

## Light Sources Enabled Science Mini-Symposium Room 121 - Session LS-MoM

### Light Sources Enabled Science Mini-Symposium

**Moderators:** Slavomir Nemsak, Advanced Light Source, Lawrence Berkeley National Laboratory, Jessica McChesney, Argonne National Laboratory

**8:15am LS-MoM-1 Microsecond Dynamics of Surface Reactions Studied by the Time-resolved Ambient Pressure XPS with Chemical Perturbations**, C. Eads, W. Wang, Max IV Laboratory, Sweden; U. Kust, J. Prumbs, Lund University, Sweden; R. Temperton, max iv Laboratory, Sweden; M. Scardamaglia, max iv laboratory, Sweden; J. Knudsen, Lund University, Sweden; **Andrey Shavorskiy**, Max IV Laboratory, Sweden **INVITED**

Recently, a new time-resolved Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) method based on chemical perturbations has been developed for studying dynamic processes with microsecond time resolution. The method uses the rapid change in the gas pressure/composition as a perturbation that drives the system away from equilibrium [1,2]. In the experiment, a sharp and strong gradient in chemical potential is created by modulating the gas composition over the catalyst via a fast valve. Such gas pulse has internal pressure in the mbar range and a rising edge of a few hundred microseconds. A time-sensitive delayline detector is synchronized with the valve operation to measure X-ray photoemission spectra with nano- to microsecond time resolution. We will present several experiments characterizing the setup's performance, including the CO oxidation reaction over Pt (111) to demonstrate the capability of the setup to correlate the gas phase composition with that of the surface during the transient supply of CO gas into an O<sub>2</sub> stream [3]. These experiments demonstrate that under CO pressure modulation conditions, the system remains active (i.e. producing CO<sub>2</sub>) at temperatures below the CO lift-off temperature under the flow conditions. We will also demonstrate that little chemisorbed oxygen is observed during the active phase of the catalytic cycle when the Pt(111) surface is saturated with the oxide. This points out a much higher activity of the O<sub>2</sub> chemisorbed towards CO oxidation than O<sub>2</sub> oxide, resolving the ongoing debate about the role of the Platinum surface oxide in the reaction.

[1] J. Knudsen *et al.* *Nat Commun* **12**, 6117 (2021). doi:10.1038/s41467-021-26372-y

[2] A. Shavorskiy *et al.* *ACS APPLIED MATERIALS & INTERFACES* **13**, 47629 (2021). doi: 10.1021/acami.1c13590

[3] C. Eads *et al.* *in preparation*

**8:45am LS-MoM-3 HAXPES at PETRA III and IV: Electronic Structure, Operando Devices and In-situ Catalysis**, **Christoph Schlueter**, Desy, Deutsches Elektronen-Synchrotron, Germany

The P22 beamline at PETRA III is a cutting-edge facility dedicated to hard X-ray photoelectron spectroscopy (HAXPES) techniques, featuring four specialized experimental end stations for high-resolution studies of electronic and chemical structures in various complex materials, device-like structures, and catalytic interfaces.

1. HAXPES Hemisphere: Known as the "workhorse" instrument, this setup offers extensive opportunities for operando device characterization, depth profiling, and chemical analysis.
1. POLARIS (Ambient Pressure XPS System): This system is tailored for investigating the catalytic properties of surfaces under industrially relevant conditions, making it crucial for practical catalysis research.
1. HarMoMic (Hard X-ray Momentum Microscope): This novel microscope explores electronic and atomic structures through wide-field imaging of band dispersions and electron diffraction patterns.
1. HAXPEEM (Hard X-ray Photoemission Electron Microscopy): Dedicated to studying laterally resolved chemical and elemental structures.

These instruments are fully operational and used in close collaboration with external user groups, reflecting the wide range of scientific fields engaged by the P22 beamline community. The P22 beamline first received light in November 2017 and conducted its first user experiments in June 2018. Since then, it has contributed to over 100 publications.

In this contribution, I will briefly present the experimental capabilities of the P22 beamline, provide an overview of the most prominent scientific results, and present an outlook towards HAXPES at PETRA IV.

**9:00am LS-MoM-4 Hard X-Ray Photoelectron Spectroscopy and Its Application to the Bonding and Electronic Structure of Metal Dihydrides**, **Anna Regoutz**, University College London, UK

Metal hydrides hold significant promise in various hydrogen-related technologies, encompassing energy storage, hydrogen compression, and hydrogen sensing. Although metal hydrides appear simple compared to many other energy materials, understanding the electronic structure and chemical environment of hydrogen within them remains a key challenge. This work presents a new analytical pathway to explore these aspects in technologically relevant systems using Hard X-ray Photoelectron Spectroscopy (HAXPES) on thin films of two prototypical metal dihydrides: YH<sub>2</sub>- $\delta$  and TiH<sub>2</sub>- $\delta$ . [1,2] By taking advantage of the tunability of synchrotron radiation, a non-destructive depth profile of the chemical states is obtained using core-level spectra. Combining experimental valence band spectra collected at varying photon energies with theoretical insights from density functional theory (DFT) calculations, a description of the bonding nature and the role of d versus sp contributions to states near the Fermi energy are provided. Moreover, a reliable determination of the enthalpy of formation is proposed by using experimental values of the energy position of metal s band features close to the Fermi energy in the HAXPES valence band spectra.

[1] C. Kalha, L. E. Ratcliff, G. Colombi, C. Schlueter, B. Dam, A. Gloskovskii, T.-L. Lee, P. K. Thakur, P. Bhatt, Y. Zhu, J. Osterwalder, F. Offi, G. Panaccione, A. Regoutz, "Revealing the Bonding Nature and Electronic Structure of Early-Transition-Metal Dihydrides", *PRX Energy*, **3**, 013003, 2024, <https://doi.org/10.1103/PRXEnergy.3.013003>.

[2] C. Kalha, N. K. Fernando, P. Bhatt, F. O. L. Johansson, A. Lindblad, H. Rensmo, L. Zendejas Medina, R. Lindblad, S. Siol, L. P. H. Jeurgens, C. Cancellieri, K. Rosnagel, K. Medjanik, G. Schönhense, M. Simon, A. X. Gray, S. Nemšák, P. Lömker, C. Schlueter, and A. Regoutz, "Hard X-ray Photoelectron Spectroscopy – A Snapshot of the State-of-the-Art in 2020", *J. Phys. Condens. Matter*, **33**, 233001, 2021, <https://doi.org/10.1088/1361-648X/abeacd>.

**9:15am LS-MoM-5 VerSoX B07-B: A Soft X-ray Beamline for High-throughput and Ambient Pressure XPS and NEXAFS**, **David Grinter**, **P. Ferrer**, **S. Kumar**, **G. Held**, Diamond Light Source, UK

Soft X-ray absorption and photoemission spectroscopy is a powerful tool for probing the chemical and electronic structure of materials. In this presentation we describe the design and capabilities of VerSoX B07-B at Diamond Light Source, (UK) a beamline dedicated to probing gas, liquid and solid interfaces across a wide pressure and temperature range.

Due to the wide photon energy range, (45-2300 eV) the beamline covers the K edges of elements from Li to P, and the L<sub>2,3</sub> edges of the first row transition metals. It is equipped with two separate endstations dedicated to UHV X-ray Photoemission Spectroscopy (XPS) and ambient pressure Near Edge X-ray Absorption Fine Structure (NEXAFS) studies, respectively. The beamline is optimised to perform routine high-throughput studies of solid samples and is also equipped with custom-engineered cells for operando electrochemical XAS measurements as well as high pressure gas (>1 bar) microreactors for catalysis research. The UHV endstation provides facilities for traditional surface science experiments and complements the ambient pressure XPS (AP-XPS) available at the neighbouring B07-C branch.

**9:30am LS-MoM-6 The Electric Double Layer at Ultra-Thin Film Electrodes and How to Experimentally Assess It**, **Maximilian Jaugstetter**, LBNL; **L. Falling**, Technical University Munich, Germany; **S. Nemsak**, **M. Salmeron**, LBNL

Understanding the structure of the electric double layer (EDL) is fundamental for the development of improved heterogeneous catalysts, batteries, and membranes for the sustainable accumulation of key materials and, generally, any process that involves a solid-liquid interface. Due to their hidden nature, the difficulty of spectroscopic detection, and the difficulty of formulating holistic molecular dynamics simulations, knowledge of the properties of these interfaces is sparse and focuses on a few example systems.

In order to obtain a better understanding of the effects of solvated ions on the interfacial water structure, local pH, and reactant adsorption, we employ soft X-ray techniques to spectroscopically investigate the atomic composition of the first few nanometers behind an X-ray transmissive electrode. For these experiments, we utilize interface-sensitive techniques

such as X-ray absorption spectroscopy/total electron yield (XAS/TEY) and X-ray photoelectron spectroscopy (XPS) in combination with nano-electrochemistry as well as nanofabrication of ultra-thin free-standing films of graphene and graphene-like 2D materials.

With these methods, we are able to demonstrate the huge implications of different electrolytes and electrode materials on the structure of the EDL as well as the contributions of individual species to its formation. A quantification of dissolved species at the interface by XPS allows us to directly relate their presence to EDL properties.

By understanding the dependence of these properties, we are one step closer to fine-tuning them to support favorable transition states in electrocatalysis or decrease inhomogeneous growth processes in energy storage.

**10:30am LS-MoM-10 In situ Synchrotron Characterization of Materials Synthesis and Electrochemical Interfaces, Katherine Harmon, Stanford University; F. Heremans, S. Hruszkewycz, M. Highland, Argonne National Laboratory**

**INVITED**

Advanced X-ray characterization tools exploiting the high coherent flux of 4<sup>th</sup> generation synchrotrons (e.g., the upgraded Advanced Photon Source) and X-ray free electron lasers promise to revolutionize our understanding of material synthesis, catalysis, and many other physiochemical processes. I will present our recent work investigating the synthesis of silicon carbide, a quintessential “polytypic” material. SiC is a versatile wide bandgap semiconductor host of optically active point defects (color centers) that may be exploited for quantum sensing and communications. SiC has also been reported to occur in over 200 polytypes, with mixed polytype inclusions being common in nominally single-polytype materials. Color centers are extremely sensitive to such heteropolytypic inclusions. Yet, the thermodynamic and kinetic drivers of polytype transformations during growth remain speculative due to a lack of characterization tools able to probe the growth process in real time. We developed a hard X-ray compatible chemical vapor deposition (CVD) reactor for the characterization of silicon carbide (SiC) polytype transformations during synthesis. Preliminary *in situ* crystal truncation rod measurements obtained using our new reactor at the Advanced Photon Source (APS) demonstrate the sensitivity to different polytypes in SiC. Notably, these measurements were carried out prior to the APS upgrade (APS-U) and did not exploit the coherent flux of the beam, which was not sufficiently high at the photon energies required to penetrate the CVD reactor walls ( $E > 24$  keV). The APS-U will provide a two order of magnitude increase in the coherent flux of the beam across the energy spectrum, enabling advanced coherent X-ray measurements, namely, X-ray photon correlation spectroscopy (XPCS), at the requisite X-ray photon energies for SiC synthesis characterization. I will outline the principles of XPCS and discuss the upcoming opportunities at the APS-U not only for characterizing and controlling polytype transformations in SiC but also more broadly for understanding material processing in cases requiring complex sample environments that were previously inaccessible.

**11:00am LS-MoM-12 Direct Imaging of Local Orbitals in Quantum Materials, Martin Sundermann, Max Planck Institute for Chemical Physics of Solids, Germany; H. Yavas, PETRA III, Deutsches Elektron Synchrotron, DESY, Germany; P. Dolmantis, C. Chang, Max Planck Institute for Chemical Physics of Solids, Germany; H. Gretarsson, PETRA III, Deutsches Elektron Synchrotron, DESY, Germany; A. Komarek, Max Planck Institute for Chemical Physics of Solids, Germany; A. Severing, Universität zu Köln, Germany; M. Haverkort, Universität Heidelberg, Germany; L. Tjeng, Max Planck Institute for Chemical Physics of Solids, Germany**

The search for new quantum materials with novel properties is often focused on materials containing transition-metal, rare-earth and/or actinide elements. The presence of the atomic-like *d* or *f* orbitals provides a fruitful playground to generate novel phenomena. The intricate interplay of band formation with the local electron correlation and atomic multiplet effects leads to phases that are nearly iso-energetic, making materials’ properties highly tunable by doping, temperature, pressure or magnetic field. Understanding the behavior of the *d* and *f* electrons is essential for designing and controlling novel quantum materials. Therefore, identifying the *d* or *f* orbitals that actively participate in the formation of the ground state is crucial. So far, these orbitals have mostly been deduced from optical, X-ray and neutron spectroscopies in which spectra must be analyzed using theory or modelling. This, however, is also a challenge by itself, since *ab-initio* calculations hit their limits due to the many-body nature of the problem.

Here we developed a new experimental method that circumvents the need for involved analysis and instead provides the information as measured. With this technique, we can make a direct image of the active orbital and determine what the atomic-like object looks like in the real solid. The method, X-Ray Raman spectroscopy or non-resonant inelastic X-ray scattering using an *s*-core level (*s*-NIXS), relies on high momentum transfer in the inelastic scattering process, which is necessary for dipole-forbidden terms to gain spectral weight. To demonstrate the strength of the technique, we imaged the (text-book example) ground-state  $x^2-y^2/3x^2-r^2$  hole orbital of the Ni<sup>2+</sup> ion in NiO single crystal [1] We will present the basic principles of *s*-NIXS and details of its experimental implementation. We will show how we can apply this technique to unveil the active orbitals in a wide range of quantum materials [2,3], including those that undergo complex metal-insulator transitions.

[1] H. Yavaş, M. Sundermann, K. Chen, A. Amorese, A. Severing, H. Gretarsson, M.W. Haverkort, L.H. Tjeng, **Nature Physics** **15**, 559 (2019)

[2] B. Leedahl, M. Sundermann, A. Amorese, A. Severing, H. Gretarsson, L. Zhang, A.C. Komarek, A. Maignan, M.W. Haverkort, and L.H. Tjeng, **Nature Commun.** **10**, 5447 (2019).

[3] A. Amorese, B. Leedahl, M. Sundermann, H. Gretarsson, Z. Hu, H.-J. Lin, C.T. Chen, M. Schmidt, H. Borrmann, Yu. Grin, A. Severing, M.W. Haverkort, and L.H. Tjeng, **Phys. Rev. X** **11**, 011002 (2021).

**11:15am LS-MoM-13 Resonant X-Ray Photon Correlation Spectroscopy on the Spin Density Waves in (La/Pr)<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub>, Hao Zheng, Argonne National Laboratory**

Intertwined spin and charge density waves (SDW and CDW) and their fluctuations have long been perceived as instrumental to the onset of non-BCS superconductivity, as extensively investigated in cuprates and Fe-based superconductors. Recently, superconductivity and intertwined SDW/CDW have been found in various layered nickelates that may or may not co-exist. These observations lead to renewed interest in the nature and dynamics of the intertwined order. Metallic nickelate Pr<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub> displays an unconventional ground state with a nearly commensurate SDW and charge density wave CDW intertwined below a metal-to-metal transition. In contrast, its lower-dimensional sibling La<sub>4</sub>Ni<sub>3</sub>O<sub>10</sub> hosts a commensurate SDW stabilized by the lattice. In this presentation, We will focus on the dynamics of the SDW order and show how we can investigate the formation and fluctuations of the SDW order using resonant X-ray correlation spectroscopy (XPCS). By tracing the speckle pattern at the SDW Bragg peak and on the L3 edge of Nickel simultaneously, our resonant XPCS provides insights into the nature of the intermediate SDW order in both nickelates.

**11:30am LS-MoM-14 Innovative High Energy X-Ray Characterization of Interfaces for Quantum Application, Andrea Sartori, J. Drnec, ESRF, France**

Small layered junctions, integral to quantum applications, typically comprise thin films, often conductors or superconductors, separated by thin oxide layers. These junctions play critical roles in various quantum devices, including Josephson junctions, thermoionic devices and parametric amplifiers. However, characterizing these structures poses significant challenges due to their small dimensions and complex compositions. Traditional techniques like cross-sectional SEM and TEM offer limited insights and may be destructive. While X-ray Reflectivity (XRR) provides valuable out-of-plane electron density profile information for these junctions, it lacks the in-plane spatial resolution required for detailed analysis. Here we introduce a novel approach utilizing High Energy XRR Tomography (HEXRR-Tomo). Unlike conventional XRR, HEXRR-Tomo enables spatial mapping of the entire surface, allowing for the potential reconstruction of a high-resolution 3D electron density map of the junction. This technique promises to offer easily accessible and non-destructive insights into the thickness, density, and roughness of individual layers within the junction, thereby advancing our understanding of their structure and properties.

In this contribution, we will present preliminary examples of the technique, demonstrating our ability to visualize the morphology and key features of various devices with specific applications. For instance, one example involves a thermoionic junction comprising complex layers of Si, SiO<sub>2</sub>, Al, and V (Fig. 1), which is utilized as a cooling device for cryogenic temperatures. Another example features NbAlAlO<sub>x</sub>AlNb films and NbTiN structures on a Si wafer, which serve as Josephson junctions for quantum computing and as parametric amplifiers, respectively. Further analysis will provide information about the roughness and thickness of each individual layer.

# Monday Morning, November 4, 2024

11:45am LS-MoM-15 Bismuth-Trimer Adlayer and Thin Film Growth on In- and Sb-Terminated InSb(111) Surfaces, Rohit Yadav, S. Huang, S. Ritter, R. Timm, Lund University, Sweden

Bismuth-semiconductor interfaces are important from both fundamental and application point of view. For example, a monolayer of bismuth on compound semiconductors like SiC and GaAs is predicted to be a 2D topological insulator with a quantum spin hall phase.<sup>[1,2]</sup> Similarly, Bi-induced trimers on Si(111) have been reported for giant Rashba splitting.<sup>[3]</sup> Here, we investigate Bi incorporation on InSb(111)A and B surfaces due to their large spin-orbit coupling and the small lattice mismatch.<sup>[4]</sup> Furthermore, individual Bi-based compounds like InBi and  $Sb_{1-x}Bi_x$  have been predicted to induce non-trivial topological states.<sup>[5,6]</sup> We are focusing on the initial deposition, from less than a monolayer up to a few monolayers of Bi.

We have employed scanning tunneling microscopy/spectroscopy (STM/S) and synchrotron-based angle-resolved photoemission spectroscopy (ARPES) and XPS to investigate surface topography, electronic properties, and chemical composition. STM topography of oxide-free InSb(111)A shows (2X2) reconstructions with In-trimers. Upon Bi incorporation, Bi mainly forms a homogeneous periodic hexagonal bilayer, highlighting the formation of large-scale Bi-induced (2X2) reconstruction, along with some areas of  $(2\sqrt{3} \times 2\sqrt{3})\text{-R}30^\circ$  reconstruction. A bias-dependent STM study shows that the Bi-film is decorated with Bi-trimers. STS on these trimers show metallic character and discrete surface states in the InSb bandgap, indicating possible band engineering upon Bi incorporation. Discrete Bi-induced surface states are further confirmed by ARPES measurement. However, Bi-incorporation into InSb(111)B results in mixed surface topography of Bi-trimers and Bi-monomer structures. Bi 5d core-level XPS for both InSb(111)A and B reveals that Bi-incorporation results in mainly Bi-Sb bonding and minor metallic Bi-Bi bonds. Interestingly, the Bi-Sb layer thickness remains self-limiting in the case of Bi/InSb(111)B, when deposited at elevated temperature. Thus, the amount of Bi-Sb remains unchanged, regardless of the number of deposition cycles.

Here, we discuss Bi-induced electronic band engineering and the formation of several 2D structures on InSb. This research highlights the metallic behaviour of decorated Bi-trimers and self-limiting BiSb film thickness in InSb(111)A and B substrates, respectively, which is highly versatile from an application point of view

## References:

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- [2] Y. Liu et al., ACS Nano 17, 5047–5058 (2023)
- [3] I. Gierz et al., PRL 103, 046803 (2009)
- [4] H. S. Inbar et al., arXiv:2302.00803 (2023)
- [5] D. Hsieh et al., Nature 452, 970 (2008)
- [6] H. Huang et al., Phys. Rev. B 90, 195105 (2014)

## Author Index

### Bold page numbers indicate presenter

#### — C —

Chang, C.: LS-MoM-12, 2

#### — D —

Dolmantis, P.: LS-MoM-12, 2

Drnec, J.: LS-MoM-14, 2

#### — E —

Eads, C.: LS-MoM-1, 1

#### — F —

Falling, L.: LS-MoM-6, 1

Ferrer, P.: LS-MoM-5, 1

#### — G —

Gretarsson, H.: LS-MoM-12, 2

Grinter, D.: LS-MoM-5, 1

#### — H —

Harmon, K.: LS-MoM-10, 2

Haverkort, M.: LS-MoM-12, 2

Held, G.: LS-MoM-5, 1

Heremans, F.: LS-MoM-10, 2

Highland, M.: LS-MoM-10, 2

Hruszkewycz, S.: LS-MoM-10, 2

Huang, S.: LS-MoM-15, 3

#### — J —

Jaugstetter, M.: LS-MoM-6, 1

#### — K —

Knudsen, J.: LS-MoM-1, 1

Komarek, A.: LS-MoM-12, 2

Kumar, S.: LS-MoM-5, 1

Kust, U.: LS-MoM-1, 1

#### — N —

Nemsak, S.: LS-MoM-6, 1

#### — P —

Prumbs, J.: LS-MoM-1, 1

#### — R —

Regoutz, A.: LS-MoM-4, 1

Ritter, S.: LS-MoM-15, 3

#### — S —

Salmeron, M.: LS-MoM-6, 1

Sartori, A.: LS-MoM-14, 2

Scardamaglia, M.: LS-MoM-1, 1

Schlueter, C.: LS-MoM-3, 1

Severing, A.: LS-MoM-12, 2

Shavorskiy, A.: LS-MoM-1, 1

Sundermann, M.: LS-MoM-12, 2

#### — T —

Temperton, R.: LS-MoM-1, 1

Timm, R.: LS-MoM-15, 3

Tjeng, L.: LS-MoM-12, 2

#### — W —

Wang, W.: LS-MoM-1, 1

#### — Y —

Yadav, R.: LS-MoM-15, 3

Yavas, H.: LS-MoM-12, 2

#### — Z —

Zheng, H.: LS-MoM-13, 2