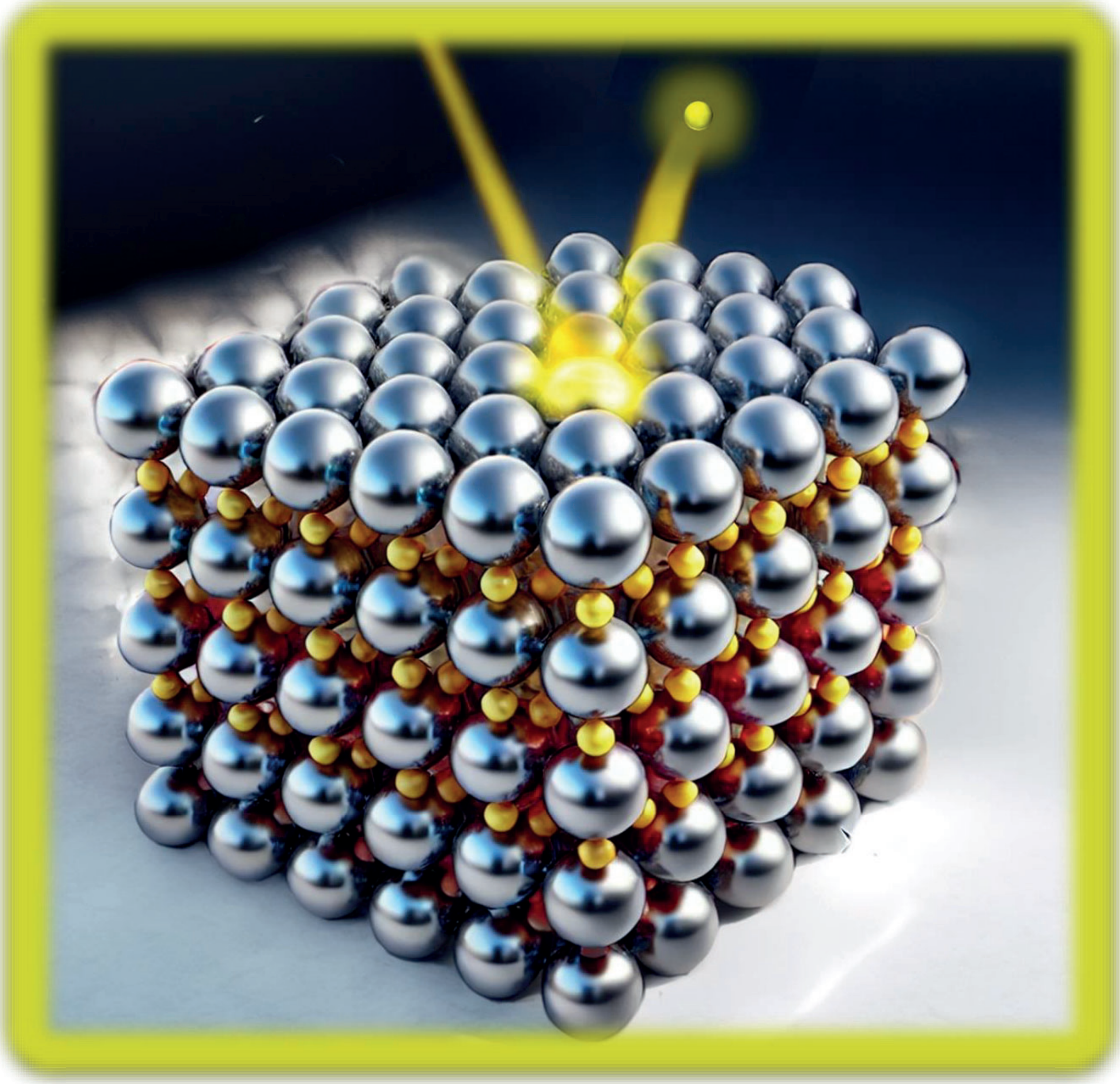
Technical Program

SWISS HAXPES WORKSHOP

FUNDAMENTALS, INSTRUMENTATIONS AND APPLICATIONS



7th - 9th May 2025

Empa, Überlandstrasse 129, Dübendorf, Switzerland

WELCOME TO THE HAXPES Workshop 2025

We cordially welcome you to the HAXPES workshop 2025: Fundamentals, Instrumentations and applications, supported by the Swiss National Science Foundation (SNSF), by Empa and by our sponsors from industry.

This workshop introduces the fundamentals and applications of Hard X-ray Photoelectron Spectroscopy (HAXPES) for investigating the chemistry and electronic structure of material surfaces, thin films, and their buried interfaces.

This workshop offers a platform for researchers, scientists, and PhD students from diverse backgrounds to explore the latest developments and applications of HAXPES in fields such as catalysis, materials science, batteries and nanotechnologies.

Throughout this workshop, participants will have the opportunity to engage in insightful presentations, interactive discussions with leading experts, to network and to start new scientific collaborations. We aim to foster collaboration and innovation, encouraging attendees to share their research findings and practical experiences with HAXPES methodologies.

Thank you for joining us in this journey of discovery and exploration. We look forward to an enriching exchange of ideas and knowledge that will enhance our collective understanding of hard x-ray photoemission spectroscopy and its impact on materials science!

Finally, we would like to thank all the speakers, presenters, participants and sponsors for their participation and support.

Wishing you a rewarding HAXPES workshop!

May 2025

Workshop organizers

Claudia Cancellieri

Claudia Cancellieri Lars P.H. Jeurgens

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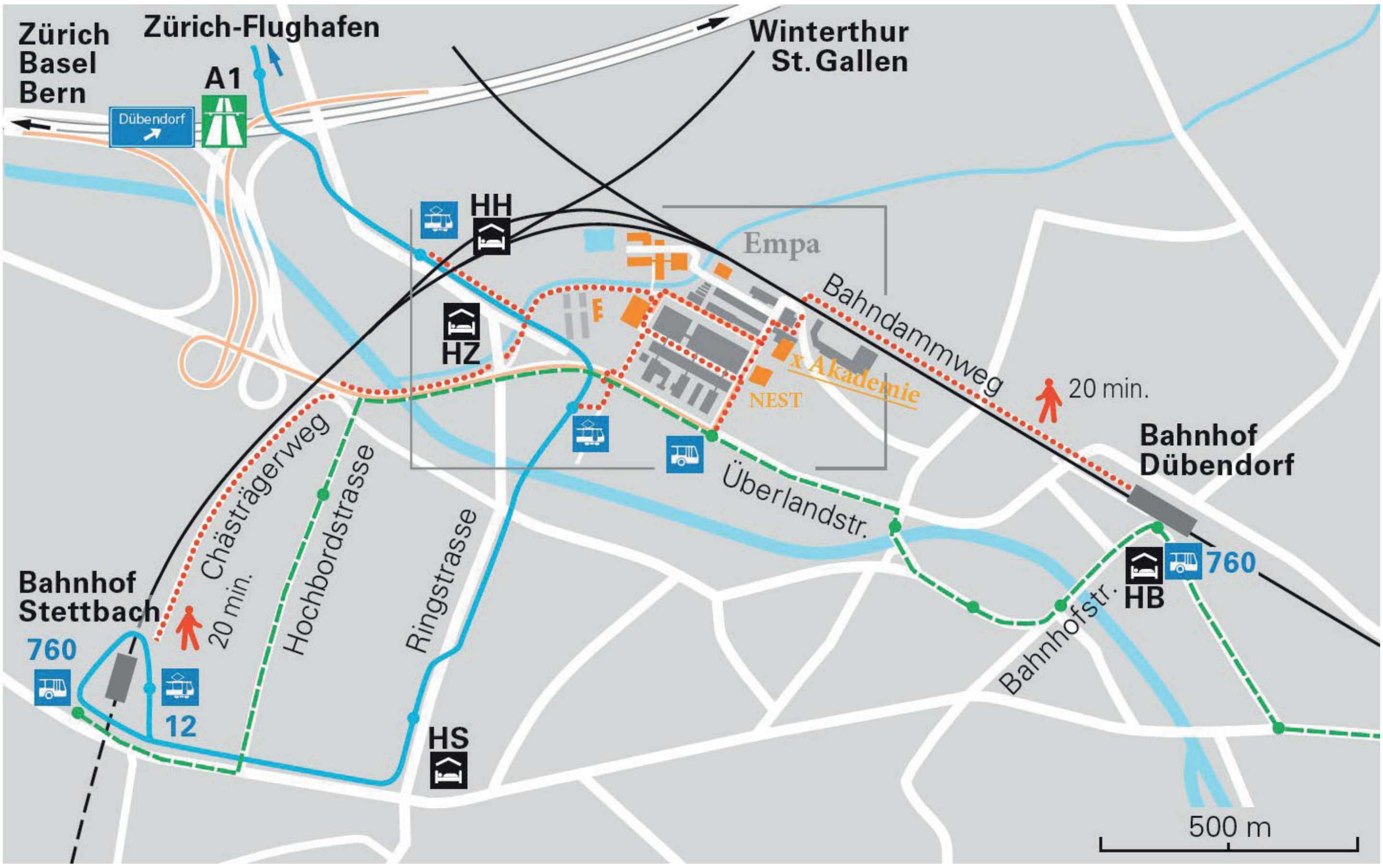

x Akademie = Workshop Haxpes

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TECHNICAL PROGRAM HAXPES WORKSHOP, MAY 7TH-9TH, 2025

	WEDNESDAY, MAY 7TH, 2025	
08:30-09:00	REGISTRATION	
09:00-09:20	OPENING – WELCOME – INTRODUCTION TO THE WORKSHOP **Lars P.H. Jeurgens, Claudia Cancellieri, Lorenz Herrmann** *Empa, Swiss Federal Laboratories for Materials Science and Technology, CH*	
09:20-10:40	**THE DEVELOPMENT OF LABORATORY-BASED HIGH ENERGY SOURCES FOR XPS** **John F. Watts** *The Surface Analysis Laboratory, School of Engineering University of Surrey, UK*	***KEYNOTE*** ***K1***
	CHARGE REDISTRIBUTION AND VALENCE BAND OCCUPANCY ON METALLIC ALLOY FORMATION: THE ROLE OF HAXPES USING AUGER PARAMETERS AND PLASMON FEATURES **John F. Watts** and **Marie-Laure Abel** *The Surface Analysis Laboratory, School of Engineering University of Surrey, UK*	***K2***
10:40-11:10	COFFEE BREAK	
11:10-11:30	**CLASSICAL VERSUS QUANTUM ASSESSMENT OF FINAL-STATE EFFECTS XPS/HAXPES OF BULK MATERIALS** **Vladyslav Turlo** *Advanced material processing, Empa, Thun, CH*	***INVITED*** ***I1***
11:30-11:50	**CHEMICAL STATE ANALYSIS FOR THE ACCELERATED DEVELOPMENT OF SEMICONDUCTING AND INSULATING THIN FILM MATERIALS** **Sebastian Siol** *Surface science and coating technologies, Empa, Dübendorf, CH*	***INVITED*** ***I2***
11:50-12:10	**FROM MOLECULAR STRUCTURES TO XPS SPECTRA AND BACK: CHALLENGES AND INTRINSIC LIMITATIONS** **Mounir Mensi** *X-ray Diffraction and Surface Analytics Platform (XRDSAP), VS – ISIC – EPFL, Sion, CH*	***INVITED*** ***I3***
12:10-13:15	LUNCH BREAK	
13:15-14:15	**CHEMICAL BONDING AND ELECTRONIC STRUCTURE OF METAL DIHYDRIDES** **Anna Regoutz** *Department of Chemistry, UCL, 20 Gordon Street, London, UK* *Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, Oxford, UK*	***KEYNOTE*** ***K3***
14:15-14:35	**IN SITU HAXPES AT SLS: ACHIEVEMENTS AND PERSPECTIVES** **Luca Artiglia** *Center for Energy and Environmental Sciences, PSI, Villigen, CH*	***I4***
14:35-14:55	**HAXPES-XPS COMBINATION REVEALS EXTENDED SURFACE STRUCTURE OF CATALYSTS** **Andreas Borgschulte** *Chemical Energy Carriers and Vehicle, Empa, Dübendorf, CH*	***I5***
15:00-15:30	COFFEE BREAK	
15:30-16:30	**LAB-SCALE HAXPES: ISSUES TO WORRY ABOUT TOWARDS IMPROVED ANALYSIS** **Olivier Renault** *Univ. Grenoble Alpes, CEA, Leti, Grenoble, FR*	***KEYNOTE*** ***K4***
16:30-16:45	SUMMARY AND CLOSING OF THE DAY/DISCUSSION **Lars P.H. Jeurgens, Claudia Cancellieri** *Joining technologies and corrosion, Empa, Dübendorf, CH*	
16:50-19:00	APERO	

	THURSDAY, MAY 8TH, 2025	
Session	ORAL SESSION PLENARY	
Room	EMPA ACADEMY	
09:00- 10:00	**ADVANCING XPS METHODOLOGIES: 1) TRANSITION METALS, 2) RARE EARTH ELEMENTS, AND 3) THE ROLE OF ADVENTITIOUS CARBON** **Mark C. Biesinger** *Surface Science Western, 2Dept. of Chemistry Western University, London ON, CA*	***KEYNOTE*** ***K5***
10:00- 10:20	**CHARACTERISATION OF CUPRIC OXIDE SURFACES GENERATED BY PLASMA OXIDATION AND RADIOCHEMICAL PROCESSES IN THE LARGE HADRON COLLIDER** **Marcel Himmerlich** *European organisation for nuclear research, CERN, Geneva, CH*	***INVITED*** ***I6***
10:20- 10:50	COFFEE BREAK	
10:50- 11:50	**ONE-STEP PHOTOEMISSION MODEL: CORE LEVELS TO VALENCE BANDS IN QUANTUM MATERIALS** **Jan Minár** *New Technologies-Research Centre, University of West Bohemia, Pilsen, CZ*	***KEYNOTE*** ***K6***
11:50- 13:15	LUNCH BREAK	
13:15- 14:15	**HAXPES INELASTIC BACKGROUND FOR CHARACTERIZATION OF NANO-STRUCTURED MATERIALS** **Sven Tougaard** *Department of Physics, Chem. and Pharm., University of Southern Denmark, Odense M, DK*	***KEYNOTE*** ***K7***
14:15- 14:35	**REAL-TIME INSIGHTS INTO ALL-SOLID-STATE BATTERIES INTERFACES WITH OPERANDO XPS** **Mario El Kazzi** *Center for Energy and Environmental Science, PSI, Villigen, CH*	***INVITED*** ***I7***
14:35- 14:55	**SURFACE CHEMISTRY OF $Li_7La_3Zr_2O_{12}$ SOLID-STATE ELECTROLYTES** **Kostiantyn Kravchyk** *Thin films and photovoltaics, Empa, Dübendorf, CH*	***INVITED*** ***I8***
14:55- 15:25	COFFEE BREAK	
15:25- 16:25	**HAXPES AT PETRA III AND IV: ELECTRONIC STRUCTURE, OPERANDO DEVICES AND IN-SITU CATALYSIS** **Christoph Schlueter** *Photon Science, Deutsches Elektronen-Synchrotron DESY, Hamburg, DE*	***KEYNOTE*** ***K8***
16:25- 16:40	**SUMMARY AND CLOSING OF THE DAY/DISCUSSION** **Lars P.H. Jeurgens, Claudia Cancellieri** *Joining technologies and corrosion, Empa, CH*	
16:40- 17:10	**LAB TOUR SHOWING HAXPES @ EMPA (OPTIONAL)**	

	FRIDAY, MAY 9TH, 2025	PART NO.
Session	**ORAL SESSION PLENARY**	
Room	**EMPA ACADEMY**	
09:00- 10:00	**PROBING EMERGENT PHENOMENA AT OXIDE INTERFACES WITH HAXPES AND STANDING WAVES** **Alexander Gray** *Department of Physics, Temple University, Philadelphia, USA*	***KEYNOTE*** ***K9***
10:00- 10:20	**SOFT-X-RAY ARPES INSIGHTS INTO K-RESOLVED ELECTRONIC STRUCTURE OF FUNCTIONAL MATERIALS** **Vladimir Strokov** *Soft-X-ray ARPES beamline, SLS, PSI, Villigen, CH*	***INVITED*** ***I9***
10:20- 10:40	COFFEE BREAK	
10:40- 11:40	**OPERANDO HAXPES OF FUNCTIONAL QUANTUM MATERIALS** **Martina Müller** *Department of Physics, University of Konstanz, Konstanz, DE*	***KEYNOTE*** ***K10***
11:40- 12:00	**HAXPES ANALYSIS OF NATIVE OXIDES ON STEEL** **Chiara Menegus** *Joining technologies and corrosion, Empa, Dübendorf, CH*	***INVITED*** ***I10***
12:00- 12:20	**SUMMARY AND CLOSING OF THE WORKSHOP/DISCUSSION** **Lars P.H. Jeurgens, Claudia Cancellieri** *Joining technologies and corrosion, Empa, Dübendorf, CH*	
12:20- 13:30	LUNCH/DISCUSSION	
	INDIVIDUAL DEPARTURE – We wish you a safe journey.	

NOTES

The Development of Laboratory-Based High Energy Sources for XPS

John F Watts
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XPS with higher energy X-ray sources is now a commercial reality with a number of systems dedicated to HAXPES available. Against this background is a rich history, and over the last fifty years a number of higher energy X-ray sources have been suggested as alternatives for the usual AlKα source, found in the first commercial XPS systems, and still the standard anode material for XPS today.

This presentation will review the development of a number of such sources, predominantly in the author's laboratory, and the rationale behind the desire to extend the binding energy range of the technique, which was mainly focussed on the desire to probe deeper core levels, rather than the increase in kinetic energy and attendant analysis depth, that has received much attention in HAXPES in recent years. The achromatic sources SiKα, ZrLα and TiKα are described along with monochromatic sources AgLα and CrKβ, both based on the standard quartz monochromator geometry but taking higher orders of diffraction. The driving force for much of this development was the desire to probe deeper core levels and attendant CCC Auger transitions. These could be combined into initial or final state Auger parameters as described in much of the work cited in this review. The additional benefits of moving Auger peaks in conventional XPS to higher binding energies, thus providing better definition of the core XPS lines of ferrous alloys with transition metal additions, will also be illustrated. The highest energy source considered is the CuKα source (hυ = 8048 e V) based around an external X-ray tube, which provides much insight into the electronic structure of steels by measurement of the Fe1s and Fe*KLL* peaks.

The last decade or so has seen a significant increase of interest in HAXPES, and all manufacturers of turn-key XPS instruments offer HAXPES options of one form or another, there are three dedicated HAXPES systems commercially available, which are very briefly described.

J F Watts, J E Castle, "The Development of Laboratory-Based High Energy Sources for XPS" *Surf Interf Anal* **56,** 408-424, (2024). https://doi.org/10.1002/sia.7300

K2

Charge Redistribution and Valence Band Occupancy on Metallic Alloy Formation: The Role of HAXPES using Auger Parameters and Plasmon Features

Marie-Laure Abel, John F Watts

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The use of higher energy sources for XPS has been carried out for more than fifty years. During this time such X-ray sources have generally been developed in-house by interested researchers or offered as an option by manufacturers of conventional XPS systems. Such developments have recently been reviewed [1] and there are now three dedicated HAXPES systems available from different manufacturers. Much recent activity has centred on the increase of analysis depth of conventional XPS transitions achievable with HAXPES, but alternative studies have made use of the additional information accrued with deeper core levels, particularly when combined with the attendant Auger transition in the form of the Auger parameter. Studies of inorganic compounds focus on changes in relaxation energies which can be related to materials chemistry and sometimes structure [1]. In the studies of metals, the situation is not so straightforward, and this contribution will cover work carried out on a systematic series of metallic alloys using Auger parameters not accessible with conventional XPS.

The starting point for such investigations was the seminal work of Thomas and Weightman [2] who studied alloys of gold with zinc and magnesium. The availability of a higher energy source than AlKα enables deeper 1s core levels to be probed that the Mg1s in the work of Thomas and Weightman. The spectrometer used in the current work was a Scienta ESCA300 system equipped with a high-power rotating anode. In addition to the usual aluminium coating on the anode an additional stripe of chromium was added, the attraction being that the CrKβ satellite line meets Bragg conditions for fourth order reflections, with only minor adjustments of the usual quartz crystal monochromator, to provide a very convenient HAXPES source with a photon energy of 5946.7 eV [3]. This provided much useful information of on a number of important alloy systems [4-7]. This gave valuable data regarding charge redistribution that occurred on alloying but, from a metallurgical perspective, the systems that really attracted attention were the steels based around iron with a variety of alloying elements. The best approach was to make use of the Fe 1s-Fe*KLL* Auger parameter, which required a source able to access the Fe1s at a binding energy of approximately 7112 eV. The solution was the development of a $CuK\alpha_1$ source with a photon energy of 7805 eV [8, 9], for the ESCA300 spectrometer. This source was used to good effect to study charge distribution in a variety of steels [10] and vanadium compounds [11]. The versatility of the source was illustrated by the quality of the 1s spectra of the 3d metals scandium through to cobalt [12].

An additional, and somewhat unexpected benefit of the study of deeper 1s orbitals is the presence of plasmon loss structures associated with many of the spectra. In conventional XPS such features are rarely observed (Al2p being the most common) and are certainly not used analytically. In HAXPES the situation changes somewhat and initial work with the CrKβ source on a series of Al alloys with Mg and Si indicated that although no charge transfer was indicated by Auger parameter measurements, in the case of the Al-25Mg alloy a common shift in plasmon energy was observed for all core levels compared to the pure metals. This shift in plasmon energy is accounted for by the formation of an intermetallic phase Al_3Mg, rather than a solid solution [13]. Using this approach, it is possible to calculate valence band occupancy in a manner similar to that used in electron energy loss spectroscopy in the TEM.

[1] J F Watts, J E Castle, *Surf Interf Anal*, **56**, 408, (2024).
[2] T D Thomas, P Weightman, *Phys. Rev. B* **33**, 5406.
[3] S Diplas, J F Watts, S A Morton et al, *J Electron Spec*, **113**, 153, (2001).
[4] S Diplas, J F Watts et al, *Intermetallics*, **7**, 937, (1999).
[5] T Mitchell, S Diplas, P Tsakiropoulos et al, *Phil Mag*, **82**, 841, (2002).
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[7] M-L Abel, J F Watts, J A D Matthew, *Surf Interf Anal*, **33**, 775-780, (2002).
[8] N Moslemzadeh, J F Watts, *Surf Interf Anal*, **36,** 1119-1121.
[9] G Beamson, S R Haines et al, *J Elec Spec*, **142,** 151 – 162, (2005).
[10] N Moslemzadeh, S Diplas, *Surf Sci*, **602**, 216-225, (2008).
[11]G Beamson, N Moslemzadeh, J F Watts, *J Elect Spec*, **162**, 19-24, (2008).
[12] N Moslemzadeh, J F Watts et al, *J Elec Spec*, **152**, 129-133.
[13] M-L Abel, J F Watts, J A D Matthew, *Surf Interf Anal,* **33**, 775-780, (2002).

K3

Chemical bonding and electronic structure of metal dihydrides

C. Kalha[1], L. E. Ratcliff[2], G. Colombi[3], C. Schlueter[4], B. Dam[3], A. Gloskovskii[4], T.-L. Lee[5], P. K. Thakur[5], P. Bhatt[1], Y. Zhu[1], J. Osterwalder[6], F. Offi[7], G. Panaccione[8], and A. Regoutz[1,9]

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[6] Physik-Institut, Universität Zürich, Zürich CH-8057, Switzerland.
[7] Dipartimento di Scienze, Università di Roma Tre, Rome 00146, Italy.
[8] Istituto Officina dei Materiali (IOM)-CNR, Laboratorio TASC, in Area Science Park, Trieste I-34149, Italy.
[9] Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, Oxford OX1 3QR, UK.

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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: $YH_{2-\delta}$ and $TiH_{2-\delta}$.[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.

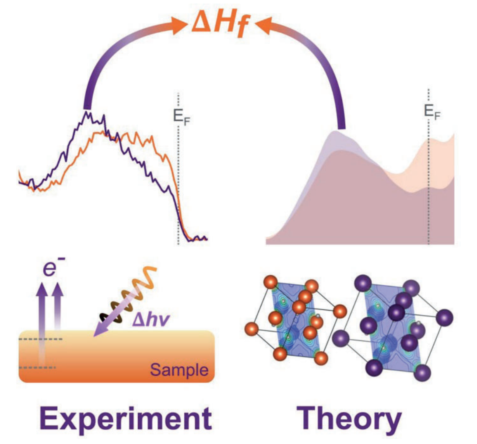


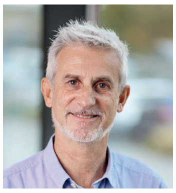
Fig. 1. Schematic overview of the core themes of this work including the comparison of experimental HAXPES spectra (top left) with density of states calculations (top right).

[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. Rossnagel, 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.

K4

Lab-scale HAXPES : issues to worry about towards improved analysis



O. Renault[1], R. Charvier[1], T. Bure[1], N. Gauthier[1], C. Robert-Goumet[2], B. Domenichini[3] and R. Lazzari[4]

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[2] *Univ. Clermont-Auvergne, Institut Pascal, 4 av. Blaise Pascal, F-63178 Aubière, France.*
[3] *Univ. Bourgnogne-Europe, 9 av. A. Savary, F-21078 Dijon Cedex, France.*
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With the advent of laboratory monochromatized hard.X-ray sources, HAXPES has become more and more popular over the recent years thanks to accessible instruments providing enhanced sub-surface sensitivity with decent enough energy resolutions for chemical fingerprinting [1-3]. Yet, the more regular use of lab-scale HAXPES faces many challenges when it comes to provide reliable and reproducible results [4]. For example, the combination of dramatically decreased ionisation cross-sections and characteristics of hard X-ray sources may result in more pronounced beam damages due to longer acquisition times or higher photon flux densities. Another challenge is related to the uniformity of a much larger sampled volume, in which non-uniform elemental depth distributions [5] and/or a potential gradient may occur. This has a big impact on the reproducibility of the elemental quantification, for which no well established, standardized procedure currently exist despite an increasing awareness on the challenges [4, 6] and some existing results in the field of transmission function correction [7]. In this talk, we will present selected examples of lab-scale HAXPES analysis which highlight some of these challenges, and in some case the solutions provided to come up with improved diagnostics. These will address the field of Mo compounds [6, 8], multilayer structures and semiconductor interfaces.

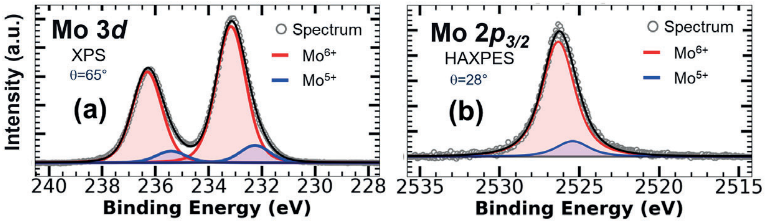

Fig. 1. The use of high-energy core lines at constant information depth for increasing the internal consistency in the quantification of sub-stoechiometric molybdenum oxide films [8].

[1] O. Renault *et al.*, "New directions in the analysis of buried interfaces for device technology by hard X-ray photoemission", *Faraday Disc*. 236, 288-310 (2022).
[2] B. Spencer *et al.*, "Characterization of buried interfaces using Ga Kα hard X-ray photoelectron spectroscopy (HAXPES)", *Faraday Disc*. 236, 311-337 (2022).
[3] S. Siol, C. Canciellieri, L. Jeurgens *et al.*, "Concepts for chemical state analysis at constant probing depth by lab-based XPS/HAXPES combining soft and hart X-ray sources", *Surf. Interface Anal*., 220, 802-810 (2020).
[4] K. Artyushkova, R. Leadley and A. Shard, "Introduction to reproducible laboratory hard x-ray photoelectron spectroscopy", *J. Vac. Sci. Technol*. A 42(5), 052801 (2024).
[5] T. Bure, O. Renault, C. Robert-Goumet *et al.*, "Assessing advanced methods in XPS and HAXPES for determining the thicknesses of high-k oxide materials: From ultra-thin layers to deeply buried interfaces", *Appl. Surf. Sci*. 609, 155317 (2023), and references therein.
[6] A. Boyer, N. Gauthier, O. Renault, *Surf. Sci. Spectra* 31(2), 024018 (2024).
[7] D. Alamarguy, N. Gauthier, T. Conard, O. Renault, R. Lazzari *et al.*, "Intensity-energy response function of Al/Cr-Kα x-ray photoemission instruments: An inter-laboratory study", *J. Electron Spectrosc. Relat. Phenom*. 276, 147486 (2024).
[8] R. Charvier, O. Renault, B. Domenichini *et al.*, *Appl.Surf. Sci*. 2025 (under review).

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K5

Advancing XPS Methodologies: 1) Transition Metals, 2) Rare Earth Elements, and 3) The Role of Adventitious Carbon

M.C. Biesinger[1,2], **J.D. Henderson**[1], **S. Buchanan**[1,3], **L. Grey**[1,2], **L. Pearson**[1,2]

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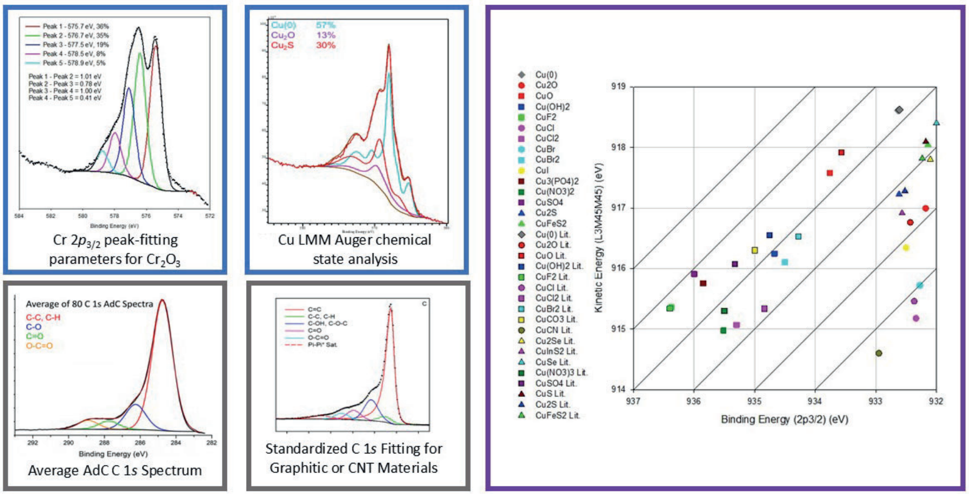
Chemical state X-ray photoelectron spectroscopic (XPS) analysis of first row transition metals and their oxides and hydroxides is challenging due to the complexity of the 2p spectra resulting from peak asymmetries, complex multiplet splitting, shake-up and plasmon loss structure, and uncertain, overlapping binding energies. Our work has shown that all the values of the spectral fitting parameters for each specific species, i.e. binding energy (eV), full width at half maximum (FWHM) value (eV) for each pass energy, spin-orbit splitting values and asymmetric peak shape fitting parameters, are not all normally provided in the literature and databases, and are necessary for reproducible, quantitative chemical state analysis.

We have worked toward a consistent, practical, and effective approach to curve fitting based on a combination of 1) standard spectra from quality reference samples, 2) a survey of appropriate literature databases and/or a compilation of literature references, 3) specific literature references where fitting procedures are available and 4) theoretical fittings, where available, of multiplet split reference spectra. The use of well characterized standard samples and fitting of the entire peak shape has been shown to increase our ability to accurately identify and (semi) quantify the various species present in mixed oxide/hydroxide systems. Additional chemical information has also been elucidated from Auger parameters and by using Wagner plots for compounds of Ni, Cu, Ga, In, Cd, and Zn. The unique spectral shapes of the LMM Auger peaks for these transition metals, particularly for Cu, as well as for Zn, In and Cd, have also been shown to be of use for chemical speciation. These methods have been shown to be effective in a wide variety of applications and are now being extended to rare earth element spectra (e.g. Er, Ce, La).

Additionally, a recent assessment of available charge corrections procedures for insulating samples will also be shown including recent work on defining the nature of adventitious carbon (AdC) and improving its merit for charge correction usage. The effect of the presence of AdC as it relates to the interpretation of the oxygen 1s spectrum will also be presented.



Cr $2p_{3/2}$ peak-fitting parameters for Cr_2O_3

Cu LMM Auger chemical state analysis

Average AdC C 1*s* Spectrum

Standardized C 1*s* Fitting for Graphitic or CNT Materials

Fig. 1. Curve-fitting examples of Cr $2p_{3/2}$ of Cr oxide (upper, left), Cu LLM of a mixed copper sample (upper, center), C 1s of an average of adventitious carbon samples (lower, left), standardized C 1s of graphitic type carbon (lower, center), and a Cu $2p_{3/2}$ – Cu LMM Wagner Plot (right).

One-step Photoemission Model: Core Levels to Valence Bands in Quantum Materials

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Angle-integrated and angle-resolved photoemission in the soft and hard X-ray regimes have become essential tools for investigating the bulk properties of various materials. In practice, enhanced bulk sensitivity can be achieved through threshold photoemission. To accurately replicate experimental results, key effects such as matrix elements, photon momentum, phonon excitations, and lattice vibrations must be properly accounted for. In this work, we present a generalized one-step photoemission model implemented within the Munich SPR-KKR program package [1, 2]. This computational framework coherently describes photoelectron excitation, transport to the surface, and emission into the vacuum. Moreover, it is applicable across a wide photon energy range, from a few electron volts to over 10 keV. The model's ability to incorporate correlation and thermal effects, in combination with the coherent potential approximation (CPA) method [3], is demonstrated through various examples. The analysis of ARPES data in terms of three-dimensional electron dispersions typically relies on the free-electron approximation for the photoemission final states. However, at high excitation energies, these final states can become significantly more intricate, involving multiple Bloch waves with distinct out-of-plane momenta. The interpretation and related treatment for multiband final states will be discussed [4]. Special emphasis is placed on the implementation of X-ray photoelectron diffraction, including the treatment of Kikuchi fine structure and circular dichroism in angular distributions (CDAD) for the core levels [5]. Furthermore, the model has been instrumental in confirming the altermagnetic lifting of Kramers spin degeneracy, a key feature of altermagnetism [6], which represents a novel class of magnetism with significant implications for both fundamental research and technological applications.

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K7

HAXPES Inelastic Background for Characterization of Nano-Structured Materials

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Quantitative characterization of nanostructures by analysis of the inelastic background in photoelectron spectroscopy (XPS and HAXPES) is now a widely used method. [1,2] The method is non-destructive, and the probing depth is considerably larger than the usually quoted 3 IMFP because the inelastically scattered electrons originate from larger depths than the electrons in the peak and it is typically ~10 IMFP but can be ~20 IMFP in cases where the background can be followed over several hundred eV. The latter is often the case with HAXPES because the separation between deep lying core electrons can be much larger compared to those excited with conventional XPS. With HAXPES, the photo electron energy and thereby the IMFP and the probing depth is also increased and several examples with analysis of structures at > 100 nm depth have been reported [2]. Since lab based HAXPES is now commercially available it is being installed in many labs and its application in nanotechnology is expected to rapidly increase considerably.

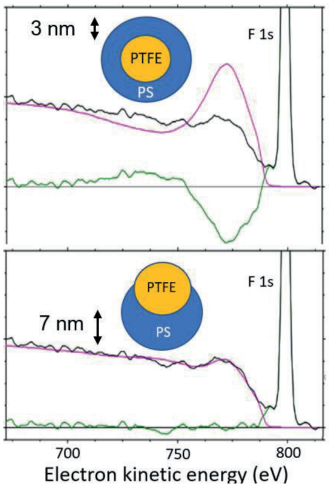

Fig. 1. QUASES analysis of a PS coated nanoparticle. The analysis shows that the coating of the PTFE core is incomplete. Data from [4]. For detailed step by step analysis, see: Video 13 in [6].

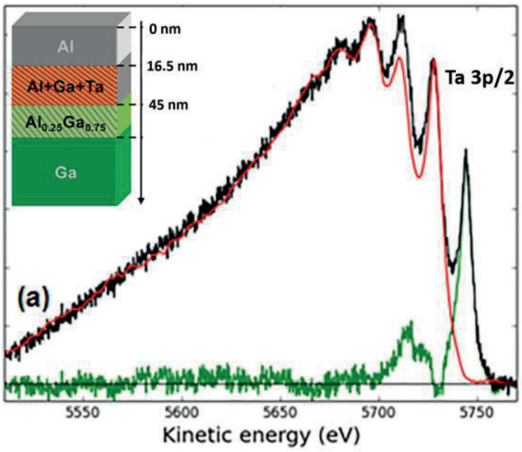

Fig. 2. QUASES analysis of a Ta layer in a stack. From [5]

In the talk, we will discuss several practical applications of the QUASES [3] software. Fig. 1 shows how it can be used to determine the core-shell thickness and determine that the shell material doesn't fully encapsulate the core [4]. Fig. 2 demonstrates its ability to determine the depth and thickness of a Ta layer in a stack [5]. The method is non destructive and in [5] the gradual diffusion of Ta atoms (both towards the surface and into the bulk) could be followed quantitatively as a function of annealing time and temperature.

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HAXPES at PETRA III and IV: electronic structure, operando devices and in-situ catalysis

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The application of photoelectron spectroscopy using hard X-rays (HAXPES) is becoming increasingly popular as a powerful spectroscopic tool in materials science. In HAXPES, electrons are excited by photons in the energy range of 2.4 – 10keV and their energy dispersion is analysed. The obtained spectra yield valuable information, not only on the chemical composition, but also on the chemical state of the elements in the sample. Analysis of their angular distribution reveals additional information on electronic band structure and atomic structure of the sample. Owing to their high kinetic energy these electrons interact weakly with matter and can travel through:

- tens of nanometres of solid – allowing for the study of buried layers,
- tens of micrometers of gas – allowing for the study catalytic reactions under realistic conditions.

This makes HAXPES particularly interesting for in situ and operando experiments. X-ray standing wave generation and photoelectron diffraction further adds the possibility to correlate electronic and atomic structure.

The X-ray undulator beamline P22 at PETRAIII is fully dedicated to hard X-ray photoelectron spectroscopy (HAXPES) techniques. As such, the beam line hosts four specialised experimental end stations for high-resolution studies of the electronic and chemical structure of complex materials, realistic device-like structures and catalytic interfaces.

The 'workhorse' instrument at P22 is a HAXPES hemisphere which is offering ample opportunities for operando device characterisation, depth profiling, and chemical analysis. The ambient pressure XPS system (POLARIS) addresses catalytic properties of surfaces in industrially relevant conditions. Anovel hard X-ray momentum microscope (HarMoMic) explores the electronic and atomic structure by wide-field imaging of band dispersions and electron diffraction patterns. The HAXPEEM setup is dedicated to investigations of laterally resolved chemical and elemental structure. All instruments are now in full user operation implemented and operated in close collaboration with external user groups and as such reflect the wide range of scientific fields currently covered by the international HAXPES community.

The P22 beamline at PETRA III received first light in November 2017 with first user experiments conducted in June the following year. Since then P22 has produced more than 100 publications.

Probing emergent phenomena at oxide interfaces with HAXPES and standing waves

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The interplay between charge, spin, and orbital degrees of freedom at oxide interfaces gives rise to emergent electronic and magnetic states, offering pathways to novel functionalities in spintronic and electronic devices. In this talk, I will present a comprehensive investigation of the electronic and magnetic structures at buried interfaces in $LaNiO_3/CaMnO_3$, $CaMnO_3/CaRuO_3$, and $VO_2/LaAlO_3/TiO_2$ heterostructures using a hard x-ray photoelectron spectroscopy (HAXPES), in conjunction with standing-wave photoelectron spectroscopy and resonant magnetic reflectivity. Our studies reveal that interfacial ferromagnetism can be stabilized in nonferromagnetic systems through precise interface engineering and thickness control, as demonstrated in $LaNiO_3/CaMnO_3$ and $CaMnO_3/CaRuO_3$ superlattices. In $LaNiO_3/CaMnO_3$, we establish a direct correlation between the depletion of Ni 3d e_g states and the suppression of interfacial ferromagnetism on Mn sites in $CaMnO_3$ [1]. In $CaMnO_3/CaRuO_3$, we show that defect chemistry, particularly the presence of oxygen vacancies, can play a crucial role in modifying the magnetic moments at the interface [2]. Finally, we show that interfacial charge transfer in $VO_2/LaAlO_3/TiO_2$ enables modulation of the VO_2 metal-insulator transition temperature over a range of 65 K without doping or strain [3]. These findings underscore the power of combining bulk-sensitive x-ray techniques to probe and manipulate interfacial phenomena, offering insights into the design of tunable correlated oxide interfaces for future electronic and spintronic applications.

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Operando HAXPES of functional quantum materials

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Materials create functionalities, and functionalities form the foundation of our technical world. Quantum materials open up the possibility of developing efficient or even novel functionalities. In these materials, it is the complex quantum mechanical interaction of electrons that leads to quantitatively new behaviour. To understand and eventually tune the emerging functionalities, one needs to see how electrons behave in real-world devices. A powerful tool to access electronic phenomena in materials and devices is hard x-ray photoelectron spectroscopy. HAXPES has recently transformed to a true operando technique to directly probe dynamic electronic functions using nanofocused x-rays and bias-driven nonequilibrium conditions [1].
Here, I will give examples for electronic functionalities of quantum materials and the possibilities of probing real-world devices. The focus will be on results obtained with ferroelectric oxides and nitrides sandwiched between metallic electrodes in prototype capacitor structures. The interplay between electronic interaction on sub-nanometer length scales ultimately determine the electrical switching, performance (in)stability and fatigue of macroscopic devices. Spectroscopic electronic fingerprints include i.a. chemical shifts, rigid binding energy shifts and valence band offsets, which give snapshots of the local and global electron distribution within a heterostructure [2]. Excitingly, defects are a key aspect of ferroelectricity – but their spectroscopic detection is much more subtle than that of atomic properties, as it means detecting something absent. This requires access to indirect signatures, often of very low intensities, and experimental condition that is difficult in practice. Our recent development includes detecting defects and oxygen/nitrogen vacancies in ferroelectric HfO2- and AlXN-based ferroelectrics. Scenarios for electronic compensation mechanisms are discussed in the frame of band alignment analyses [3].

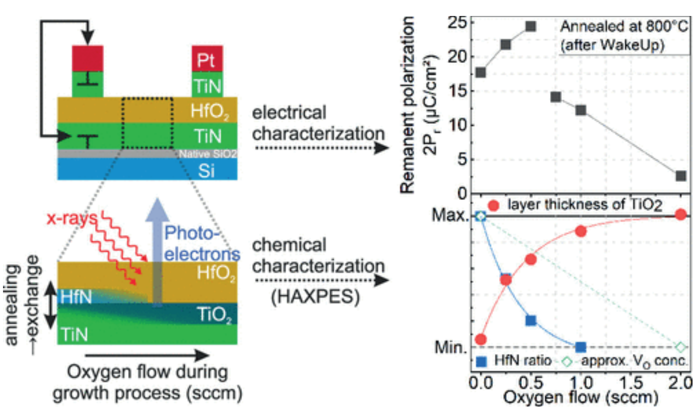

Fig. 1. Interface formation between ferroelectric HfO₂ and TiN electrodes studied by HAXPES, directly correlated to the ferroelectric polarization characteristics of TiN/HfO₂/TiN capacitors. The maximum ferroelectric remanent polarization is tied to a threshold oxygen vacancy concentration, enabling the controlled design of ferroelectricity in HfO2-based capacitors [1].

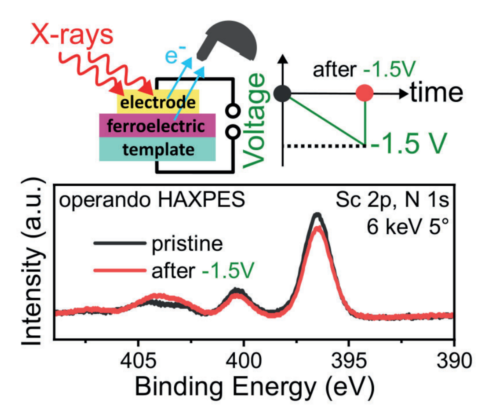

Fig. 2. Scheme of operando HAXPES experiments under applied bias voltage. Example of a AlScN ferroelectric capacitor measured in pristine and biased state. The Sc2p core level shifts indicate accelerated oxidation when electrically switched [2].

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NOTES

Classical versus quantum assessment of final-state effects in XPS/HAXPES of bulk materials

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Final-state effects in XPS correspond to the relaxation of electronic subsystem in response to the core-hole creation. Such effects can be effectively isolated experimentally by measuring Auger parameter shifts with respect to a reference phase, with HAXPES enabling characterization of bulk material by extracting Auger electrons well below the surface. Classical electrostatic theory enables interpretation of final-state effects in compounds dominated by extra-atomic relaxation i.e., polarization of nearest-neighbor ligands [1]. We have demonstrated that such theory combined with ab-initio-accurate atomistic simulations can describe Al-O-based compounds, predicting effective polarizabilities of O and OH ligands (see Fig. 1 and Ref. [2]). Alternatively, quantum assessment of final-state effects can be done using Δ-Kohn-Sham scheme [3], as shown in Fig. 2 for bayerite. However, to avoid Coulomb interactions across periodic boundaries in bulk supercells, the compensating charge has to be added to the system after core-electron removal, which leads to an underestimation of the extra-atomic relaxation component. In this talk, we will discuss the strategies to bridge classical and quantum approaches for solids to enable predictive modeling.

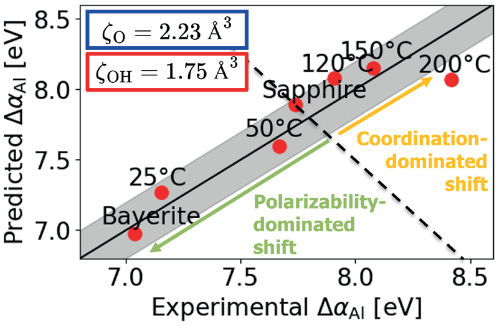

Fig. 1. Predicted vs. experimental Auger parameter shifts for amorphous alumina thin films (atomic layer deposited at different temperatures) as well as crystalline compounds [2]. The -O and -OH ligand polarizabilities are extracted from atomistic simulations and the electrostatic theory of extra-atomic relaxation [1].

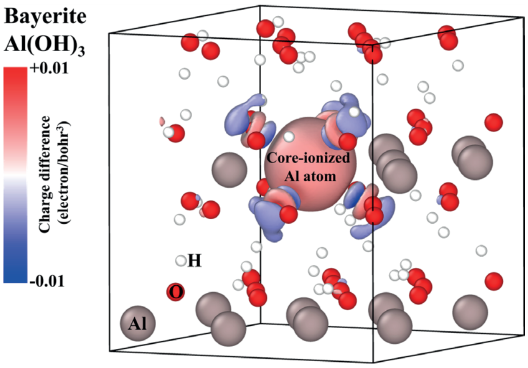

Fig. 2. -OH ligand polarization visualized by charge density change in response to the core-hole insertion in the central Al atom, with blue and red isosurfaces indicating charge depletion and charge gain areas, respectively [unpublished]. Calculations are done with AiiDA + Quantum Espresso using the Δ-Kohn-Sham scheme [3].

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I2

Chemical State Analysis for the Accelerated Development of Semiconducting and Insulating Thin Film Materials

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Functional thin films are critical for advancing technologies across various applications. As the demand for tailored material properties grows, the complexity of materials and their associated parameter spaces increases significantly. To address these challenges, high-throughput experimental approaches have become increasingly prevalent in research laboratories worldwide.

Despite its importance in conventional materials development, X-ray photoelectron spectroscopy (XPS) remains rather underutilized in high-throughput materials development. This presentation will demonstrate how XPS analysis can complement other high-throughput characterization techniques, offering unique advantages for accelerating materials discovery and optimization.

Results will be presented for a range of material systems, including oxides [1] and nitrides [2,3]. Additionally, the discussion will include best practices for analyzing insulating or semiconducting materials. These materials often exhibit differential charging and sometimes even X-ray-induced photovoltages. A particular focus will be placed on Auger parameter (AP) measurements as a robust tool for chemical state analysis. This method is uniquely suited for insulating materials as it is insensitive to surface charging of erroneous calibration of the binding energy scale.[4] In addition, the AP is highly sensitive to changes in the local chemical environment and can provide important insight into chemical state and binding environment of the constituent elements. It will be shown that using the AP even changes in coordination can be resolved making it a valuable tool in the exploration of new phase spaces. This is especially useful in materials with low crystallinity where conventional phase screening via X-ray diffraction often leads to ambiguous results (see Fig. 1). The concepts and methodologies discussed are applicable to both XPS and HAXPES analysis. Whereas HAXPES enables access to previously inaccessible transitions.

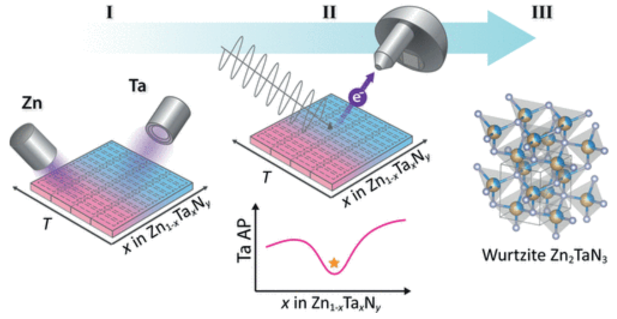

Fig. 1. Chemical state analysis offers great utility in the exploration of new materials with low crystallinity.

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From Molecular Structures to XPS Spectra and Back: Challenges and Intrinsic Limitations

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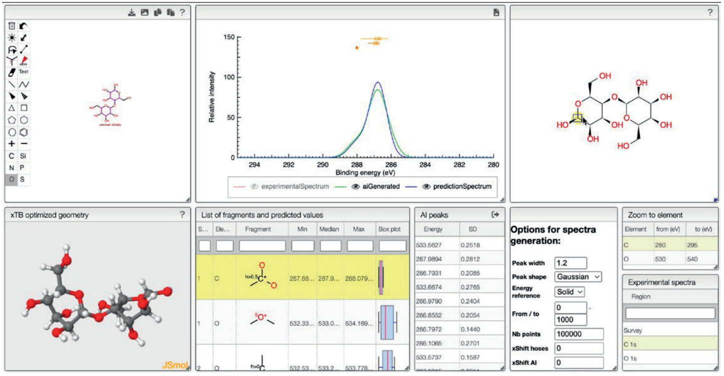
As materials grow more complex, the demand for advanced analytical techniques rises. These techniques are essential to (i) unravel the chemical and physical structures of materials and (ii) link these structures to their properties and performance. X-ray Photoelectron Spectroscopy (XPS) stands out as a powerful method, delivering rich, detailed data. Yet, the intricate nature of XPS signal formation presents serious challenges to anyone willing to extract reliable insight from the measurement spectra. These challenges can be mitigated by the appropriate use of statistical methods, simulations techniques such as density functional theory (DFT), and more recently digital innovations such as machine learning (ML) and artificial intelligence (AI). For what matters to us - namely XPS predictions and data interpretation; DFT has the ability to provide robust estimates of binding energies within established limits. These computationally intensive estimates can then be extended by ML into larger 'predicted' datasets at a fraction of the cost. Finally, AI has the ability to analyzes these extended datasets, enhancing the potential to interpret XPS spectra.

This presentation will center on molecular structures - often introduced into materials for passivation, band structure tuning, interfacial effects, or biomedical surface chemistry, with e.g., DNA interactions with functionalized substrates. Molecular structures might be seen as deceptively simple: a series of atoms bound together following some sets of rules. Nevertheless, the complexity explodes combinatorially. Moreover, the surjective nature of XPS signals complicates matters, as multiple structures can produce nearly identical spectra within experimental resolution. This raises a critical question: even with flawless simulations and digital tools, how far can we go in retrieving molecular structures from experimental data? Drawing on a digital workflow firmly grounded in experimental reality, I will outline the steps needed to gain insight and assess the inherent boundaries of translating XPS spectra into molecular candidates.



xTB optimized geometry

List of fragments and predicted values

S...	Ele...	Fragment	Min	Median	Max	Box plot
1	C		287.88...	287.9...	288.079...	
1	O		532.33...	533.0...	534.169...	
2	O		532.53...	533.2...	533.778...	

AI peaks

Energy	SD
533.5627	0.2518
287.9894	0.2812
286.7931	0.2085
533.6674	0.2765
286.9790	0.2404
286.8552	0.2054
286.7972	0.1440
286.1065	0.2701
533.5737	0.1587

Options for spectra generation:

Peak width: 1.2
Peak shape: Gaussian
Energy reference: Solid
From / to: 0 - 1000
Nb points: 100000
xShift hoses: 0
xShift AI: 0

Zoom to element

Element	from (eV)	to (eV)
C	280	295
O	530	540

Experimental spectra

Region

Survey
C 1s
O 1s

methods. The signal from each atom can be interactively revealed.

I4

In situ HAXPES at SLS: achievements and perspectives

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Since 2012, research groups at PSI and ETH have designed and built an ambient pressure X-ray photoelectron spectroscopy setup consisting of a commercial Scienta R4000 HiPP-2 analyzer connected to suitable experimental chambers.[1] Such a setup has been commissioned to investigate solid-gas and liquid interfaces with soft and tender X-rays at the Swiss light source synchrotron.[2,3] In 2018, the endstation has been permanently connected to the X07DB site and named In Situ spectroscopy (ISS) beamline. Meanwhile, first the university of Zurich and then EMPA have joined the consortium and expanded the research activity towards the investigation of buried (solid-liquid) interfaces by means of tender X-rays.[4]

In my presentation, I will describe the main research activities at ISS and focus on results obtained in the investigation of buried interfaces. I will describe the development of the solid-liquid interface chamber (see Figure 1), showing some scientific highlights regarding the dip and pull technique. Positive and negative aspects will be listed, with some emphasis on possible future developments.

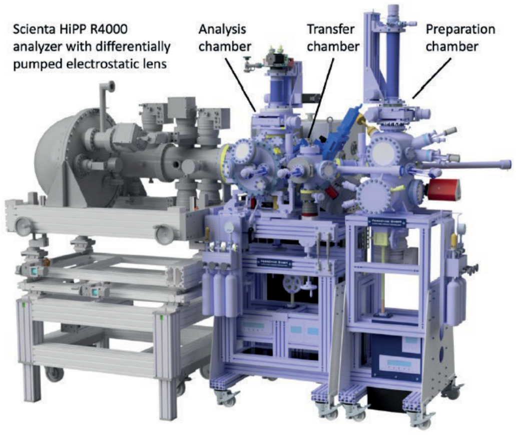

Fig. 1. Sketch of the solid-liquid interface chamber connected to the Scienta R4000 Hipp-2 analyzer available at the ISS beamline.

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HAXPES-XPS combination reveals extended surface structure of catalysts

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Only the chemical state of the surface of a catalyst defines its performance. However, the surface depends on the applied external conditions and the underlying bulk. We will present two examples from thermo-catalysis and electrocatalysis showcasing how the interplay of external conditions and bulk chemistry affects the performance of a catalyst. The chemical analysis of surface and bulk is a great challenge as most methods reveal either the surface or the bulk. We demonstrate the use of the HAXPES-XPS combination as a powerful, practical and non-destructive tool for quantitative surface (~1 nm) and subsurface/bulk (~10 nm) chemical composition analysis of catalysts.

As a first example, we introduce the perovskite-type material $Er_{0.15}La_{0.15}Sr_{0.55}Ti_{0.95}Cu_{0.05}O_3$ (ESTN) as a promising cataluminescence material, which converts chemical energy directly into light [1]. The chemical composition of its surface and the subsurface changes upon reduction and reoxidation, a behavior, which is very typical in doped perovskites. The corresponding optical changes are visible even by eye and are relevant for the cataluminescence performance. The observed diffusive reflectance UV-Vis spectra (DRUVS) are typical for light-plasmon interactions, indicating the formation of Cu-nanoparticles on the surface. The HAXPES-XPS analysis confirms the exsolution of Cu upon reduction and reveals the associated electronic structure changes as a function of depth.

After the introductory example of a thermo-catalytic system, we will showcase the methodology of XPS/HAXPES combination on an electro-catalytic surface. Fe-Ni surfaces are known for their excellent performance for the oxygen evolution reaction (OER) [2]. Here reduction and oxidation are induced by the electro-chemical potential applied to the electrode. Like the thermo-catalytic example, optical changes give insights into the chemical and structural changes of the oxide formed during OER. However, the complexity of the associated redox-reactions and segregation phenomena led to a controversial debate in the community on the active surface/sites. The XPS/HAXPES unravels the various oxide-, hydroxide- and oxyhydroxide- phases, and the segregation of Fe. The results underscore the complexity of the system, however, being a post-mortem method, the question of the active surface remains elusive.

We will conclude the talk with an overview of catalytic systems studied by post-mortem XPS/HAXPES combination and discuss its advantages and limitations.

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Characterisation of cupric oxide surfaces generated by plasma oxidation and radiochemical processes in the Large Hadron Collider

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After the first long shutdown (LS1) that included venting of the Large Hadron Collider (LHC) beam vacuum system, an increment of the beam-induced heat load to the cryogenic system, which was distributed irregularly across the sectors of the accelerator ring, occurred during operation throughout the experimental run 2 [1,2]. After the second shutdown (LS2), a further degradation was noticed [3], which is indicating critical limitations for the future when the system is planned to be operated at higher proton bunch population to achieve higher luminosity [4]. The process of electron cloud formation was identified as the reason for the observed changes. The resulting electron density is strongly dependent on the secondary electron yield (SEY) of the beam pipe material, which is sensitive to chemical surface transformations and work function changes.

In LS2, several beam screens from sectors with different heat load were removed from selected superconducting LHC magnets. Samples from the Cu surfaces that face the proton beam were extracted for material analysis. Measurements by classical X-ray photoelectron spectroscopy with Al K_α radiation revealed the formation of a cupric oxide (CuO) surface layer in regions with high heat load, while magnets with relatively low heat load exhibit merely a Cu_2O-like surface oxide layer [5]. This difference in chemical nature has also consequences on the SEY of the surface during operation, and thus on the density of the formed electron cloud. Considering the special environmental conditions of pressures in the 10^{-12} mbar range in the cryogenic beam vacuum of the LHC and beam screen surface temperatures between 5 and 20 K, the formation of CuO was surprising and could only be explained by radiochemical transformation processes on the Cu surface due to exposure of the adsorbate-loaded surface by electrons. Model experiments on lab scale revealed that the CuO formation process requires cryogenic temperatures and depends on the quantity of surface adsorbates, e.g. hydrocarbon and hydroxide bonds.

Moreover, as the CuO surface layer significantly influences the SEY, it is essential to know its thickness and ideally its composition profile. There are several technical challenges for such analyses on copper surfaces: 1. depth profiling leads to immediate decomposition of the CuO layer, thus falsifying results in XPS or TOF-SIMS, 2. the kinetic energy of the Cu 2p electrons excited by Al K_α photons is very low as is their depth of information which limits angular-dependent measurements, 3. a proper identification of the oxidation state of Cu requires the comparative analysis of photoelectron spectra, including binding energy and shape of satellite features, and Auger-Meitner [6] electron spectra, and 4. technical Cu surfaces with different adsorbates and mixed compounds are complicated to characterise. We have addressed the thickness and film composition determination using Cr K_α based HAXPES measurements of the extracted beam screen samples and of artificial CuO layers on Cu created in a remote oxygen plasma. I will discuss the results of the measurements and thickness estimations, the limitations of this methodology and potential pathways for further analysis refinement using additional available photon lines for photoelectron spectroscopy.

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I7

Real-time insights into all-solid-state batteries interfaces with *operando* XPS

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All-solid-state batteries (ASSBs) offer a promising alternative to conventional Li-ion batteries by increasing the volumetric energy density and enhancing safety. However, their performance is often hindered by the limited Li-ion transport across the solid electrolyte (SE)/active materials (AMs) interfaces. This limitation arises primarily from the SE's narrow thermodynamic stability windows and the parasitic (electro-)chemical side reactions with the AMs. These interfacial processes lead to the rise of cell impedance and performance degradation over time. [1, 2]
The comprehensive understanding of the SE oxidation/reduction byproducts and the interface chemical evolution remains elusive, largely due to the buried nature of these interfaces and the limitations of conventional surface-sensitive analytical techniques, especially during *operando* conditions.

In this talk, we will present recent advancements in *operando* X-ray photoelectron spectroscopy (XPS),[3] enabling real-time monitoring of the interfacial (electro-)chemical evolution in operational ASSB working electrodes. *Operando* XPS measurements are made possible thanks to the low vapor pressure of the SE in ultra-high-vacuum (UHV) and to the unique and versatile electrochemical custom-made cell, ensuring reliable electrochemistry.[4] We will demonstrate how the in-house *operando* XPS using Al Kα X-ray source is a powerful method to probe the electrified solid-solid interfaces, providing valuable insights into: (i) identifying and quantifying the potential-dependent redox byproducts of the SE, (ii) the (electro-)chemical evolution of the SE/AMs interfaces, (iii) unveiling the complex reversible redox reactions of cathode or anode AMs, and (iv) determining the electrical properties of the interface byproducts. Through various case studies on working electrodes (e.g., Li_3PS_4:VGCF, Li_3PS_4:$LiCoO_2$,[5] and Li_3PS_4:SnO_2,[6]), we will illustrate the dynamic surface and interfacial processes occurring in real-time during battery cycling.

Finally, we will discuss the versatility of our *operando* electrochemical cell for applications beyond soft XPS including hard XPS, Auger/XPEEM imaging,[7] and XAS measurements at laboratory or synchrotron facilities.

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I8

Surface Chemistry of $Li_7La_3Zr_2O_{12}$ Solid-State Electrolytes

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The current battery research landscape is witnessing a significant shift toward substituting liquid electrolytes in Li-ion batteries with safer, nonflammable solid alternatives, particularly focusing on $Li_7La_3Zr_2O_{12}$ (LLZO) with garnet-type structure [1, 2]. LLZO solid-state systems hold promise not only in addressing the pressing need for safe and temperature-tolerant batteries but also in enhancing their energy density and cycle life compared to traditional liquid-electrolyte-based counterparts. Such prospects stem from intrinsic properties of LLZO including its superior thermal stability, high Li-ion conductivity of up to 1 mS cm^{-1} at room temperature (RT), relatively low electronic conductivity of *ca*. 10^{-8} S cm^{-1} at RT, and chemical stability in contact with metallic Li. However, integrating LLZO solid-state electrolytes (SSEs) into batteries has encountered substantial challenges, particularly in sintering processes. Major issues revolve around maintaining the proper Li stoichiometry (cubic LLZO structure, c-LLZO) after sintering, ensuring reproducibility of the LLZO microstructure, and addressing cost and scalability concerns associated with the sintering process. In response, recent efforts have focused on innovative sintering technologies for LLZO ceramics, including microwave-assisted sintering, spark plasma sintering, flash sintering, and ultrafast (UF) sintering.

This study presents an in-depth analysis of the surface chemistry of UF-sintered LLZO using comprehensive techniques, including hard X-ray photoelectron spectroscopy (HAXPES), depth-profiling X-ray photoelectron spectroscopy (XPS) and focused-ion-beam time-of-flight secondary ion mass spectroscopy (FIB-TOF-SIMS) [3, 4]. Our investigation uncovers a striking difference between the surface of UF-sintered and conventionally sintered LLZO, revealing predominant surface contamination by Li_2O up to *ca*. 40 nm depth in the case of UF processing. Comparative synchrotron X-ray diffraction data during UF and conventional sintering elucidate the origin of surface contamination. We propose a viable solution to this issue through an additional heat treatment (HT) step at 900 °C after UF sintering, as corroborated by XPS and FIB-TOF-SIMS measurements. Furthermore, we present a comparative assessment of the electrochemical performance of Li/LLZO/Li symmetric cells based on UF-sintered LLZO pellets, both with and without the post-HT step, underscoring the pivotal role of an uncontaminated LLZO surface.

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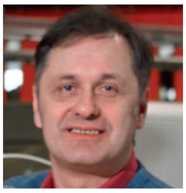
I9

Soft-X-ray ARPES insights into k-resolved electronic structure of functional materials



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Fundamental characteristics of solid-state systems such as electron dispersions, Fermi surface, electron-boson coupling, etc. resolved in **k**-space are essential for understanding their physical properties. This information can be gained with angle-resolved photoelectron spectroscopy (ARPES). Pushing this technique to soft-X-ray energies around 1 keV adds larger probing depth, sharper definition of three-dimensional **k**, and chemical-state specific resonant photoexcitation. At the same time, the Debye-Waller factor and recoil effects, depleting the coherent spectral intensities, remain moderate in this energy range. These properties make soft-X-ray ARPES ideal for 3D bulk materials, buried interfaces/heterostructures and impurity systems relevant for electronic and quantum devices.

Bulk materials. – Applications of soft-X-ray ARPES to bulk materials employ sharper definition of out-of-plane **k** due to delocalization of photoelectrons over larger escape depth. Examples include 3D-nested Fermi surface of VSe_2 forming exotic charge-density waves [1], 3D topological structures such as Weyl cones and chiral fermions [2], etc.

Buried heterostructures. – Semiconductor systems are illustrated by AlN/GaN high-electron-mobility transistor (HEMT) heterostructures. Soft-X-ray ARPES resolves band dispersions and an anisotropic Fermi surface (Fig. 1) of interfacial quantum-well states [3]. A representative semiconductor/superconductor interface is GaN/NbN. We identify a large **k**-space separation between the valence band maximum of GaN and the Fermi states in NbN (Fig. 2) which protects its superconductivity [4]. A paradigm example of an oxide interface is $LaAlO_3/SrTiO_3$. Here, resonant photoexcitation at the Ti *L*-edge resolves the interfacial charge carriers, whose peak-dip-hump spectral lineshape identifies multiphonon polarons with intrinsically small mobility [5].

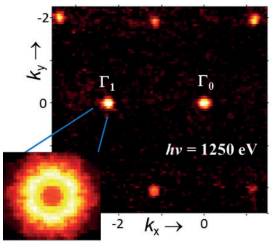

Fig. 1. Fermi surface of the interfacial quantum-well states in AlN/GaN HEMTs. Its anisotropy propagates to anisotropy of the saturation current in these HEMTs.

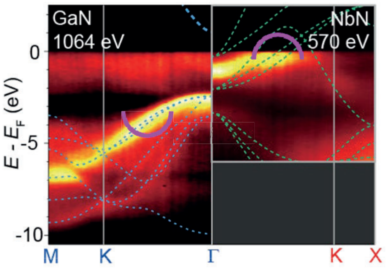

Fig. 2. Bandstructures of GaN and NbN matching at tGaN/NbN heterojunction. Large separation of GaN bands from the Fermi states in NbN (magenta semicircle) protects superconductivity.

Impurity systems. – A paradigm impurity system is Ga(Mn)As, a dilute magnetic semiconductor. Resonant photoexcitation at the Mn *L*-edge identifies energy alignment and hybridization of Mn impurities with host GaAs, elucidating their ferromagnetic interaction [6]. Further topics include magnetic impurities in topological matter.

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HAXPES analysis of native oxides on steel

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This study employs Hard X-ray Photoelectron Spectroscopy (HAXPES) to investigate the chemical composition of native oxides on steel surfaces, with a focus on their interaction with hydrogen.

In the context of a growing hydrogen economy, a detailed understanding of hydrogen interactions with steel surfaces is becoming increasingly critical. While the detrimental effects of hydrogen embrittlement in steels are well documented, the role of the thin native oxide layer that spontaneously forms on steel surfaces has received comparatively little attention.

Native oxides, only a few nanometers thick, are known to offer some protection against corrosion but may also influence hydrogen ingress, trapping, and diffusion. Understanding the role of native oxides in hydrogen uptake and transport is essential for developing effective mitigation strategies.

This study focuses on the chemical changes occurring within native oxide layers on steel surfaces upon hydrogen exposure. Hydrogen was introduced electrochemically using a custom-designed flow cell operating inside an argon-filled glovebox, vacuum-connected to the HAXPES instrument. This setup allows precise control of the environment during hydrogen charging, minimizing surface contamination and preventing unwanted oxidation or reduction processes. One side of each sample was exposed to hydrogen through electrochemical charging, while the opposite side remained in contact with inert gas, preserving the surface of interest from oxygen exposure.

XPS/HAXPES was used to characterize the native oxide layer before and after hydrogen charging. The results reveal significant changes in the oxide composition, including the reduction of Fe^{3+} to Fe^{2+} and metallic Fe, as well as the reduction of Cr^{3+} to metallic Cr.

This work demonstrates the potential of HAXPES as a powerful tool for studying hydrogen interactions with steel and other materials. The findings contribute to a deeper understanding of hydrogen interactions with native oxides and pave the way for the development of more resistant steel alloys for industrial applications.

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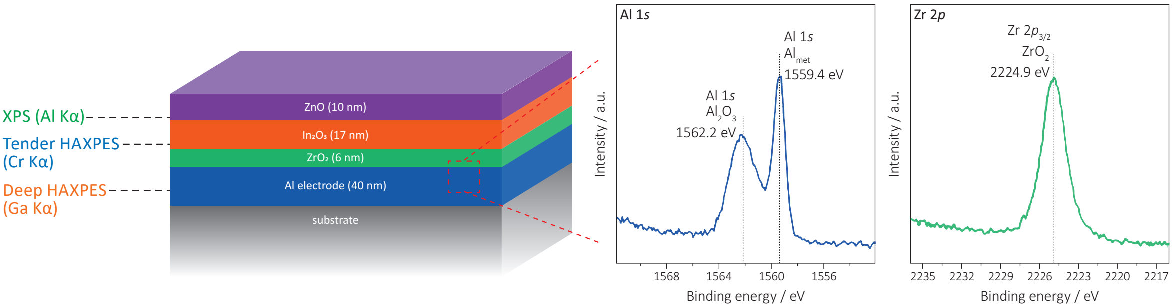
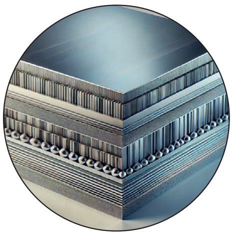
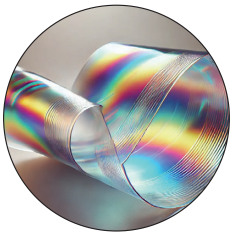

XPS (Al Kα)
Tender HAXPES (Cr Kα)
Deep HAXPES (Ga Kα)
ZnO (10 nm)
In₂O₃ (17 nm)
ZrO₂ (6 nm)
Al electrode (40 nm)
substrate
Al 1s
Al 1s
Al$_{met}$
1559.4 eV
Al 1s
Al$_2$O$_3$
1562.2 eV
Intensity / a.u.
1568
1564
1560
1556
Binding energy / eV
Zr 2p
Zr 2p$_{3/2}$
ZrO$_2$
2224.9 eV
Intensity / a.u.
2235
2232
2229
2226
2223
2220
2217
Binding energy / eV



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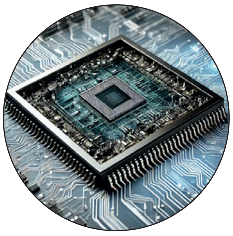

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