Charles S. Fadley Memorial Session
Room Naupaka Salon 5-7 - Session CF-TuM1

Charles S. Fadley Memorial Session III: Hard X-ray Photoelectron Spectroscopy

Moderators: Gerd Schönhense, Johannes Gutenberg-Universität, **Trevor Willey**, Lawrence Livermore Laboratory

8:00am **CF-TuM1-1 Probing Quantum Materials Interfaces with HAXPES at the GALAXIES Beamline, SOLEIL Synchrotron***, **Jean-Pascal Rueff**,* Synchrotron SOLEIL, France **INVITED**

We will review recent HAXPES results obtained at the GALAXIES beamline, SOLEIL Synchrotron [1] regarding interfacial properties of metal oxides specially when combined to standing waves. This approach started at GALAXIES in collaboration with C.S. Fadley in CCMO [2] and continues today in different systems including CMO / YCO superlattices [3]. The functionality of novel quantum materials derives from the competition between the internal degrees of freedom (electrons, spin, orbital, topology, spin-orbit coupling) most notably observed at interfaces. An intense research activity has been set off for fabricating and manipulating interfacial properties of quantum materials leading to a frenzy of scientific discoveries including 2DEG, interfacial superconductivity, etc. HAXPES appears as a major probe of electronic interfacial behavior due to its superior probing depth and sensitivity to the local atomic properties. Extension of this work to investigating materials properties in operando conditions or characterizing ultrafast charge dynamics as recently obtained in GeSe [4] will be discussed. These results will be put in the context of the 4th generation (DLSR) synchrotron sources with much reduced H source size which offer new possibilities for in-depth interfacial characterization.

References

[1]J.-P. Rueff *et al.*, *J. Synchrotron Rad.***22**, 175 (2015)

[2]M. Marinova *et al.*, Nano Letters **15**, 253 (2015)

[3]L. Cambou *et al.*, *J. of Vacuum Science & Technology A***39**, no. 5, 053204 (2021)

[4]Z. Chen *et al.*, *Nature Communications Physics***4**, no. 1, 138 (2021).

8:40am **CF-TuM1-3 Hard X-ray Photoemission Spectroscopy (HAXPES) at the Advanced Photon Source: A Legacy of Charles S. Fadley***, **Jeff Terry**,* Illinois Institute of Technology

Over my career few scientists have helped me as much as Charles S. (Chuck) Fadley. He was always willing to provide advice, analysis code, and a pep talk when needed. Unfortunately, we were only able to put together one document out of all of our shared interests. This document, "**Study of Complex Materials and Nanostructures Using Hard X-ray Photoemission Spectroscopy,"** has played an important role at the Advanced Photon Source (APS). The APS had no hard x-ray photoemission facilities dedicated to photoemission measurements prior to our writing this document. The APS now has 3 HAXPES instruments and one intermediate energy PES system of which 3 of are used primarily of photoemission, one is utilized more for detection of x-ray standing wave measurements. In this talk, I will highlight some of the measurements performed using HAXPES at the APS and discus how Chuck's passion and dedication to the development of HAXPES within the US will continue to shape the future of photoemission for the foreseeable future.

9:00am **CF-TuM1-4 Bulk Sensitive PhotoElectron Spectroscopy on Metal Hydrides***, G. Panaccione,* IOM- Consiglio Nazionale delle Ricerche (CNR), Italy*; **Curran Kalha**, A. Regoutz,* University College London, UK*; L. Ratcliff,* University of Bristol, UK*; F. Offi,* Università Roma III, Italy*; C. Schlueter, A. Gloskovskii,* DESY, Germany*; J. Osterwalder,* University of Zurich, Switzerland*; G. Colombi,* Technical University of Delft - TU Delft, Netherlands

Efficient hydrogen storage is a key process for energy, transport and electrochemistry technology and metal hydrides have demonstrated high capacity of reversible storage, tuneable diffusion rate, and thermodynamic stability [1]. In terms of electronic structure, the identification of the electronic character vs. thickness and the hybridization between hydrogen and the metal host are fundamental values to be known, and a number of Photoelectron Sepctroscopy works captured many relevant characteristics of the metal-hydrides properties, such as i) the high reactivity of the surface and formation of more or less stable intrinsic oxides (influencing catalytic properties), and ii) the changes in the electronic character of the extended valence states upon formation of the hydrides (influencing the (semi)-metallic or semiconducting behaviour) [2-6]. Though, these results have been mainly obtained with a strong surface sensitivity in the VUV or soft X-ray region. As the hydrides are extremely reactive and their surfaces easiloxidise under ambient conditions, a precise determination of H-related features was difficult, leaving significant uncertainties in the understanding of hydrides both experimentally and theoretically

In this work, we exploit the bulk-sensitivity of Hard X-ray PhotoElectron Spectroscopy (HAXPES) to probe the electronic structure of metal-hydrogen states of two technologically relevant metal hydrides titanium (TiHx) and yttrium hydride (YHx). By means of energy dependent core level peak analysis we are able to disentangle the hydride, the main oxide and hydroxide spectral line shapes, and precisely determine their thicknesses and their chemical shifts (related to their valence oxidation number) (Fig.1). Analysis of valence band spectra and comparison with model calculations allow to attribute the metal-hydrogen states, as well as to identify the d vs sp contribution in the electronic states near the Fermi level, thus providing estimate of the charge-transfer between the metal and H, a value strongly affecting the conductivity of the system.

References

[1] B. Sakintuna et al. International Journal of Hydrogen Energy32, 1121 (2007)

[2] E. Billeter et a. J. Phys. Chem. C , 125, 25339 (2021)

[3] J. H. Weaver, D. T. Peterson,and R. L. Benbow, Phys. Rev. B20, 5301 (1979); J. H. Weaver, D. J. Peterman, D. T. Peterson,and A. Franciosi, Phys. Rev. B23, 1692 (1981).

[4] T. Riesterer, Z. Physik B - Condensed Matter66, 441 (1987); J. Osterwalder et al. Z. Phys. B - Condensed Matter 61, 113-128 (1985)

[5] S.J. Kerber et al. J. Vac. Sci. Technol. A 14(3),(1996)

[6] A Fujimori and L Schlapbach J. Phys. C: Solid State Phys. 17 , 341 (1984)

9:20am **CF-TuM1-5 Synergies between Synchrotron and Lab-Based X-Ray Techniques for the Studies of Complex Materials and Interfaces***, **Alexander Gray**,* Temple University **INVITED**

X-ray photoelectron spectroscopy, or photoemission, is a powerful and well-established experimental technique for probing the electronic structure and chemical composition of matter. Since the pioneering measurements in the 1950s, to the most recent angle-, spin-, and time-resolved studies, photoemission had and continues to have major impacts on condensed-matter physics in emerging fields, such as the studies of topological phenomena, strong electronic correlations, high-temperature superconductivity, and 2D materials. In this talk, I will describe several new directions in the field of photoemission that were pioneered by the Fadley Group, with a particular focus on the enhancement and control of the depth sensitivity and selectivity of the measurements through high-energy excitation and the use of standing waves. I will further discuss some of the latest studies that utilize hard x-ray and standing-wave photoemission in synergy with complementary synchrotron and lab-based x-ray spectroscopic and electron imaging techniques.

10:20am **CF-TuM1-8 In Situ Observation of Electrochemical Lithiation and Delithiation in Silicon Electrodes in All-solid-state Battery Configuration***, **Takuya Masuda**,* National Institute for Materials Science, Japan

We have developed an in-situ/operando XPS apparatus equipped with a bias application system and investigated electrochemical lithiation/delithiation reactions of a silicon electrode in contact with a solid electrolyte in an all-solid-state battery configuration. Not only lithium silicides but also lithium oxides, lithium silicates and lithium carbonates are formed due to the lithiation of silicon and native oxide, followed by undesired side reactions with residual oxygen and carbon dioxide in the chamber. Lithium silicides reversibly respond to the successive lithiation/delithiation cycles. However, lithium oxides, lithium silicates and lithium carbonates are remained at the surface as irreversible species. The lithium silicide peak drastically shifts during the successive delithiation after preceding lithiation up to certain level. This is attributed to the phase transition of a crystalline lithium silicide to an amorphous phase. The effect of this phase transition on the cycle performance will be discussed on the basis of nanomechanical aspect.

References

[1] R. Endo, T. Ohnishi, K. Takada, and T. Masuda, "In Situ Observation of Lithiation and Delithiation Reactions of a Silicon Thin Film Electrode for All-

Solid-State Lithium-Ion Batteries by X–ray Photoelectron Spectroscopy", J. Phys. Chem. Lett. 2020, 11, 6649–6654.

[2]R. Endo, T. Ohnishi, K. Takada, T. Masuda, "Instrumentation for tracking electrochemical reactions by x-ray photoelectron spectroscopy under conventional vacuum conditions", Journal of Physics Communications, 2021, 5, 015001.

[3] R. Endo, T. Ohnishi, K. Takada, T. Masuda, "Electrochemical Lithiation and Delithiation in Amorphous Si Thin Film Electrodes Studied by Operando X–ray Photoelectron Spectroscopy", J. Phys. Chem. Lett. 2022, 13, 7363-7370.

10:40am **CF-TuM1-9 Structural Investigation of Ruthenium Silicide Si 2p Core Level Surface States Using X-Ray Photoelectron Diffraction*, Jonathan Denlinger,*** Lawrence Berkeley National Laboratory

The Si 2p core-level photoemission spectra of URu_2Si_2, a heavy-fermion superconductor with a famous unexplained 'hidden'-order transition at 17.5K, provides a distinct signature of the (001) cleaved-surface termination, which is important for the interpretation of valence band electronic structure studies. The Si-terminated surface, in particular, exhibits multiple distinct Si 2p peaks shifted to lower binding energy than the bulk component. Density functional theory calculations of the core-level spectra predict an unexpected structural site assignment and energy ordering of the top surface dangling bond surface state relative to a sub-surface Si site. Structural investigation with these surface states is explored using photon- and angle-dependent measurements of the Si 2p x-ray photoelectron diffraction intensities in comparison to EDAC scattering simulations.

Author Index

Bold page numbers indicate presenter