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BOOK OF ABSTRACTS

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Book of Abstracts

CONTENTS

PLENARY LECTURES	6
KEYNOTE LECTURES	11
ORAL PRESENTATIONS.....	26
Biomaterials engineering and analysis.....	26
Catalysis.....	38
Corrosion.....	48
Energy storage and conversion	59
Heritage and geology	79
<i>In-situ</i> and near ambient pressure analysis.....	81
Machine learning in surface science	91
Metals.....	92
Modelling.....	101
Nanomaterials and nanostructuring	107
Polymers.....	120
Semiconductor materials	125
Surfaces of porous materials	143
Technique development and metrology.....	151
Thin films and coatings.....	184
POSTERS	209
Biomaterials engineering and analysis.....	209
Catalysis.....	213
Corrosion.....	226
Data analysis	227
Glasses, Ceramics, and Oxides	231
<i>In-situ</i> and near ambient pressure analysis.....	236
Machine learning in surface science	240
Metals.....	243
Nanomaterials and nanostructuring	248
Semiconductor materials	256
Surfaces of porous materials	258
Technique development and metrology.....	261
Theoretical modeling of surfaces and interfaces	267
Thin films and coatings.....	270

PLENARY LECTURES

Investigation of reactions at liquid-vapor interfaces by X-ray photoelectron spectroscopy

Hendrik Bluhm (*Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin, Germany*)

Heterogeneous reactions at liquid-vapor interfaces play a major role in the environment and atmosphere. The investigation of chemical reactions and transport processes, in particular at aqueous solution-vapor interfaces, at realistic partial pressures, temperatures and time scales, is thus of great importance for a better understanding and theoretical modeling of some of the most important processes in the environment and atmosphere. This talk discusses the challenges and obstacles for measuring heterogeneous chemical reactions at liquid-vapor interfaces using X-ray photoelectron spectroscopy (XPS) and suggests experimental strategies to overcome these challenges. We will also demonstrate how inelastic scattering effects can be used to overcome the inherent depth-resolution limit in XPS. The talk will in addition showcase an investigation of trace gas uptake by an aqueous solution, which indicates that the mechanism of gas uptake at the interface differs markedly from uptake in the bulk of the solution, which has implications for the modeling of interfacial reactions in the atmosphere.

Keywords: Liquid-vapor interfaces, XPS, Heterogeneous reactions

Electronic Structure and Depth-Resolved Chemical State Analysis of Functional Materials by Laboratory XPS and HAXPES

Claudia Cancellieri (*Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland*)

Understanding the chemical bonding and electronic structure of materials at the atomic scale is essential for the development of advanced functional materials and devices. In this talk, I discuss how laboratory-based X-ray and hard X-ray photoelectron spectroscopy (XPS/HAXPES) can provide depth-resolved insights into the chemical and electronic structure of surfaces and interfaces in functional materials. Combining XPS and HAXPES enables selected core levels to be measured at different kinetic energies and correlated with Auger transitions of comparable probing depth. This allows chemical state analysis at nearly constant information depth through evaluation of the Auger parameter (AP), which is intrinsically independent of charging and band-bending effects and therefore provides a robust descriptor of local chemical bonding.

Several case studies involving different classes of materials illustrate the capabilities of this approach. AP shifts in metallic nanometric multilayers are shown to sensitively probe electronic charge transfer at buried interfaces. For Al_2O_3 and TiO_2 thin films prepared by atomic layer deposition, anodization, and thermal oxidation, Auger parameter analysis reveals subtle variations in oxide polymorphism and local coordination environments, even in amorphous phases. Complementary valence band measurements of TiO_2 films spanning amorphous, partially crystalline, and fully crystalline structures, including mixed phases, provide insight into the evolution of the electronic structure. Correlating these valence band features with core-level shifts and Auger parameter variations establishes a consistent picture linking short-range structural order to the evolution of the electronic structure across amorphous, mixed-phase, and crystalline TiO_2 . In amorphous Al_2O_3 , Auger parameter shifts correlate with hydrogen incorporation and are supported by machine-learning-assisted atomistic simulations that reveal hydrogen-induced changes in the local Al electronic structure and coordination. The interaction of atomic hydrogen with passive oxides on steels is further investigated using an integrated electrochemical cell–glovebox–XPS approach.

Finally, new experimental approaches enabling dynamic measurements will be presented, including in-operando XPS during voltage cycling of solid-state batteries. A specially designed sample holder allowing in-situ voltage cycling, combined with high-speed snapshot XPS acquisition, enables real-time monitoring of core-level shifts during lithiation and delithiation as a function of the dynamic electrochemical state.

Together, these examples highlight the potential of combined XPS/HAXPES for electronic structure analysis and quantitative, depth-resolved chemical state analysis of functional materials under realistic and operando conditions.

Keywords: HAXPES/XPS, Auger parameter analysis, Interface Chemistry, operando XPS

The need for speed in adsorbent evaluation: Rapid measurements of multicomponent isotherms and kinetics

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For each adsorbent considered in a separation process, the adsorption thermodynamics and kinetics must be known to evaluate the technical and economic viability of the process. Because multiple adsorbates are present in any separation (e.g., CO₂ and water vapor in carbon capture), multicomponent experiments are critical for industrial process optimization. However, measuring multicomponent adsorption is complex and time-consuming. Breakthrough methods, by far the most common approach, illustrate these limitations. While this method provides robust multicomponent adsorption data, each breakthrough experiment yields data for only one gas mixture composition before the sample must be reactivated, making this approach too slow to collect full multicomponent isotherms. Measurements of adsorption kinetics are even more challenging. Hence, multicomponent diffusion measurements are rare due to limitations of available measurement methods.

In this contribution, a new temperature-step methodology will be presented that enables the rapid measurement of multicomponent adsorption and kinetics. Central to this approach are custom miniaturized heaters capable of heating up a small adsorbent sample (< 1 mg) in milliseconds. To measure multicomponent isotherms, thermal desorption is triggered after equilibration at every atmosphere composition, and the desorbed guest molecules are quantified downstream using mass spectrometry. Compared to breakthrough measurements, the temperature-step approach is much faster because much smaller adsorbent quantities are used, thereby decreasing equilibration times, and because no separate reactivation step is necessary in between measurements. To illustrate this advantage, 'isotherm surfaces' that quantify the uptake of each adsorbate for 99 mixed atmosphere compositions were acquired within the same time needed for only a few breakthrough measurements (Figure 1). For kinetic measurements, the required out-of-equilibrium conditions were achieved by a rapid temperature step rather than by the typical concentration change in the atmosphere surrounding the adsorbent (*i.e.*, moving between two isotherms rather than along one isotherm). The transient uptake/release profiles were measured using a sampled approach. Finally, the speed of the temperature-step method was used to assess the cycling stability of adsorbents, enabling rapid evaluation of capacity retention and degradation under realistic conditions.

Keywords: Adsorption, Multicomponent isotherms, Adsorption kinetics, Metal-organic frameworks, Measurement methods

Interpreting Thin Film Characterization Using AI-enhanced Atomistic Modeling

Vladyslav Turlo (Empa – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland)

A central challenge in surface and interface science is the interpretation of characterization signals in terms of underlying atomic structure and chemistry. Measurements such as RBS/ERDA as well as XPS/HAXPES/Auger electron spectroscopy provide rich information on thin films, but their physical origin is often difficult to resolve in complex materials. This is especially true for amorphous systems, where disorder, environmental effects, and impurities can produce coupled changes in structure, bonding, and measured response.

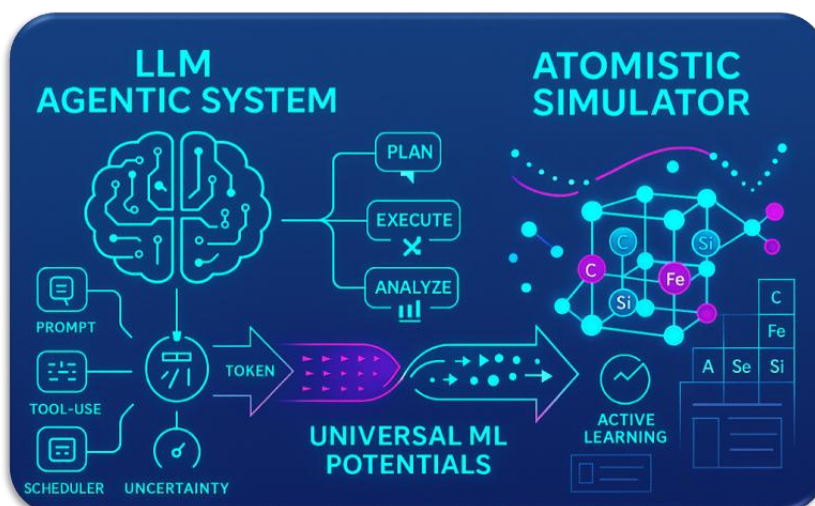
Atomistic simulations with *ab initio* accuracy provide a powerful route to bridge this gap by directly linking atomic-scale mechanisms with experimentally accessible observables, often reaching quantitative agreement and enabling predictive modeling. The explosive growth of *ab initio* training datasets has catalyzed the emergence of foundational machine learning interatomic potentials (MLIPs) capable of describing interactions across much of the periodic table. In this talk, I will demonstrate how hydrogen chemical state in H-supersaturated atomic layer deposited (ALD) amorphous alumina coatings can be revealed by reproducing Auger parameter chemical shifts of Al cations measured by XPS/HAXPES using novel simulation sample preparation technique enhanced by the foundational Matlantis potential [1]. Furthermore, I will show the rigorous proof of the applicability of complete and simplified electrostatic models to analysis of Auger parameter chemical shifts of Al cations in Al-based compounds, and reveal the structural building blocks of ALD alumina polymorphs at different temperatures, potentially guiding the development of high-performance nanoporous gas separation membranes [2].

Finally, I will demonstrate how such advanced simulation workflows can be made accessible to everyone by using foundational large language models (LLMs), enabling agentic computing systems that can plan, execute, and reason over the results (see figure attached). To bring foundational MLIPs and LLMs together in a single accessible platform, we developed OptiMat Chat (www.optimat.chat) – unified platform for conversational AI agents designed to democratize access to advanced computational tools and simulation-driven materials research. Such agentic systems may ultimately help connect spectroscopy, atomistic simulation, and materials design within unified, autonomous research workflows, opening new possibilities for data-driven surface science.

References:

- [1] S. Gramatte, O. Politano, N. Jakse, C. Cancellieri, I. Utke, L. P. H. Jeurgens, V. Turlo, *npj Computational Materials* 11 (2025) 170. <https://doi.org/10.1038/s41524-025-01676-5>
- [2] S. Gramatte, X. Wang, M. A. Hernández Bertrán, C. Cancellieri, G. Pizzi, D. Prezzi, I. Timrov, O. Politano, I. Utke, L. P. H. Jeurgens, V. Turlo, *Journal of Materials Chemistry A* (2026) accepted. <https://arxiv.org/abs/2408.08255v2>

Keywords: Auger parameter analysis, amorphous oxides, hydrogen chemical state, machine learning interatomic potentials, agentic AI



Adsorption at the Atomic Scale: Unraveling Surface Interactions Through Theory and Experiment

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Density Functional Theory (DFT) is a cornerstone of surface science, enabling the atomic-scale exploration of molecular adsorption on metal and oxide surfaces. By predicting adsorption energies, charge transfer, and bonding geometries, DFT facilitates the tailored functionalization of surfaces, unlocking customized properties for applications in corrosion protection, adhesion, and organic electronics. This presentation will highlight how DFT synergizes with key experimental techniques—such as Scanning Tunneling Microscopy (STM), X-ray Photoelectron Spectroscopy (XPS), Infrared Spectroscopy (IR), and Atomic Force Microscopy (AFM)—to create a powerful feedback loop.

In this talk, we will illustrate the theory-experiment dialogue with concrete examples related to corrosion, adhesion, and electronics. In corrosion science, the combination of DFT with XPS and ToF-SIMS elucidates the mechanisms of inhibitor adsorption, validating theoretical models of corrosion mitigation. For adhesion and biomolecular interactions, XPS, AFM and IR provide nanoscale insights into molecular bonding, while DFT refines our understanding of interfacial forces. In organic electronics, STM reveals the structural order of self-assembled monolayers, with DFT offering critical insights into the driving forces for adsorption and resulting electronic properties.

This integrated approach bridges atomic-level theory with macroscopic observations, enabling the design of functional surfaces with tailored properties.

Keywords: Atomic Scale, Theory, Surface Interactions

KEYNOTE LECTURES

Exchange of thiol containing molecules in chemisorbed monolayers: a XPS and ToF-SIMS study

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Self-assembled monolayers (SAMs) of organic thiolates on metal surfaces, are known to strongly modify the chemical, physical and electronic properties of the surfaces and their interfaces. Owing to the possibility to deliberately steer and modify the surface properties with SAMs, they are useful in organic electronics, chemical sensors and medical or biological applications. We have investigated the composition of pure and mixed SAMs of two different aromatic thiol-containing molecules, namely 2,3,4,5,6-pentafluorothiophenol (PFBT) and 4-(methylsulfanyl)thiophenol (MeSTP) (see Figure 1; bottom), on gold surfaces by means of x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Due to their different chemical composition, the two molecules can be clearly discriminated in XPS by the S-CH₃ bond (MeSTP) and the C-F bonds (PFBT). The analysis by means of ToF-SIMS is more complex, because of the many different detectable molecular fragments. Therefore, we have successfully applied multivariate analysis (MVA) in order to determine the mixing of the two different molecules by means of ToF-SIMS.

By first covering half of a silicon substrate with a thin film of gold (*Surface A*) and then dipping the substrate into *Solution 1*, a monolayer containing one of the two molecules is prepared on *Surface A*. Subsequently, a thin film of gold is deposited onto the other half of the substrate (*Surface B*), and the entire substrate is dipped into *Solution 2*, which contains only the other thiol (see workflow in Figure 1). Our spectroscopy results clearly show that on *Surface A*, some of the molecules that had formed a monolayer from *Solution 1* were replaced by molecules from *Solution 2*, while no molecules from *Solution 1* are detected on *Surface B*. Furthermore, we observed that the replacement of PFBT by MeSTP is more efficient than the replacement of MeSTP by PFBT. When PFBT is deposited first, less than 20% of the PFBT molecules are left after dipping into the MeSTP solution. Vice versa, when MeSTP is deposited first, only small amounts are subsequently replaced by PFBT. The degree to which the first molecule is replaced by the second molecule can be further steered by varying the time of immersion into *Solution 2*. This clearly indicates the difference in bonding strength between MeSTP and PFBT on gold. For the future, we hope that the sequential adsorption and deterministic replacement of thiolates on gold surfaces can be exploited for the fabrication of electronic devices, e.g., to functionalize electrodes of different devices with monolayers of different thiolates.

Keywords: chemisorbed molecular layers, molecular replacement, XPS, ToF-SIMS

Domain Expertise as the Key to ML-Driven Corrosion Insights: A SECCM Case Study on 316L

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High-throughput local electrochemical measurements generate rich datasets whose full informational content often remains inaccessible through conventional analysis. Scanning electrochemical cell microscopy (SECCM) is a prime example: hundreds of spatially resolved chronoamperometric (CA) measurements can be acquired on a single specimen. We argue that a critical (and underexploited) step in such workflows is expert-guided supervised labelling: rather than relying solely on unsupervised learning or prediction-oriented approaches, researchers should actively leverage their domain knowledge to annotate data, because it is this labelling that ultimately enables machine learning (ML) to reveal new mechanistic insights.

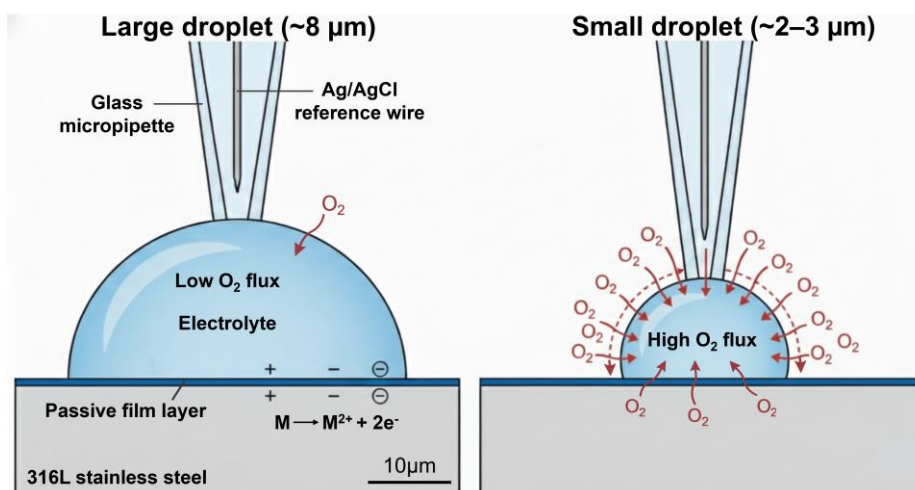
SECCM measurements were performed on industrially produced 316L stainless steel in 0.01 M NaCl at +1.20 V vs Ag/AgCl (60 s potentiostatic hold, 205 individual tests). Natural evaporation during sequential measurements progressively reduced micro-droplet footprint size (2–8 μm), creating an intrinsic oxygen availability gradient that was exploited as a controlled variable to investigate how aeration modulates passive film evolution and metastable pitting. Each CA curve was characterised by quantitative descriptors capturing nucleation, growth, and repassivation kinetics.

Crucially, transient events were manually classified by domain experts into two physically meaningful categories: peak-type (classical metastable pitting, sharp current spikes) and belly-type (gradual passive film thinning), yielding 91 labelled events. This supervised labelling step, grounded in domain expertise, was the cornerstone of subsequent ML analysis. Linear Discriminant Analysis (LDA) was applied to electron backscatter diffraction (EBSD)-derived crystallographic features to assess whether microstructural descriptors could discriminate between the expert-defined transient categories, allowing the relative contribution of crystallography to corrosion susceptibility to be evaluated in comparison with oxygen availability effects.

The analysis revealed that oxygen availability dominates over grain crystallography in controlling both general dissolution and transient event characteristics. Higher aeration produced faster-forming but less protective passive films, with longer belly-type events indicating a protectiveness–repassivation trade-off consistent with Point Defect Model principles.

This work illustrates how the combination of expert classification, quantitative descriptor extraction, and supervised ML transforms high-throughput local electrochemical data into mechanistic understanding, highlighting both the power and the interpretive care required when applying ML to surface science datasets.

Keywords: 316L stainless steel, SECCM, Metastable pitting, Passive film, Supervised machine learning



Grafting of anti-adhesive polydentate polymers onto gold surface

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Gold nanoparticles show great potential for biomedical applications, particularly in the fields of imaging and therapy. However, their use requires functionalisation to make them stable in solution and prevent them from adhering to components of the biological environment. We are working on polydentate polymers (cyclic and linear), as alternatives to the standard surface functionalisation, thiol-polyethylene glycol (HS-PEG). The polydentate polymers are designed with four binding functions and six or seven anti-adhesive functions. The binding function is dithiolane (TA) and the anti-adhesive function is polysarcosine (pSar). The polymers are characterised by being monodisperse, with a perfectly controlled structure. The gold surfaces consist of quartz crystals coated with gold.

We investigated the adsorption, stability and anti-adhesive properties of our polymers using QCM-D, XPS and ToF-SIMS.

The grafting process monitoring revealed the systematic formation of a polymer layer on gold, the amount of which varies depending on the conditions. This layer consists of polymers covalently bonded to gold and a multilayer structure. In 0.1% TFA, we observe a limitation on the formation of multilayers, unlike in ultrapure water, where these multilayer structures are uncontrolled. The S 2p core level allows us to identify and quantify the thiolate bonds (S-Au) as well as the molecular adsorption. ToF-SIMS spectrometry confirms the chemical characterisation of the various bonds involving sulphur atoms. Furthermore, the systematic detection of gold by XPS and ToF-SIMS suggests that the deposition mode is not fully covering. A kinetic analysis of the QCM-D data confirms the grafting mechanism and allows comparison of the adsorption rates.

The stability of polymers deposited on gold in 0.1% TFA was assessed at different concentrations of dithiothreitol (DTT) and compared with the behaviour of HS-PEG. In the case of linear polymers, at 0.01 M DTT, we observe little or no desorption by QCM-D compared to the HS-PEG reference. In contrast, at 0.1 M DTT, only the cyclic polymer Cyc (6pSar14;4TA) exhibits desorption comparable to that of HS-PEG, suggesting that it is the least robust. XPS and ToF-SIMS analyses show the presence of residual polydentate polymers on the surface, whereas the monodentate HS-PEG is no longer detected after 0.1 M DTT.

We also evaluated the anti-adhesive effect of the grafted polymers in presence of BSA using QCM-D. The results show that the cyclic polymer Cyc (6pSar14;4TA) exhibits the best anti-adhesive properties.

These polymers represent a promising approach to surface functionalisation of gold nanoparticles.

Keywords: polymers, adsorption, anti-adhesive, XPS, ToF-SIMS, QCM-D

Control of stiction phenomena at the rotor/pad interface in automotive braking systems

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Corrosion attack grey cast iron brake rotors might cause stiction phenomenon in automotive braking systems. This consists of a strong adhesion of the pad material on the brake rotor and is associated with the penetration of iron corrosion products into the friction material. This might result in severe damage of the pad, reduced braking performance and even immobilization of the vehicle in most severe cases.

A dedicated electrochemical cell was developed to investigate the stiction phenomenon between a brake pad sample and a disc sample (gray cast iron). The adhesion force between disc and pad can be measured by means of a test bench, providing a quantitative parameter to assess stiction susceptibility of friction materials.

This work investigates the mechanism of stiction at the rotor/pad interface and discusses different approaches based on the use of corrosion inhibitors to reduce the stiction susceptibility of model friction materials. These include organic corrosion inhibitors, with particular focus on their potential suitability for friction materials used in electric vehicles; inorganic corrosion inhibitors; as well as hybrid approaches that combine different inhibition strategies.

Keywords: corrosion, stiction, rotor/pad interface, automotive braking systems

Testing the Consistent Retardation Assumption for XPS transmission function determination

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Quantitative XPS relies on knowing the intensity-energy response function, commonly known as the transmission function (TF). The TF converts the raw data into an approximation of the true XPS spectrum from a sample. One of the commonly used methods to determine TFs relies upon an assumption that the TF is a simple function of the retardation ratio: the ratio of electron kinetic energy to analyser pass energy. We call this method the "Consistent Retardation Assumption" (CRA) procedure. To the best of our knowledge, the CRA method has not been rigorously compared to other methods. In this presentation we describe a wide-ranging comparison of CRA TF correction to NPL reference data. This interlaboratory study was initiated and organised by Neal Fairley of CASA XPS.

We demonstrate that the CRA method may be performed either with, or without, knowledge of true intensities from reference materials. For some XPS instruments, in certain operating modes, the method works extraordinarily well. For an exemplar instrument and operating mode, the agreement with NPL reference intensities for gold is within a few percent across pass energies from 30 eV to 200 eV. For the same instrument, but with a different selection of apertures, the method fails to provide agreement with NPL reference data, with more than 20 % deviation.

We conclude the presentation with recommendations for using the CRA method and highlight examples of failure. In such cases, the alternative approach of calibrating each pass energy individually using reference data is recommended.

Keywords: XPS, Calibration, quantification, metrology, accuracy

Cryo-XPS analyses of membrane vesicles from bacterial cells

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Membrane vesicles (MVs) are formed and dispatched from all types of cells including mammalian, plant and microbial cells. These have a range of biological functions. In bacterial systems they may be used for cell signalling, for discarding waste, remodelling the cell membrane, as decoys for antimicrobial agents and to harvest nutrients. MV interactions with the surroundings are governed by their physicochemical properties, including surface chemistry. This presentation will describe work performed to characterize the surface chemistry of bacterial MVs using cryogenic X-ray Photoelectron Spectroscopy (cryo-XPS). The methodology for analysing MVs in PBS as frozen droplets will be described, as well as methodological challenges that may arise both during sample preparation and analysis. Furthermore, a data treatment methodology will be described that was used to determine the macromolecular composition of the sample. It enables quantification of lipids, proteins, polysaccharide as well as remnants of iodixanol from the gradient centrifugation step of the vesicle purification. This methodological information is expected to provide a good starting point facilitating future cryo-XPS characterization work of cell-derived MVs but also for analyses of bacteriophages or viruses subjected to similar isolation and purification methodologies as vesicles.

Keywords: cryo-XPS, membrane vesicles, bacteria

A Study of the chemistry of Mary-Rose timber hull core samples using XPS and ToF SIMS

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The Mary Rose, one of the most important maritime artefacts in the United Kingdom is to be found in Portsmouth. It was the favourite warship of Henry VIII and was retrieved from the Solent in 1982 long after it sank in 1545. In order to preserve integrity of the artefact, various "washing" methods were used initially, followed by a spray of polyethylene glycol (PEG) of three different molecular weights inspired by the protocol followed for the Vasa [1] in Sweden. Previous work has shown that the PEG was found at a depth of at least 20mm and that some of the data indicate initial degradation of the polymer. In this piece of work, we will compare the results obtained for the three cores investigated with the kind permission of the Trust. Said core samples were taken by the Mary Rose Trust in various locations on the ship and three of those were tested at the Universities of Surrey, using X-ray photoelectron spectroscopy and secondary mass spectrometry. These core specimens were sectioned at regular intervals to investigate the chemistry of the timber as a function of depth into the hull. Both sides of the specimens were analysed using a specially designed rotating sample holder. Elements indicative of the wash using tap water (e.g. calcium) and seawater (e.g. chlorine and sodium) were observed. The presence of PEG was demonstrated for a depth of between 17 to 20mm. Its presence is inhomogeneous, probably because of the structure of the wood as well as the presence of cracks within the material. In addition, the drop in PEG concentration as a function of depth is concomitant with the uptake in concentration of sodium and chlorine possibly indicating that the initial water wash was not entirely successful for the full thickness of the planks. Other chemicals containing nitrogen may indicate the presence of bacteria especially when present together with sulphur or amino acids. Other traces are slightly more difficult to assign such as iron, chromium or even uranium. Some of those may be assigned to the paint of the cradle supporting the ship or contamination in the Solent waters. In addition, further insight will be provided using chemometrics.

Selected references [1] Hocker, E., Almkvist, G. & Sahlstedt, M., 2012. The Vasa experience with polyethylene glycol: A conservator's perspective. *Journal of Cultural Heritage*, 13(S), pp. 175-182.

Keywords: Mary-Rose, ToF-SIMS, XPS, Conservation, Chemometrics

Operando SIMS to Monitor Degradation in Solid-State Batteries

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The cathode electrolyte interphase (CEI) is a key determinant of the performance and long-term stability of solid-state batteries (SSBs). Forming at the interface between the cathode active material (CAM) and the solid electrolyte (SE), the CEI contributes substantially to impedance growth and capacity fading during cycling. Nevertheless, its dynamic evolution, chemical composition, and potential redox activity as a function of the state of charge (SoC) remain poorly understood, particularly in argyrodite-based systems. In this work, a novel operando ToF-SIMS sample holder was developed that enables real-time electrochemical characterisation of SSBs directly within the SIMS instrument under applied pressure. This configuration permits the simultaneous acquisition of electrochemical data and surface-sensitive mass spectrometric information throughout charge and discharge. The model system comprised $\text{LiNi}_{0.82}\text{Co}_{0.11}\text{Mn}_{0.07}\text{O}_2$ (NCM) as the CAM, $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI) as the solid electrolyte, and $\text{In}|\text{(InLi)}_x$ as the anode.

SoC-dependent changes in the ToF-SIMS mass spectra were monitored across the first charge–discharge cycles. Key CEI-related secondary ion fragments – including PO_3^- , SO_3^- , PS_2^- , and NiO_2^- – exhibited reversible intensity variations closely correlated with the applied cathode potential, while displaying a continuous overall increase upon cycling. The systematic increase of phosphate and sulphate fragments during charging and their subsequent attenuation during discharging strongly indicate that the CEI in LPSCI-based SSBs is partially redox-active within the relevant electrochemical potential window. Two principal decomposition pathways were identified: electrochemical oxidation of the solid electrolyte, yielding Li_3PS_4 , elemental sulphur, and LiCl , and CAM-involved oxidation producing transition metal phosphates, sulphates, and chlorides. Complementary electrochemical impedance spectroscopy (EIS) was employed to quantify CEI growth kinetics as a function of SoC. Invoking the Wagner diffusion model and plotting impedance magnitude of the interfacial contribution against $\sqrt{t}$, the CEI growth rate constant k was extracted, revealing a pronounced dependence on applied potential in the range of 3.5–3.9 V vs. $\text{In}|\text{(InLi)}_x$. Operando XPS measurements performed in parallel showed no discernible compositional changes, an outcome attributed to the inherently lower surface sensitivity of this technique under the conditions employed.

Collectively, these findings substantiate the hypothesis that the CEI in argyrodite-based SSBs is electrochemically active and undergoes partially reversible compositional changes during cycling. Future work will aim to deconvolute overlapping decomposition processes and elucidate their individual kinetic contributions, advancing the mechanistic understanding of CEI formation in solid-state battery systems.

Keywords: Operando, Battery, Secondary Ion Mass Spectrometry, Electrochemistry, Kinetics

Surface and Interface Analysis as a Key to Understanding ZnFe₂O₄@TiO₂ Direct Z-Scheme Photocatalysts for CO₂ Reduction

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Photocatalytic CO₂ conversion into useful chemicals is a promising approach for sustainable energy storage and climate change mitigation. Because these reactions occur at the catalyst surface, photocatalytic efficiency is governed by surface chemistry, interfacial contact, and the lifetime of photogenerated charge carriers. Z-scheme heterostructures are attractive systems to suppress charge recombination, yet their rational design is still limited by a lack of direct insight into charge transfer processes and surface-active sites. In this work, we investigate direct Z-scheme ZnFe₂O₄@TiO₂ photocatalysts, with ZnFe₂O₄ as the reduction photocatalyst and TiO₂ as the oxidation component.

As a first step, we focus on gaining synthetic control over the morphology and structural properties of ZnFe₂O₄. ZnFe₂O₄ particles are initially prepared via wet-chemical co-precipitation, while their morphology is tailored using hydrothermal treatment. By systematically varying hydrothermal synthesis and post-treatment parameters, we demonstrate how crystal structure, particle size, and optical absorption can be tuned. The resulting materials are characterized using established bulk and microstructural techniques, including X-ray diffraction, Raman spectroscopy, diffuse reflectance spectroscopy, and electron microscopy.

This initial study provides a well-defined material platform for constructing ZnFe₂O₄@TiO₂ heterojunctions with controlled morphology and interfacial contact. However, bulk characterization alone cannot explain photocatalytic performance, as photochemical reactions depend on charge transport to the surface and reactions at specific active sites. This highlights the need for surface- and interface-sensitive analysis methods to move beyond empirical structure-activity correlations.

Keywords: ZnFe₂O₄, structural characterization, chemical co-precipitation, morphology, interfacial contact

A multiple X-ray beam approach for angle-resolved photoelectron analysis of dielectric thin film stacks

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Over the past two decades, thin layers have become central to semiconductor device performance as scaling has driven the adoption of high- κ gate dielectrics, metal gate stacks, ultra-thin interconnect barriers, and complex multi-layer passivation schemes. The transition from SiO_2 to Hf-based dielectrics in CMOS technology and the widespread use of atomic layer deposition for nanometer-scale layer control highlight the growing need for reliable characterization of ultra-thin and buried film stacks.

Techniques such as ellipsometry, TEM, SIMS, and XRR offer advantages including rapid thickness determination, structural information or high depth resolution, but often suffer from limited chemical specificity, destructive sample preparation, or complex data interpretation. These trade-offs make it challenging to obtain a complete, non-destructive, and chemically resolved picture of multilayer stacks using a single technique.

Angle Resolved X-ray Photoelectron Spectroscopy (AR-XPS, $\text{Al K}\alpha$) is a well-established method for probing thin film stacks, providing non-destructive, chemically specific depth sensitivity through variation of the photoelectron emission angle. State-of-the-art AR-XPS approaches combine advanced modelling and data analysis to extract layer thicknesses and compositional gradients, though they remain limited by the restricted information depth of conventional laboratory X-ray sources. On the other hand, Angle Resolved Hard X-ray Photoelectron Spectroscopy (AR-HAXPES, using $\text{Cr K}\alpha$ in this work) allows the characterization of much deeper layers but suffers from a lack of surface sensitivity while significant changes in composition can be expected in the first top nm.

The use of a multiple X-ray beam approach, combining conventional XPS with HAXPES in an angle-resolved configuration, complements thus the high surface sensitivity of XPS with the significantly increased probing depth of HAXPES while preserving chemical sensitivity, thereby enlarging the precision and robustness of the depth-resolved analysis of thin film stacks with buried layers. In this work, thin film dielectric stacks consisting of HfO_2 , Al_2O_3 , and SiO_2 on Si substrates with total stack thicknesses ranging from 2 to 20 nm are examined using AR-XPS, AR-HAXPES, and a combination of AR-XPS and AR-HAXPES. Prior to experimental analysis, simulations are performed to determine the optimal combination of XPS and HAXPES spectra, considering parameters such as effective attenuation lengths, relative sensitivity factors, and the depth positioning of the constituent elements. Using this setup, the advantages of the combined multiple X-ray beam approach over standard AR-XPS analysis are demonstrated. A special focus will be put on the examination and discussion of the limitations, sources of error, and uncertainties associated with this combined approach.

Keywords: Angle Resolved X-ray Photoelectron Spectroscopy (AR-XPS), Angle Resolved Hard X-ray Photoelectron Spectroscopy (AR-HAXPES), thin film stacks, depth-resolved chemical analysis

Depth-resolving the pSEI formation and Redox Mechanism of Delithiated NMC 811 Electrodes by Lab-Based Soft and Hard XPS

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Layered transition metal oxides $\text{Li}_x\text{Ni}_w\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC_{wyz}, $w+y+z=1$) represent state-of-the-art positive electrode materials for Li-ion batteries. In these electrodes, charging occurs through Li^+ deintercalation and redox reactions, producing a strong stoichiometric gradient between the surface and the bulk during electrochemical cycling. Investigating the redox process requires a non-destructive approach that probes changes in the local electronic structure of the transition metals and oxygen atoms during cycling at the sub-nanometer scale. X-ray photoelectron spectroscopy (XPS) is a well-established technique to study the redox process and the positive electrode Solid Electrolyte Interphase (pSEI) in $\text{Li}_x\text{Ni}_w\text{Mn}_y\text{Co}_z\text{O}_2$ materials. However, interpreting the final state electronic structure and determining the formal oxidation state of the metal atoms upon charge remain challenging due to the high surface sensitivity of XPS and the overlap of Auger features with transition-metal core levels when using soft X-ray energies.

In this study, combined soft and Hard X-ray photoelectron spectroscopy (resp. XPS, Al $K\alpha$, 1.5 keV and HAXPES, Cr $K\alpha$, 5.4 keV) were employed to study the impact of lithium disinsertion on the electronic structure of $\text{Li}_x\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrodes, with $x \approx 1, 0.7, 0.4, 0$. Within the first 15 nm, we elucidate the respective contributions of metal and oxygen species to the charge-compensation mechanism. Furthermore, by employing reference metal oxides with well-established formal oxidation states, we develop a protocol to quantify surface and bulk contributions using laboratory-derived HAXPES sensitivity factors for delithiated states during the first charge. These results are analyzed with respect to the formation of the pSEI and its influence on the evolution of the surface stoichiometry.

Keywords: Li-ion batteries, Electronic structure, Photoelectron spectroscopy, positive electrode materials, XPS spectroscopy

Characterization of Ultrathin ALD-Grown VS_x Films for Electrical Contacts to MoS_2

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Two-dimensional transition metal dichalcogenides (TMDs), such as MoS_2 , have attracted significant attention for next-generation ultra-scaled electronic devices [1], [2]. However, contact engineering remains a critical bottleneck due to high contact resistance and interface degradation induced by conventional metals [3]. In this context, vanadium sulfides (VS_x), and in particular semi-metallic VS_2 , emerge as promising candidates for forming efficient contacts to MoS_2 [4]. In this work, we develop a two-step ALD/MLD and annealing process to synthesize and crystallize VS_x thin films using a novel vanadium precursor and 1,2-ethanedithiol. Film growth is performed in a custom-built ALD/MLD reactor, enabling *in situ* monitoring via spectroscopic ellipsometry and residual gas analysis to gain insight into growth mechanisms. Special attention is given to annealing processes performed after the first step of deposition.

The chemical composition and electronic structure of the films are primarily investigated by angle-resolved X-ray photoelectron spectroscopy (ARXPS) *in quasi in situ* conditions, enabling depth-resolved analysis of chemical states and their evolution upon annealing. The samples transfer without air exposure, allow us to preserve interface chemistry and prevent oxidation. These conditions provide a unique opportunity to investigate phase transformations within the V-S system, known for its complex phase diagram and metastable compounds. These measurements are complemented by hard X-ray photoelectron spectroscopy (HAXPES) to probe both surface and subsurface regions, including sulfur distribution within the VS_x layer and across the VS_x/MoS_2 interface. Furthermore, synchrotron-based EXAFS *in situ* measurements performed at the SOLEIL facility provide detailed insights into the local atomic structure and coordination environment in the VS_x films during the growth. Additional complementary techniques, including Raman spectroscopy, SIMS, and TEM, support the chemical and microstructural analysis.

Overall, this multi-scale and *quasi in situ* approach should establish clear correlations between processing conditions, structural properties, and electric behavior, paving the way for optimized VS_x -based contacts for MoS_2 optoelectronic devices.

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Keywords: ARXPS, HAXPES, ALD, Synchrotron, 2D Materials

Electrochemical Additive Manufacturing of Sub-100 nm Metals via Chemical Focusing

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The growing demand for high-aspect-ratio, complex nanoscale features is driven by emerging applications in nanorobotics, quantum technologies, nanoelectronics, sensing, and energy storage. Among high-resolution additive manufacturing techniques, electrochemical methods uniquely enable the fabrication of fine conductive metallic structures through confined electrodeposition via localized delivery of precursor ions. Although this approach allows the creation of complex three-dimensional architectures with micro- and sub-microscale resolution, almost unlimited aspect ratios, and broad material compatibility, producing features below 100 nm has remained a major challenge. Here, we systematically test the resolution limits of nanoconfined electrochemical additive manufacturing and demonstrate, through experiments and mathematical modeling, a strategy that enables true nanoscale printing that is otherwise unattainable by electrochemical additive manufacturing in liquid. Using chemical focusing—scavenging stray ions that leave the nanoscale gap under the nozzle with a chelating agent—we achieve metallic features of varying complexity with enhanced mechanical performance arising from refined microstructure.

Keywords: electrodeposition, nanopipette, nanoprinting

An evolution in standard operando surface chemical analysis

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Instrumental requirements evolve alongside technological needs. New analytical techniques are becoming increasingly available and continue to push the limits of existing tools.¹ Therefore, hardware must also continuously evolve.

The EnviroESCA², launched in 2015, already introduced solutions for automated near-ambient pressure (NAP) operando X-ray photoelectron spectroscopy (XPS) studies for research in surface science and standard analytical environments. The scientific community is now pushing further into new research areas such as renewable energies, advanced electrochemical studies, and increasingly challenging material types.³ To support and drive this development, the EnviroESCA Release II continues to set a new standard in surface analysis.

The EnviroESCA II is based on the AEOLOS 150 NAP electron analyzer, the AD-CMOS true pulse-counting detector, and the μ FOCUS 450 three-color monochromatic X-ray source. This combination enables high-throughput, flexible NAP-(HA)XP(E)S surface analysis under environmental conditions with excellent surface sensitivity.

The EnviroESCA II builds on ten years of experience with the successful first release. It maintains the unique operational concept for NAP-XPS measurements, while offering higher operational performance and adding new optional techniques and capabilities:

- Parallel angle-resolved XPS (PAR-XPS),
- Hard X-ray photoelectron spectroscopy (HAXPES),
- Near ambient pressure ultraviolet photoelectron spectroscopy (NAP-UPS),
- Optical analytical methods, e.g., FTIR, IRRAS, and/ or Raman spectroscopy,
- Dual beam charge compensation, and
- up to 5 process gases.

The EnviroESCA II will be a significant step forward to evolve operando surface analysis under environmental conditions into a standard technique with excellent surface sensitivity that can be corroborated by additional methods such as NAP-UPS, IR and/or Raman spectroscopy.

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Keywords: Parallel angle-resolved XPS (PAR-XPS), Hard X-ray photoelectron spectroscopy (HAXPES), Operando NAP-XPS, NAP-UPS, ESCA

Surface and Interface Study of ENEPIG Metallization on AlSiCu Pads for SiC Power Devices

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The increasing electrification of transportation and energy systems demands high-performance power electronics based on wide bandgap semiconductors such as silicon carbide (SiC). Reliable device operation under high voltage, high temperature, and high switching frequency conditions critically depends on the integrity of surface metallization and interfacial chemistry. In this context, Pb-free surface finishes compliant with the Restriction of Hazardous Substances Directive (RoHS) have become essential, with Electroless Nickel–Electroless Palladium–Immersion Gold (ENEPIG) emerging as a key metallization strategy for advanced power modules.

In this work, ENEPIG stacks were deposited on AlSiCu pads of SiC wafers using different electroless processes. A comprehensive surface and interface characterization was performed by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Dynamic SIMS depth profiling enabled detailed investigation of elemental distribution, layer thickness, and interfacial composition within the Ni–P/Pd/Au multilayer system. Complementary static SIMS analysis was employed to detect trace contaminants and evaluate surface cleanliness, particularly on the polyimide (PI) passivation layer.

The results reveal distinct differences in phosphorus incorporation within the electroless nickel layer (≈ 4 at.% vs. ≈ 7 at.%), potentially impacting the mechanical and corrosion properties of the metallization stack. In addition, trace metallic residues were identified on the PI surface, indicating process-related contamination pathways that may affect long-term device reliability.

This study demonstrates the capability of ToF-SIMS to provide molecular- and depth-resolved insight into complex multilayer metallization systems and highlights its critical role in process optimization and reliability assessment of next-generation SiC power electronics.

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Keywords: SiC Power Devices, ENEPIG metallization, ToF-SIMS

ORAL PRESENTATIONS

Biomaterials engineering and analysis

Interfacial Analysis of ExoPolymeric Substance (EPS) Adsorption on Chromium by Coupled QCM–ARXPS

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An approach combining real-time Quartz Crystal Microbalance (QCM) and Angle-Resolved X-ray Photoelectron Spectroscopy (AR-XPS) was developed to elucidate the adsorption and structural organization of EPS on oxidized chromium surfaces under marine-mimicking conditions. This coupled approach enables *in situ* kinetic measurements of mass uptake and post-adsorption surface chemical analysis, providing complementary insight into polymer–metal interactions at the nanoscale.

EPS T14, produced by *Bacillus licheniformis* strain T14, consists of a γ -polyglutamic acid (γ -PGA)–rich high-mass fraction (>200 kDa) and a polysaccharide-rich low-mass fraction (<200 kDa). QCM measurements performed in artificial seawater (ASW) reveal rapid and quasi-irreversible adsorption of both fractions, forming nanometric films ($\approx 3\text{--}4$ nm). Adsorbed masses range from 0.27 to 0.44 $\mu\text{g}\cdot\text{cm}^{-2}$, with the complete biopolymer yielding intermediate values, indicating co-adsorption of both fractions in comparable proportions. No desorption occurs after 6 h immersion in ASW, demonstrating strong interfacial stability. A slight mass increase suggests water uptake by the hygroscopic γ -PGA component.

Depth-sensitive AR-XPS reveals that adsorption induces significant chemical reorganization compared to the native biopolymer composition. Nitrogen-containing species and amide groups are preferentially located near the chromium oxide surface, whereas aliphatic C–C/C–H groups dominate the outermost layer. This stratified architecture indicates selective interfacial anchoring of nitrogen-rich polysaccharide domains, with outward-oriented hydrophobic chains. Preconditioning with bovine serum albumin strongly suppresses EPS adsorption, confirming the key role of nitrogenous functionalities in interfacial binding.

By coupling real-time *in situ* mass uptake measurements with depth-resolved surface chemical analysis this methodology provides mechanistic insight into biopolymer adsorption, interfacial structuring, and film stability. The formation of a robust, nanostructured organic layer on chromium under saline conditions highlights potential implications for biointerface engineering, antifouling strategies, and corrosion-related surface modification of alloys such as stainless steels in marine environments.

Keywords: Biopolymer–metal interface, Quartz Crystal Microbalance (QCM), Angle-Resolved XPS (AR-XPS), Surface chemical characterization, Nanostructured EPS films

Reactive landing of peptides on tailored surfaces using gas cluster ion beams

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The controlled fabrication of functional biointerfaces with nanometer-scale precision is essential for applications ranging from biosensing to surface-based bioengineering. Conventional biomolecule immobilization strategies predominantly rely on solution-phase processes, which inherently suffer from limited spatial control, solvent-induced perturbations and competitive side reactions. In this work, we demonstrate a solvent-free and vacuum-based approach for the covalent immobilization of a model cyclopeptide, Cyclo-(RGDfK), onto chemically tailored gold surfaces using gas cluster ion beam (GCIB)-assisted sputtering. Gold substrates were functionalized with NHS-terminated self-assembled monolayers (SAMs) to promote amide bond formation with primary amine groups of the peptide. Using time-of-flight secondary ion mass spectrometry (ToF-SIMS), we provide molecular-level evidence of peptide transfer, surface reactivity, and covalent attachment under ultra-high vacuum conditions. A characteristic peptide-SAM covalent adduct, identical to that observed following conventional aqueous coupling, is selectively detected after GCIB-assisted deposition onto reactive SAMs and persists after extensive rinsing, confirming the formation of stable covalent bonds. The influence of GCIB parameters on peptide integrity and surface reactivity is systematically investigated. Increasing the cluster size, thereby lowering the energy per atom, significantly reduces peptide fragmentation while preserving surface reactivity. Furthermore, a dose-dependent transition from a reactive, surface-limited regime to a multilayer deposition regime is identified, revealing the critical role of surface coverage in governing covalent immobilization efficiency. These results establish GCIB-assisted sputtering as a versatile and charge-independent platform for reactive landing of biomolecules, extending vacuum-based biofunctionalization strategies beyond ion-based deposition methods and opening new perspectives for the controlled fabrication of solvent-free biointerfaces.

Keywords: reactive landing, peptide, ToF-SIMS, biointerface, GCIB

Enzymatic Surface Nanostructuring of Biopolymer-Silica Hybrid Materials

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Sustainable surface engineering strategies require a detailed understanding of interfacial transformations occurring at the nanometer scale. Enzymatic degradation of hybrid organic-inorganic materials, represents a mild and selective alternative to conventional chemical or thermal treatments [1]; yet the surface mechanisms governing such bio-induced nanostructuring remain insufficiently understood. Here, we demonstrate how a correlative multi-technique surface analysis approach provides a coherent understanding of the enzymatic nanostructuring of gelatin-silica hybrid systems.

Hybrid thin films were fabricated by dip-coating silicon wafers using gelatin as a biopolymer matrix and tetraethyl orthosilicate (TEOS) as a silica precursor, forming an interpenetrated organic-inorganic network. Enzymatic treatment was performed using extracellular proteases contained in the supernatant of the marine bacterium *Alteromonas macleodii*, previously reported for its ability to degrade biopolymers such as gelatin [2]. The treatment selectively targets the organic phase of the hybrid system.

The degradation process was investigated by combining complementary surface-sensitive techniques probing different length scales and information depths. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) provided morphological evidence of progressive surface restructuring, revealing pore formation, increased roughness, and nanoscale texturing. X-ray photoelectron spectroscopy (XPS), with a sampling depth of a few nanometers, enabled quantitative monitoring of chemical-state evolution at the outer surface, showing a marked decrease of nitrogen- and carbon-containing species associated with gelatin and a relative enrichment in silicon-oxygen environments characteristic of the inorganic network. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), probing the uppermost molecular layers, delivered complementary molecular information, confirming the depletion of organic fragments and mapping their spatial distribution through two-dimensional chemical imaging and depth profiling.

The combined interpretation of topographical (SEM/AFM), elemental and chemical-state (XPS), and molecular (ToF-SIMS) datasets provides a consistent picture of selective enzymatic removal of the biopolymer phase at the surface (Figure 1). This correlative approach reveals how controlled bio-degradation drives the emergence of nanoscale porosity and modifies surface chemistry in hybrid materials. The study highlights the power of multi-technique surface analysis to unravel bio-induced interfacial processes and establishes enzymatic treatment as a sustainable tool for tailoring nanostructured hybrid interfaces.

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Keywords: Hybrid materials, Nanostructuring, Enzymatic degradation, Surface analysis

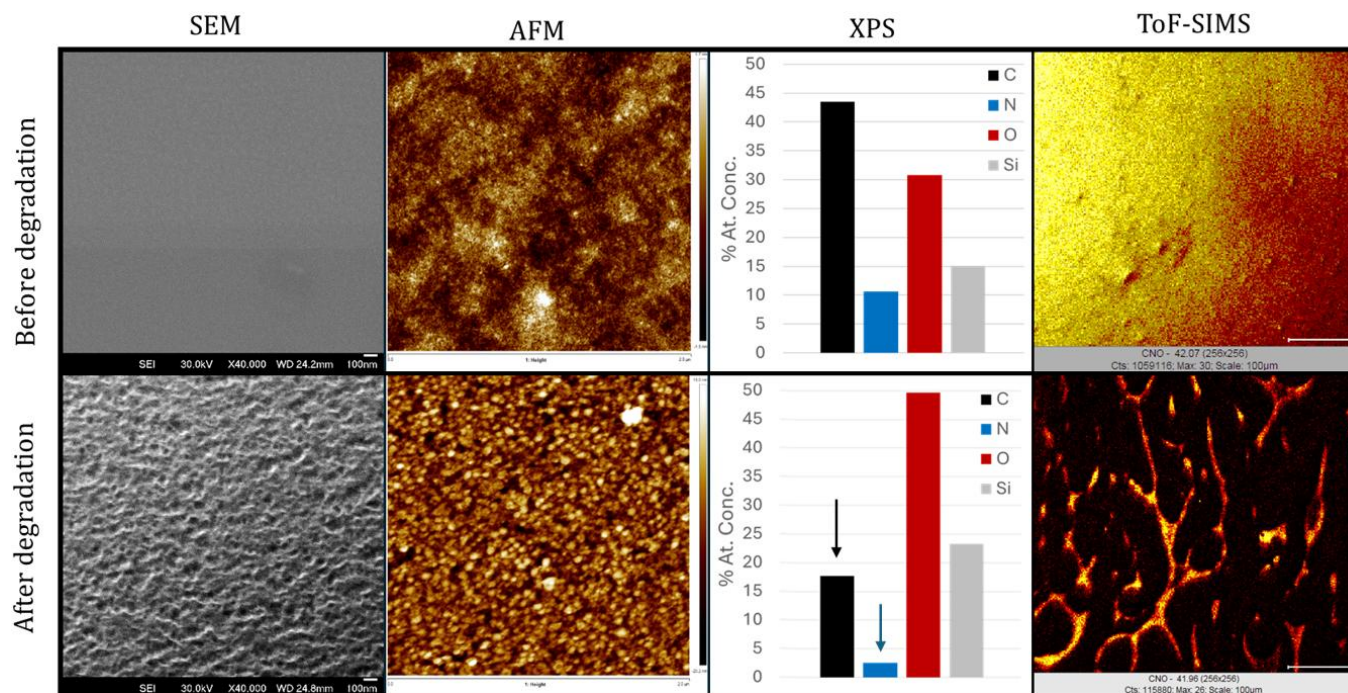


Figure 1. SEM, AFM, XPS, and ToF-SIMS characterization of gelatin-silica hybrid films before and after enzymatic degradation.

Interaction of protein-functionalized silica with f-block elements using surface analysis

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The f-block elements find applications in multiple industrial fields including nuclear fuel production, high tech products, hybrid materials for low-carbon energy systems and many others. Given the increasing demand and the rising of geopolitical tensions, achieving self-sufficiency in its consumption of f-block elements becomes a major challenge for European Union. There is an urgent need to minimize waste and develop low energy, cost-effective extraction processes from industrial waste. Recently, biomaterials have emerged as a promising alternative to conventional extraction methods [1]. Especially, the use of proteins such as the lanmoduline (LanM), a small protein with a mass of 12 kDa and a size of 5 nm (133 amino acids) having a stable disordered structure in complex environments, has shown very interesting extraction properties. In the presence of f-block elements, the protein folds to fit the high-affinity complexation sites required for their retention. This peptide chain folding during complexation drives selectivity: only f-block elements can provide the activation energy required for this folding. In aqueous solution, LanM has picomolar affinities on three complexation sites (from 5 to 35 pM), and a selectivity 5-6 orders of magnitude higher for lanthanides than for classical competing cations such as Ca^{2+} , Cu^{2+} or Zn^{2+} . In addition, this protein releases f-block elements at pH 2 [2]. To prepare functionalized materials for f-block element extraction, we have studied the functionalization of silica surface with this protein and its behavior in f-block element electrolyte solutions. To reach this goal, X-ray reflectivity was used to ensure that protein was properly grafted onto the surface of solid quartz substrates. Combined with atomic force microscopy, we were able to determine the arrangement of the immobilized LanM and highlight a surface density around 1 LanM per 5 to 8 nm². To go deeper in the behavior of grafted LanM during complexation and release of f-block elements (in situ experiment), neutron reflectivity analyses were performed (D17, ILL). Several cycles of complexation/release have been completed with XCl_3 solutions (X = f-block elements) prepared in D_2O . The results obtained showed that the folding of the grafted LanM during the complexation of f-block elements and their unfolding during the release. In these experimental conditions, LanM remains effective for at least two cycles.

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Keywords: Protein, Surface functionalization, f-block elements, AFM, X-ray and neutron reflectometry

Effect of Salicylic Acid Treatment on Human Keratinized Skin Investigated by XPS Cluster Depth Profiling

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Stratum corneum is the skin's outermost layer, whose main constituent is keratin. The treatment of dermatological diseases showing hyperkeratosis is a serious problem in dermatology and cosmetics seriously affecting the population showing increasing prevalence. One of the treatment is a peeling agent like salicylic acid (SA), categorized as a keratolytic agent, however its mode of action is not fully understood. X-ray photoelectron spectroscopy (XPS) is a method for monitoring the changes of surface composition at atomistic level in 5–10 nm depth. The development of argon cluster sputtering enabled the investigation of deeper regions (nanometric level) even for biomaterials. In this pilot study, the mode of action of SA has been studied at atomistic level for the first time. Different concentrations of SA (3, 5, 10 wt%) in different time frames (1 day, 1 week, 1 month) was applied on human keratinized skin. The carbon, nitrogen and oxygen peak have not shown changes during the treatment, not showing the suggested desmolytic mechanism of SA. However, significant changes were observed in the sulfur peak, with increasing time and concentration the rate of sulfonate and sulfate was increased compared to thiol group indicating the break of sulfide bonds between the polypeptide chains in keratin, indicating that keratolysis happens at nanometric level. Already a 1 week-10 wt% SA treatment resulted in higher rate of sulfate compared to sulfonate indicating further oxidation of the keratolytic product. However, 1 month-10 wt% treatment resulted in the same surface composition as 3 wt%-1-month treatment indicating that enough time with low concentration can exert the same effect as higher concentrations. These findings have relevance in the design of future SA-based dermatologic therapies and that XPS can contribute to medical therapy monitoring. The measurement method and XPS results related to the sulfur peak is summarized in Fig.1. [1]

Acknowledgments: Discussions with Dr. A. Sejk are highly acknowledged. No funding was received for this work.

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[1] A.S. Racz Atomistic insights into salicylic acid treatment on human keratinized skin by XPS combined with argon gas cluster sputtering, Surf. Interfaces, 55, 2024, 105452

Keywords: XPS, Cluster sputtering, Skin, Keratin, Salicylic acid

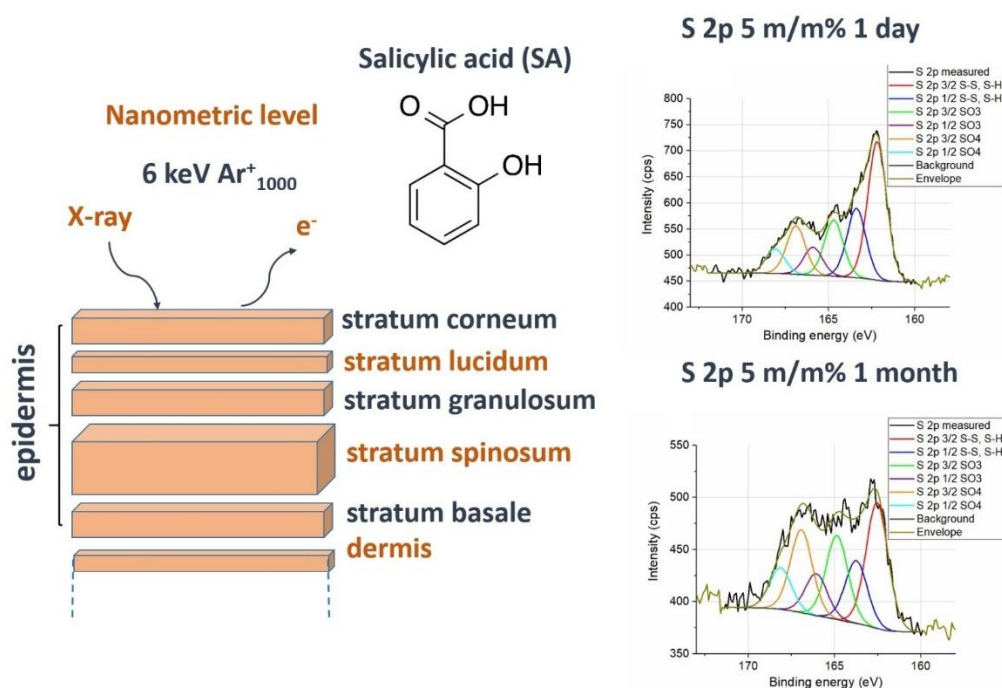


Fig.1 Following the effect of salicylic acid treatment of keratinized skin by XPS cluster depth profiling

Mapping Surface Topographies in Biofilms Using Neutral Atom Microscopy

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Understanding the structure and function of microbial biofilm surfaces is key to solving numerous problems across medical/materials science and yet remains a major challenge in surface and interface science. Biofilms form protective extracellular polymeric substance (EPS) matrices composed of polysaccharides, proteins, lipids and extracellular DNA, creating a dynamic interface that shields embedded microbes from thermal, chemical and mechanical stresses. Traditional imaging modalities, such as optical, confocal and electron microscopies, struggle to resolve this outermost layer due to its thin, transparent nature, and because sample preparation can introduce artefacts or obscure native surface features.

The scanning helium microscope (SHeM) offers a fundamentally different approach to surface visualisation. Using neutral helium atoms with energies of ~60 meV, the SHeM interacts exclusively with the outermost electron density of a material, enabling non-destructive, charge-neutral, true surface imaging without dyes, stains or metal coatings. Recent studies have demonstrated the SHeM's ability to reveal EPS topographies in *Pseudomonas aeruginosa* and *Clostridioides difficile* biofilms, including the effects of enzymatic disruption of eDNA within the matrix [1,2].

In particular, comparative imaging using SHeM, SEM and confocal microscopy shows that the SHeM uniquely visualises EPS-rich regions that are invisible or weakly expressed in electron or optical modalities. Overlays of SHeM and confocal images reveal enhanced EPS coverage, consistent with the SHeM's extreme surface sensitivity. Haralick texture analysis further quantifies these differences, with SHeM images exhibiting higher contrast and lower energy values, indicative of richer topographical information and greater sensitivity to subtle surface variations. These results reinforce the SHeM's role as a complementary technique capable of resolving surface features that conventional microscopies cannot access.

Looking forward, we outline the design principles for an Environmental SHeM (ESHeM) capable of imaging hydrated or "wet" biological materials across cryogenic to ~600°C conditions and at pressures up to ~0.03 mbar. Such an instrument could bridge the long-standing "pressure gap" in surface science, enabling in situ studies of biofilm interfaces under extreme temperature and pressure relevant to natural and engineered environments. Together, these advances position neutral-atom microscopy as a transformative tool for probing soft, hydrated, and environmentally stressed surfaces with unprecedented fidelity.

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Keywords: Biofilms, Neutral Atom Microscopy, Surface Imaging

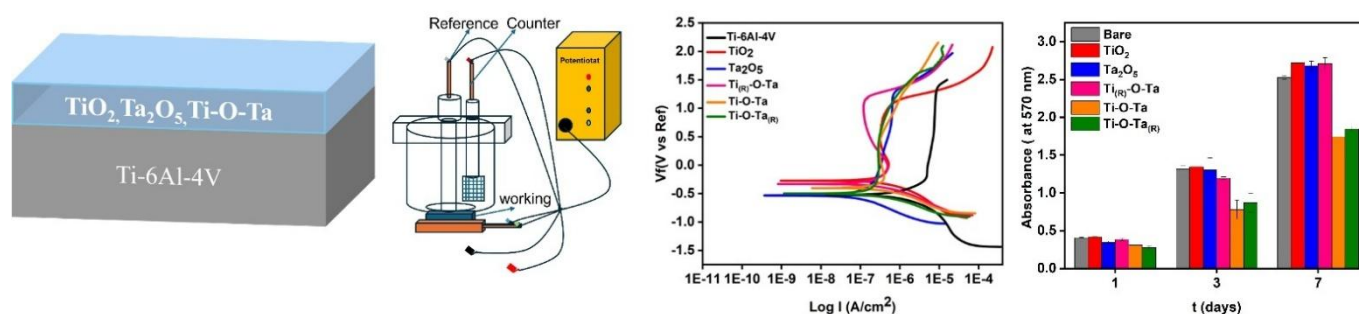
Cost effective corrosion resistant and biocompatible coatings for Ti-6Al-4V biomedical implant

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Titanium and Ti-6Al-4V are widely used implant materials for their good mechanical properties and antibacterial behaviour, but their surfaces require modification to address compromised corrosion resistance and biocompatibility. In this regard, coating plays a key role in encouraging osteoblast and tissue ingrowth, thus minimising the risk of loosening and enhancing corrosion resistance. Thus, this study focuses on modifying Ti-6Al-4V surfaces via a cost-effective bottom-up sol-gel method to prepare Titanium dioxide (TiO_2), Tantalum pentoxide (Ta_2O_5), and Ti-O-Ta nanocomposites with varying Ti/Ta atomic ratios by spin coating. TiO_2 offers antibacterial activity and corrosion resistance, whereas Ta_2O_5 provides excellent biocompatibility and scratch resistance. The resulting nanocomposites combine these attributes, prompting a comparative evaluation of their improved surface properties. Microstructural characterisation of the prepared films reveals different morphologies, roughness, uniform thickness and stoichiometric formation of the desired metal oxides and composites. A detailed corrosion study, including electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation, performed in Hank's solution, shows improved passivity and corrosion resistance for the coated films compared to the bare alloy substrate (Ti-6Al-4V), with I_{corr} values in the order of 10^{-8} A/cm^2 for the Ta_2O_5 -coated film. Furthermore, Pull-off adhesion testing confirms excellent film-to-substrate adhesion strength ranging between 15-26 MPa for the coated samples, effectively addressing one of the most common limitations of the sol-gel-derived coatings. In addition, most of the coated samples exhibited superior cell viability and attachment relative to the bare Ti-6Al-4V in both the MG-63 (human osteosarcoma) and NIH/3T3 (mouse embryonic fibroblast) cell lines across 1, 3, and 7 days. Overall, the study demonstrates the efficacy of the spin coated films TiO_2 , Ta_2O_5 and Ti-O-Ta composite films to enhance the surface properties of bare Ti-6Al-4V implant.

Acknowledgment: I would like to acknowledge the Defence Research and Development Organisation (DRDO) project (ERIP/ER/202302005/M/01/1824) for funding this study.

Keywords: Titanium dioxide (TiO_2), Tantalum pentoxide (Ta_2O_5), corrosion resistant, biocompatibility, adhesion strength



Surface chemistry of Lipid Nanoparticles polymorphic transitions induced by -80 °C freeze-thaw cycle

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Lipid Nanoparticles formulations critical quality attributes monitoring in transport and long-term storage conditions is required to ensure the efficacy of an emergency-ready and resilient public health response to pandemic threats.

One of the major challenges is transport and long-term storage of the colloidal formulations. Usually closely controlled low temperatures are required to maintain a high efficacy. While currently formulations which can be stored at up to +4 °C and methods for long term storage, e.g., lyophilisation with reconstitution right before use, are developed, it is generally necessary to understand how LNP formulations behave under storage and transport conditions.

Most commonly performed is LNPs physical characterization however, looking only at physical changes (in particular size and size distribution) of the particles is usually not sufficient to provide guidance for optimized formulations. Chemical characterization of LNPs is less commonly performed, both X-ray photo-electron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) used to study LNPs surface chemistry in combination with bulk chemical analysis techniques (e.g. HPLC). Therefore, it is crucial to combine physical and chemical characterization to obtain comprehensive information on the changes the particles when exposed to storage conditions.

In this study TEM, AF4-MALS-Raman and ToF-SIMS were used to simultaneously investigate the physicochemical changes LNPs undergo during freezing at -80 °C. LNPs of different compositions were characterized before and after freezing and their change encapsulation efficiency has been determined as a proxy for their efficacy. Changes in particle size distribution, particle morphology, zeta-potential, shape factor, density and characteristic Raman and SIMS signals are correlated to the changes in encapsulation efficiency. The results indicate that LNPs which undergo more severe changes during freezing can already be recognized before freezing. Thus, it may be possible to recognize unstable formulations upfront without time-consuming stability tests. Furthermore, the chemical changes determined by Raman and ToF-SIMS indicate that the physical changes are a result of molecular reorganization at least of the particle surface.

The study highlights the necessity of a combined physical and chemical analysis for a comprehensive investigation of LNP behavior.

Keywords: Quality Control, LNP-Blebs, ToF-SIMS, online-FFF-Raman, TEM

Interfacial Reactivity of ZnO-coated 3D Titanium Scaffolds

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Titanium alloys are extensively used in orthopaedic implants, yet challenges such as poor osseointegration and limited antibacterial properties remain. In this context, additive manufacturing offers new opportunities through the fabrication of three-dimensional (3D) scaffolds that can serve as bone substitutes, providing a favorable microenvironment for cell colonization. Despite these advances, surface functionalization remains crucial to simultaneously enhance bioactivity, biocompatibility, and resistance to infection—two major causes of implant failure.

In this work, Ti-6Al-4V 2D substrates and 3D scaffolds were fabricated by selective laser melting and subsequently functionalized with ZnO-based coatings. Following acid polishing to remove unmelted particles, a two-step strategy was implemented for surface functionalization: (i) deposition of ZnO nanoparticles, acting as seeds, followed by (ii) the growth of ZnO nanowires. Initially optimized on flat substrates, this approach was successfully extended to complex 3D architectures, ensuring homogeneous coating throughout the entire scaffold, including internal pores surface.

The interfacial reactivity of the coatings in culture medium—critical for governing biological response—was thoroughly investigated. Surface characterization (SEM, XPS, Raman spectroscopy) was coupled with ICP-MS analysis probing zinc ions release in solution. ZnO nanowire-coated surfaces exhibited bioactivity, as demonstrated by the rapid formation of a calcium phosphate-based layer in DMEM. In parallel, antibacterial activity was observed against *Escherichia coli*, while a more moderate effect was obtained for *Staphylococcus aureus*. Importantly, the coatings showed no cytotoxicity; however, nanowire architectures were found to hinder cell adhesion.

These findings demonstrate the potential of ZnO-functionalization on additively manufactured titanium scaffolds as implant materials. Ongoing work is focused on protein adsorption, a key early event governing cell–material interactions and subsequent tissue integration.

Keywords: Coating, Reactivity, Nanostructures

Surface-Functionalized Nanoparticles for Amplified QCM Detection of *Listeria monocytogenes*

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The agri-food sector is subject to very strict regulations regarding microbial contamination of raw and processed foods. In the dairy sector, European legislation [1] requires “the absence of pathogens in 25g of product.” Existing detection methods for *Listeria monocytogenes* (*Lmo*) are time-consuming, typically requiring one to several days to confirm the absence of contamination. In addition, these methods must have very low detection thresholds in order to detect the slightest contamination. There is therefore a critical need for rapid, sensitive and selective detection strategies. To achieve this, we are developing a bacteria nanoparticle-assisted capture strategy with Quartz Crystal Microbalance (QCM) detection for rapid and real-time monitoring of *Lmo* in milk and dairy products.

Surface biofunctionalization was done on flat gold surfaces and gold-magnetic nanoparticles, and thoroughly characterized by X-ray Photoelectron Spectroscopy (XPS) and Polarization Modulation Reflection–Absorption InfraRed Spectroscopy (PM-RAIRS), confirming successful covalent grafting and orientation of ligands of interest.

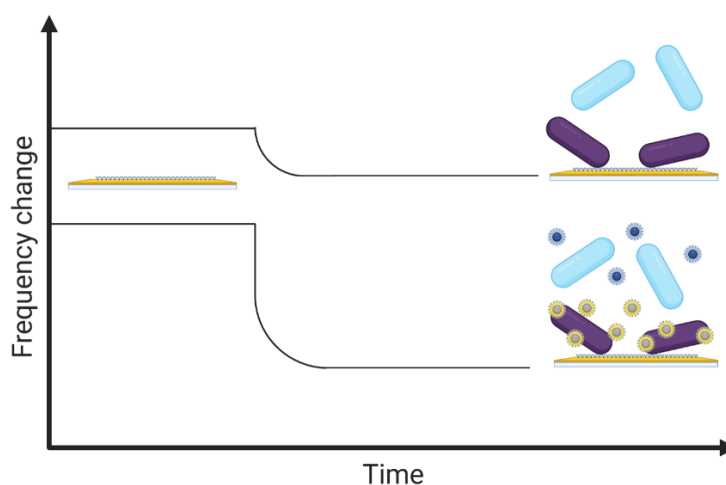
An anti-*Lmo* antibody was employed as the recognition ligand to confer selective binding to the target bacterium. Static capture assays demonstrated strong selectivity, with 94% discrimination against *E. coli* and 77% against *L. innocua*, despite the close phylogenetic relationship within the *Listeria* species, validating thus the specificity of the biointerface.

Dynamic interactions were investigated using QCM under flow conditions. Coupling bacteria to functionalized nanoparticles resulted in a significant enhancement of the QCM frequency shift [2] and dissipation, compared to bacteria alone (Figure), demonstrating mass amplification and modified viscoelastic interfacial behavior [3] respectively. This sandwich-like device approach combines surface chemistry, selective biorecognition, and amplified gravimetric detection, offering a promising strategy for rapid pathogen detection in complex dairy matrices.

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Keywords: Surface biofunctionalization, QCM sensing, Nanoparticles, Selective pathogen capture, Surface characterization



Development of a microfluidic separation device to recover CD34+ stem cells

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The need of stem cells for applications in regenerative medicine and hyperthermia-based anti-cancer therapy has gained interest over the years. CD34 is an antigen discovered in 1984 on haematopoietic stem cells [1]. These stem cells are present at very low concentrations in cord blood (less than 2% of the total cell population). Traditional recovery techniques such as Magnetic Activated Cell sorting and Fluorescence Activated Cell sorting require cell labelling and costly to produce [2].

In this project, we present a reusable microfluidic device system for the recovery of CD34+ stem cells without cell labelling and use of expensive immobilizing drugs.

This project started with the development of specific biointerface on gold substrates for static and dynamic capture of CD34+ stem cells. Two specific biointerfaces were developed; 1. Classical Thiol-MUA with EDC/NHS activation to graft CD34-antibodies. 2. Thiol-streptavidin biointerface to graft biotinylated-antibodies. The specific biointerfaces were characterized by XPS, FTIR and WCA. Cell types were classified as adherent or non-adherent as a basic model to evaluate how cord blood cell lines interact with our biointerfaces. Results showed biotin-streptavidin biointerface with 81.2% specificity to CD34+ stem cells as compared to Thiol-MUA with 73.1% specificity.

Reversible capture was done after CD34+ stem cell capture by comparing the use of Accutase and 0.1 M Glycine-HCl after cell capture to detach cells from the specific biointerface. Results showed that Accutase was gentler on the cells during cell detachment and maintained a higher cell viability of 80.8% after recovery. On the contrary, 0.1 M Glycine-HCl was harmful to the cells with a cell viability of 0% after recovery.

For dynamic capture, real-time in situ functionalization and capture of CD34+ stem cells on our specific biointerface were performed with commercial QCM. Quantification analysis after capture showed only up to 10% capture efficiency. In this project, we designed a new microfluidic chamber with a reduced flow cell height to improve capture efficiency and enable real-time imaging of captured cells using high-magnification microscopic imaging.

In conclusion, we successfully developed two distinct specific biointerfaces for the capture of CD34+ stem cells under both static and dynamic conditions, with reversible capture using Accutase.

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Keywords: CD34 Stemcell, Microfluidic, Recovery, Biointerface, Device

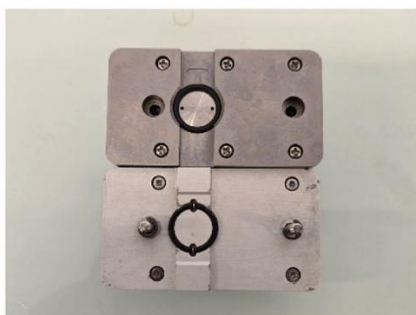
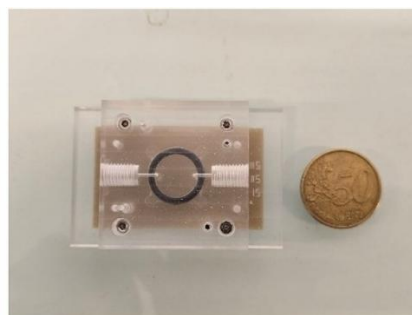


Figure: Commercial flow chamber



Custom-built microfluidic cell

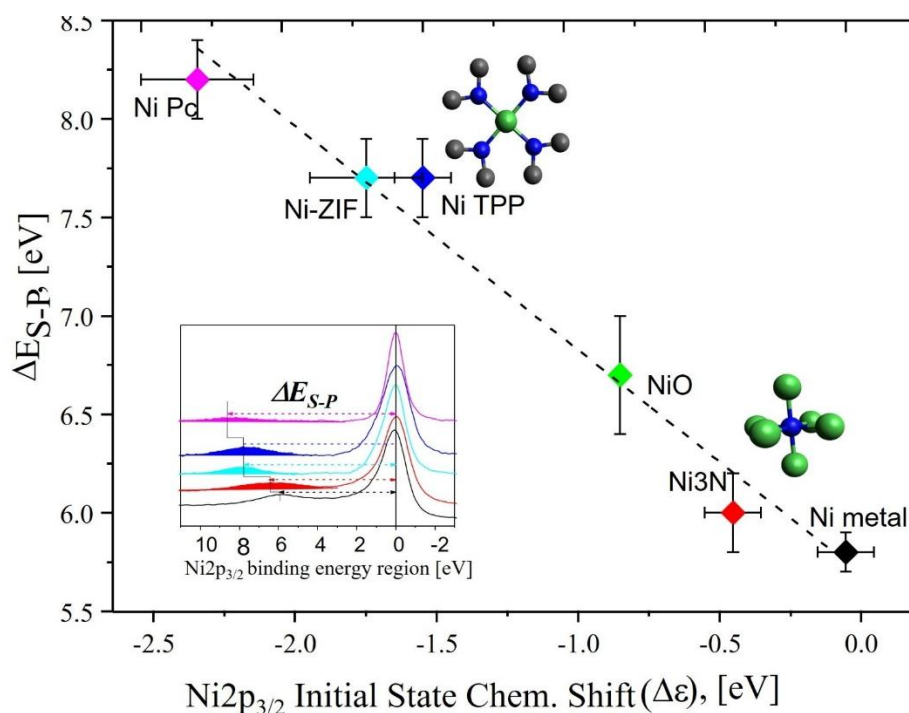
Catalysis

Characterizing Nickel state in Oxide-Free Nickel- Nitrogen Compounds: A Comparative XPS, XRD, and TEM Study

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The family of metal–nitrogen–carbon single-atom catalysts (SAC) have emerged as a rapidly advancing class of electrocatalyst for CO₂ reduction and for various redox reactions. Among them Ni–N–C catalyst has demonstrated exceptionally high catalytic activity. However, a fundamental understanding of their working mechanism is still missing the comprehensive experimental insight. The catalytic activity is governed by the metal oxidations state and metal–nitrogen coordination and is influenced by the formation of metal oxides. In the present work we examine the covalency and nickel–nitrogen coordination in an oxygen-free SAC nickel–nitrogen–carbon catalyst prepared from a Ni–imidazole framework precursor (Ni–ZIF). The Ni–ZIF is compared to the oxide-free nickel–nitrogen compounds with N/Ni atomic ratios ranging from 1:3 to 8:1. Thin film (Ni₃N) with Ni:N=3 was prepared via *in-situ* low energy N₂ ion implantation into pure nickel foil. Oxygen free thin films of Ni(II) Phthalocyanine (Ni Pc) (Ni:N=1:8) and Nickel(II) Tetraphenylporphyrin (Ni TPP) (Ni:N=1:4) were thermally evaporated in the XPS spectrometer. The study employs XPS in combination with TEM and XRD. TEM imaging of Ni–ZIF confirms Ni atoms atomically dispersed in the carbon matrix. The covalency of the Ni–N bonding is assessed through analyses of satellite structures in the Ni2p XPS spectra and correlated with the initial chemical shift ($\Delta\epsilon$). The $\Delta\epsilon$ and final state effect (relaxation energy ΔR) were estimated from the modified Auger parameter. Given the similarities in Ni:N ratios, modified auger parameters, $\Delta\epsilon$, and ΔR , between Ni–ZIF and Ni TPP, we speculate that Ni–ZIF also adopts square-planar structure, with Ni–N₄ configuration. We find that the satellite separation from the main Ni2p_{3/2} XPS peak (ΔE_{S-P}) is proportional to the $\Delta\epsilon$, while the satellite intensity monotonically decreases with the $\Delta\epsilon$. We propose that ΔE_{S-P} can serve as a quantitative descriptor of Ni–N bond covalency in oxide free compounds. Comparative analysis of the degree of covalency revealed the following trend: Ni₃N > Ni TPP, Ni–ZIF > Ni Pc. This finding is likely generalizable across a broad range of 3d transition metal–nitrogen materials.

Keywords: XPS, single atom electrocatalyst, Nickel Nitride



Titanium sulfide-based 2D nano(photo-)catalysts under reactive conditions

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To overcome challenges in the energy transition, heterogeneous (photo)catalysis is a key technology. Our target is to develop sustainable noble-metal free (photo-)catalysts by combining reduceable oxides with 2D surface materials, based on the surface-science approach: To overcome experimental limitations under technical conditions, we investigate model systems by using well-defined (single crystal) samples from ultra-high vacuum ($< 10^{-9}$ mbar) to *operando* conditions (usually few mbars). Combining insights from spectroscopy, microscopy and reactivity studies can gain a comprehensive picture down to the atomic level.^{1,2,3}

To replace critical elements such as platinum group metals (PGM) and many other transition metals, Titanium is an excellent candidate due to its availability and attractive sustainability footprint. As defects in TiO_2 are potent sites for small molecule conversion and greenhouse gas activation,^{4,5} herein recent results on hybrid Ti-based model systems for (photo-)catalytic reactions will be presented, especially combinations of oxides and nanostructured sulfides. For example, 2D TiS_2 nanoparticles on metal and oxide surfaces will be introduced as potential candidates for future photocatalytic applications.⁶

The synthesis chemical potential of S was identified as the key to tailor the shape and edge structure of single layer TiS_2 particles on $\text{Au}(111)$.⁶ These particles exhibit a bright edge feature in scanning tunneling microscopy similar to the quasi-metallic edge of MoS_2 .⁶ In comparison to $\text{Au}(111)$, the TiS_2 particles appear to interact more strongly with oxide substrates, here rutile TiO_2 (110), leading to more elongated shapes and a limited thermal stability. NEXAFS allows a chemically sensitive identification of structural features across both substrates. Finally, the surface chemistry of titanium sulfides was studied in reductive (molecular H_2) and mildly oxidative (H_2O) atmospheres in a wide temperature range, indicating a high stability of the TiS_2 basal planes under catalytically relevant conditions.

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Keywords: 2D Nanomaterials, Titanium, Sulfides, Oxides, Catalysis

Tuning TiO₂/AlInP Interfaces by Surface Preparation and ALD Chemistry for Unassisted Photoelectrochemical Applications

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Record unassisted solar-to-hydrogen efficiencies in photoelectrochemical (PEC) water splitting have been demonstrated using dual-junction III–V tandem cells based on epitaxially grown III–V photoabsorbers. However, these materials suffer from chemical instability under aqueous reaction conditions, necessitating effective corrosion-protection strategies. In state-of-the-art PEC devices, GaInP top photoabsorbers are combined with a highly *n*-type-doped AlInP(100) electron-selective contact for photogenerated electrons and a thin TiO₂ protection layer that provides chemical stability and selective charge carrier transport. The efficiency of these devices critically depends on precise control of the heterointerfaces between the III–V semiconductor and the metal-oxide protection layer, as interfacial chemistry governs recombination losses and, together with band alignment, determines photogenerated charge carrier extraction. Recent studies of the TiO₂/InP(100) heterointerface [Adv. Funct. Mater. 2025, 2506105] using X-ray and ultraviolet photoelectron spectroscopy (XPS/UPS) combined with *ab initio* molecular dynamics simulations have revealed pronounced interface-induced band bending, the formation of interfacial InPO_x related to phosphorus-rich InP(100) surface terminations, and a strong sensitivity of the interfacial chemistry to atomic-layer-deposition process conditions. These findings highlight the critical role of III–V surface preparation prior to metal-oxide deposition in determining the electronic structure of metal-oxide/III–V heterointerfaces.

Here, we relate these findings to AlInP(100) surfaces grown on GaInP photoabsorbers, prepared either with atomically well-ordered reconstructions or with thin native oxide layers formed after wet-chemical etching. TiO₂ was deposited by atomic layer deposition using titanium isopropoxide or titanium tetrachloride as Ti precursors with H₂O as the oxidant at different substrate temperatures. Using XPS and UPS, we analyze interfacial oxide formation, contaminant incorporation, and valence-band alignment at TiO₂/AlInP heterointerfaces, and elucidate how III–V surface preparation prior to atomic layer deposition and Ti-precursor chemistry govern the chemical composition, electronic band alignment, and bulk and surface properties of the TiO₂ films. We observe precursor-dependent differences in contaminant species within the TiO₂ bulk, at the surface, and at the TiO₂/III–V heterointerface, with concentrations strongly influenced by deposition temperature and post-growth annealing. We complement these results with synchrotron-based photoelectron spectroscopy measurements on selected samples prepared using different Ti precursors. By correlating oxide states and valence-band positions with those of InP-based reference systems, we demonstrate how AlInP surface preparation, together with ALD process parameters, governs the formation and electronic structure of TiO₂/III–V heterointerfaces.

Keywords: TiO₂/III–V heterointerfaces, XPS/UPS surface analysis, Atomic layer deposition (ALD)

U–Ce charge transfer in ceria-uranium mixed oxide: implications for thermochemical water splitting

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Reducible metal oxides are crucial for applications such as catalysis and solar energy conversion. Among these, cerium oxide (CeO_2) stands out for its stability and activity, yet its necessary reduction to promote Ce^{3+} active sites and associated oxygen vacancies requires high energy. Ceria doping or mixing with other elements has been proven successful in increasing the conversion from Ce^{4+} to Ce^{3+} . In addition to iso-valent and alio-valent doping with cations of lower oxidation state than Ce^{4+} , mixing ceria with metallic cations of higher oxidation state can induce a charge transfer that promotes and stabilizes Ce^{3+} sites. Among these elements, uranium cations are the most suitable candidates: substituting a fraction of Ce^{4+} with U^{4+} results in a charge-transfer process that promotes the formation of Ce^{3+} and U^{5+} states. In particular, the production of H_2 via thermochemical water splitting (TCWS) has been shown to increase significantly in powder samples with about 20% U content [1], which has been theoretically linked to lower oxygen vacancy formation energies [2].

The fundamental study of the charge-transfer process requires model systems, as heat- and mass-transfer limitations are largely absent in polycrystalline powders. Using in-situ X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED), we explored the redox properties and structural stability of 6 to 8 nm thick epitaxial (111)-oriented Ce_1 -

Keywords: Ceria, Uranium, XPS, TCWS, DFT+U

Reaction of Reduced Ti-Centers with N₂O in Hetero- & Homogeneous Coordination: From Oxides to Organometallic Environment

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The limited availability, toxicity, and socio-ecological impact of conventional (noble) metal catalysts such as gold or platinum necessitate the development of alternative catalytic systems based on earth-abundant and environmentally benign elements^[1]. Titanium represents a promising candidate in this context. It is highly abundant, exhibits comparatively low environmental impact, and offers rich redox chemistry across multiple oxidation states combined with a broad range of established ligand frameworks^[2,3]. These characteristics enable systematic tuning of titanium-based catalytic systems for diverse applications.

Using nitrous oxide (N₂O), a potent greenhouse gas and potential source of atomically bound oxygen as a model reactant, we investigate the reactivity of reduced titanium centers in both heterogeneous oxide environments and homogeneous organometallic coordination spheres. This comparative approach allows us to elucidate how the coordination environment governs electronic structure, oxidation behavior, and oxygen transfer processes.

Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) demonstrates that reduced TiO₂, the most prevalent titanium-containing compound, activates N₂O under atmospheric pressure. In this process, reduced titanium centers (Ti³⁺ and Ti²⁺) are irreversibly oxidized. Complementary ultra-high vacuum XPS (UHV-XPS) experiments reveal that the presence of Ti²⁺ species enhances the thermal stability of adsorbed N₂O on the rutile TiO₂ (110) surface. However, at pressures as low as 10⁻⁸ mbar N₂O, partial oxidation of these highly reduced centers is observed.

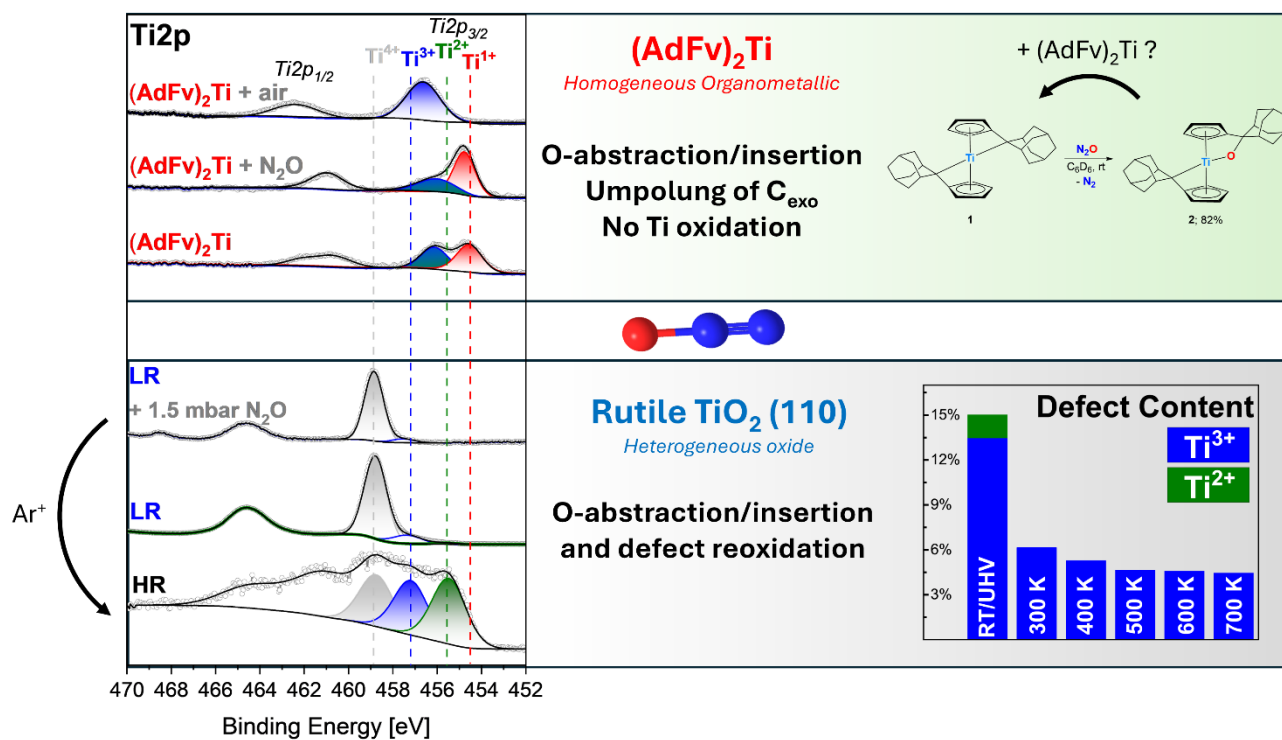
In contrast, the reaction of organometallic (adamantylidenebisfulvene)titanium complexes with N₂O proceeds via oxygen abstraction through insertion into the Ti–C_{exo} bond. Remarkably, this process does not lead to substantial oxidation of the titanium center. Combined XPS measurements and DFT calculations reveal the presence of a Ti¹⁺ species in the precursor complex. The oxygen insertion induces only a minimal formal charge redistribution at the titanium center, indicating that the redox burden is largely accommodated by the ligand framework rather than the metal^[4].

The contrast between irreversible oxidation in heterogeneous TiO₂ systems and the redox-buffering behavior observed in homogeneous organometallic complexes highlights the decisive role of ligand participation and electronic delocalization in stabilizing low-valent titanium species. The results presented here therefore provide fundamental insight into how coordination environment controls the redox chemistry of early transition metals during small-molecule activation.

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Keywords: (Near-Ambient Pressure) X-Ray Photoelectron Spectroscopy, Nitrous oxide, Titanium dioxide, Titanium complexes, Ligand framework



Correlating Surface Science and Catalysis Data: Enantioselective Hydrogenation, Deoxygenation and Olefin Metathesis

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Measurements in conventional surface science are carried out under conditions far removed from those found in actual heterogeneous catalysis reactions. Pressure-gaps, materials-gaps and temperature-gaps are some of the terms used to emphasize the differences between the two domains. Nevertheless, in both cases, the key chemistry obviously involves molecules or molecular fragments in close contact with surfaces: the more the surfaces involved are similar the more the observations from both domains are likely to dovetail. We present examples from our studies where surface science observations closely match observations made under catalyst operating conditions. The first study uses precisely defined chirally-modified Pt(111) surfaces as models for enantioselective hydrogenation catalysts. In the second study, poorly defined molybdenum carbide surfaces serve as models for deoxygenation and olefin metathesis catalysts. Both of the studies reveal crucial mechanistic details that were hitherto unknown from even *operando* catalysis studies. The work illustrates some of the compromises, pitfalls and advantages involved in looking at heterogeneous catalysis through the lens of surface science. The studies were performed using XPS, TPD, STM, RAIRS, and DFT.

Keywords: enantioselective hydrogenation, STM, RAIRS, DFT, olefin metathesis

Ce-Induced Nanod defect Engineering and Electronic Regulation for Efficient CO₂ Electroreduction to Formate over Bi₂O₂CO₃

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Electrochemical CO₂ reduction reaction (CO₂RR) to formate is a promising carbon-neutral pathway but remains limited by insufficient catalytic activity and selectivity. Herein, a nanod defect-rich Ce-Bi₂O₂CO₃ nanosheet catalyst was synthesized via ion exchange from a Ce-BiOCl precursor, enabling simultaneous regulation of nanod defects and electronic structure. CeO_x nanoclusters formed during the synthesis of the BiOCl precursor act as structural regulators in the subsequent ion-exchange process, inducing abundant nanod defects and undercoordinated active sites while preserving the two-dimensional morphology, while Ce doping induces electronic reconstruction through Ce-O-Bi interactions. Benefiting from the synergistic nanod defect and electronic effects, the catalyst exhibits outstanding CO₂RR performance, achieving a formate Faradaic efficiency of 96.2% at a current density of 31.8 mA cm⁻² at -1.1 V (vs. RHE) in an H-type cell with excellent stability over 30 h. In a flow cell, a maximum Faradaic efficiency of 96.8% is achieved at -1.0 V (vs. RHE), corresponding to a formate partial current density of 394.1 mA cm⁻², while a maximum current density of 466.2 mA cm⁻² is obtained at -1.2 V (vs. RHE). In situ FTIR and density functional theory calculations reveal that oxygen vacancies derived from defect engineering act as key active sites to stabilize the *OCHO intermediate and facilitate selective CO₂-to-formate conversion, while Ce-induced electronic effects effectively suppress the competing hydrogen evolution reaction.

Keywords: CO₂RR, Formate, Bi₂O₂CO₃, Nanod defect, Electronic Regulation

Effect of Pt Decoration and its Thickness on Catalytic Properties of Cu–Zn Electrocatalysts

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Cu–Zn-based materials have been widely investigated as promising catalytic platforms owing to their tunable electronic structures, earth-abundant compositions, and industrial relevance. Noble metal decoration, particularly with Pt, has been recognized as an effective strategy for enhancing catalytic activity; however, the interplay between Pt thickness, dealloying-induced surface reconstruction, and the evolution of catalytically active sites remains poorly understood.

In this study, we systematically investigated the thickness-dependent surface chemistry of Pt-modified Cu–Zn electrodes and its impact on active-site formation. Cu–Zn alloy electrodes were prepared by electrodeposition and subsequently decorated with Pt via sputtering for 300 and 600 s to precisely control the Pt thickness. Acid-induced dezincification was performed using 5 M HCl for 1 min and 5 min, enabling controlled surface reconstruction. Chloride adsorption was employed as a surface-sensitive probe of the electronic structure and stability, and the reconstructed surfaces were characterized by scanning electron microscopy and energy-dispersive X-ray spectroscopy.

The selective dissolution of Zn during the acid treatment resulted in Cu-rich reconstructed surfaces with Pt-decorated domains. The chlorine content exhibited a pronounced dependence on the Pt thickness and treatment time. For the thin Pt layers (300 s sputtering), non-monotonic variation in chlorine content was observed, with the chlorine content decreasing from 11.24 % to 9.64 % upon prolonged acid exposure, indicating dynamic surface restructuring and reversible chloride adsorption. In contrast, thicker Pt layers (600 s sputtering) showed a substantial increase in the chlorine content from 14.34 % to 28.13 %, indicating stabilization of Pt–Cl species and formation of electronically modified Pt domains.

Finally, we proposed a thickness-dependent active-site model. Thin Pt layers partially covered the Cu–Zn substrate, exposing Cu-rich interfacial sites that underwent continuous restructuring and provided a dynamic catalytic environment. In contrast, thicker Pt layers formed continuous Pt domains that stabilized chloride species and suppressed interfacial Cu–Zn exposure, leading to distinct electronic and adsorption properties. These findings reveal that the Pt thickness critically governs the surface reconstruction pathways, chloride stabilization, and active site evolution in Cu–Zn–Pt catalytic systems.

This study provides fundamental insights into surface-reconstruction-driven active-site control in noble-metal-modified alloy catalysts and offers a rational design strategy for optimizing the catalytic performance through noble-metal thickness tuning.

Keywords: Cu–Zn, Pt thickness, sputtering, Cu–Zn–Pt catalytic

Revealing the Impact of pH on Nanoscale Hydrogen Evolution Catalysis via Operando Optical Microscopy

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Molybdenum disulfide (MoS_2) has emerged as a promising non-precious catalyst owing to its excellent catalytic performance.[1] Although the mechanism of the Hydrogen evolution reaction (HER) on MoS_2 has been studied across a range of structural forms, its dependence on pH remains comparatively underexplored, despite its potential to provide important mechanistic understanding.[2]

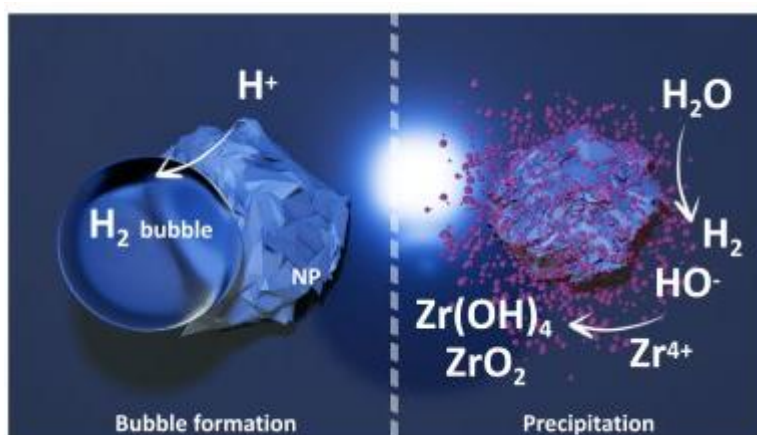
In this work, HER activity was examined at the single-nanocatalyst level using MoS_2 and Pt/C nanoparticles as model systems, with a methodology that can be extended to other nanocatalysts. A custom-built reflective microscopy platform was employed to monitor catalytic processes in real time. This technique enables simultaneous visualization of proton reduction and water reduction by directly detecting their reaction products: hydrogen bubble formation during proton reduction—an established indicator of catalytic activity [3]—and the formation of metal hydroxide (or oxide) precipitates during water reduction (Fig. 1).

Building on our previous studies [4][5], we investigate the pH-dependent catalytic behavior of individual nanocatalysts by evaluating onset potentials associated with both bubble nucleation and precipitate formation. In addition, detailed analysis of bubble growth and precipitation dynamics was performed. The results show strong agreement with prior macroscopic studies while introducing a novel approach for probing catalytic activity at the nanoscale.

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Keywords: Optical Microscopy, Hydrogen Evolution Reaction, Catalysis, Molybdenum disulfide, nanoscale



Corrosion

Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling for the Study of Oxidation and Prevention of Wear

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Understanding and preventing surface degradation of metal-based components when exposed to operational environments is crucially important for many industrial sectors. Typical degradation mechanisms include corrosion, oxidation and wear. Spectroscopic and microscopic techniques are valuable in determining the thickness and chemical composition of surface layers formed as a result of corrosion or high temperature oxidation. These techniques can also be applied to studying thermochemical surface treatments and vapour deposited coatings to protect against wear. XPS sputter depth profiling has traditionally been employed to monitor changes in chemical composition and chemical state information as a function of depth. However, drawbacks of the technique include preferential sputtering effects and the profiling depth being limited to a few microns in practical time scales. The recent introduction of femtosecond laser ablation (fs-LA) as a novel XPS depth profiling method has enabled these drawbacks to be overcome. fs-LA XPS depth profiles have been using a femtosecond laser with a pulse length of 160 fs and wavelength of 1030 nm. Use of SEM cross-sections combined with fs-LA XPS depth profiles to understand changes in the chemical composition and chemical state information as a function of depth for thick oxide scales, nitriding treatments, PVD wear resistant coatings etc will be presented. The ability of fs-LA XPS to retain the true chemical information and ability to profile to depths > 50 μm will be demonstrated, highlighting the importance of this new technique for the study of high temperature oxidation and protection of surfaces through different surface engineering processes.

Keywords: XPS, Depth Profiling, Femtosecond Laser Ablation, High Temperature Oxidation, Surface Engineering

Analysis of Sodium Phosphate as a Corrosion Inhibitor for Grey Cast Iron Brake Discs in Automotive Applications

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In brake disc assemblies, adhesion between the brake pads and the disc due to corrosive phenomena, commonly known as the stiction phenomenon, represents a critical issue for vehicle braking systems, especially when the braking system is exposed to aggressive environments. Such conditions include contact with moisture, pollutants, or chlorides, which are typical of winter driving conditions.

This phenomenon is closely related to the corrosion of grey cast iron discs, which leads to the formation of corrosion products capable of penetrating the porosity of the friction material, particularly during the application of the parking brake. The development of friction materials with low susceptibility to stiction is therefore essential for improving the performance and reliability of braking systems.

This objective can be pursued through careful selection of the components of the friction material, including the use of corrosion inhibitors capable of controlling the local conditions at the pad–disc interface. The present study focuses on the use of phosphates as environmentally friendly corrosion inhibitors.

To investigate the inhibition mechanism, the corrosion behavior of grey cast iron samples was analyzed in different electrolytes simulating the typical conditions of the pad–disc interface, with the addition of phosphates. The analysis was carried out using a wide range of electrochemical techniques along with complementary characterization methods.

In addition, a specific form of pitting corrosion affecting grey cast iron discs was examined. This corrosion morphology occurs under mildly alkaline conditions and in the presence of phosphates. The results of this study provide significant insights for the design of friction materials with improved resistance to corrosion-related effects and offer an analysis of a particular pitting corrosion morphology that has been scarcely addressed in the current corrosion literature.

Keywords: cast iron, stiction phenomenon, tubular pitting corruptions

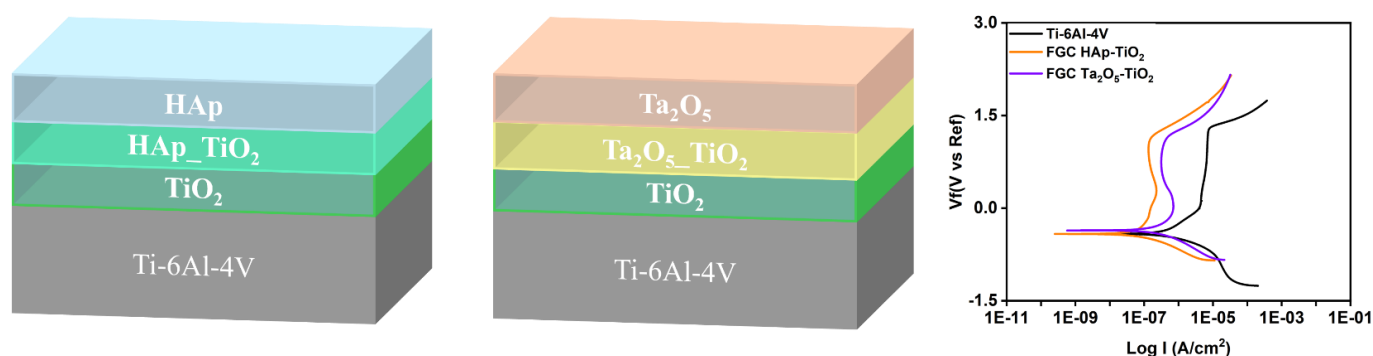
Development of High quality functionally graded coating (FGC) on Ti-6Al-4V as biomedical implant

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Numerous metal oxide and nitride coatings are the subject of a vast number of studies to improve the compromised adhesion strength, biocompatibility, and corrosion resistance of Ti-6Al-4V alloys for biomedical implants. However, single-layer coatings on Ti-6Al-4V generally demonstrate limited improvements in terms of these desired characteristics, durability and additional incurred cost, which could be primarily attributed to the interface incompatibility between the coating and that of the substrate. To overcome these, a multi-layer approach consisting of functionally graded coatings (FGCs) is employed here, wherein FGCs are fabricated on Ti-6Al-4V using a cost-effective sol-gel method followed by spin coating. Compositional gradients consisting of Tantalum pentoxide-Titanium dioxide ($\text{Ta}_2\text{O}_5/\text{TiO}_2$ - $\text{Ta}_2\text{O}_5/\text{TiO}_2$) and Hydroxyapatite (HAp)-Titanium dioxide (HAp/HAp- $\text{TiO}_2/\text{TiO}_2$) are developed using optimised process parameters, following which a detailed microstructure, corrosion, biocompatibility and adhesion tests are conducted. The intermediate layer is found to play a vital role in minimising the compatibility mismatch between the top and the bottom layers. Microstructural analyses using scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), and atomic force microscope (AFM) reveal uniform, stoichiometric films with desired roughness, while X-ray diffractometry (XRD) asserts the formation of preferred phases. A detailed corrosion study performed in Hank's solution, including electrochemical impedance spectra (EIS) and Potentiodynamic polarization (Tafel analysis) reveals reduced for both these FGCs relative to bare and single-layer coated substrates. Notably, the HAp/HAp- $\text{TiO}_2/\text{TiO}_2$ configuration is found to demonstrate superior passivation and corrosion resistance as compared to the ($\text{Ta}_2\text{O}_5/\text{TiO}_2$ - $\text{Ta}_2\text{O}_5/\text{TiO}_2$) configuration. Furthermore, a comparable average adhesive strength of 23-25 MPa is achieved in both these configurations in the Pull-off adhesion test. In vitro assays using MG-63 (human osteosarcoma) and NIH/3T3 (mouse embryonic fibroblast) cell lines over 1, 3, and 7 days indicated enhanced cell viability and attachment on both configurations relative to the uncoated alloy. Overall, the results demonstrate that both FGCs provide a simple, low-cost strategy to significantly improve the corrosion resistance and biological performance of Ti-6Al-4V implants.

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Keywords: Hydroxyapatite (HAp), Tantalum pentoxide(Ta_2O_5), functionally graded coatings (FGCs), electrochemical impedance spectra (EIS), biocompatible



How Late Can Corrosion Inhibitors Be Released? Local inhibiting layer formation and re-immersion stability

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Understanding how late an inhibitor can be released after corrosion initiation and how stable inhibiting layers are once inhibitor has been depleted from the coating are important but unattended factors for the design of anticorrosion coatings. In this work, we investigated the influence of Ce(III) release timing as function of AA2024-T3 dealloying and the stability of the resulting inhibiting layers during re-immersion in non-inhibited salt solutions. To gain information at sub intermetallic particle level, we used operando (in-situ) reflected light microscopy with high time and spatial resolution combined with electrochemical noise. Image correlation at pixel level revealed the kinetics of inhibiting layer local deposition and growth as well as degradation and stability at high spatial resolution (submicron).

To assess the effect of delayed inhibitor availability, $\text{Ce}(\text{NO}_3)_3$ was introduced at 0, 30, 60, and 180 s after the start of immersion in NaCl aq. solution to reach a final concentration of 0.001 M. Results show that thicker inhibiting layers are obtained when the dealloying is more advanced. When $\text{Ce}(\text{NO}_3)_3$ was supplied within 60 s of immersion, surface activity related to degradation slowed earlier. This indicates that corrosion protection can still be achieved even after the onset of localized activity, provided inhibitor release occurs sufficiently early. To further evaluate the durability of the inhibiting layers formed on AA2024-T3, the samples were re-immersed in un-inhibited salt solutions. Re-immersion activity varied with IMP composition, spatial distribution, and the extent of Ce(III) precipitation. IMPs were classified into four categories based on whether their activity was high or low during both the initial immersion and re-immersion stages. Notably, most particles showing high activity during re-immersion (i.e. more instability) had exhibited low activity during the initial immersion, highlighting the heterogeneous and dynamic nature of local protection. Overall, it was found that inhibiting layers formed after a brief delay in inhibitor supply (30 s) offered same stability (protection) than layers formed during 72h immersion with no pre-dealloying (0s).

The results highlight the high quantification potential of reflected light microscopy for operando studies of local corrosion inhibition and provides design rules to develop more efficient anticorrosion systems considering the dimensionality of release time and inhibiting layer stability.

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Keywords: corrosion inhibitor, local corrosion, intermetallic particles, new techniques

A computer vision approach for linking outdoor surface wetting states to atmospheric corrosion sensor signals

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Atmospheric corrosion sensors are playing an increasingly important role in monitoring and managing corrosion in changing environments¹⁻³. However, their electrochemical signals are shaped not only by the ambient conditions, but by the evolving surface electrolyte state that determines when and how the surface becomes electrochemically active. Quantifying this electrolyte state in the field remains challenging, leading to uncertainty in sensor interpretation and limiting the transferability of laboratory insights to outdoor exposure.

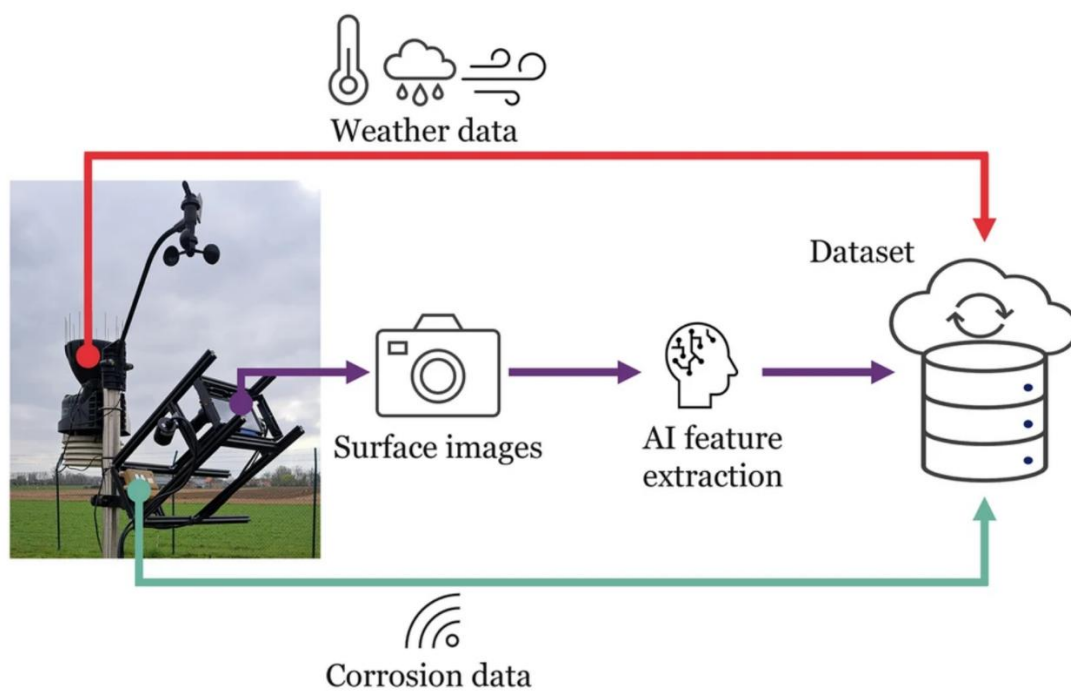
In earlier work, we demonstrated that AI-based image analysis can track condensation-driven droplet growth and reveal time-dependent links between electrolyte evolution and sensor response under controlled conditions³. More recently, we implemented a field-deployable monitoring approach combining imaging, environmental logging, computer vision and real-time corrosion sensing, and showed that image-derived electrolyte descriptors improve predictive performance relative to weather-only models during distinct wetting events⁴.

Here, we extend this methodology to longer outdoor exposure periods and use it to compare how multiple atmospheric corrosion sensor types respond when subjected to the same evolving environment. The extended monitoring window also captures progressive changes in surface state, including corrosion product build-up, and evaluates how this alters electrolyte formation, persistence and redistribution over time. The results provide a pathway toward more physically grounded interpretation of corrosion sensor data, more robust data-driven prediction, and improved alignment between laboratory wetting protocols and outdoor electrolyte behaviour.

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Keywords: Computer vision, Atmospheric corrosion sensors, Electrolyte layer dynamics, In-field monitoring, AI

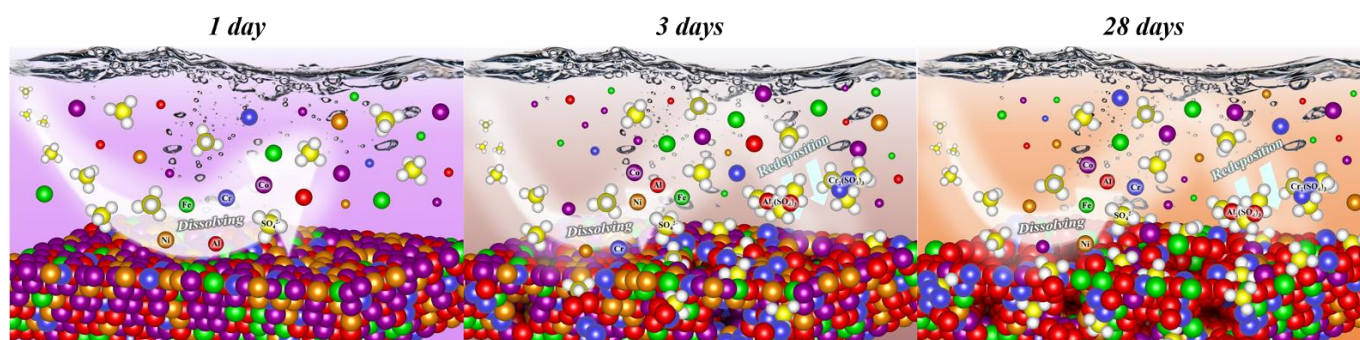


Passivation and Corrosion of AlCoCrFeNi HEA Revealed by Hard and Soft XPS

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Recently, high-entropy alloys (HEAs) have attracted significant attention due to their exceptional properties, including high yield strength, enhanced ductility, and excellent corrosion resistance, which challenge conventional alloy design strategies. In this study, the corrosion behavior of AlCoCrFeNi HEAs in 0.5 M H₂SO₄ solution under ambient conditions was investigated using soft and hard X-ray photoelectron spectroscopy (XPS) for surface and bulk analyses (~5 nm and >10 nm probing depths, respectively). Surface and bulk compositional information was obtained and compared using a switchable target system, in which Al K α (1486.6 eV) and Cr K α (5414.8 eV) sources generated X-rays for conventional XPS and hard X-ray photoelectron spectroscopy (HAXPES), respectively. HAXPES enables more accurate compositional analysis of the bulk region while minimizing interference from Auger electron signals originating from neighboring transition metals. In addition, the dissolution of metallic ions in the H₂SO₄ solution was analyzed using inductively coupled plasma–mass spectrometry (ICP–MS) and correlated with the XPS/HAXPES results. The analysis revealed that Al and Cr compounds redeposited on the HEA surface, whereas Fe, Co, and Ni continued to dissolve into the acidic solution. It is suggested that the dissolution of Fe, Ni, and particularly Co may reduce the dissolution rate of Cr. Consequently, a passivation layer composed of Cr hydroxide/oxide forms and protects the HEA from further corrosion. Although Al tends to leach out prior to the formation of the Cr passivation layer, Al compounds remain the dominant species on the HEA surface. These findings, revealed through the combined XPS/HAXPES analytical approach, provide new insights into corrosion mechanisms in HEAs and may offer a new paradigm for the quantitative analysis of complex alloy systems.

Keywords: High-entropy alloys, Hard X-ray, HAXPES, Corrosion behavior, Surface analysis



Quantitative and Time-Resolved Low Energy Ion Scattering of Thin Oxide Film Growth on HEA

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Low Energy Ion Scattering (LEIS) provides direct access to the outermost atomic layer of materials, enabling truly surface-specific and quantitative compositional analysis. In this contribution, we demonstrate how reference-based LEIS quantification, combined with complementary modelling and spectroscopy, resolves dynamic processes governing surface composition and evolution in technologically relevant systems.

First, we establish robust quantitative reference systems as a basis for reliable LEIS analysis of oxides. By combining LEIS with SDTrimSP sputtering simulations, we investigate the depth-dependent compositional evolution during sputtering and surface treatment of oxide standards for oxygen quantification, including SiO₂, ZnO, and TiO₂. These model systems allow us to disentangle sputtering-induced mixing, preferential sputtering, and surface contamination effects. A consistent reference-based quantification strategy is developed using well-defined single-crystal facets and materials, providing transferable calibration schemes. This approach is not limited to oxides but can be extended to other compound classes such as nitrides, establishing a general framework for quantitative LEIS analysis.

In a second step, we apply this methodology to the investigation of time resolved early-stage oxidation and passivation in complex alloys, including equiatomic CrMnFeCoNi, CrFeNi, and FeCr17.5Ni10 stainless steel. Using an *in-situ* LEIS approach with stepwise oxygen dosing, we monitor elemental redistribution in real time within the outermost atomic layers. Complementary XPS and angle-resolved XPS measurements confirm the formation of chemically stratified native oxides, characterized by Fe-rich outer layers, Cr- and Mn-enriched intermediate regions, and Ni/Co enrichment in the subsurface.

The results reveal oxidation kinetics consistent with the Cabrera–Mott model. Importantly, Cr oxidation initiates the process, establishing the electric field that drives subsequent cation migration and layered oxide formation. Mn rapidly oxidizes when present, while Ni and Co are displaced into subsurface regions. At higher oxygen exposures, Fe resurfaces and partially replaces Cr and Mn, resulting in the characteristic layered passivation structure.

Together, these studies demonstrate that LEIS uniquely captures dynamic, atomic-scale surface processes, linking reference-based quantification with real material behavior. The findings highlight that surface composition is governed by dynamic, process-dependent phenomena rather than static bulk properties, providing key insights for thin film processing and the design of corrosion-resistant multi-component alloys.

Keywords: LEIS, passivation, oxide films, ion scattering, XPS

Selective Oxidation of Low Cu and Cu Enriched EAF Steels: A Combined SEM–XCT Study

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Electric arc furnace (EAF) steelmaking is a key route to reduce energy consumption and CO₂ emissions, but recycling inevitably leads to the accumulation of tramp elements such as copper (Cu) in scrap-based steels. Cu is known to cause hot shortness during high temperature processing due to the selective oxidation and Cu enrichment at the steel-scale interface. This work investigates the high temperature oxidation susceptibility of two medium-carbon EAF steels with different Cu levels (0.02 and 0.16 wt.%). Isothermal oxidation tests are being conducted between 1000 and 1200 °C for holding times of 20, 40, 60, and 120 min. Oxidation kinetics, scale growth exponent, and activation energies are being determined from mass-gain measurements, while the oxide scale morphology and Fe–Cu partitioning are being characterized using cross-sectional and surface electron microscopy. In addition, X-ray computed tomography (XCT) is being employed to obtain three-dimensional oxide thickness distributions and to quantify internal voids, spallation cracks, and blisters. By correlating 2D microscopy with 3D XCT observations, the study aims to clarify the oxide formation and damage mechanisms in Cu-containing EAF steels.

Keywords: Oxidation, Electric Arc Furnace, Sustainability, Tramp elements

Effect of hydrogen on the native oxides of steels

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In the context of a growing hydrogen economy, we must confront an increasing number of challenges rising from hydrogen interaction with steel across various stages of production, storage, transportation, and utilization. The oxide layer forming on the metal has a key role in defining the interaction with hydrogen from the environment, because it is the first barrier of the material against hydrogen surface reaction and transport. Hydrogen influences the corrosion resistance of stainless steels due to its interaction with their nm-thick oxide layer and its possible reduction, and once inside the material, it can cause embrittlement of susceptible steels ultimately leading to mechanical failure.

While extensive research has been performed on the bulk embrittlement effect of hydrogen, interaction with the material surface is still unclear.

To advance the mechanistic understanding of the oxide hydrogen-interaction, the behavior of native oxides present on Fe and FeCr alloys was investigated focusing on modification due to oxide-hydrogen chemical interaction studied by surface analytical methods.

The goal was to understand whether and according to which mechanism hydrogen can cause a partial or complete reduction of the oxides, and if the addition of chromium in the alloy could influence and slow down the process.

Electrochemical hydrogen charging was carried out inside a glovebox, performing hydrogen exposure on one side of the sample while maintaining an inert argon atmosphere on the opposite side. The samples were subsequently transferred directly to the X-ray photoelectron spectroscopy (XPS) analysis chamber without exposure to air, though a UHV vacuum transfer system. This approach minimizes surface polarization and prevents unintended modifications, such as reoxidation due to interaction with air, thereby enabling reliable assessment of hydrogen-induced changes.

The XPS analysis focuses on determining the oxide layer thickness, composition, oxide/hydroxide phase distribution, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio within the oxide, the chemical states of elements at and near the oxide/alloy interface, and degree of carbon contamination. To ensure a reliable fitting of the XPS spectra, reference samples of the different oxide components were measured and fitted.

This approach offers new insights into hydrogen-oxide reaction pathways within steel surface layers, enhancing our understanding of hydrogen-steel interactions.

Keywords: Native steel oxides, Hydrogen-oxide interaction, Electrochemical hydrogen charging

Functionally graded corrosion resistant coatings on Ti-6Al-4V for biomedical implant applications

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The integrity and performance of biomedical implants are often compromised by harsh physiological environments. To alleviate these challenges, this study develops functionally graded coatings that create a gradual transition in composition and properties between the implant substrate and the biological environment, reducing interfacial stress and preventing issues such as cracking and poor adhesion. Consequently, these coatings improve mechanical compatibility and bioactivity while enhancing the long-term stability of the implant. In the present study, two functionally graded coating systems (FGCs), deposited on Ti-6Al-4V alloy via RF magnetron sputtering, are investigated: Hydroxypapatite-Titanium dioxide (HA-TiO₂) with HA as the top layer and Tantalum pentoxide-Titanium dioxide (Ta₂O₅-TiO₂) with Ta₂O₅ as the top layer. Additionally, multilayer coatings of HA-(HA+TiO₂)-TiO₂ and Ta₂O₅-(Ta₂O₅+TiO₂)-TiO₂ with intermediate ratios of 1:1, 2:1, and 1:2 are designed to enhance the corrosion resistance and biocompatibility of titanium alloy implants. Functionally graded and multilayer HA-TiO₂ and Ta₂O₅-TiO₂ coatings employ TiO₂ as an adhesion-promoting interlayer on Ti-6Al-4V, while HA and Ta₂O₅ provide bioactivity and chemical stability, leading to enhanced corrosion resistance under simulated physiological conditions. The effectiveness of the fabricated thin films is assessed through comprehensive corrosion testing using Electrochemical Impedance Spectroscopy and Potentiodynamic polarization in Hank's solution, a medium that emulates physiological body fluids. Furthermore, the films are characterized for their microstructure and compositional make-up via an array of experimental techniques, whereas their mechanical durability and adhesion to the substrate are evaluated through adhesion tests. Furthermore, MTT assays are conducted employing MG-63 (human osteosarcoma cells) and NIH 3T3 (mouse fibroblast cells) cell lines for 1, 3 and 7 days to assess cell viability, attachment and proliferation. Electrochemical results establish that the Ta₂O₅-TiO₂ FGC generates strong passive layer with high impedance and capacitive response, yielding excellent corrosion resistance and exceedingly low corrosion current densities in the range of 67.15 to 86.93 nA/cm² among the tested coatings, whereas HA-TiO₂ FGC films perform moderately and uncoated Ti-6Al-4V remains the least protected in the simulated physiological medium. These films also promote superior cell attachment and growth over 7 days, indicating their biomedical potential for implant applications in a biological environment. Overall, the results demonstrate that these coatings effectively enhance both the electrochemical stability and biological performance of biomedical implants.

Keywords: RF magnetron sputtering, Corrosion resistance, Functionally graded coatings, Biocompatibility, Biomedical application

Energy storage and conversion

Accelerating Advanced Materials Innovation in the age of Artificial Intelligence

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Technological progress and sustainable development fundamentally rely on the discovery of advanced materials that enable cleaner energy, smarter devices, resilient infrastructure, and efficient resource use. From energy storage and conversion to electronics, catalysis, and structural applications, new materials are the foundation of transformative innovation. Yet, conventional trial-and-error approaches to materials discovery remain slow, expensive, and increasingly inadequate to address the growing complexity and urgency of today's scientific and technological challenges. The decades-long development cycles observed in areas such as lithium-ion batteries clearly demonstrate the limitations of traditional methodologies. Across diverse application domains, there is an urgent need to accelerate the discovery of high-performance, cost-effective, non-toxic, earth-abundant, and environmentally sustainable functional materials. In this talk, I will present FULL-MAP, a pioneering European initiative designed to transform the way materials and interfaces are discovered. By integrating laboratory automation, high-throughput experimentation, and artificial intelligence and machine learning-driven multiscale, multiphysics modeling, FULL-MAP establishes a closed-loop, data-driven framework for systematic and adaptive experimentation. This approach accelerates discovery, reduces cost and risk, and demonstrates a new paradigm for materials innovation—one that can be extended beyond batteries to a wide range of advanced material systems critical to future technologies.

Keywords: Materials Discovery, Surface and Interface, Energy storage and conversion, Artificial Intelligence, Materials Acceleration Platform



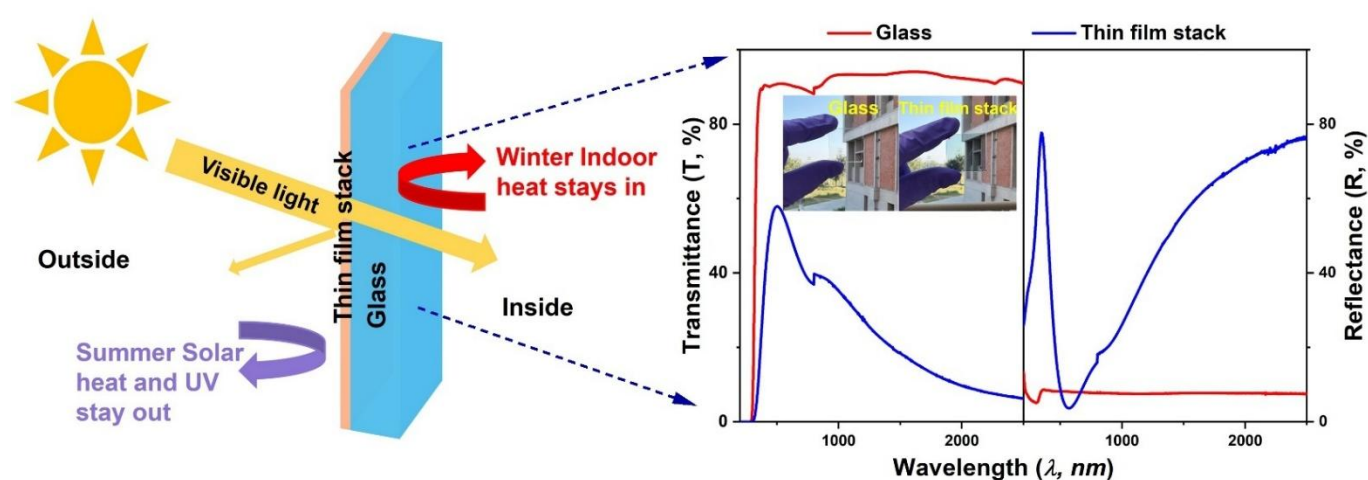
Developing Cost effective low-Emissivity coating as energy saving window

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With the increasing demand for energy supply, the development of smart window technologies has become critical. A major portion of the sun's radiation incident on the Earth's surface consists of infrared (IR) (~49%), which contributes significantly to undesired heating inside buildings, vehicles, etc. Smart window coatings provide a practical solution by reducing heat ingress while maintaining adequate visual transparency. In this regard, low-emissivity (Low-E) coatings are a widely investigated class of smart windows due to their ability to provide high visible transmittance and strong IR reflectance without requiring any external power supply. Conventionally, Low-E coating uses noble metals to reflect infrared radiation. This metal layer is encapsulated between multiple dielectric layers to protect it from environmental degradation. However, noble metal-based configurations often suffer from high material costs, poor long-term stability, and an unpleasant appearance (such as a brownish tint). In this regard, a range of configurations involving single or multiple metallic layers in combination with the dielectrics are reported in the literature. In this work, a novel multilayer configuration consisting of aluminium (Al), aluminium nitride (AlN), and titanium dioxide (TiO₂) thin film-based stack is designed on soda-lime glass substrates using RF magnetron sputtering at room temperature. The entire stack consists of TiO₂/AlN/Al/AlN/TiO₂. Al is selected for its low cost and neutral appearance, while AlN layer functionally serves as both an antireflection coating and a protective barrier, preventing oxidation of the Al layer during subsequent TiO₂ deposition. The TiO₂, with its high refractive index, enhances the visible-range anti-reflective behaviour, thereby improving luminous transmittance. The maxima of the visible transmission is found to shift towards the longer wavelength due to the interference effects resulting from varying AlN and TiO₂ layer thicknesses, thereby confining the optical tunability through precise thickness control. Moreover, for this stack, luminous transmittance is found to be ~ 49% in the entire visible range of 380-780 nm with an IR reflectance of ~ 77% (at $\lambda = 2500\text{nm}$), demonstrating its performance as a low-E coating, i.e., providing adequate visible transparency while preventing heat transfer through it. Furthermore, the indoor temperature by using this stack is lowered by ~ 6-7 K when compared with a bare glass window. These results demonstrate the potential of the Al, AlN, and TiO₂-based multilayer design as a cost-effective and durable low-E coating for energy-efficient window applications.

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Keywords: low-E coating, ultra-thin Al film, luminous bandwidth selectivity, optoelectronic properties, thermal insulation



The role of oxygen in the degradation of the $\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ solar absorber

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$\text{Cu}(\text{In}_x\text{Ga}_{1-x})\text{Se}_2$ is an efficient solar absorber material, with efficiencies reaching up to 23.6%. [1] While many improvements were performed to reach such record efficiency, the stability of the solar device is also of primary importance to guarantee the durability. Although the aging of CIGS solar cells has been addressed in the literature, [2] the influence of each specific factor of aging (relative humidity, temperature, oxygen, pollutants...) still remains insufficiently explored. Recent results of our team have proved the great impact of relative humidity [3] and illumination [4] on the degradation of the CIGS surface.

Here, we propose to investigate the evolution of the CIGS absorber surface under the influence of environmental oxygen alone using Lab X-ray photoelectron spectroscopy (XPS) and Near-Ambient Pressure XPS in a synchrotron facility. Within this scope, two aging setups were implemented: the first one where CIGS absorbers were exposed to drastic conditions of high relative humidity (90% RH) and high illumination, without any assistance of oxygen; the second one where other samples were submitted to different fluxes of O_2 in a NAP-XPS system.

If no surface alteration was noticed in the absence of dioxygen, as soon as dioxygen was introduced in the NAP system, oxide phases started to grow. Interestingly, the kinetics of oxide formation differed according to the element observed, as well as the amount of dioxygen introduced. Indeed, the formation of In oxide phases requires an O_2 pressure higher than 1 mbar, whereas Se oxidation already begins at 0.5 mbar. Additionally, in this case, both elemental selenium (Se^0) and selenium oxide phases are observed simultaneously from the early stages of exposure to oxygen, deviating from the typical two-step process where Se^0 usually appears first, followed by its gradual evolution into Se oxides after extended exposure times. These results identify molecular oxygen as a key driving force for surface degradation in CIGS absorbers. Molecular oxygen is thus a key trigger for surface degradation in CIGS absorbers.

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Keywords: solar energy, degradation, XPS, NAP-XPS

Unveiling reactivity differences between Cd and Te faces in CdTe(111) by coupling XPS photopeaks and X-AES transitions

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Cadmium telluride (CdTe) is a widely used material for thin-film photovoltaic cells. During the fabrication process, depending on the crystal orientation of CdTe with a zinc blende structure, the resulting CdTe(111) surface can be predominantly composed of cadmium atoms (Cd face) or tellurium atoms (Te face). However, environmental exposure can compromise the long-term stability of these faces through surface degradation. In this context, knowing the chemical difference between the two faces becomes essential, and can be carried out using X-ray photoelectron spectroscopy. In order to obtain chemical information at different depths using the same source (Al K α) and without sputtering, coupling the XPS photopeaks with the X-Auger (X-AES) transitions of Cd and Te that are close in kinetic energy (Cd M_{4,5}N_{4,5}N_{4,5} and Te M_{4,5}N_{4,5}N_{4,5}; Cd 3d and Te 3d; Cd 4d and Te 4d) is an interesting approach to explore.¹

To achieve this, we adopted a two-step approach: first, the identification of secondary phases (oxides, hydroxides, and/or carbonates) likely to form when the Cd and Te faces are exposed to the environment (XRD study and XPS analyses), followed by the application of this approach to the study of the aging of the Cd and Te faces. A tellurium–oxygen–based secondary phase (TeO₂), as well as three cadmium–oxygen–based secondary phases (CdO, Cd(OH)₂, and CdCO₃), were identified, and each of them was the subject of a dedicated study using reference powders.

The XRD study showed that only the CdCO₃ powder was pure, whereas the CdO and Cd(OH)₂ powders contained residual CdCO₃, complicating photopeaks and X-Auger transitions decomposition. Thus, to first isolate the pure chemical environment of CdO, a vectorial method was employed². In contrast, XPS analysis of the Cd(OH)₂ powder, unlike XRD analysis, also revealed the presence of CdO. Consequently, the decomposition of the chemical environment of Cd(OH)₂ was obtained by deduction, by separating it from the chemical environments of CdO and CdCO₃.

Establishing these standards finally allowed monitoring chemical changes on Cd and Te faces of CdTe(111) after 25, 200, and 700 h of aging (80% RH, 20 °C, 3500 lux). The study shows an increase of Cd(OH)₂ and CdCO₃ on both faces, along with significant TeO₂ growth, with stronger secondary phase formation on the Te face, suggesting higher chemical reactivity compared to the Cd face.

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Keywords: Solar cells, CdTe(111) aging, Photoemission spectroscopy, X-AES transitions

Operando XPS: A novel approach to study sulfide based all solid-state-batteries in realistic condition

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Characterizing and understanding the dynamic processes at the solid/solid interface in solid-state Li-ion batteries SSBs is crucial for designing resilient, durable, and high-energy density SSBs [1]. Nevertheless, in the constructed solid-state Li-ion batteries (SSBs), direct access to these buried interfaces remains challenging. In situ and operando characterization techniques offer unique insights into the continuous evolution of interfacial phenomena [2]. X-ray photoelectron spectroscopy (XPS), one of the most used surface analysis techniques for battery materials, can provide valuable quantitative and chemical state information from the surface. Specifically, Operando XPS is an advanced approach that enables monitoring the chemical changes of the electrolyte-electrode interface in SSBs during battery operation[3].

In this work, we developed a methodology that applies operando XPS to the cross-section of SSBs in a full-cell configuration, enabling simultaneous detection of chemical changes within both the composite solid electrolyte (SE) and the cathode layers. Our dedicated operando XPS cell enables simultaneous electrochemical measurements and XPS data acquisition under controlled pressure and temperature conditions, allowing direct comparison with standard-pressure cells commonly used for SSB cycling. We also provide guidelines for SSB cross-section preparation and highlight the effect on the battery performance. Finally, we demonstrate the application of this approach to a sulfide-based system, revealing its redox behaviour during battery operation.

Keywords: Operando XPS, Cross-section samples, Solid State Batteries, Sulfide State Batteries

Cryo ToF-SIMS to Study Sodium Transport and Storage in Hard Carbon Anodes

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Among anode materials for sodium-ion batteries (SIBs), hard carbon has emerged as the most promising candidate owing to its relatively high reversible capacity, moderate operating potential, and compatibility with standard electrolyte systems. Despite considerable progress, the underlying sodium transport kinetics and storage mechanisms remain insufficiently understood, hampering the rational design of high-rate electrodes. Conventional electrochemical techniques such as galvanostatic intermittent titration (GITT) yield macroscopically averaged kinetic parameters but cannot resolve the spatial distribution of sodium within the carbon microstructure. To overcome this limitation, we employ thin-film model electrodes and investigate sodium transport and storage by ToF-SIMS in a controlled diffusion experiment.

Resol-resin-derived hard carbon thin films, deposited under well-defined conditions, replicate the essential structural features of electrode-grade hard carbon while eliminating the geometric complexity inherent to porous composite electrodes. Sodium is deposited on these films via physical vapour deposition, establishing well-defined initial concentration profiles. Subsequent ToF-SIMS depth profiling tracks the temporal evolution of the sodium distribution at varying temperatures, providing spatially resolved diffusion data inaccessible by electrochemical methods alone. Given the exceptionally fast sodium transport and high reactivity, all diffusion experiments are performed in situ within the SIMS instrument under cryogenic conditions.

A critical prerequisite for this model electrode strategy is verifying that the thin-film material faithfully represents the microstructure of composite electrodes. Transmission electron microscopy (TEM) is employed to compare local structures at the nanoscale, with particular focus on pore size distributions in both thin films and practical electrode materials. This structural validation establishes the essential link between the model system and real-world electrode conditions, lending credibility to the calculated diffusion coefficients. To derive quantitative diffusion coefficients from the SIMS depth profiles and rationalise the observed sodium distributions, the profiles were fitted using a finite element diffusion model that extracts a concentration-dependent diffusion coefficient, yielding improved consistency with diffusion coefficients obtained from GITT measurements and accurately reproducing the experimental SIMS depth profiles.

In summary, the integration of thin-film model electrodes, temperature-dependent ToF-SIMS depth profiling, TEM structural characterisation, and grain-based finite element modelling affords unprecedented spatial and temporal resolution of sodium diffusion mechanisms in hard carbon, providing essential insights for the rational design of anodes in next-generation SIBs.

Keywords: Battery, Secondary Ion Mass Spectrometry, Diffusion, Transmission Electron Microscopy

Probing surface reactivity of carbon group anodes for sodium-ion batteries by XPS and SEM

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Rechargeable batteries are central to the transition toward sustainable energy systems. While lithium-ion batteries dominate current applications, concerns related to resource availability and cost have raised interest in sodium-ion batteries (SIB) as a complementary alternative. According to the greater abundance and lower cost of sodium, SIB have paid increasing attention, despite their lower theoretical energy density compared to LIB, as continuous discoveries in electrode materials reduce the gap between the energy density of SIB and LIB.

In this work, we investigate the electrochemical, morphological, and surface properties of novel anode materials for SIB based on carbon-group elements, including hard carbon, Sn, Pb, and their blends. We also screen different electrolytes such as glyme-based and carbonate-based systems, and show that glyme-based electrolytes exhibit better electrochemical performance. To elucidate the origin of the observed behaviours in the discharge capacity, we employ a complementary post-mortem approach combining X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDXS). This approach provides detailed insights into surface chemistry, including metal alloying processes, and the formation and structural evolution of the solid electrolyte interphase.

Taken all together, these results provide a deeper understanding of interfacial processes in carbon-group-based anodes and pave the way for the development of improved electrode materials and electrolytes for SIB.

Keywords: sodium-ion batteries, XPS, SEM

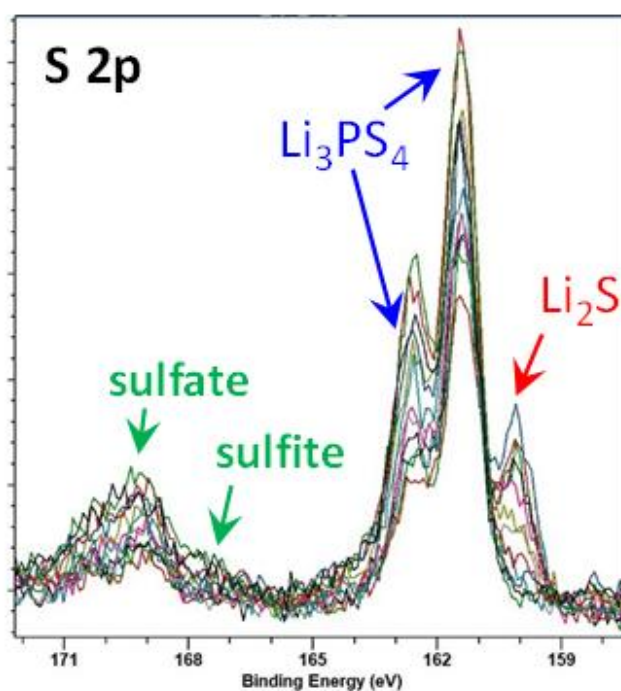
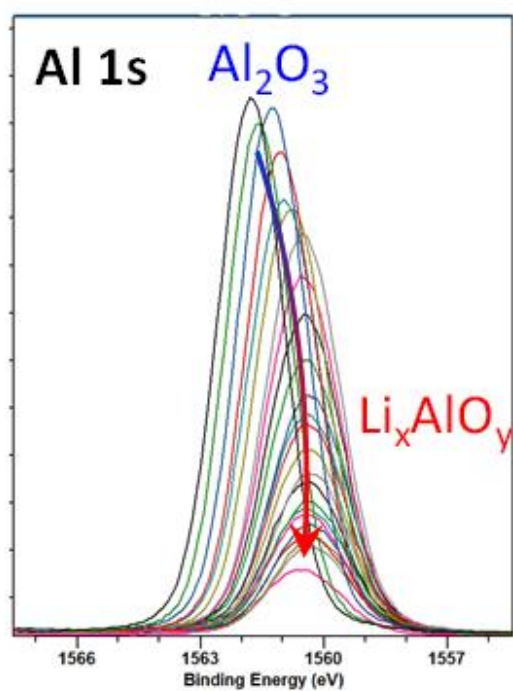
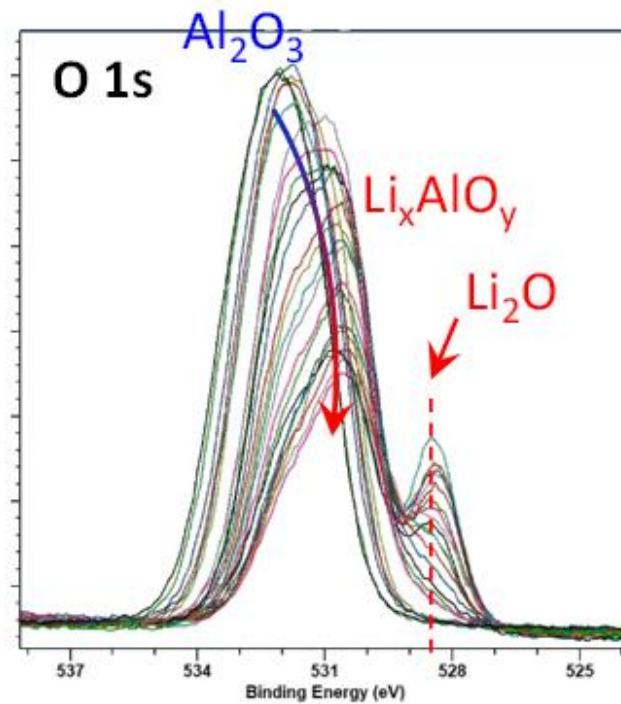
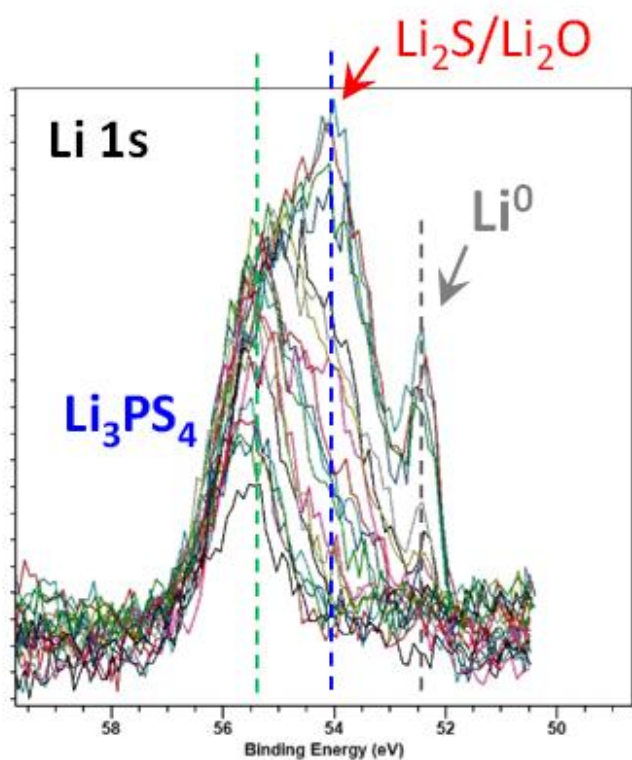
In situ XPS investigation of the lithium/solid electrolyte interfaces in all-solid-state batteries

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Good operation of Li-ion batteries requires a good mastering of electrode/electrolyte interfaces. The so-called Solid Electrolyte Interphase (SEI) formed at the surface of the graphite anode in a classical Li-ion battery is one of the best examples. Today, the development of new battery chemistries, like all-solid-state batteries, leads scientists to solve emerging problems regarding the chemical and electrochemical reactivity at these new interfaces.

Investigation of electrode/electrolyte interfaces requires good analytical tools to characterize their chemical composition, due to their complexity depending on many parameters, such as electrolyte composition, nature of electrode materials, binders, impurities, cycling conditions, temperature, etc... Moreover, characterization of interphases is all the more difficult that they are only a few nanometers thick and extremely moisture- and air-sensitive. X-ray Photoelectron Spectroscopy (XPS), coupled to thorough experimental conditions to prevent the analyzed surfaces from any contact with air (argon environment), has made a great contribution to our knowledge of electrode/electrolyte interfaces in batteries. However, scientists are today searching for *in situ* and *operando* approaches to prevent from risks of modifying the chemical nature of the surfaces during the sample's preparation. In this study, we have investigated the interface between metallic Li and a sulfide solid electrolyte (Li_3PS_4) by *in situ* XPS (obtained by direct Li evaporation onto the solid electrolyte in the analysis chamber) and evaluated the stabilization of this interface when a 4 nm-thick Al_2O_3 coating is deposited at the surface of the solid electrolyte before Li evaporation. A photon energy of 2300 eV was used to better access the buried interfaces. This study highlights the reaction mechanisms between Li and Li_3PS_4 , as well as the protection mechanisms of the oxide coating.

Keywords: solid electrolytes, lithium, sulfides, *in situ*, HAXPES



ToF-SIMS for the analysis of interfaces in liquid and solid state Li-ion batteries

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The technology of Li-ion batteries is currently expanding rapidly into the electric vehicle market, as well as into many other industrial sectors such as portable electronic devices, intermittent renewable energy systems, aviation or railways. These applications often require not only high energy densities, but also long life and a high level of safety. To meet these requirements, new electrode materials and electrolytes are developed, whose ageing mechanisms (capacity loss and/or high polarization) are critical to understand and control. Ageing of Li-ion batteries arises from multiple and complex causes, involving interactions between electrode materials and electrolytes, parasitic reactions, outgassing and more. Controlling the different interfaces is therefore a key factor in improving battery performances. The aim of this study is to gain a better understanding of the mechanisms that lead to the formation of degradation compounds at these interfaces, by identifying the chemical species formed using surface analysis techniques especially Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) in combination with X-ray Photoelectron Spectroscopy (XPS) and Auger microscopy. ToF-SIMS enables the determination of the elemental and molecular composition of nanometric layers, such as the SEI (Solid Electrolyte Interface) and CEI (Cathode Electrolyte Interface), as well as the 2D and 3D spatial distribution of species of interest, thanks to its imaging and depth-profiling capabilities. A focus will be done on TiNb_2O_7 anode material as a promising candidate for high potential and fast charging applications [1]. The impact of several cycling parameters such as temperature, end-of-charge voltage, counter electrode type and electrolyte composition will be assessed.

Interfaces in All-Solid-State Li-ion Batteries (ASSBs), where the Solid-State Electrolyte (SSE) consists either of a Solid Polymer Electrolyte (SPE) or Sulfide-based SSE, will also be investigated. The development of a specific in-situ cycling cell for ASSBs allowing ToF-SIMS analysis of solid-solid interfaces immediately after cycling and without any further handling will be presented [2].

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Keywords: Li-ion batteries, electrode/electrolyte interfaces, surface analysis, ToF-SIMS

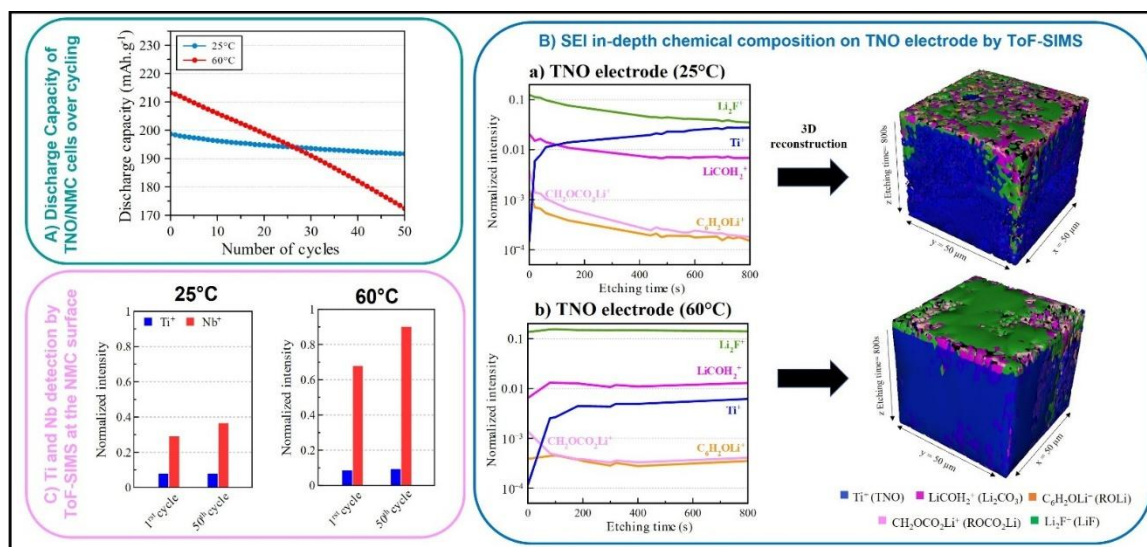


Figure 1: A) Discharge capacities of TNO/NMC full cells for 50 cycles at either 1.2V/25°C (blue) or 1.2V/60°C (red). B) Normalized ToF-SIMS depth profiles and 3D image reconstructions over 800s etching time of species of interest detected after 50 cycles at the TNO electrode surface cycled in TNO/NMC full cells at a) 1.2V/25°C and b) 1.2V/60°C. C) Histograms representing the normalized intensities of Ti^+ and Nb^+ species detected by ToF-SIMS at the NMC electrode surface at 25°C and 60°C for the 1st and the 50th cycles.

Operando XPS with Coupled Mass Spectrometry on Dual Electrolyte Solid-State Batteries

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Dual electrolyte solid-state batteries (SSBs) that combine a sulfide solid electrolyte (SE) separator with an (oxy)halide SE in the positive electrode composite represent a promising SSB architecture. However, the interface where both SEs meet near the active material, the so-called triple-phase boundary, has been identified as a critical site of electrochemical degradation that severely limits cycling stability [1]. Understanding the degradation mechanism at this buried interface requires surface-sensitive techniques capable of operating under electrochemical bias.

We present an *operando* X-ray photoelectron spectroscopy (XPS) approach coupled with simultaneous residual gas analysis by mass spectrometry (MS) to investigate the potential-dependent decomposition reactions at the sulfide(oxy)halide triple-phase boundary. A custom composite working electrode, consisting of $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI), Li_3InCl_6 (LIC), and conductive carbon additives, was designed to maximize the interfacial area accessible to the X-ray beam while mimicking the triple-phase boundary without the complications of active material volume changes. The *operando* cell was polarized stepwise from OCV (~ 2.5 V vs. Li^+/Li) up to 4.7 V and back, with XPS spectra acquired during constant-voltage holds after current relaxation below 5 μA .

The In 3d and S 2p core-level spectra reveal that LPSCI begins to form polysulfides (P_2S_x) already at 3.0 V, while LIC remains stable up to ~ 4.0 V. Once the potential exceeds the oxidation stability limit of LIC at ~ 4.3 V, a sharp increase in the InCl_3 signal is observed, accompanied by massive formation of elemental sulfur and oxidized sulfide species (S_8 , Li_2S_n with $3 \leq n \leq 8$). Critically, the simultaneously recorded chamber pressure and MS signals reveal gas evolution exclusively at potentials ≥ 4.3 V. The MS detects Cl_2 ($m/z = 35, 37$) from LIC oxidation and a strong $m/z = 32$ signal. By comparing the counts($m/z = 32$)/counts($m/z = 16$) ratio with a pure O_2 reference measurement (~ 2.75 vs. ~ 7.25 during the experiment), the excess $m/z = 32$ intensity is unambiguously attributed to sulfur-containing gaseous species rather than O_2 alone. These degradation products persist when the potential is reduced back to OCV, demonstrating the irreversibility of the interfacial decomposition.

A control experiment using only LPSCI and carbon, without LIC, shows significantly less degradation and no gas evolution, confirming that the synergistic reaction between the two SEs at the triple-phase boundary is responsible for the enhanced decomposition and sulfur gas release.

Keywords: *operando* XPS, mass spectrometry, solid-state batteries, triple-phase boundary, interfacial degradation

XPS investigation of trapping functionalities in Li-ion batteries

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Lithium-ion batteries (LIBs) are the dominant energy-storage technology for portable electronics and electric vehicles thanks to their high gravimetric and volumetric energy densities, low self-discharge and competitive cycle life. Despite these advantages, long-term safety and reliability are still limited by complex interfacial degradation phenomena occurring at electrode/electrolyte interfaces. Parasitic side reactions, including transition metals (TMs) dissolution from the positive electrode, electrolyte decomposition, result in a loss of stability of the solid electrolyte interphase (SEI), which is manifested by capacity fade, impedance growth and gas generation. [1] These effects ultimately constrain battery lifetime and can pose safety risks under abusive conditions.

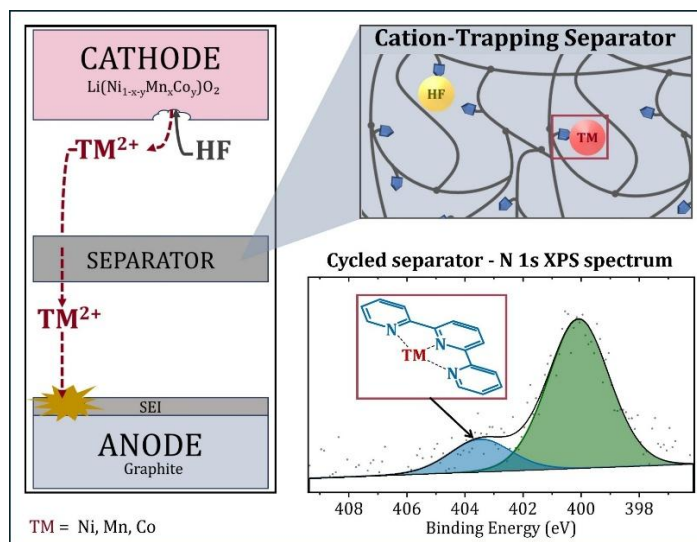
In this study, we have investigated the effect of “smart” components introduced in the battery’s separator to prevent from these effects, i.e. trapping functionalities targeting dissolved TMs and protons in the electrolyte, to stabilize the SEI. X-ray photoelectron spectroscopy (XPS) was employed as the principal analytical technique to probe the chemical composition and oxidation states of species for pristine and cycled materials. Separators were analyzed after synthesis to verify the successful incorporation of trapping functionalities. Then the graphite electrodes were examined ex-situ after electrochemical cycling to identify organic and inorganic SEI constituents, quantify TMs deposition; cycled separators were also analysed to check the presence of trapped degradation products and then to evaluate the efficiency of modified separators, in regard with the electrochemical performances.

Taken together, these surface-sensitive insights establish direct correlations between material design and interfacial chemistry, providing a mechanistic basis for the rational optimization of smart components aimed at enhancing lifetime and safety. More broadly, the study highlights how innovative materials and functional strategies can stabilize interfaces, scavenge harmful species and impart resilience to next-generation LIBs, ultimately contributing to safer and longer lasting energy storage systems.

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<https://doi.org/10.1002/aenm.202102652>.

Keywords: Li-ion batteries, Functional materials, Electrode degradation mitigation, Cross-talk, XPS



Guide to Improving XPS Analysis for Studying the SEI in Li-ion Batteries

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During the initial cycles of a Li-ion battery, electrolyte reduction at the negative electrode surface forms the solid electrolyte interphase (SEI), a layer of decomposition products that strongly influences the battery stability, performance, and safety. Because this layer is complex and easily altered, characterizing it without inducing changes remains challenging [1]. XPS is widely used for SEI analysis due to its surface sensitivity and chemical specificity, but UHV requirements and the volatility of electrolyte species complicate sample handling. Sample preparation and measurement conditions often affect the observed composition and binding energies, contributing to inconsistencies in the literature. In this study, we outline best practices for obtaining reliable post-mortem SEI XPS data, including preparation procedures, measurement conditions, and data-analysis strategies.

This study examines lithiated and delithiated commercial graphite electrodes after 1.5 and 2 charge-discharge cycles, respectively. The graphite electrodes were cycled against nickel-rich ($\text{Ni} > 80\%$) lithium-nickel-manganese-cobalt-oxide (NMC) as positive electrode using 1.0 M LiPF_6 in ethylene carbonate and diethyl carbonate (1/1 wt/wt, LP40) as electrolyte using a 0.265 mA constant current cycling protocol. The electrodes are either left unwashed or washed in dimethyl carbonate by one of three procedures. The surface homogeneity and reproducibility of these washing procedures are evaluated for both lithiated and delithiated graphite electrodes.

During XPS measurement using a laboratory X-ray source (Al K α), all electrodes showed SEI compositional changes induced by X-ray exposure. Using a large X-ray spot at low power density (yet high total power) reduces this beam damage while improving signal quality. Such changes can easily remain hidden because most XPS instruments output spectra averaged over multiple repeats by default. Therefore, we recommend acquiring and evaluating single spectra iteratively before averaging. Additionally, the insulating nature of the SEI can lead to charge buildup and binding energy shifts. Although charge neutralizers are often used to counteract this effect, we found that both electron neutralizers and low-energy Argon beams give inconsistent energy corrections and frequently modify the SEI's apparent chemical composition. For reliable SEI characterization, neutralizers should therefore be avoided or used only with great care. Finally, we discuss binding energy calibration, peak fitting, quantification, and how to avoid common mistakes during the data analysis of XPS spectra of the SEI. This research provides guidelines for sample preparation, measurement, and data analysis procedures for more reliable XPS studies on the SEI.

Keywords: Li-ion battery, Solid electrolyte interphase (SEI), XPS, Post-mortem analysis, Measurement conditions

Fatigue crack growth kinetics of PV relevant laminates based on polyolefinic encapsulants and tinned copper substrates

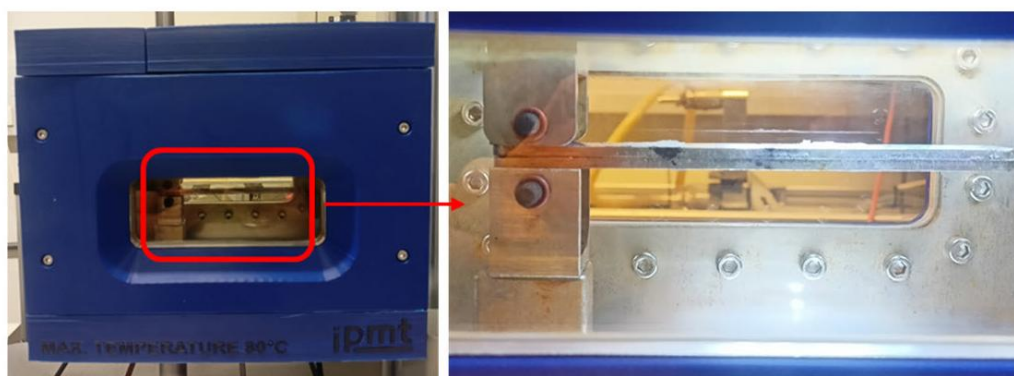
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Photovoltaic (PV) modules play a central role in the transition to renewable energy, where long-term reliability is essential to ensure stable power generation and to reduce CO₂ emissions. Among the degradation processes affecting service life, delamination at encapsulant/metal interfaces is one of the most critical mechanisms, as it initiates interfacial failure and compromises both electrical performance and mechanical integrity. This work examines the fatigue crack growth behaviour of encapsulant/metal laminates representative of PV module interconnects, focusing on the combined influence of elevated temperature and controlled humidity.

Double cantilever beam specimens were prepared with tin-based solder alloys (SnPb, Sn100Ni, and SnAgCu) bonded to encapsulants widely used in PV modules: UV-transparent ethylene-vinyl acetate copolymers (EVA) and polyolefin elastomers (POE). Fatigue crack growth tests were carried out at 60°C under 10% and 50% relative humidity, applying a compliance-based procedure to evaluate crack propagation. Data were interpreted within a linear elastic fracture mechanics framework using the strain energy release rate (G) as the fracture parameter. The modified Hartman-Schijve (HS) model was employed to represent crack growth kinetics. Optical microscopy (OM) and X-ray photoelectron spectroscopy (XPS) were conducted to characterize the fractured surfaces optically and chemically.

Fatigue crack growth curves revealed the highest crack growth resistance for SnAgCu laminates, followed by Sn100Ni and SnPb. Higher humidity generally accelerated crack growth, although in POE-based laminates with SnPb an improvement was observed. In most cases POE exhibited lower interfacial adherence to the soldering than EVA. Fractured surfaces revealed predominantly interfacial failure, irrespective of encapsulant type. Hence, the adherence at the encapsulant/solder boundary governs crack propagation. By XPS, a humidity-driven oxidation of the solder surfaces and degradation mechanisms in EVA were confirmed. Overall, the solder alloy composition and the encapsulant chemistry affected significantly the fatigue debonding under temperature and humidity.

Keywords: photovoltaics, encapsulant, tinned copper, delamination, environment



Environmental test chamber and double cantilever beam specimen made from EVA/ or POE/tinned copper laminates.

Advances of secondary ion mass spectrometry metrology in battery applications

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Batteries are very important to achieve the EU net zero target by 2050. Understanding battery electrode surfaces, solid electrolyte interphase (SEI) evolution and solid-state electrolyte structures ¹ is very helpful for developing next generation batteries. Surface chemical analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy are often used but they have their limitations. XPS analysis cannot always resolve overlapping binding energies for some key SEI elements such as the F 1s and Ni LMM Auger peak, and SEI often exhibits a weak Raman signal. Owing to the high sensitivity, chemical specificity and ability to image in 2 and 3-dimensions, secondary ion mass spectrometry (SIMS) has become a popular method to study battery interfaces.

In an operando Raman battery study, SIMS was used to post-mortem map SEI component ions over a 9 mm × 9 mm area². SIMS maps of Li⁺, OH⁻ and F⁻ exhibited spatial inhomogeneities, revealing the differences in SEI formation in outer and inner regions caused by the stack pressure difference related to the cell window, thus informing improvement of operando cell design.

Battery SEI is composed of organic and inorganic components. To date, most SIMS studies have focused on the inorganic components ³, neglecting the organic components. We will share our recent progress in building a more complete picture of SEI by characterising both organic and inorganic components using OrbiSIMS.

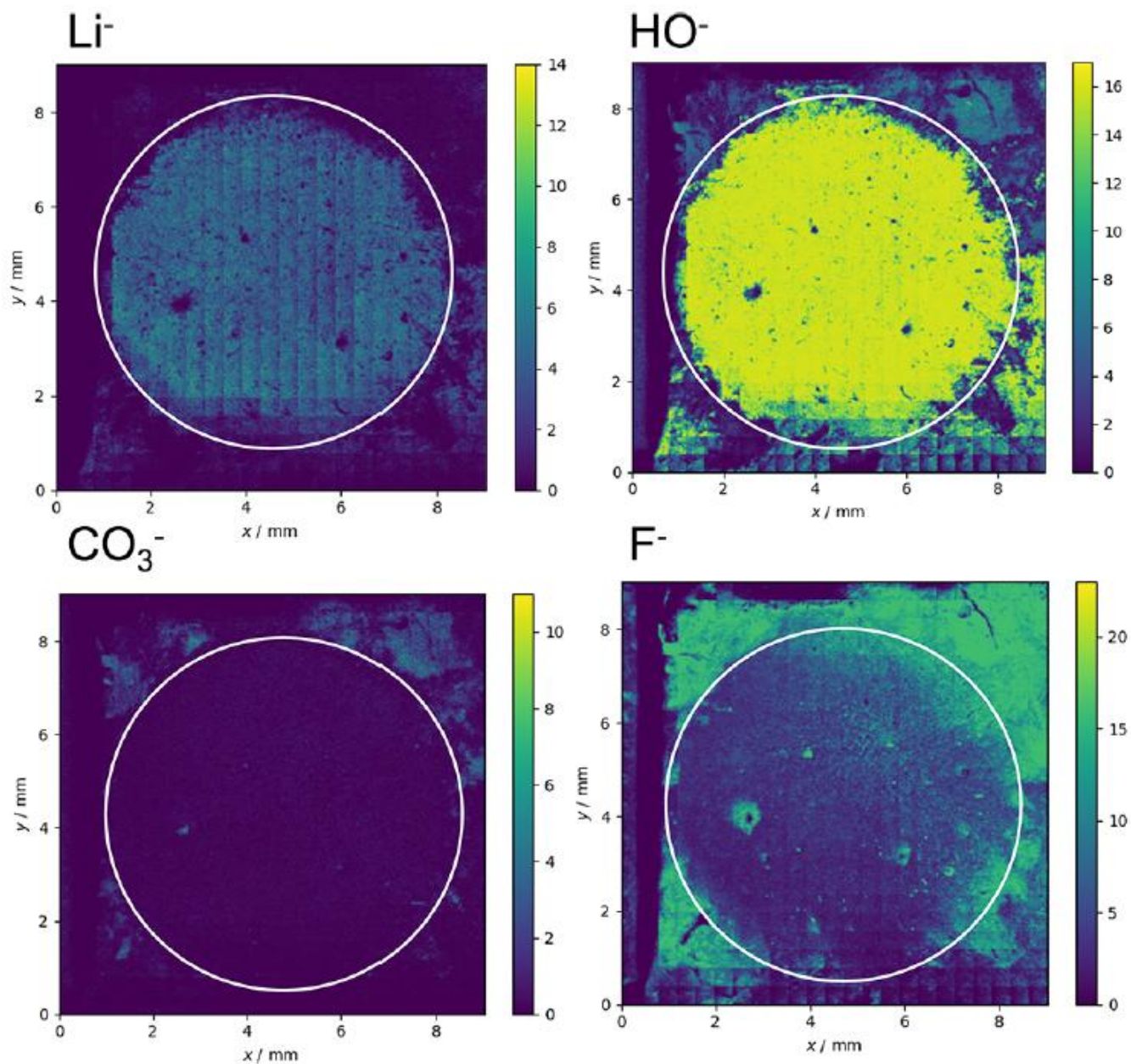
Early cell failure of solid-state batteries is caused by instability between cathode and solid electrolytes. To investigate the causal chemical mechanisms, we have designed an operando sample holder for SIMS analysis of solid-state batteries whilst operating charging/discharging cycles. Our recent progress for operando SIMS characterisation of cathode – solid electrolyte interface will be presented.

We will also report our efforts to quantify the sputter yield of LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ with 2 keV Cs and O₂ to enable calibration of the SIMS sputter depth, and determination of the relative sensitivity factor of Co in carbon.

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Keywords: secondary ion mass spectrometry, solid electrolyte interphase, OrbiSIMS, operando SIMS, metrology



Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling of Lithium-Ion Batteries

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A detailed understanding of the chemical compositions of multi-component electrodes and solid-electrolyte interphases (SEI) within lithium-ion batteries is essential for enhancing cell longevity and capacity. In this work, Li-ion batteries were tested in a half cell configuration consisting of a graphite/NMC/LFP working electrodes [DC1] and lithium metal as the counter electrode. These were immersed in organic carbonate solvents (EC: EMC) containing dissolved lithium salts within a CR2032 cell casing[DC2]. The batteries were then cycled galvanostatically to form the interphases. The recently developed technique of femtosecond laser ablation (fs-LA) XPS depth profiling has been employed using a 1030 nm peak wavelength, 160 fs pulse length laser to produce high quality depth profiles. The solid electrolyte interphase (SEI) and bulk electrodes (50-60 μm thickness) of Li ion battery electrodes were tested without inducing chemical damage typically associated with argon ion sputter depth profiling. This approach provides direct chemical insights which have historically been challenging to obtain, often requiring reliance on indirect electrochemical measurements or computational models. The results presented will show important chemical state information as a function of depth allowing a more accurate characterisation of SEI compositions and electrode interactions as a function of depth, advancing our understanding of the complex interfacial chemistry within Li-ion cells.

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Keywords: XPS, Femtosecond laser ablation, Lithium Ion battery, Solid electrolyte interface

Probing the Local Electrochemistry of Li-ion Batteries Using Scanning Electrochemical Cell Microscopy

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The heterogeneity of materials in Li-ion batteries is known to cause battery degradation and failure [1][2]. Despite extensive studies of battery materials with various advanced spectroscopy and microscopy techniques [1][3][4], this long-standing puzzle remains unresolved. In this work, we address this complex research question with the latest scanning electrochemical cell microscopy (SECCM) [5], enabling the electrochemical probing within the contact area of a droplet (meniscus) formed at the end of a micropipette probe. With its high lateral resolution and versatility, we can probe sub-micron to micron-scale electrochemical properties of battery electrode materials.

SECCM has gained popularity in recent years but is rarely used in battery research due to numerous practical challenges. In this study, we introduced a Pt/PPy (platinum wire coated with partially oxidized polypyrrole) quasi-reference/counter electrode (QRCE) in SECCM-based experiments for Li-ion batteries [6][7]. This demonstrated excellent compatibility and stability with the aprotic electrolytes used in Li-ion batteries, essential for reliable long-term SECCM measurements. Additionally, we introduced a specially formulated ionic liquid electrolyte, allowing us to probe battery reactions in ambient atmosphere with a simple humidity control system. These novel implementations led to reliable SECCM characterizations on the thin-film LMO model system. We have addressed some of these challenges and with further optimization, this approach can investigate composite electrodes and help comprehend the origin of heterogeneity in Li-ion batteries.

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Keywords: Battery materials, Scanning Electrochemical Cell Microscopy, Local electrochemistry

Accurate quantification of transition metal ratios in battery materials using combined XPS and HAXPES

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X-ray photoelectron spectroscopy (XPS) is a critical analytical tool for advancing battery materials research, providing direct insight into surface chemistry, elemental composition, and oxidation states of the active electrode material and the solid–electrolyte interphase (SEI) layers formed during charge/discharge cycles. This capability makes XPS essential for diagnosing battery chemical failure mechanisms, guiding materials design, and accelerating the development of next-generation high-performance batteries.

The current state-of-art battery materials, such as lithium nickel manganese cobalt oxide (NMC) and sodium nickel iron manganese oxide (NFM), are dependent on transition metal oxide matrices. Quantification of transition metals in XPS is not trivial and there are many pitfalls that an inexperienced analyst may fall into. For example, a typical XPS spectrum will contain spectral features other than the primary photoelectron peaks, such as the Auger-Meitner peaks. For XPS analysts, these Auger-Meitner peaks are often a nuisance because they can overlap the primary photoelectron peaks, confounding quantitative analysis.

One method to get around this issue was suggested by Marchesini *et al.* They recommended using the lower binding energy core levels (<140 eV) of the transition metals, that is the 3p and 3s peaks[1]. Whilst these core levels have lower absolute intensities compared to the 2p peaks therefore requiring longer acquisitions to achieve an acceptable signal-to-noise ratio, they do not overlap with any Auger-Meitner features, and the core levels occupy a smaller range of kinetic energies reducing quantification errors from energy-dependent escape depth and analyser transmission differences.

Recently, commercial XPS instruments offer dual anode monochromated sources with higher energy X-rays, allowing the use of hard x-ray photoelectron spectroscopy (HAXPES). The kinetic energy position of Auger-Meitner peaks is fixed, so using HAXPES separates their intensity contributions from the principal core levels, allowing for easier quantification. Furthermore, this work, which has been developed on reference materials and electrodes of NMC622 and verified using X-ray fluorescence (XRF), shows that an intensity-scaled HAXPES spectrum can be used to subtract the Auger-Meitner contributions from the XPS spectrum and increase the accuracy of the XPS quantification therefore providing atomic composition at multiple information depths[2].

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Keywords: XPS, HAXPES, batteries, transition metals, surface analysis

Surface interaction of hydrogen isotopes with native iron oxide studied by ToF-SIMS

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Hydrogen is widely regarded as a key energy carrier for the transition toward low-carbon energy systems due to its potential to substantially reduce greenhouse gas emissions. Nevertheless, its interaction with steel components used in infrastructure—such as pipelines and storage vessels—remains a major concern. Hydrogen can diffuse into metallic structures, promoting hydrogen embrittlement and thereby increasing the risk of mechanical degradation or failure. Previous studies based on hydrogen permeation measurements have shown that surface oxide layers, either naturally formed or generated under controlled conditions, can influence hydrogen transport in steels by slowing diffusion or increasing the characteristic permeation time [1,2]. Therefore, probing hydrogen interactions at the material surface is crucial, as interfacial processes are the initial stage that governs hydrogen uptake and subsequent transport into the bulk.

In this work, the early stage of hydrogen interaction with native iron oxide surface was investigated using in situ gas exposure in Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). A mixture of hydrogen and deuterium gases ($\sim 10^{-6}$ mbar) was introduced under controlled conditions, allowing the evolution of surface species to be monitored through isotopic labeling using static-SIMS. This approach enables the observation of adsorption processes and a depth profile is added to provide insight into possible diffusion or penetration phenomena after exposure. The results reveal an obvious increase of D^- and OD^- signals on the iron oxide surface, indicating adsorption and surface reactions involving deuterium. To further improve our understanding of hydrogen surface adsorption, identical experiments were performed on a Pd-coated surface as a reference system known for its high hydrogen affinity. A more pronounced increase of the D^- signal is observed on the Pd-coated surface, highlighting a quicker adsorption of deuterium compared with the oxide surface.

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Keywords: hydrogen, iron oxide, gas exposure, ToF-SIMS

Heritage and geology

Using XPS to Determine Iron Oxidation State in Metamorphic Fe-Ti-oxides, Adirondack Mts, New York

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This presentation explores the application of X-ray Photoelectron Spectroscopy (XPS) for analyzing geological samples, specifically a rock sample from the Adirondack Mountains, N.Y. [1] The Adirondacks are notable due to their complex history and high-temperature metamorphic mineral compositions. These rocks represent the roots of an ancient mountain belt that have been exposed by uplift and erosion. The central Adirondack Highlands were metamorphosed, 1090 to 1020 million years ago, at pressures of ~0.8 GPa (depths of ~25 km) and temperatures up to 850 °C, transforming the mineral-chemistry of many of the rocks. [2-3] The unique geochemistry provides an interesting test case for applying XPS analysis to this metamorphic transformation.

Of particular interest to geochemists is the ability to determine the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in ilmenite and magnetite that can be used to infer peak-metamorphic temperatures. Traditional techniques like electron microprobe analysis have limitations in accurately differentiating these oxidation states. XPS, with its capability for detailed chemical state analysis, offers a promising complementary technique. However, Fe oxides are notoriously difficult to separate when multiple species are present, due to peak overlaps and changes in relative intensities of the satellite structure.[4] A library of $\text{Fe}^{2+}/\text{Fe}^{3+}$ results for quantitative analysis is important for successful identification. In addition to a polished Adirondack rock sample, multiple hematite, magnetite, and ilmenite standards were measured. This library will be used to determine the oxidation states of iron within the rock's mineral phases.

The PHI Genesis has unique XPS capabilities in that it scans a focused ($< 5 \mu\text{m}$) X-ray beam across the sample surface. Using a combination of an optical image and PHI's unique scanning X-ray imaging capability, areas of interest on the petrographic thin section can be found quickly. The PHI scanning microprobe enables XPS analysis exclusively from ilmenite or magnetite sections of the rock. The Fe $2p_{3/2}$, Fe 3p, O 1s and valence band spectra from each of these two areas will be analyzed, by comparing relative intensities and binding energies of the peaks and satellite structures when present.

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Keywords: mineral phase, iron oxidation states, xps, scanning microprobe

Marble Waste Reuse for Wastewater Treatment: a Contribution of XPS

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This work is part of an ongoing investigation into the reuse of powder waste generated during the processing of limestone from Sardinian quarries and marble from the Carrara district (Tuscany, Italy). Previous feasibility studies on the removal of lead and zinc from aqueous solutions using high-purity commercial calcium carbonate demonstrated removal efficiencies consistently above 97%. Marble waste (MW), however, contains variable amounts of inorganic phases such as dolomite, and its particles may be coated with organic additives used during stone cutting and polishing. These factors can influence the reactivity of the material.

In this investigation, we characterized the surface chemistry of MW samples by X-ray photoelectron spectroscopy (XPS), focusing on how different processing technologies—diamond blade gangsaws, diamond disc saws, and grinding/polishing machines—affect particle surfaces. Our goal was to evaluate whether microdust collected directly from quarries and stone-processing plants can be used in technical-scale removal tests, bridging the gap between laboratory experiments and industrial applications.

Microfine dust samples were collected from the marble producing area in Orosei (Sardinia, Italy) in three different points: beneath chainsaw cutting equipment (supplied by Fantini) mounted on a backhoe loader, on the quarry floor where the bottom cut of the bench was carried out by another chainsaw machine blocks. The third set of samples were from dewatered sludge obtained under the filter-press plates of the water-treatment plant. All those fine scraps were sieved to obtain particles in the 38–45 μm range. XPS analyses were performed on the as-received samples and after a cleaning procedure in which the powders were suspended in absolute ethanol, stirred, filtered through an 8 μm Whatman® grade 40 filter, dried at 383.2 K for 24 hours, cooled in a desiccator, and pressed into aluminum cuvettes. A description of the XPS-analysis conditions is in [1].

XPS spectra from all sampling points confirmed that the microdust consists almost entirely of CaCO_3 , with no detectable compositional differences.

Ethanol-washed MW samples were then used in Cd removal tests, which involved 30 minutes of contact with a 5 mg/kg Cd solution. pH monitoring and ICP-OES analyses were used to track reaction progress. These results will be compared with those obtained using untreated MW to assess the sorbent reactivity of industrial calcium-carbonate fractions.

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Keywords: limestone, marble, calcium carbonate, cadmium removal, XPS

***In-situ* and near ambient pressure analysis**

XPS of wet samples: past, present and future

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Wet samples, especially solid-aqueous solution interfaces, are common in nature and responsible for the mediation and catalysis of (a)biotic environmental processes, including reactions in organisms. Experimental exploration of the interface composition is crucial to our understanding of key phenomena in nanotechnology, nature, and life.

Historical overview of different attempts and approaches to explore liquid and wet samples since the beginning of XPS era is given with focus on conventional XPS [1]. These include liquid beam, moving wetted wire, rotating cone (all in Siegbahn laboratory); deep freezing followed by ice sublimation (freeze-drying developed in Ratner's lab); fast-freezing of aqueous solution drops (Burger's group); liquid microjet filaments (Faubel's group at synchrotron).

Development in the field resulted in NAP-XPS and cryogenic XPS. Most important applications nowadays are shortly overviewed including experimental protocols [2]. Brief comparison of NAP- and cryo-XPS as well as fast-freezing and freeze-drying *pro et contra* is given.

Future development necessary in instrumental setups, experimental challenges, and new potential applications in material science, biotechnology, biology and medicine are discussed.

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Keywords: XPS, wet samples, fast-freezing, freeze-drying, NAP-XPS

What is the Role of Water in the Electrochemical Double Layer of Emerged Electrodes?

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The electrochemical double layer (EDL) plays a crucial role in electrochemical processes such as electrocatalysis at the three-phase boundary in fuel cells or corrosion of metals. To characterize the EDL under *in situ* conditions, the concept of the emerged electrode was developed to another level to overcome the problematic thick layer of water that usually prevents the use of most analytical tools. The electrode is immersed in an electrolyte so the EDL can form. A potential is applied and maintained during the emersion of the electrode so that only the EDL remains on the surface without the bulk electrolyte. On the example of gold, it was validated that the emerged electrode transferred in UHV¹ or humid nitrogen² has a more or less intact EDL of the order of a few monolayers. The absence of water in UHV raises questions about the structure of water in the electrochemical double layer of the emerged electrodes and its impact on the potential.

In this study, we systematically investigated the EDL across the full humidity range of 1-95% RH. We extended the investigation to include iridium and platinum and performed first *in situ* studies during polarization induced by suitable gas phase changes.

For this study, a homemade set-up was built to investigate emerged electrodes using various characterization techniques in a controlled environment. Cyclic voltammetry was performed to clean the surfaces and reveal the chemical reactions occurring in the system.

The input gases inside the analysis chamber can be adjusted to enable *in situ* measurement: the humidity can be set from dry N₂ (1-3% RH) to wet (90-95% RH); hydrogen and oxygen can be added to increase or decrease the potential *in situ* without new emersion. The Kelvin Probe was used to measure the electrode potential^{3,4}, providing information about the surface, including the presence and reorientation of water². Fourier-Transform Infrared Spectroscopy provided information about the reorientation of the water layer⁵ and the presence and relative quantity of ions from the electrolyte. Additional characterizations were used to obtain more information about the EDL, including ellipsometry and X-ray Photoelectron Spectroscopy.

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Keywords: Electrochemical Double Layer, Emerged electrode, Kelvin Probe, Infrared Spectroscopy

Soft X-ray Spectroscopy of Spinel Oxides for Photocatalytic Water Splitting

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As active components in photocatalytic water splitting, spinel oxides (general formula AB_2O_4) have attracted much attention with regards to their electronic structure. In addition to variation in oxidation states for reducible spinels, the effect of coordination geometry is also of key importance to the electronic structure and reactivity. One parameter of merit is the inversion degree, which indicates the relative populations of tetrahedral and octahedral sites within the lattice.

Our group has employed synchrotron-based soft X-ray spectroscopy (XPS, NEXAFS and XMCD) to understand the bulk and surface behaviour of ferrite spinels ($CoFe_2O_4$, $CuFe_2O_4$, $ZnFe_2O_4$ nanoparticles and single crystal surfaces). We complement these experimental results with DFT modelling of the spectra and the materials. Particle size, composition, and thermal treatments are all observed to play important effects in the behaviour and inversion degree of the spinels.

The talk will present our recent results as well as describing the in-situ and operando soft X-ray spectroscopy capabilities available at the B07 beamline at Diamond Light Source.

Keywords: XAS, XPS, Spinel, Photocatalysis

Monitoring reversible surface modifications of SrMoO₃ thin films by combining laboratory and synchrotron NAP-XPS

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Perovskite-type oxides have attracted interest due to their remarkable electronic and optical properties. Among them, SrMoO₃ (SMO) is a promising candidate for transparent conducting oxide applications because of its very high electrical conductivity, which is related to partially filled Mo 4d states near the Fermi level associated with Mo⁴⁺ (4d²) in the SMO crystal structure^{1,2}. However, the high surface reactivity of this material raises important questions about its chemical stability under reactive environments and the tendency to generate insulating layers involving stable Mo⁶⁺ species.

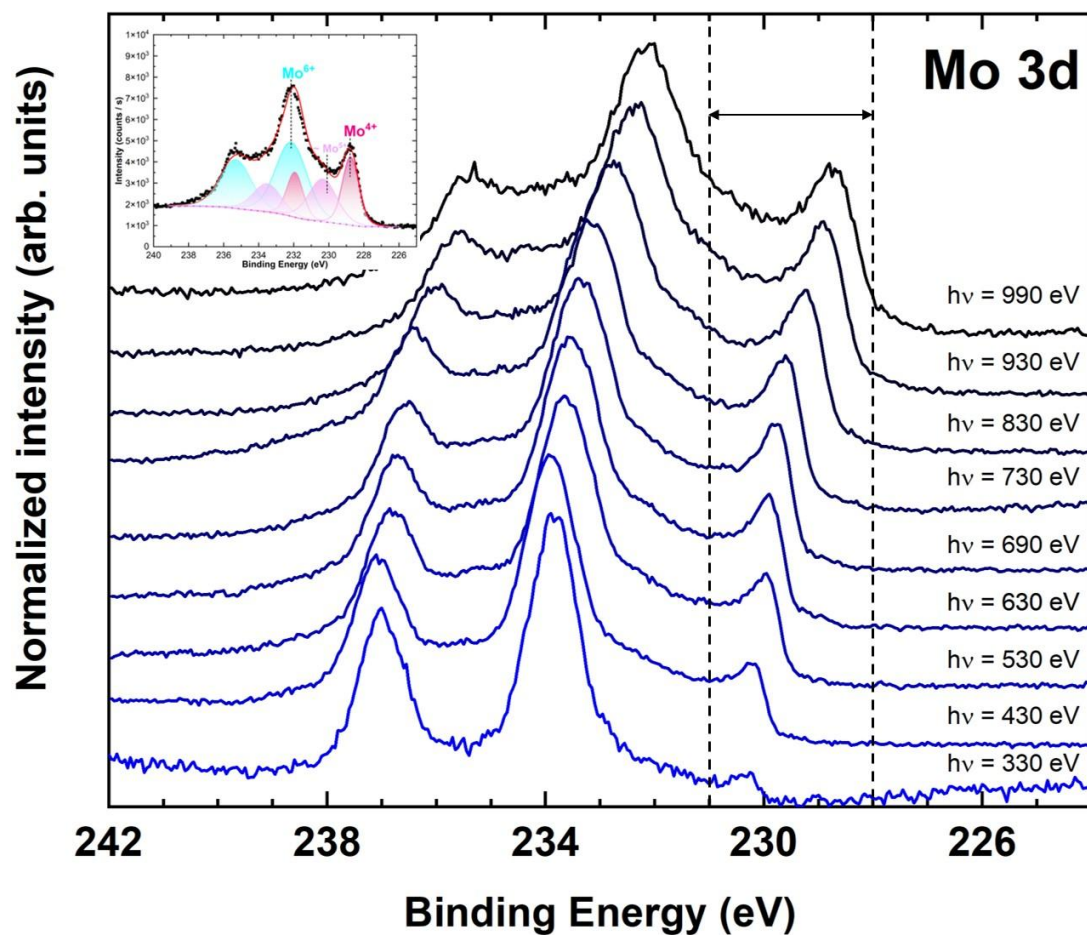
In this work, the surface chemical evolution of SrMoO₃ thin films deposited on SrTiO₃ substrates by pulsed laser deposition (PLD) is investigated using near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS). Experiments were performed both in a laboratory NAP-XPS system and at a synchrotron radiation facility.

Measurements were performed under O₂ and H₂ atmospheres up to 3 mbar with temperature variations, allowing the monitoring of surface oxidation and reduction. The evolution of the Mo 3d core level shows a rapid surface oxidation under O₂ exposure, leading to the formation of Mo⁶⁺ species even at room temperature. In contrast, exposure to H₂ induces a reduction process with the reappearance of Mo⁴⁺, showing the reversible character of the surface redox processes. Measurements at different sample positions help distinguish beam effects from the reactive atmosphere.

Complementary synchrotron experiments performed at different excitation energies provide additional information on the surface and near-surface regions of the films. The figure shows the XPS spectra in the Mo 3d region for different excitation energies, with a tentative reconstruction in the inset highlighting the binding energy difference between Mo⁴⁺ and Mo⁶⁺. A clear evolution is observed, indicating that the conductive perovskite oxide (characterized by Mo⁴⁺) is covered by a nanometric film containing Mo⁶⁺. In addition, SrMoO₃ samples capped with LaAlO₃ and AlOx layers were also investigated in order to complete this study. The comparison between capped and uncapped samples shows that the capping layers modify the electronic environment of SrMoO₃ and influence the distribution of molybdenum oxidation states. In particular, capped samples show stronger contributions from reduced molybdenum states in the initial condition, suggesting that the passivation layers help preserve these reduced states against surface oxidation.

These results highlight the strong surface reactivity of SrMoO₃ and demonstrate the reversible nature of its surface redox processes. The combination of laboratory and synchrotron NAP-XPS provides valuable insight into the chemical stability of this highly conductive perovskite oxide.

Keywords: SrMoO₃ thin films, Near-ambient pressure XPS, Surface oxidation–reduction, Perovskite oxides, Synchrotron radiation



Operando APXPS Reveals Distinct Wet and Dry Carbonation Pathways of $\text{Ca}(\text{OH})_2$

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Calcium hydroxide ($\text{Ca}(\text{OH})_2$) is an effective sorbent for carbon dioxide (CO_2), and is being explored as a reactive material in emerging Direct Air Capture (DAC) technologies.^{1,2} Despite the apparent simplicity of the $\text{Ca}(\text{OH})_2$ carbonation reaction, its surface mechanism remains poorly understood. In particular, a proposed two-step carbonation pathway involving surface-adsorbed water is supported by higher reaction rates under humid conditions,^{3–5} yet the structure and dynamics of this interfacial water layer and its influence on CO_2 adsorption and activation are not well established.

Here, the surface mechanisms of $\text{Ca}(\text{OH})_2$ carbonation are investigated *operando* using Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) and X-ray Absorption Spectroscopy (XAS), with emphasis on the role of interfacial water. $\text{Ca}(\text{OH})_2$ particles (<1 micrometer) derived from steel-slag calcium were suspended in ethanol, drop-cast onto Au substrates, and studied in an APXPS flow reaction cell where CO_2 and H_2O partial pressures were controlled by mass flow.

Under vacuum, the initial C 1s spectrum shows contributions from carbonate (CO_3^{2-}) and aliphatic/adventitious carbon. When 0.5 mbar CO_2 is introduced under dry conditions, an additional carbon peak appears, indicating the onset of surface carbonation. Upon adding H_2O vapor (0.5 mbar) together with CO_2 , the C 1s spectral region changes dramatically: the additional carbon peak disappears and the aliphatic component diminishes, leaving primarily the carbonate signal. This clear change in carbon speciation reveals a fundamental difference between dry and wet carbonation pathways. At higher H_2O pressures (> 1 mbar), the C 1s signal disappears entirely, consistent with the formation of a hydrated surface layer that attenuates photoelectrons and masks carbonate species beneath the interface. Together, these results demonstrate that even trace amounts of water strongly modify the surface chemistry of $\text{Ca}(\text{OH})_2$, promoting interfacial hydration and fundamentally altering the carbonation mechanism, an effect that has important implications for optimizing Ca-based materials for DAC technologies.

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Keywords: Calcium hydroxide, Carbonation, APXPS, CO_2 capture, Surface chemistry

Size- and shape-dependent reactivity: a NAP-XPS study of Cu₂O nanoparticles as model catalysts

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Cu₂O-based catalysts are promising alternatives to noble-metal-based catalysts in several reactions, such as the water-gas shift reaction, propylene oxidation, and selective oxidation processes.^[1] Their catalytic performance, however, is strongly hindered by the tendency of Cu₂O to oxidise to CuO under reaction conditions: a deeper understanding of their behaviour is needed to fine-tune the reactivity and avoid unwanted modifications.

CO oxidation on copper is commonly reported to proceed through a Mars-van Krevelen mechanism, yet the exact active site is not well determined: Huang et al.^[2] found Cu₂O to be the main active phase, but Wan et al.^[3] showed that the activity is improved by the presence of a mixed Cu(I)/Cu(II) valence state.

To shed light on this topic, multiple shapes and sizes of Cu₂O nanoparticles (cubes for (100) facets, octahedra for (111), spheres, in the range of 15–600 nm) were investigated by Near-Ambient Pressure XPS: nanoparticles with controlled morphology are the perfect candidates to bridge the “material gap” between ideal (e.g., single crystals) and real (powder) catalysts. Morphology and crystallinity were verified by SEM, TEM, and XRD.

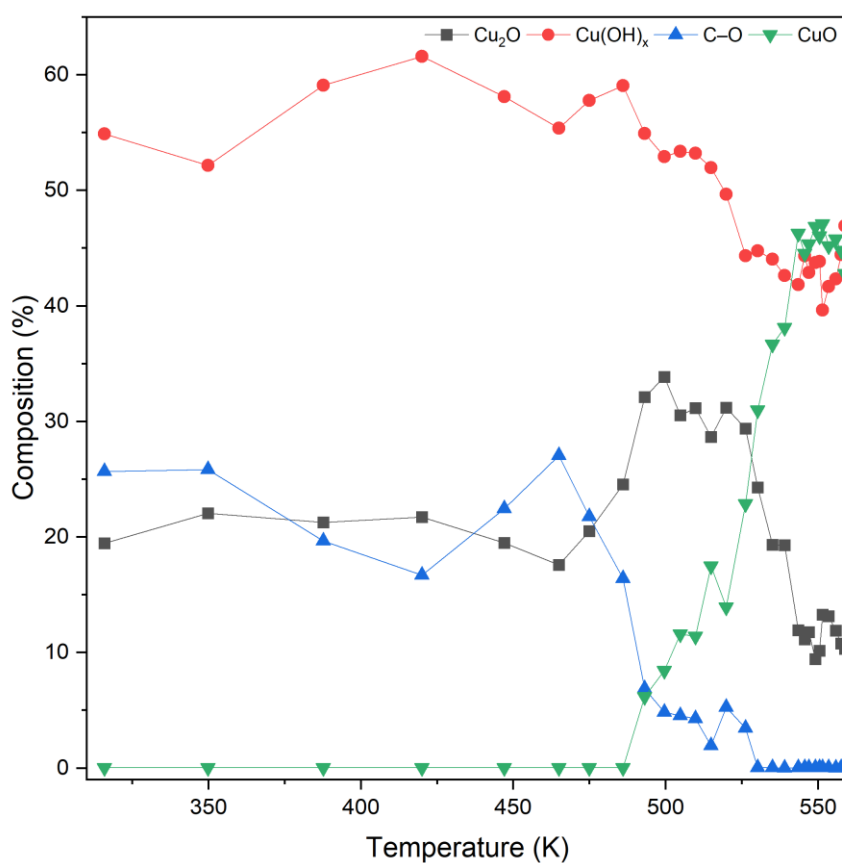
Temperature-dependent oxidation experiments (1 mbar O₂, up to 600 K) reveal that the Cu₂O oxidation temperature depends on the size and the morphology, showing two different reaction regimes depending on the size. On a series of 6 cube sizes, cubes below 80 nm show kinetics limited by surface reaction, while in bigger particles the reaction is limited by diffusion. Furthermore, carbon reactivity was found to be independent from copper: it is then possible to selectively remove the adventitious carbon contamination before oxidising the nanoparticles, while morphology is fully retained. The accompanying figure displays the decomposition of the O 1s spectrum in function of the temperature. This results in the possibility to prepare clean surfaces in model materials for catalytic studies.

Having established this, carbon-depleted samples were exposed to a mixture of CO and excess O₂ in the NAP-XPS chamber to monitor their behaviour in CO oxidation. Cu 2p, O 1s, and C 1s spectra were acquired at multiple temperature steps (420, 470, 520 K), while reaction products were monitored by in-line mass spectrometry, allowing identification of the various copper, oxygen, and carbon species and their relative surface abundance depending on temperature.

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Keywords: NAP-XPS, Nanoparticles, Cu₂O, CO oxidation



Oxidation behaviour of model 304 stainless steel exposed to water vapour at 500°C: An in situ XPS study

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Stainless steels are used in many industries because of their exceptional corrosion resistance provided by the passive film which forms instantly under ambient conditions. The various oxidizing agents to which the surface is exposed, such as oxygen and water vapour, influence the film structure and its corrosion resistance. The precise role of water vapour during the earliest stages of film formation is not completely understood. It can be studied on pristine surfaces in ultra-high vacuum (UHV) conditions. A recent study involving the exposure of a (100)-oriented surface of Fe-18Cr-13Ni (model SS304) to water vapour at room temperature (RT) and 250°C revealed that the alloy surface undergoes layer-by-layer growth of a mixed oxide-hydroxide film independent of pressure, with faster kinetics and reduced hydroxide content observed at 250°C [1]. At higher temperatures, the reaction kinetics, film structure and stability are likely to be modified, with a possible influence of pressure. In this work, the same alloy surface was exposed at 500°C to water vapour at pressures ranging from 3×10^{-7} to 1.5×10^{-6} mbar, while the O 1s signal was simultaneously recorded by *in situ* XPS. The reaction kinetics was found to be initially linear, followed by a sudden transition to exponential growth at an oxide thickness of 0.7 monolayers (ML) then saturation at a thickness of 3 ML. This behaviour was consistently observed across different water vapour pressures and initial surface compositions. It was demonstrated that these parameters only influence the initial oxidation kinetics. The repeatable transition to rapid exponential growth is probably due to a catalytic effect that occurs when a specific surface structure is achieved. At saturation, a Cr-rich oxide film with a thickness 0.65 nm (3 ML) is observed. The composition and structure of the film at different stages of the reaction, analysed by angle-resolved XPS, was characterized. This study is an essential step towards the design of improved corrosion-resistant surfaces with specific compositions and structures.

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Keywords: Stainless Steel, Oxidation behaviour, Growth kinetics, X-ray Photoelectron Spectroscopy, Single crystal

Microfluidic Chip for In Situ Surface Mass Spectrometry

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Time-of-flight secondary ion mass spectrometry (ToF-SIMS) enables label-free chemical imaging with high spatial resolution and is used for the characterization of biomaterials and complex biological systems. However, direct analysis of samples prepared within enclosed microfluidic environments remains challenging due to the incompatibility of typical microfluidic devices with vacuum-based surface analysis techniques. In this work, we present a microfluidic chip designed to enable direct ToF-SIMS characterization of biomaterials formed inside microchannels. The device incorporates a membrane that maintains integrity during microfluidic operation while enabling controlled exposure of the sample surface prior to analysis. The membrane can be selectively removed prior to measurement, and the chip design eliminates the need for cleanroom-based fabrication while facilitating a straightforward transition from microfluidic experiments to mass spectrometric analysis. The platform was validated using hydrogel-based biomaterial systems containing model compounds, including the antibiotic low-molecular-weight moxifloxacin (MXF; 401 Da) and poly(styrene sulfonate)(PSS; Mw 70,000), a high-molecular-weight polyelectrolyte. ToF-SIMS imaging demonstrated successful detection and localization of both species within the dried microfluidic environment. This approach enables in situ chemical imaging of biomaterials and offers new opportunities to investigate molecular transport, drug distribution, and biomaterial–tissue interactions. Furthermore, the methodology shows potential compatibility with Cryo-SIMS, enabling analysis of hydrated biological samples in near-native states.

Filed with the European Patent: Characterization of a material in a microfluidic device (European Patent Application No. EP25189373.1).

Keywords: TOF SIMS, Microfluidic, Biomaterial

Machine learning in surface science

ML-framework for deconvolution in X-ray Photoelectron Spectroscopy

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Spectral fitting is a fundamental step in the characterization of materials; however, despite significant methodological progress, the interpretation of spectroscopic data remains a major source of uncertainty and misinterpretation¹. Conventional analysis workflows often depend on user-defined fitting parameters, which can introduce subjectivity and variability between spectroscopists. Consequently, there is a growing need for approaches that improve the reliability and objectivity of spectral analysis². In this work, we present a machine learning (ML)-based framework designed to address these challenges. As an application, the framework is applied to X-ray photoelectron spectroscopy (XPS), which is an indispensable surface-sensitive technique for investigating the chemical states of materials.

The proposed framework is based on convolutional neural networks (CNNs) trained on a large dataset of synthetically generated XPS spectra with predefined oxidation-state compositions. The synthetic spectra are generated to closely replicate realistic experimental conditions, incorporating features such as peak overlap, variable peak widths, and instrumental noise. This strategy enables the generation of large and diverse training datasets while maintaining full control over the ground-truth chemical composition. When evaluated on unseen synthetic test spectra, the trained model achieves over 92% accuracy in detecting the presence of specific chemical bonds and approximately 96% accuracy in quantifying the relative concentrations of oxidation states.

The framework is applied to spectra containing multiple chemical environments within the C 1s core level. The C 1s region is among the most frequently analyzed in XPS due to the widespread presence of carbon-based materials. The results show that the model can reliably identify and quantify multiple overlapping chemical states within this spectral region.

The proposed framework is not limited to the C 1s orbital and can be easily extended to other core levels, such as O 1s, N 1s, F 1s, P 2p, and Zr 3d. Compared with conventional peak-fitting workflows, the AI-powered approach reduces human-induced biases, which increases reproducibility, and significantly accelerates spectral interpretation. Overall, this work highlights the potential of data-driven methods to aid spectroscopists by partially replacing traditional spectral fitting procedures, paving the way for more consistent spectroscopy analysis.

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Keywords: Machine Learning, Framework, X-ray Photoelectron Spectroscopy, carbon

Metals

Applications of XPS in an industrial production environment

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The company Plansee SE fabricates products based on the refractory metals Mo, W and Ta for various applications in the fields of diagnostics in medicine, consumer electronics, semiconductor manufacturing and high-temperature processing. We employ powder metallurgy as the main production technology.

XPS, as a very surface-sensitive technique, is usually not very suitable for the investigation of parts/samples from a production environment, as handling of the materials, machining processes and annealing treatments are not necessarily designed to yield a clean surface. However, in specific fields, surface cleanliness or the oxidation state at the surface play an important role for the application. Additionally, different versions of cleaning or annealing treatments can be compared regarding their effect on the material surface that can influence the performance in the final application.

One example for the application of XPS is the characterization of potential contamination sources in high-temperature annealing treatments (up to 2500 °C). For this purpose, e. g. sheets of Mo or W, can be inserted into the furnace at different positions as probes. By comparing the surface composition before and after the annealing process, sources of contamination can be located. Thus, valuable input is generated for the optimization of the annealing treatments. This is especially useful for processing alloys, e. g. Mo with 0.7 wt% La_2O_3 , to check for accumulation of the added substance in the furnace, which would create the risk of surface contamination in the following annealing treatment.

For specialized applications, e. g. in extreme ultraviolet (EUV) lithography, the surface state of the utilized material has an impact on its performance. In this regard, the oxidation state of Mo and the thickness of the oxide layer can be crucial. The fabrication route and cleaning treatments influence these properties significantly. To determine the oxide layer thickness as reliably as possible, considering also potentially present contaminants, two approaches are employed: sputter depth-profiling relative to a standard and determination of the oxidation state by fitting the Mo 3d region with a self-developed fit model. Based on the latter, the oxide layer thickness is estimated with the single-overlayer model. The evolution of the O 1s, C 1s and Mo 3d peak areas in the depth profile yields valuable information on surface topography, the contamination layer and the oxide layer itself, while the single-overlayer calculation provides a different estimate, which is more independent of the contamination.

Keywords: molybdenum, oxide thickness, industry, contamination

Quasi in situ monitoring of GaAsSb Plasma Surface Preparation

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6G communication technologies based on GaAsSb are designed to meet the requirements of the next-generation telecommunication by operating at ultra-high frequencies (300 GHz)[1].

In order to perform CMOS-compatible III/V high performance contact, plasma surface preparation process has been developed to investigate native oxide cleaning and electrical performance[2]. Unavoidable air exposure between wet surface treatment and metallization induces inevitable regrowth of native oxides[2][3]. That's why in-situ surface preparation is essential to achieve oxide-free surfaces prior to metallization while preserving surface morphology, roughness[2].

In this work, quasi-in-situ pARXPS is employed to quantitatively assess oxide removal efficiency from GaAsSb surfaces, using Argon or Helium plasma treatments, in the PC XT chamber of an Applied Endura® 300 mm platform. Argon (Ar) and Helium (He) plasma were generated using a dual RF generator providing power to an inductively coupled plasma source. Processes etch rate were evaluated on SiO₂ thin film in the range 1 to 5nm/min. Plasma exposure time varied between 15 to 150 s. The chamber pressure during plasma processing ranged from 0.1 to 3.8 mTorr. pARXPS measurements were performed using a customized Theta 300 from Thermo Scientific™. A specific 300mm carrier's transfer setup[4] allows to perform quasi in-situ analyses without any air exposure between process and measurement. pARXPS gives access to angle resolved information without any wafer tilt and at each acquisition.

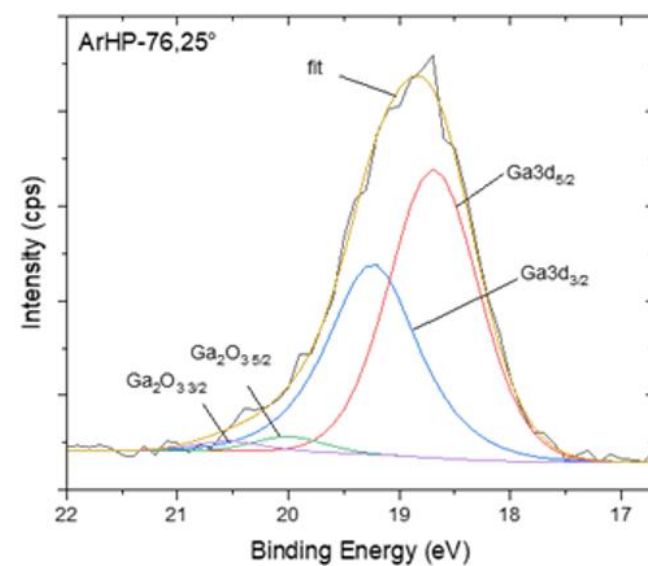
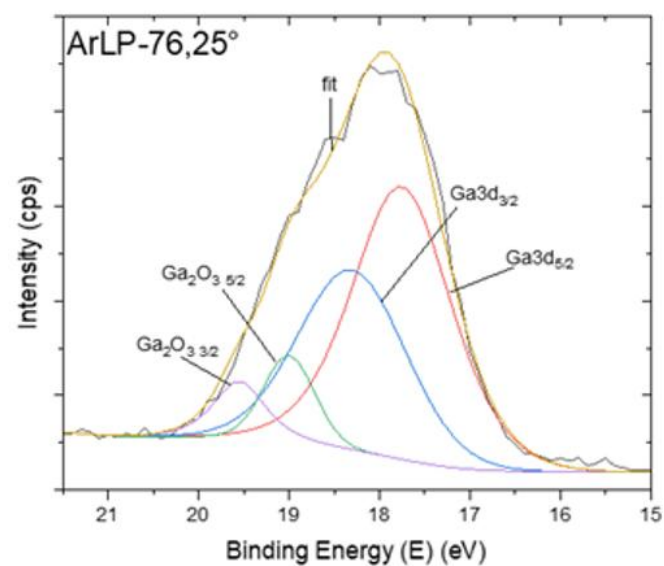
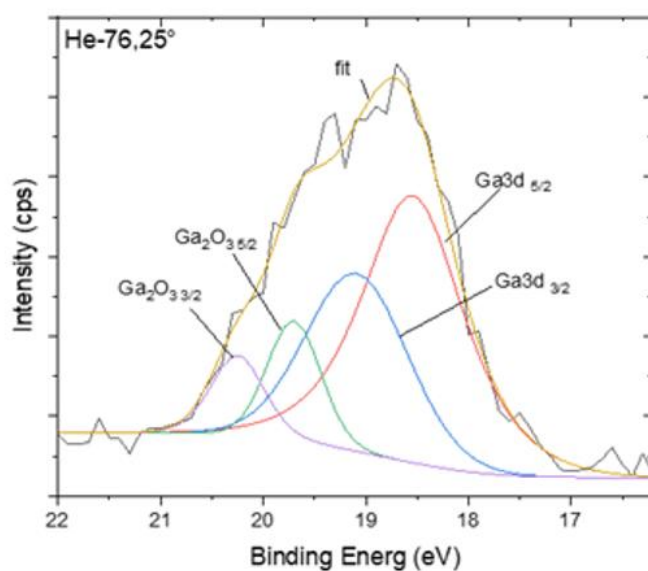
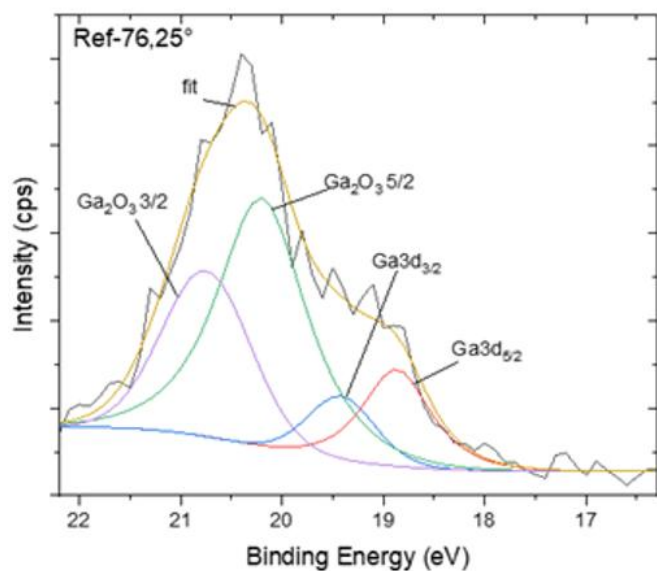
Figure 1 presents the Ga spectra acquired at an angle of 76.25°, with surface enhanced sensitivity, after Ar and He plasma pre-clean treatments. Both Ar and He plasmas effectively reduced the native oxide components. High-power Ar (ArHP) plasma resulted in complete removal of native oxides. In contrast, low-power Ar (ArLP) and He plasmas led to partial oxide removal. He & ArLP plasmas mainly enables chemical assisted oxide removal with limited damage, whereas ArHP plasma promotes dominant physical etching. A critical trade-off between complete deoxidation and material preservation.

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Keywords: III-V Materials, surface preparation, impact_X XPS, deoxidation, material preservation

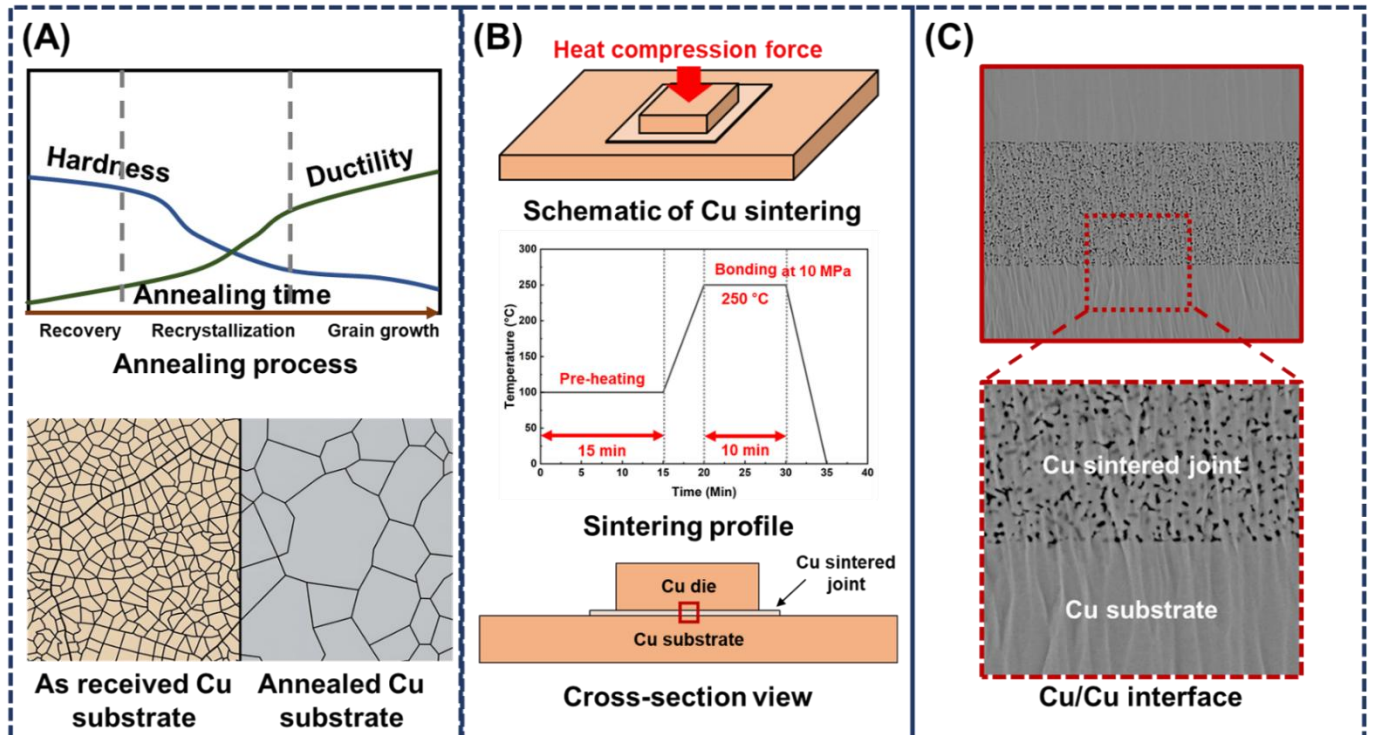


Effect of Microstructure and Surface Orientation of Cu Substrate on Interfacial Reaction in Cu Sinter Bonding Process

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Cu sinter bonding technology has received attention as a die-attach material for wide-bandgap semiconductor to replace Ag sinter bonding. With the recent surge in silver prices, the demand for transitioning to copper-based materials is increasing. Cu sinter is compatible with a wide range of substrate and metallization, such as active metal active metal brazed Cu, Cu lead frame, and backside metallization of power semiconductor. Due to variation in manufacturing process for substrate and metallization, these exhibits distinct microstructure and crystallographic texture. As a result, grain size, texture, dislocation density, and residual strain can vary depending on substrate type. These microstructural differences can influence diffusion behavior, neck growth, and Cu/Cu interface formation during Cu sintering, which may lead to variation in final bonding strength and joint quality. This study systematically investigates how annealing induced microstructural evolution in Cu substrates affects Cu/Cu interfacial connectivity and mechanical performance in Cu-sintered joints, using EBSD based surface and interface analysis. To simulate industrial substrate conditions and examine annealing effects, Cu specimens were annealed using two approaches. Time dependent annealing was performed at 500 °C for 0.1 ~ 10 h to promote grain growth and reduce deformation-induced defects. In addition, temperature dependent annealing was conducted for 1 h at 50 ~ 800 °C to obtain microstructures ranging from recovery to recrystallization states. The annealed microstructures were analyzed by EBSD to examine grain structure and texture evolution through inverse pole figure (IPF) mapping. Grain boundary distribution and kernel average misorientation (KAM) were further evaluated to quantify grain boundary density and local misorientation related to dislocation structures and residual strain. Cu sintered joints were prepared at 250 °C under pressure of 10 MPa for 10 min in a nitrogen atmosphere. Cross sectional analyses were performed to quantify interfacial connection ratio and porosity distribution along the Cu/Cu interface. EBSD mapping near the interface was conducted to assess grain continuity across the Cu/Cu interface and to identify bonded regions along the interface. Mechanical performance was evaluated by die shear testing, followed by statistical correlation analysis relating EBSD derived microstructural parameters to interfacial connectivity and shear strength. Overall, the results suggest that annealing controlled changes in Cu substrate microstructure, particularly grain structure and defect and strain state, are closely associated with Cu/Cu interfacial connectivity and shear strength, highlighting the importance of substrate pre-conditioning for robust Cu sintered joints in power electronic packaging.

Keywords: Cu sintering, EBSD, Interfacial connectivity, Microstructural evolution, Annealing



Determination of oxide-layer-thickness on ~50 μm high-alloyed steel spheres by use of XPS

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Today, materials science offers a broad range of characterization methodologies for determining the thickness of an ultrathin layer on top of a substrate material. However, most of these methods are limited by one or more of the following factors: the roughness, geometry, and flatness of the sample; the thickness of the layer; and the elements within the layer.

Most lab-source based methods are highly limited when it comes to characterizing ultrathin layers (1–10 nm) of material on top of non-flat substrates. For example, it is not possible to determine the thickness of a nm-thick oxide layer on a μm -sphere of high-alloyed steel using XRD, TXRF, XRR or SEM-EDX. Alternatively, one could cut out a FIB lamella and use STEM-EELS or STEM-EDX, which would entail long working days and a high risk of losing the sample. Additionally, transferring the sample through air and the cutting process itself may affect the material's chemistry and compromise the results. XPS offers the opportunity of analyzing very thin layers and using the relative signals of metallic and oxidized species to simulate the oxide thickness using the SESSA software¹. After calibrating the method, one can use an Ar-ion sputter gun to remove some of the oxide layer until the underlying metal becomes visible in XPS and then determine the thickness by adding the estimated sputter depth to the final thickness value. Using this method, we were able to determine oxide thicknesses in the range of 3–10 nm of high-alloyed steel spheres that were the result of different synthesis approaches. Compared to the FIB/STEM approach, preparation and measurement times are reduced by around 80% to about 2 hours in total.

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2 peak fitting was performed according to suggestions provided by Biesinger et al. on <https://www.xpsfitting.com>

Keywords: steel particles, oxide films, thickness determination, XPS

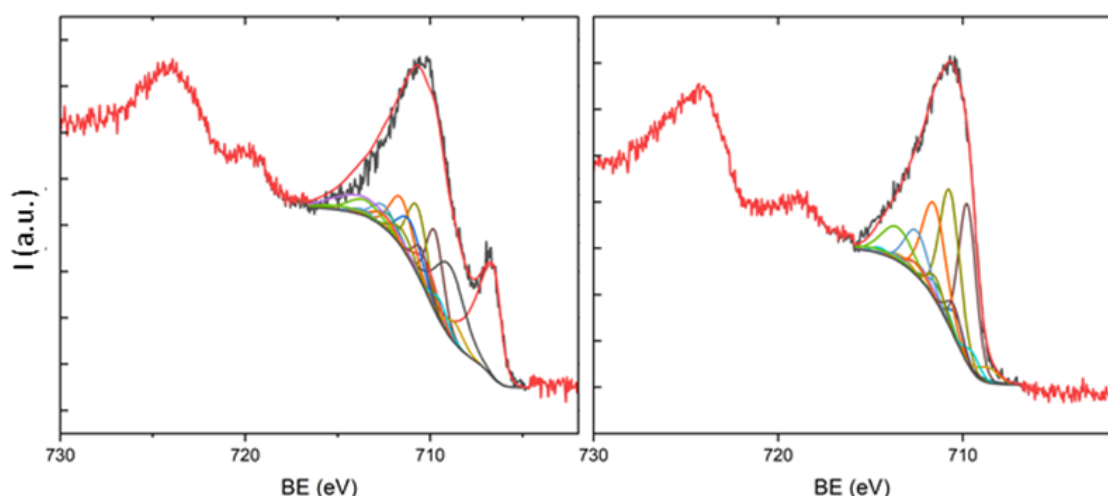


Figure 1: XPS spectra of the Fe2p region measured on steel particles with different thicknesses of iron oxide on top. While the metallic signal is visible in the left figure (untreated sample) the metallic signal vanishes after surface treatment (right figure). Application of the SESSA software enables simulation of the corresponding layer thickness in the left sample, while both Ar-ion-sputtering and simulation are needed to determine the oxide thickness on the treated samples.

In situ XPS analysis of iron oxide reduction for hydrogen detection in advanced high-strength steels

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Hydrogen embrittlement (HE) is a hydrogen-assisted degradation mechanism that turns a ductile into a brittle behaviour, threatening structural integrity of materials in service. Thus, a thorough understanding of hydrogen in HE sensitive materials is of great importance. Our custom-built *in situ* cell (Figure 1a) can charge zinc-coated advanced high-strength steel from the entry (charging) side with hydrogen while the opposite exit (detection) side is monitored by X-ray photoelectron spectroscopy (XPS) [1]. Hydrogen is generated via the reaction of perchloric acid (HClO_4) with the zinc coating and diffuses through the steel to the opposite sample side. Upon reaching the exit side, hydrogen reduces surface iron oxides from its third Fe^{3+} to the second Fe^{2+} oxidation state. These changes are observable in the high-resolution Fe2p spectra through shifts in the main line and satellite features (Figure 1b). By varying the acid concentration, we tune the hydrogen input signal and observe corresponding changes in the reduction rate of iron oxides at the exit side. Open-circuit potential (OCP) measurements determine the time required to fully dissolve the zinc coating, thereby defining the temporal profile of the hydrogen input at the entry side and providing a boundary condition for diffusion modelling. This gives the possibility to predict the time-dependent hydrogen concentration at the exit surface, which can further be correlated with the XPS-derived reduction kinetics to identify the predominant surface reaction mechanism. This *in situ* XPS approach enables indirect yet sensitive detection of diffusing hydrogen in advanced high-strength steel and promises a deeper understanding of hydrogen embrittlement mechanism.

Keywords: Advanced high-strength steel, XPS, Hydrogen, in situ

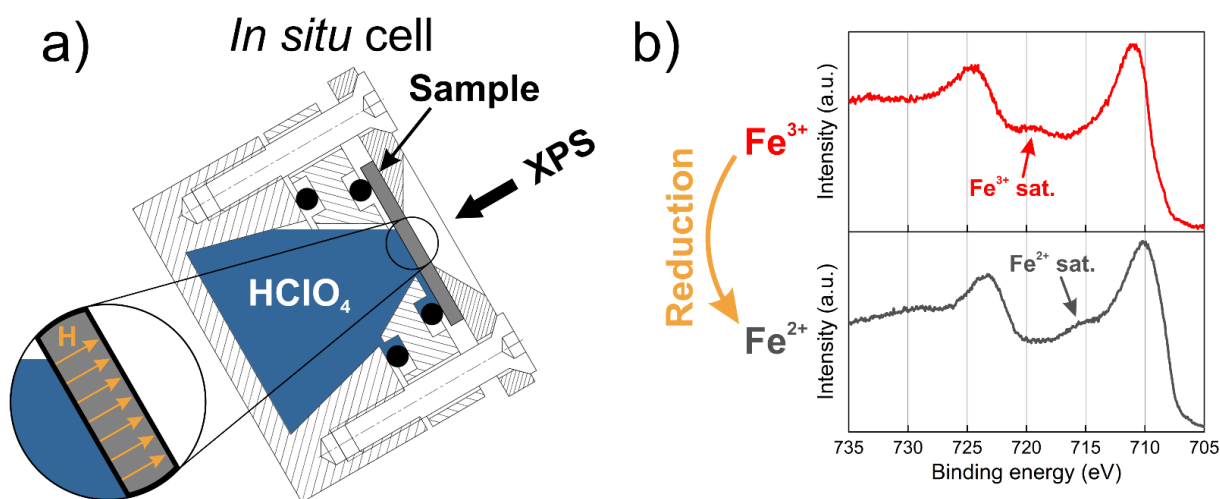


Figure 1. a) Schematic drawing of the *in situ* cell. b) Changes in the Fe2p spectrum due to diffused hydrogen.

Stretch Induced Evolution of Gallium Oxide in Liquid Metal Interconnects in flexible stretchable electronic devices

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Galinstan, a Gallium based liquid metal alloy is increasingly explored as conductive interconnects in intrinsically flexible and stretchable electronic sensors due to its high electrical conductivity and fluidic nature at ambient conditions. A key feature governing the device's performance is the formation of an ultrathin Gallium native oxide layer (typically ~3-6 nm), which critically influences mechanical stability, wetting behaviour, and electrical reliability.

In this work, the surface chemistry and strain (stretch) dependent evolution of the native oxide layer on Galinstan are systematically investigated under both static and mechanical deformation conditions using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and Scanning Electron Microscopy (SEM). Measurements performed on Galinstan under ambient laboratory conditions reveal an oxygen-rich surface (~50 at%), predominantly composed of Ga_2O_3 . High-resolution Ga $2p_{3/2}$ spectra estimate an oxide thickness of approximately 3 nm. However, mechanical manipulation of the oxide skin demonstrates its ability to undergo localized rupture, thinning, and accumulation. Testing actual sensors with encapsulants as base and Galinstan traces shows significant variations in the metal-to-oxide (M:O) ratio across the sensor. Highly strained regions exhibit an increased Ga metallic fraction (M:O~0.5), indicating oxide rupture, whereas low-strain regions maintain a stable oxide composition (M:O~0.2). Depth profiling via controlled sputtering further reveals a Ga_2O_3 rich subsurface region beneath a thin SiO_2 containing layer. The origin of Si remains unresolved. However, SEM images reveal a wrinkled surface, suggesting oxide breaking and rolling, and transport of Si from the underlying polymer substrate during deformation is proposed as a plausible mechanism, indicating the importance of the encapsulant material on the performance characteristics of the sensor. These findings highlight the dynamic nature of the oxide layer and encapsulants under mechanical loading and its critical role in governing interconnect reliability.

Current work focuses on the characterization of embedded liquid metal structures within polymeric matrices. Ongoing efforts employ cryogenic cross sectioning techniques to preserve interfacial features and understand oxide distribution and its impact on device performance.

Keywords: Galinstan, Gallium oxide, Stretchable electronics, Liquid metal interconnects

Mitigation of chromium release in high-temperature heat exchangers via alumina-forming Ni-based alloys

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Stainless steels are widely used in high-temperature heat exchanger (HT-HEX) systems due to their excellent properties. However, under operating conditions ($T > 600$ °C, moisture and oxygen), they release toxic Cr(VI) species. This release leads to corrosion issues, electrochemical degradation of fuel cell and electrolyzer stacks, and potential pre-contamination during the initial HT-HEX welding. To address these challenges, a collaboration between Bosal Group and Vrije Universiteit Brussel (VUB) aims to develop Cr-free HT-HEXs.

To date, a Ni-based alloy is being investigated as a potential alternative to conventional stainless steels. The alloy is specifically designed to form a stable and protective alumina (Al_2O_3) at high temperatures. Oxide formation and surface chemistry were characterized using SEM/EDS, Raman spectroscopy, and XPS analyses. In parallel, chromium evaporation was quantified by ICP-MS through the analysis of aliquots taken in-service conditions. Ongoing work is focusing on coating technologies and welding processes to identify scalable, and industrially compatible solutions to mitigate chromium evaporation in HT-HEX systems.

Acknowledgements: The authors gratefully acknowledge the financial support of Flanders Innovation & Entrepreneurship (VLAIO) under the R&D project "Mitigation of Chromium Evaporation in Electrolyser and Fuel Cell Systems (VLAIOO44)". The authors also thank Prof. Yue Gao and Prof. Martine Leermakers for their support with chromium analysis, and Bart Lippens for sample preparation.

Keywords: High-temperature heat exchanger, Stainless steels, Chromium release

Modelling

Atomistic Insights into Surface Reactivity: From Thermochemical Energy Storage to Catalysis and Bio-mineral Interfaces

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Understanding and controlling surface reactivity is central to the rational design of functional materials for energy, environmental, and biomedical applications. In this contribution, density functional theory (DFT) is employed as a unifying tool to investigate the chemical behaviour of three distinct but complementary classes of materials, illustrating how atomistic modelling can guide material optimization across diverse fields.

First, the potential of MXenes as active materials for reversible thermochemical heat storage (RTHS) is explored. Heat represents the largest global energy end use, and improved storage technologies are urgently needed to reduce large-scale energy waste. The water adsorption properties of representative MXenes (Ti_3C_2 , Mo_2C and Mo_2N) with different surface terminations are investigated in terms of thermodynamics, electronic structure, and chemical bonding. The results indicate that functionalized MXenes constitute a promising and tunable platform for next-generation RTHS systems.

Second, the mechanisms governing the formation of reactive oxygen species (ROS) on supported metal catalysts are addressed through a detailed study of Ag_{13} clusters on amorphous SiO_2 . DFT calculations reveal how interfacial interactions influence O_2 and H_2O activation, charge transfer, and reaction pathways. These insights highlight the crucial role of the metal-support interface in promoting ROS generation and provide guidelines for the rational design of highly active catalytic surfaces.

Finally, the surface chemistry of calcium oxalate, a biologically and geochemically important mineral, is examined. Because calcium oxalate surfaces consist of molecular ions, different crystallographic faces exhibit markedly different chemical environments and reactivities. The varying exposure of calcium ions leads to surface-dependent interactions with charged species in solution, offering an atomistic explanation for the selective vulnerability of specific crystal faces to chemical attack.

Together, these case studies demonstrate how first-principles modelling enables a fundamental understanding of surface processes in materials ranging from advanced energy storage systems to heterogeneous catalysts and bio-mineral interfaces. The work underscores the versatility of computational surface science as a powerful approach for designing materials with tailored reactivity and functionality.

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Keywords: Modelling, MXenes, Silica, Biological Minerals, DFT

Facet- and defect-dependent adsorption of toluene on CeO₂ surfaces: a DFT study

Amanda Fernandes Gouveia (MONARIS, Sorbonne Université, Paris, France), **Monica Calatayud** (MONARIS, Sorbonne Université, Paris, France)

Volatile organic compounds (VOC), widely released from industrial processes and urban transportation, pose significant risks to both the environment and human health[1]. A valid strategy to remove VOCs relies on heterogeneous catalysts performing oxidation reactions under mild conditions. In the present work we will investigate the role of cerium dioxide (CeO₂) [2] to activate toluene, focusing on the role of exposed terminations as well as the presence of defects. Density functional theory (DFT) calculations at the PBE+D3 level, were carried out using the VASP code [3], to examine the adsorption of toluene on CeO₂ (111), (200), and (220) surfaces in the presence and absence of oxygen vacancies. The results reveal a strong dependence on surface orientation, with the (200) facet exhibiting the strongest interaction with toluene. Oxygen vacancies play a critical role in modulating adsorption, with their impact varying according to their position (surface or subsurface) and the crystallographic facet. Bader charge analysis indicates significant electronic redistribution at the adsorbate–surface interface, characterized by charge transfer from the toluene molecule to the CeO₂ surface, leading to electron depletion in toluene and electron accumulation on the oxide. These findings demonstrate the synergistic influence of surface structure and oxygen defects on the adsorption and activation of aromatic VOCs on CeO₂, offering valuable insights for the rational design of improved oxide-based catalytic materials.

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Keywords: DFT, heterogeneous catalysis, surface defects

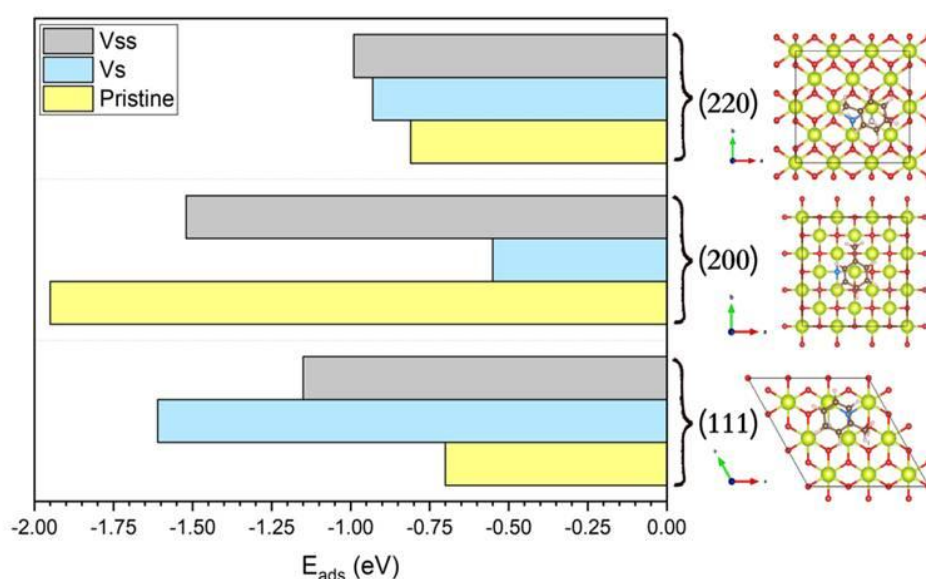


Figure 1. Comparison of adsorption energies for pristine and defective models, including surface (Vs) and subsurface (Vss) oxygen vacancies, on CeO₂ (111), (200), and (220) surfaces, and selected structures for the adsorption systems.

XPS–REELS Analysis and KMC Modeling: Toward Controlled Organization and Chemical Composition of InGaN Droplets on GaN

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Indium gallium nitride ($\text{In}_x\text{Ga}_{1-x}\text{N}$) quantum dots are of great interest for optoelectronics due to their spectral tunability, which is exploited in LEDs, lasers, photodetectors, and photovoltaic cells. Precise control of the indium composition which determines the emission wavelength remains a major challenge, requiring high structural quality and chemical homogeneity of the layers. Droplet epitaxy is emerging as a promising alternative to conventional growth modes (Stranski-Krastanov). This technique links on the prior formation of metallic $\text{In}_x\text{Ga}_{1-x}$ droplets, followed by nitridation under a nitrogen flux. Understanding the self-organization and chemical homogeneity of these droplets before nitridation is therefore crucial for optimizing the properties of the final quantum dots.

In this work, we combine X-ray photoelectron spectroscopy (XPS) and reflection electron energy loss spectroscopy (REELS) to probe chemical composition and surface distribution of $\text{In}_x\text{Ga}_{1-x}$ droplets on GaN(0001) at the early stages of growth. In parallel, kinetic Monte Carlo (KMC) simulations, based on substrate deformation induced by local stretching at the liquid-solid interface, were performed. Calculating the substrate displacement caused by this stretching makes it possible to evaluate the elastic free energy generated by a droplet deposited on the substrate. This energy, similar in nature to that associated with a strained epitaxial island, allows us to model droplet formation using effective elastic constraints that depend on the liquid surface tension ($\gamma_l(\text{Ga})$ and $\gamma_l(\text{In})$) and on the elastic properties of the GaN substrate. Introducing these elastic effects into the simulations enables us to study the influence of mechanical stresses on the spatial distribution and segregation of species within the droplets. By comparing the theoretical model with experimental results (XPS, REELS, and SEM), we gain deeper insight into the mechanisms governing the growth of nanometric droplets, allowing us to control their density and spatial distribution and to highlight the key role of surface tension in their organization. This approach combines XPS and REELS with multiscale modeling, providing new insights into the self-organization of precursor droplets. It opens promising perspectives for advanced control of $\text{In}_x\text{Ga}_{1-x}\text{N}$ quantum dot growth by droplet epitaxy on GaN substrates.

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Keywords: Kinetic Monte Carlo (KMC), elastic effect, growth of nanodroplets, self organisation

Defect mediated surface modification of TiO₂ surface using Grignard reagent in explicit solvation model

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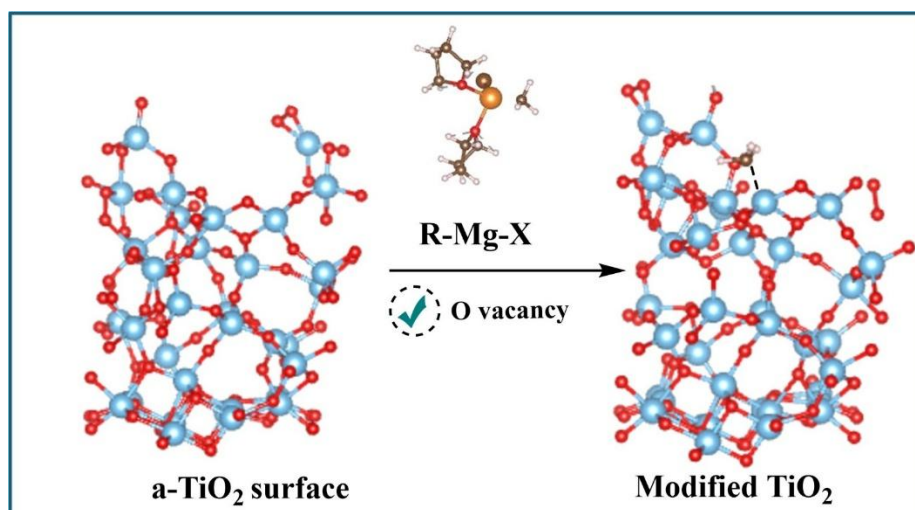
Titanium dioxide (TiO₂) is a material of great importance in heterogeneous catalysis, photocatalysis and adaptable surface chemistry¹. Among its crystalline polymorphs, anatase TiO₂ exhibits superior catalytic performance, largely attributed to its high surface area and undercoordinated active sites. In addition, amorphous form of TiO₂ plays a crucial role in sorption, separation, and catalytic technologies owing to its structural disorder, enhanced surface area, and electronic mobility. Traditional surface modification strategies typically rely on oxygen-based anchoring groups² such as phosphonic acids and silanes; however, organometallic functionalization provides a more direct and tunable approach to covalent surface engineering. In particular, Grignard reagents enable the formation of direct Ti–C³ or Ti–O–C linkages⁴, thereby enhancing electronic coupling and facilitating interfacial charge transfer.

In this study, density functional theory calculations with a Hubbard correction (DFT+U) are employed to systematically investigate the adsorption behaviour and reactivity of methyl magnesium bromide (CH₃MgBr) on both anatase and amorphous TiO₂ surfaces. Pristine surfaces as well as intrinsically defective models⁴ which includes incorporating oxygen vacancies, titanium vacancies, and combined Ti–O vacancies are examined to elucidate the role of defects on adsorption geometries, chemical bonding, and electronic structure. Furthermore, the influence of explicit solvent coordination, specifically tetrahydrofuran, is explored through *ab initio* molecular dynamics to assess its impact on the thermodynamic and kinetic aspects of surface functionalization. The results demonstrate that solvent-mediated dynamics play a critical role in stabilizing intermediates and promoting Ti–C bond formation. These findings provide fundamental mechanistic insight into solvent and defect-driven Grignard reactivity and establish design principles for the directed organometallic functionalization of TiO₂ surfaces.

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Keywords: Titania, Density functional theory, surface modification, Grignard reagent, adsorption studies



Why Zinc is a good Barrier for Hydrogen

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Understanding the origins of the excellent H-barrier performance of Zn coatings is essential for optimizing their use as coatings on high strength steels and performance in various H-containing environments. We compare H-trapping energies associated with point defects in the metals Al, Cu, Ni, Pd, Cr, Fe, V, Mg, Ti, and Zn. Zn shows exceptionally weak interaction with H, with trapping energies ranging from 0.19 to 1.20 eV/at, far from the threshold of -0.6216 eV/at for irreversible trapping. Al and Mg also have low H-affinities, while Ti shows the strongest H-affinity. Band-structure projections reveal that all metals except Zn and Al form a localized Hmetal hybrid band, indicating that an available d-band is critical for strong H-bonding. In Zn, the fully filled d-band lies too low in energy to contribute to H bonding, explaining its low H-trapping energies. The d-band center position correlates with the trapping energies in different defect configurations. ZnO provides a more favorable site for H than metallic Zn, suggesting enhanced diffusion along partially oxidized grain boundaries. Stronger trapping at Zn/Al₂O₃, Zn/Fe, and Zn/ZnO interfaces also has implications for electroplating, where H generated during deposition may become immobilized at such interfaces, reducing the effectiveness of post-deposition bake-out treatments.

Keywords: Hydrogen embrittlement, Zinc, Steel, DFT, Corrosion

Prediction of in-service behaviour of aerospace aluminum alloys

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Corrosion control of metals and alloys is of high importance to prolongate their service life across diverse applications. Eventually, a complex coating system consisting of several (organic) coating layers is added to provide barrier corrosion protection. Additional corrosion inhibitors contribute to active corrosion protection. Dedicated evaluation of corrosion protective properties of these (active) corrosion protective layers is strictly necessary. While laboratory trial procedures and outdoor test programs are personnel and time intensive and accelerated corrosion tests can lead to limited service performance information, predictive modeling of the durability and lifetime of (coated) metal alloys under (long-term) environmental corrosion can provide a promising alternative.

Predictive modeling of (coated) metal alloys aims to develop a deterministic modeling and simulation concept that allows to forecast the onset and propagation of corrosion of a simplified corrosion protection scheme. Furthermore, it allows to generate fundamental understanding of corrosion processes and surface and interface phenomena, of important parameters and boundary conditions and constitutes an important first step towards more complex and accurate predictive deterministic and/or hybrid models, allowing the development of surrogate models and digital twins to aid material and coating design.

In this work, a finite element modeling (FEM) approach is developed and validated to model the corrosion critical conditions on aerospace aluminum alloys, focusing on the alloy microstructure and surface properties over time, with and without active corrosion protection, under static and dynamic electrolyte film conditions.

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Keywords: modeling, corrosion, aluminum

Nanomaterials and nanostructuring

Relationship between the dry surface state of CuO nanopowders and its zeta-potential in solution

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CuO nanoparticles (NPs) have great potential in various applications, including catalysis, batteries, medicine, printable electronics and nano-joining. However, CuO NP surfaces are extremely reactive and thus highly sensitive to storage and processing conditions. Such atmospheric aging results in irreproducible NP surface properties both in the solid state, but also when dispersed in a solution for preparing a colloidal NP dispersion for e.g. electrophoretic deposition or printing. In this contribution, a surfactant-free strategy is presented to optimize the colloidal stability and electrophoretic mobility of CuO NPs in non-aqueous solutions by tuning their surface defectiveness and resulting space-charge region in the dry state. To this end, various commercial and in-house synthesized CuO nanopowders (with unknown synthesis, storage and atmospheric aging histories) were subjected to mild, organic-free surface treatments (e.g., washing and annealing in O₂ or O₃). These surface treatments reduce the surface defect density – as confirmed by combining XPS and positron annihilation lifetime spectroscopy (PALS) – which sharpens the surface space-charge region, thereby effectively increasing the z-potential in solution. This enables the fabrication of coherent, uniform, porous CuO coatings with micrometer-scale thickness by electrophoretic deposition (EPD) without the common addition of surfactants or other chemicals. These findings enable the development of efficient, up-scalable and environmental-friendly EPD manufacturing routes of organic-free NP-based oxide coatings and membranes, independent of the nanopowder type and aging history.

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Keywords: CuO nanoparticles, surface state, zeta-potential, XPS, positron annihilation lifetime spectroscopy (PALS)

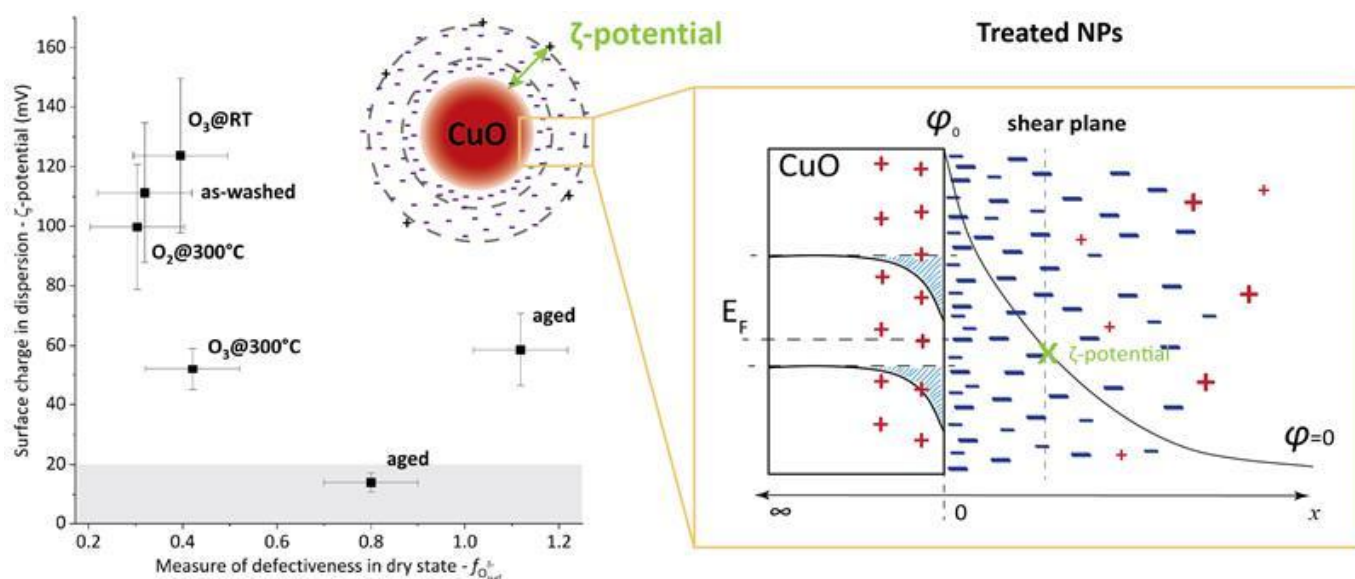


Figure caption: [LEFT] Measured ζ -potentials of aged and differently surface-treated CuO nanoparticles dispersed in ethanol plotted versus respective fraction of defective oxygen (sub)surface species. The fraction of defective oxygen (sub)surface species corresponds to the area ratio between the defective surface and bulk CuO components, as resolved from the O 1s spectra recorded by XPS in the dry state. The grey band marks the region where the surface charge in solution is low for performing electrophoretic deposition. [RIGHT] Sketch illustrating the correlation between the surface space charge (SSC) region in p-type CuO and its corresponding ζ -potential in solution. The measured ζ -potential at the oxide/liquid interface is related to the potential drop in the electrical double layer (EDL), as established to screen the build-in electrostatic surface potential.

Reliable ToF SIMS Depth profiling of Hybrid nanomaterials via Reactive high-energy per molecule Oxygen GCIB sputtering

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Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an advanced technique widely employed for the characterization of diverse samples, ranging from inorganic systems in microelectronics to organic and biological materials. However, an ongoing challenge persists regarding the characterization of hybrid materials and nanocomposites that integrate both organic and inorganic moieties within their architecture. This difficulty arises from the significantly different instrumental conditions required to analyze such disparate components. While inorganic materials generally require energetic monoatomic primary beams to overcome sputtering threshold energies, organic species typically necessitate Gas Cluster Ion Beams (GCIB) to limit chemical damage and enable molecular depth profiling. [1] Furthermore, under analysis conditions suited for organics, the erosion rates of inorganic components are generally between two and three orders of magnitude lower; [2] this discrepancy leads to instrumental artifacts, the development of roughness, and data that are overall complex to interpret. To overcome these limitations, our novel approach proposes the implementation of reactive, high-energy-per-molecule O₂-GCIB sources. By delivering higher energy per incident molecule, these clusters effectively erode inorganic materials; moreover, the reactive nature of the oxygen species prevents the chemical damage and cross-linking that would otherwise lead to the loss of molecular information on the organic counterpart. [3] By addressing historical limitations in SIMS-based depth profiling, the proposed approach provides a novel and reliable means to characterize technologically significant hybrid materials paving the way for high-fidelity results on these intricate architectures.

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Keywords: hybrid nanomaterials, ToF-SIMS, Oxygen clusters

Operando X-ray Photoemission Microscopy: Unveiling the Energy Landscape of 2D Material-Based Devices

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As two-dimensional (2D) materials are increasingly incorporated into electronic and optoelectronic devices, understanding their electronic structure under realistic working conditions becomes a central challenge. Once integrated into device architectures, these materials are no longer isolated systems but are instead in contact with metal electrodes and dielectric environments while operating under applied electrical bias, conditions under which their intrinsic properties may substantially deviate from those of pristine materials.

In this context, scanning X-ray photoemission microscopy (SPEM) [1] emerges as powerful technique to directly access to the local energy landscape and electric-field distribution in operating 2D-material-based devices. By exploiting the sub-micrometer spatial resolution of SPEM, we investigate field-effect transistors (FETs) based on single-flake transition metal dichalcogenides (TMDs) and van der Waals heterostructures under applied bias. The technique enables simultaneous mapping of the out-of-plane gate-induced field and the in-plane vectorial electric-field components across the device channel [2].

Our results demonstrate that this approach acts as a sensitive local probe of device architecture, flake geometry, thickness, and morphology, parameters that strongly influence nanoscale current pathways within the device channel [2]. The measurements highlight finite-size effects and reveal the spatial distribution of electric fields at flake interfaces [3]. Ultimately, this *operando* methodology enables a correlative description linking the bias-modified local energy landscape to the macroscopic electrical response, offering a pathway toward systematic and rational optimization of nanoelectronic devices, including, but not limited to those based on 2D materials.

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Keywords: Scanning X-ray photoemission microscopy (SPEM), Van der Waals heterostructures, 2D transition metal dichalcogenides (TMDs), Field-effect transistors (FETs), Electric-field distribution

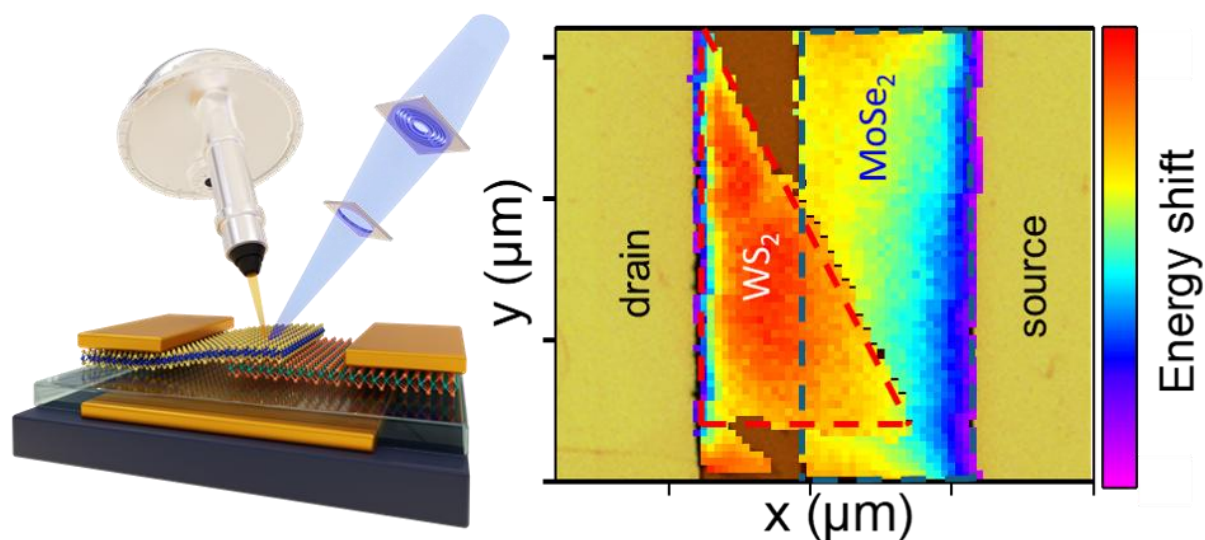


Figure 1: Left: Schematic of the FET, whose channel consists of a $\text{WS}_2/\text{MoSe}_2$ heterostructure spatially probed by SPEM. Right: Energy-shift map revealing the gate-induced energy variation within the heterostructure under an applied gate bias ($V_{\text{GS}} = +5 \text{ V}$ is applied; $V_{\text{DS}} = 0 \text{ V}$).

Direct Visualization of Buried Surface Chemistry in the van der Waals Gap between Graphene and Platinum by In Situ SEM

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Atomically thin materials supported on solid substrates form confined interfacial spaces in which chemical reactions can proceed under conditions distinct from those on open surfaces. In particular, the van der Waals (vdW) gap between graphene and a metal substrate can host intercalated molecules whose transport and reactivity are strongly modified by nanoscale confinement. Here we show that the overall reaction rate beneath graphene is limited primarily by the supply of molecules into the vdW gap.

We investigate the intercalation and confined reactivity of CO, H₂, and O₂ molecules beneath graphene on Pt using in situ scanning electron microscopy (SEM) combined with reactive molecular dynamics simulations, XPS and LEEM. Unlike other experimental techniques, the in situ SEM experiments enable direct observation of multilayer graphene etching in inverse-wedding-cake configuration during exposure to reactive gases at elevated temperatures, providing real-time insight into reaction dynamics at the buried graphene–Pt interface.

The experiments reveal substantial differences in etching kinetics depending on the gas species. In particular, CO induces significantly faster etching of the buried graphene layer than hydrogen or oxygen. Molecular dynamics simulations indicate that H₂ and O₂ primarily diffuse along the Pt surface inside the confined gap, whereas CO molecules move through the gap in a quasi-gas-phase regime before readsorbing. This mechanism results in a more efficient supply of CO to the reactive buried graphene edge.

Our results demonstrate that nanoscale confinement can fundamentally alter mass transport mechanisms and thereby control the apparent reactivity of molecules at buried interfaces. At the same time, we show that the vdW space-confined reactions may proceed via alternative reaction pathways, being promising for e.g. confined catalysis, etc.

This research was supported by Quantum materials for applications in sustainable technologies (QM4ST)—project No. CZ.02.01.01/00/22_008/0004572 under OP JAK, call Excellent Research.

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Keywords: intercalation, electron microscopy, diffusion, graphene

Quantitative and spectral analysis of electron transmission through stacked bi-layer graphene

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Graphene membranes can be utilized to suppress ion-backflow in gas electron multiplier detectors for high-energy physics experiments. While graphene is expected to successfully block ion transmission, its transmissivity for electrons T_e needs to be known. We have measured T_e of stacked bi-layer graphene, that was transferred from CVD-grown single-layer graphene on Cu foils, onto Au grids with 50 % optical transparency. Two different geometries were realized: while the primary electrons with variable energy ($1 \text{ eV} < E_p < 1800 \text{ eV}$) impacted the surface perpendicularly in both cases, the measurements of transmitted electron current were performed by biasing the sample negatively, and either using a positively biased Faraday cup to collect electrons at the sample backside or by measuring the electron current on a less negatively biased back-plate (potential difference 20-70 V) with low secondary electron yield (SEY maximum 0.5) to minimize electron reflection. The energy-dependence of the obtained transmission curves was identical for both experiments and revealed slight variations at low electron energy (5-50 eV), where T_e is $< 30\%$, that resemble electronic transitions observed in electron energy loss spectroscopy (EELS) studies. On the other hand, for $E_p > 200 \text{ eV}$, T_e exceeds unity with a maximum of $\sim 180\%$ detected at $E_p = 550 \text{ eV}$. The found energy-dependence is similar to secondary electron yield curves of solids typically measured in reflection geometry. Both aspects indicate that two irregularly stacked graphene layers are sufficient to induce significant scattering events that generate a high number of low-energy secondary electrons. To validate this, we have also measured the full spectral distribution of the transmitted electrons (TEELS) at low and high E_p . As in reflective REELS, the typical features of elastically scattered electrons and inelastic electronic and plasmon excitations are detected together with a high quantity of secondary electrons with kinetic energy $< 10 \text{ eV}$. However, the intermediate energy region of the traditionally called "back-scattered electrons" (between 10 and 300 eV in this case for $E_p = 500 \text{ eV}$) differs significantly when comparing with REELS data of HOPG. This disparity is attributed to different scattering pathways when comparing the cascade of events that occur when electrons are reflected from a solid to the transmission of electrons through two layers of graphene. The measured number of transmitted electrons and the measured amplification effect for primary electrons with $E_p > 200 \text{ eV}$ is remarkable and likely linked to a multitude of scattering events occurring between the two graphene sheets.

Keywords: graphene, electron transmission, secondary electrons, energy distribution, quantification

Reliable Workflows for the elemental analysis of Graphene-Related 2D Materials with SEM/EDS and XPS

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Reliable quantification of the chemical composition of graphene-related 2D materials (GR2M) as powders and liquid suspensions is a challenging task. Analytical methods such as X-ray photoelectron spectroscopy (XPS), inductively coupled plasma mass spectrometry (ICP-MS), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) are recommended by documentary standards.[1] Specific parameters to be measured are defined in a classification framework, e.g. the oxygen-to-carbon (O/C) atomic ratio, metal impurities, or functional groups.[2]

Recently, we develop workflows for the reliable quantification of the O/C ratio and impurities with the fast and widely available energy-dispersive X-ray spectroscopy (EDS) at a scanning electron microscope (SEM) (see Figure 1). It should be noted that the standardless quantification was used. The results were validated by comparison with the established XPS analysis.[3] Furthermore, an ionic liquid was selected as reference material for the quantification of the light elements. The functional groups of the materials were analysed using XPS.

The study clearly demonstrates the reliability of SEM/EDS as a standard method for the quantitative elemental analysis of GR2M and, furthermore, the potential for quantifying light elements also in other materials.

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Keywords: Graphene Related 2D Materials, X-ray Photoelectron Spectroscopy, Energy-Dispersive X-ray Spectroscopy, Quantification

Electrochemical probing of the radiation damage caused by an electron beam

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Electron Microscopy (EM) is one of the most widely used imaging methods in the domain of surface analysis, and is heavily relied upon in methodologies like Identical-Location Electron Microscopy (IL-EM) [1]. While the adverse effects that electron beams can have on samples (i.e. sputtering, sintering of NPs, growth of a carbon layer, etc.) are well established, assessing their direct impact on the electrochemical activity of a surface can be difficult due to the limited size of the irradiated region. This is primarily because standard macroscopic electrochemical techniques average out the signal from the highly localized irradiated zones, rendering microscale beam damage effectively undetectable.

In this work, we demonstrate how Scanning Electrochemical Cell Microscopy (SECCM), a powerful scanning probe technique offering a high spatial resolution, allows us to overcome this challenge. We mapped the electrochemical activity of gold nanoparticles (Au NPs) that have either been or not exposed to an electron beam. The effects of the irradiation on both the electrodisolution of gold, a highly surface sensitive process [2] and the activity towards the Oxygen Evolution Reaction (OER) of the carbon film support are discussed. The growth of a carbon layer being dependent on the availability of carbonaceous material at the surface of the sample, we perform our analysis on colloidal Au NPs with citrate as surfactant or surfactant-free NPs [3]. The effects of the irradiation parameters (accelerating voltage and electron dose) and the effectiveness of a conventional glow discharge cleaning method were assessed. X-ray Photoelectron Spectroscopy (XPS) was used to further investigate the processes responsible for the observed variation of electrochemical activity.

The results obtained demonstrate the impact of the electron beam exposure on the local electrochemical behaviour, thanks to the high spatial resolution of SECCM which allows us to directly compare within a single electrochemical mapping both pristine and irradiated regions. From this work, we believe that the electrochemical scanning probe microscopies constitute promising tools for investigating the radiation damage caused by an electron beam.

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Keywords: SECCM, Electron beam damage, Carbon contamination, Electron Microscopy, Identical Location

Engineering Silica Capsules via Pickering Emulsion Templating: Advances in Porosity and Surface Functionality

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This study presents a novel approach to engineering nanostructured silica capsules with controlled porosity and mechanical properties, specifically designed for applications in catalysis and microreactor technologies. Using Pickering emulsions stabilized by hydrophobized silica nanoparticles (~80 nm), we demonstrate the precise control of interfacial sol-gel kinetics to fabricate porous silica shells confining ionic liquid cores. The capsules (~15 µm diameter) were synthesized under varied sol-gel conditions (pH, water-to-alkoxysilane molar ratio, temperature, and reaction time), enabling the systematic tuning of nanoscale textural and mechanical properties.

Key findings include the critical role of drying techniques in preserving the native nanoporous architecture. Supercritical CO₂ drying effectively mitigates capillary-induced shrinkage, which compromises porosity during ambient drying. The sol-gel process parameters were further optimized to achieve tailored surface area, pore size distribution, and shell flexibility. Acidic conditions (pH < 2) favored the formation of linear polymeric networks, resulting in highly mesoporous and flexible shells, while basic conditions produced rigid, microporous structures prone to fracture. The water-to-alkoxysilane molar ratio and reaction temperature were also found to significantly influence micro- and mesoporosity, with higher ratios and temperatures promoting branched networks and denser structures.

Advanced characterization techniques, including nitrogen physisorption (BET, BJH, and HK methods), optical and electron microscopy, and gas chromatography, were employed to elucidate the relationship between synthesis parameters and nanostructure. Interparticle voids from nanoparticle packing contributed distinct mesopores (12–50 nm), while sol-gel dynamics controlled micropores (<12 nm). These findings provide practical guidelines for the design of nanostructured capsules with optimized surface and interface properties.

This work underscores the importance of precise nanostructuring in tailoring material functionality for surface-sensitive applications. By combining controlled sol-gel kinetics with advanced drying protocols, we demonstrate the potential of silica capsules as versatile platforms for encapsulation, controlled release, and catalysis.

Keywords: Pickering emulsion, Silica Capsules, Interfacial sol-gel, Surface Functionalization, Porosity control

Revealing Distributed Kinetics in Electrochemical Nucleation and Growth through Local Electrochemistry

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Electrochemical nucleation and growth (EN&G) is a fundamental process governing the formation of metallic nanostructures on electrode surfaces. However, the earliest stages of nanostructure formation remain difficult to resolve experimentally because conventional electrochemical measurements average the response of a vast number of active sites, obscuring the true distribution of activity and nucleation behaviors across the surface.

In our work, we combine Scanning Electrochemical Cell Microscopy (SECCM), co-located microscopy, and statistical analysis to probe electrochemical nucleation at the scale where these variations actually arise and to directly quantify spatial differences in activity across heterogeneous substrates. By performing hundreds of independent measurements on fresh regions of the same surface, this high-throughput approach captures the stochastic nature of nucleation events while preserving spatial resolution and enabling electrochemical and structural information to be compared at the same scale^[1].

Our measurements reveal that both overpotential and surface state strongly influence the probability of nucleation, leading to a broad dispersion of nucleation kinetics between neighboring surface regions. These observations show that EN&G cannot be fully described by a single nucleation rate, but instead reflects a distribution of site-specific activation barriers associated with local surface features^[2].

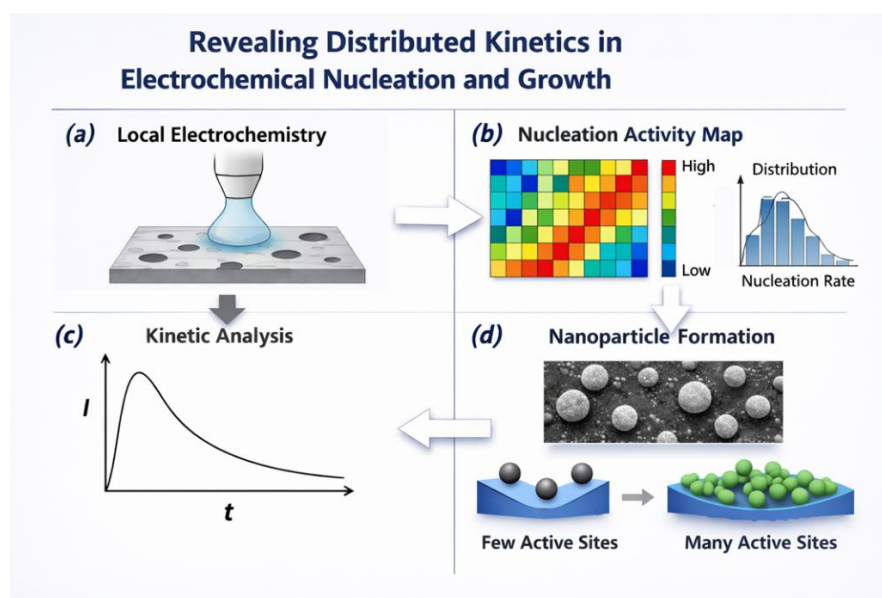
To rationalize this behavior, we introduce a distribution-based kinetic framework that accounts for the variability of nucleation rates across the surface. Within this approach, classical constant-rate descriptions emerge as a limiting case of a broader distributed rate law, in which the characteristic rate sets the overall time scale, and the local parameters provide a quantitative description of kinetic dispersion^[3].

This framework links microscopic variability with macroscopic electrochemical observables, connecting local activity distributions to ensemble current transients and nanoparticle formation. More broadly, the results show how local electrochemistry combined with statistical and analytical modeling can uncover hidden distributions of activity at electrochemical interfaces. Ultimately, this approach provides new insight into interfacial phase formation and supports the rational design of tailored electrochemical interfaces and functional nanostructures.

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Keywords: Electrochemical Nucleation, Nanoparticles, SECCM, Active Sites



Nanoscale Observation of Ag Nanowire Growth at the Step Edges of Atomically Flat Si(111) Surface

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Silicon nanosheets with thickness below 5nm are promising materials for next-generation transistors and sensors. However, a major challenge in fabricating Si nanosheets, such as silicene, is achieving a fully hydrogenated structure that is both air-stable and exhibits a semiconductor band gap. One way of approaching is to scale down the bulk into atomically thin layers. By proposing a method to fabricate ultrathin Si layers from a silicon-on-insulator (SOI) wafer through a fully wet chemical process, we aim at producing atomically thin, hydrogen passivated Si layers.

Our approach employs Ag nanowires as nanoscale “scissors” to assist the etching of atomically flat staircase structures on the Si (111) surface. For straight and continuous etching, Ag nanowires must grow uniformly along the step edges of Si(111) surface. However, during the sequence development it is: (1) common to encounter Ag particles deposited on top of the nanowire^[1], and (2) there is an unknown relation between deposited Ag and the nucleation sites beneath it due to limited resolution by observation of amplitude-modulation atomic force microscopy^[2].

To address the first issue, we want to modify the sequence of the wet process to obtain a more homogeneous Ag nanowire and suppress the particle formation. Next, we investigate the Ag-deposited Si(111) surface at the sub-nanometer scale using atomic force microscopy with different modes.

Our first principles study suggests that Ag prefers to form nanowires when Si step edges are hydrogen-terminated, whereas nano clusters tend to form on hydroxyl-terminated edges. By this consideration, we adjust the pH of wet process solution from 8 (Figure 1a) to 5 (Figure 1b) where we succeed to reduce the particle formation. Subsequent non-contact AFM imaging over 100×100 nm² area (Figure 1c) indicates the presence of the nanowire at edges along with unidentified adsorbates at terraces. Further scanning probe observations will be needed to clarify the nanowire structure and the origin of unknown adsorbates.

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Keywords: Wet process, Amplitude-modulation AFM, Non-contact AFM, First principles calculations

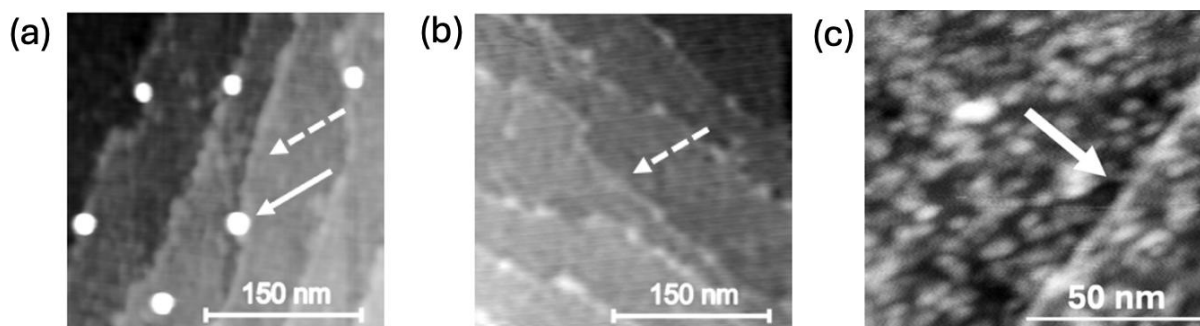


Figure 1. 300×300nm² amplitude-modulation AFM image of Ag-deposited Si immersed in (a) pH = 8 and (b) pH = 5 solution. Dashed arrow indicates nanowire, and solid arrow indicates particle. (c) 100×100 nm² non-contact AFM image of Ag-deposited Si immersed in pH = 5 solution showing thin nanowire indicated by solid arrow. In (c), unknown adsorbates exist at terraces.

Advanced Glass Surfaces: Optical, Wetting, and Biological Control via Texturing and Chemistry**Wageesha Senaratne** (*Surface Science and Technology, Corning Incorporated, Corning, USA*)

Advanced control of surface chemistry and micro-/nano-scale texturing enables simultaneous tuning of optical, wetting, and/or biological functionalities on glass. This work presents integrated strategies for engineering transparent glass surfaces with anti-glare, light-management, anti-fingerprint, anti-smear, and antimicrobial performance, targeting demanding applications in consumer electronics, automotive displays, and life sciences.

Glass substrates engineered with precise micro-structures are employed to produce display cover glass features for next-generation anti-glare surfaces; these are designed through optimized multi-scale textures to reduce sparkle and washout while preserving low haze and high clarity of reflected images. All-glass light guide plates are also described, incorporating lenticular and extraction structures that achieve superior local dimming, greater brightness uniformity, and enhanced thermal and dimensional stability compared to polymer alternatives. Combining low-surface-energy chemistries with hierarchical micro and nano surface textures, we demonstrate routes to modulate wetting behavior across regimes ranging from oleophobic to deliberately oleophilic surfaces, highlighting the trade-offs between fingerprint transfer, visual visibility, durability, and optical clarity. Moreover, this platform extends beyond optics to multifunctional surfaces with biological effects. Lithography-free nano-structuring approaches, including metal dewetting-assisted patterning, are used to fabricate transparent antimicrobial coatings based on copper nanoparticle systems with controlled ion release, durability, and optical neutrality.

Collectively, these results present cohesive materials and surface-engineering strategies for multifunctional glass, supporting scalable and robust solutions that combine optical excellence with chemical and biological performance for advanced display, touch, and life science technologies.

Keywords: Micro/nano textures, Surface Chemistry, Optical Properties, Wetting Behavior, Antimicrobial Performance

Polymers

XPS fs-laser depth profiling of polymer materials and polymeric samples

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X-ray Photoelectron Spectroscopy (XPS) is a powerful and widely used technique for surface and interface analysis, delivering quantitative elemental composition and detailed chemical state information from the top few nanometers of a material. While ideally suited to thin films and surface treatments, extending XPS into the depth dimension through sputter profiling presents significant challenges for polymeric and other organic materials. Conventional monoatomic ion sputtering can induce chemical damage, crosslinking, preferential sputtering, and atomic mixing, resulting in distorted depth distributions and loss of meaningful chemical state information.

The introduction of gas cluster ion beams (GCIBs) marked a breakthrough in polymer depth profiling. By distributing the total ion energy across hundreds or thousands of atoms, cluster ions achieve a very low energy per atom, enabling gentle, near-surface material removal with minimal subsurface penetration. This significantly reduces chemical damage and preserves molecular structure, allowing accurate profiling of multilayer polymer systems. However, even cluster ion beams are typically limited to profiling depths on the order of single microns, constraining their application for thicker coatings, laminates, and bulk-modified materials.

The integration of femtosecond (fs) laser ablation with XPS represents a further step change in capability. Ultrafast laser pulses deposit energy on timescales shorter than thermal diffusion processes, enabling highly confined material removal with reduced heat-affected zones and minimal chemical modification. In contrast to cluster ion sputtering, fs-laser ablation can remove tens to hundreds of microns of material rapidly, dramatically extending the accessible depth range while maintaining a high degree of chemical integrity. This approach enables the analysis of thick multilayer assemblies, buried interfaces, and subsurface defects that were previously inaccessible by ion-based methods alone.

In this study, we systematically evaluate the performance of fs-laser-assisted depth profiling across a range of polymer systems under varied processing conditions. We assess depth resolution, chemical state preservation, surface morphology, and potential laser-induced artifacts. Furthermore, we demonstrate real-world application examples including thick multilayer coatings that would be impractical or impossible to characterise using cluster ion beams alone. The results highlight the complementary nature of fs-laser ablation and cluster ion sputtering, establishing fs-laser depth profiling as a transformative tool for advanced polymer and soft-material characterisation.

Keywords: fs-laser, depth profiling, XPS, ablation

Efficiency and UV stability of interference-pigmented thermoplastic encapsulants for double-glass photovoltaic modules

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Aesthetic integration of photovoltaic (PV) modules into buildings and vehicles requires durable, color-stable solutions without compromising optical performance. Embedding interference pigments in the front encapsulant is a promising approach because it relies on spectrally selective reflection with minimal absorption, resulting in high efficiencies of the PV modules. While the inorganic nature of the pigments suggests robust ageing behavior, long-term color stability is governed not only by pigment chemistry but also by interactions at the pigment–matrix and glass–encapsulant interfaces. This study investigates the weathering stability of interference pigments embedded in a thermoplastics polyolefin (TPO) encapsulant. The functional principle of these interference pigments is shown in Figure 1a [1]. Eight encapsulant films, supplied by Lenzing Plastics, were laminated at 155 °C, 800 mbar for 20 minutes between two low-iron float glasses. The double-glass laminates were artificially aged in a xenon arc test chamber Q-SUN Xe-1 (continuous irradiation at 0.5 W/m² @340nm, 65 °C) to assess UV-induced changes in the pigments, the TPO matrix, and interactions at the pigment–matrix and encapsulant–glass interfaces. Hemispheric reflectance was measured after 1000 h, 4000 h and 8000 h from 380 to 780 nm in 5 nm steps on a Lambda 950 UV/Vis/NIR spectrometer. Colorimetric analysis (CIE Lab*) and the corresponding color difference ΔE were calculated; all colors exhibited superior stability with $\Delta E < 1$ after 8000 h of irradiation. The expected modules efficiency using the different encapsulant films was estimated by measuring hemispheric transmittance and weighting the spectra with an AM 1.5 source and the spectral response of a silicon solar cell [1]. Most colors exhibit high efficiencies above 90 %. However, gold and blue require further optimization of pigment selection, with efficiency losses of 27 % and 23 %, respectively. To illustrate perceived color, photographs (see Figure 1b) of the films and laminates placed over a chessboard pattern demonstrate the strong background dependence, with little to no apparent color against a white background.

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Keywords: encapsulation, thermoplastics polyolefin, interference pigments, spectroscopy

Fluorine Quantification in Polymer Matrices via TOF-SIMS: Supporting Compliance with Emerging EU PFAS Regulations

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In light of the impending EU PFAS restrictions slated for late 2026¹, precise solid state fluorine quantification has become a critical requirement for regulatory compliance. However, the inherent chemical resistance of high performance polymers often renders conventional digestion or dissolution techniques non-feasible, additionally traditional wet chemical approaches result in the irreversible loss of critical spatial information. Standard techniques like XPS (0.1-1 at.%)² and LIBS (≈ 50 mg/kg)³ frequently fail to reach the detection limits required for compliance, as their theoretical sensitivities are rarely achievable in practical analysis, or only offer bulk information without spatial context.

While negative-mode ToF-SIMS offers exceptional fluorine sensitivity, it is notoriously subject to matrix effects, which must be carefully managed during quantification. To evaluate the method's performance despite these effects an in-house produced standard series was prepared, comprised of a polyimide solution, spiked with a fluorine containing aromatic compound with concentrations from 10 mg/kg up to 10,000 mg/kg, then spin-coated onto a Si-wafer substrate. By utilizing negative mode on the IONTOF ToF-SIMS V with Cs⁺ sputtering to enhance ion generation and capture representative bulk data, a calculated LOD of 14 mg/kg was achieved. These preliminary results outperform existing solid sampling techniques, providing a viable pathway for meeting future regulatory obligations while preserving the integrity and spatial information of the sample. Expanding on these results quantitative imaging and depth profiles are investigated with real samples. These findings demonstrate the viability of ToF-SIMS in the evaluation of PFAS in solid samples.

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Keywords: ToF-SIMS, Polymer, Fluorine, Quantification, Spin-coating

Impact of PDMS molecular weight and crosslinker functionality on mechanical and surface properties of soft PDMS networks

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The aim of this project is to develop and characterise model soft materials, whose moduli are below the MPa, to provide the international contact mechanics community with relevant and universal mechanical laws for elastic and viscoelastic materials. The objective of these laws is to get a simple comprehension and reasonable estimates of the involved mechanisms in micro/nano indentation experiments, whether adhesion is present or not. We decided to use crosslinked polydimethylsiloxane (PDMS) networks, as study materials, since publications [1], [2] have shown that it is possible to control the structure of the network and, therefore, the final properties of the material.

Elastomer networks were synthesized by varying the average molecular weight of vinyl-terminated PDMS chains and employing crosslinkers with different reactive site densities (bi-, tri-, and tetra-functional). Reactants were fully characterized by size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR). The build-up of the networks was followed by Fourier Transformed InfraRed (FTIR) spectrometry and rheological measurements. The results show that the gel and equilibrium times depend only on the amount of catalyst added to the reaction. Simultaneously, mechanical characterization, performed via rheology, DMA, tensile and indentation tests, reveals a proportionality of the Young's and shear modulus with molecular mass between entanglements of the networks, which depended on the PDMS chain/crosslinker ratio, functionality of the crosslinker and average molecular weight of the PDMS chains before crosslinking, allowing for a broader range of achievable stiffness.

The surface properties were characterized using contact angle measurements (wettability), revealing that surface energy of the silicone is little to non-impacted by the ratio of crosslinker, and average molecular weight between entanglements of the PDMS networks. AFM (Atomic Force Microscopy) both in tapping, contact modes, LFM (Lateral Force Microscopy), as well as adhesion at macroscopic scales are also planned to have a better understanding of the surface's properties.

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Keywords: PDMS, Soft Material, Mechanical properties, Surface properties

Gadolinium sorption on chitosan: an XPS investigation

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Rare earth elements (REEs) are critical materials for advanced technologies [1], making sustainable recovery strategies an important challenge. Chitosan, a biopolymer obtained from waste-derived chitin, is a low-cost and environmentally friendly sorbent suitable for REE removal and consistent with circular-economy principles. In this work, a commercial chitosan powder previously characterized by XPS [2], with a deacetylation degree of 93(2) %, was tested for Gd^{3+} uptake. Suspensions were contacted for 3 h with Gd^{3+} solutions from 0.5 to 100 mg/kg. ICP-OES measurements showed high removal efficiency, with nearly quantitative uptake up to 10 mg/kg and sorption capacities between 0.05 and 4.63 mg g⁻¹. The reduced efficiency at higher concentrations is attributed to solution acidification and partial protonation of chitosan –NH₂ groups.

To clarify the surface chemistry involved in the sorption process, X-ray Photoelectron Spectroscopy (XPS) was used to analyse chitosan after Gd uptake. Interpreting lanthanide XPS spectra is challenging because their main photoelectron lines show complex multiplet structures; for Gd, the 4d region is particularly intricate due to spin–orbit coupling and electron–electron interactions. Despite its relevance, a consistent curve-fitting strategy for Gd 4d in oxide systems is still poorly documented.

Therefore, reference spectra of metallic Gd and Gd oxide were examined to establish a fitting model for the Gd 4d region. The model includes four components assigned to the ⁹D and ⁷D final states, plus two components linked to ligand-ion exchange involving hydroxide and carbonate species present in both reference samples. These fitting parameters were applied to the Gd 4d signal recorded on chitosan after sorption, enabling quantification of surface-bound gadolinium and providing insight into the interaction between Gd^{3+} ions and chitosan functional groups.

The study demonstrates that chitosan is a promising, low-cost sorbent for recovering rare earth elements, and it provides a new, well-defined XPS fitting strategy for interpreting complex Gd 4d spectra.

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Keywords: Chitosan, XPS, Gadolinium, Rare Earth Elements, Surface chemistry

Semiconductor materials

Quantitative study of ion beam-enhanced reactivity of MoS₂

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Monolayer Molybdenum disulfide (MoS₂) is a two-dimensional transition metal dichalcogenide whose structure is highly sensitive to defect engineering. In our work, we present a quantitative X-ray photoelectron spectroscopy (XPS) investigation of ion beam-enhanced reactivity in monolayer MoS₂, using air oxidation kinetics as a probe of defect-mediated chemical activity. Controlled ion irradiation was employed to introduce a tunable density of lattice defects, including sulfur vacancies. The evolution of surface chemistry upon ambient air exposure was then systematically monitored by XPS. High-resolution Mo 3d core-level spectra reveal a pronounced increase in oxidation rate with increasing ion fluence. Pristine monolayers exhibit minimal oxidation under ambient conditions, whereas irradiated samples show, in comparable timescales, progressive formation of higher oxidation states associated with Mo-O bonding. The oxidation kinetics are expected to follow a defect-density-dependent trend, consistent with vacancy-mediated oxygen adsorption. By correlating ion dose with the fraction of oxidized Mo species, we extract effective reaction rate constants and activation behavior as a function of defect concentration. The data support a model in which ion-induced sulfur vacancies act as primary nucleation centers for oxidation, lowering the kinetic barrier for oxygen chemisorption and accelerating lattice destabilization. At higher fluences, defect clustering further enhances reactivity, leading to spatially non-uniform oxidation and increased chemical heterogeneity.

Importantly, the study distinguishes between direct beam-induced chemical modification and subsequent ambient-driven processes, demonstrating that ion irradiation alters reactivity. These findings provide insight into how controlled ion beam treatment modulates chemical reactivity in molybdenum disulfide. The results have implications for defect engineering and patterning strategies in MoS₂-based electronic and optoelectronic devices, where balancing functionalization and degradation remains critical.

Keywords: XPS, Reactivity, Oxidation kinetics, MoS₂, 2D materials

Surface Analysis of GaN after Ar Ion Irradiation

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Gallium nitride (GaN) exhibits excellent properties such as a high breakdown voltage and high electron mobility and is regarded as a key material for power and high-frequency devices in next-generation energy technologies. Accurate evaluation of the GaN surface state is essential for development high-performance and reliable devices, as surface conditions strongly influence material properties.

Surface analysis techniques such as XPS, AES, and SIMS are widely employed. In these measurements, Ar ion sputtering is commonly used for removing oxide layers and contaminants and for depth profiling. However, ion irradiation can induce selective sputtering of nitrogen, leading to changes in composition, chemical state, and electronic structure, which may affect both analytical results and device performance. These effects have not been sufficiently clarified.

In this study, GaN surfaces before and after Ar ion irradiation were investigated by angle-resolved hard XPS (AR-HAXPES) and ion scattering spectroscopy (ISS) to non-destructively evaluate the depth-dependent elemental analysis from the topmost atomic layer to the near-surface region. In addition, the electronic structure of the GaN surface was examined by XPS.

The Ga 3d spectrum obtained by HAXPES showed an increased peak intensity around 18 eV after Ar ion irradiation, while the valence band spectrum measured by XPS exhibited enhanced intensity near the Fermi level, indicating a metallic modification of the GaN surface. The AR-HAXPES analysis revealed a significant reduction in the N/Ga ratio toward the surface, suggesting selective nitrogen desorption and the formation of Ga–Ga bonds. Complementary ISS measurements, which selectively probe the topmost atomic layer, showed that nitrogen remains present on the topmost surface even after Ar ion irradiation.

These results demonstrate that Ar ion irradiation induces depth-dependent compositional modifications and electronic-structure changes in GaN. The combined use of AR-HAXPES and ISS enables non-destructive depth profiling of composition, while XPS provides insights into the associated electronic-state modification.

Keywords: XPS, HAXPES, GaN, Ar ion sputtering, Ion scattering spectroscopy

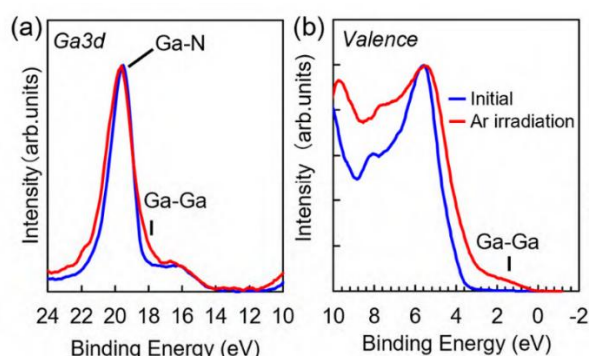


Figure 1. (a) Ga 3d spectra obtained by HAXPES, (b) valence band spectra obtained by XPS before and after Ar ion irradiation.

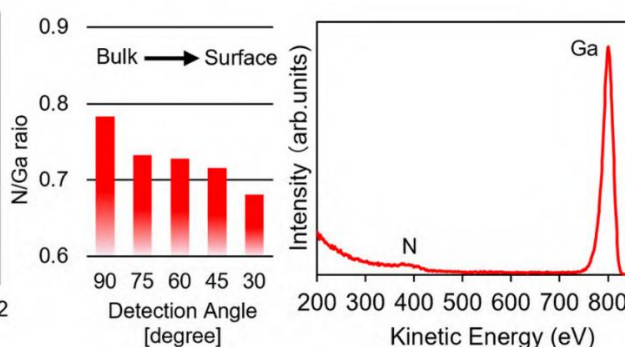


Figure 2. Detection angle dependence of N/Ga ratio after Ar ion irradiation.

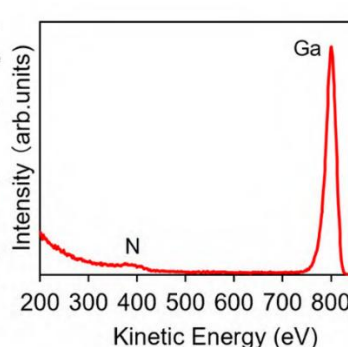


Figure 3. ISS spectrum of the GaN surface after Ar ion irradiation.

pARXPS investigations of HCl-deoxidized InP surfaces exposed to different atmospheres

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Indium Phosphide (InP) represents a key compound semiconductor for electronic and optoelectronic devices, where controlling surface composition after HCl treatment remains a major challenge. Surface species formed on InP (100) surfaces upon interaction with HCl were therefore investigated by parallel Angle Resolved X-ray photoelectron spectroscopy (pAPXPS) under various atmospheres.

In this study, the analyses were carried out using a pARXPS equipped with a large-angle electron analyzer for simultaneous acquisition of 8 angles without any sample tilt. This allows to access systematically to enhanced surface sensitivity as well as significant depth information.

HCl treatments were conducted in a N₂-purged glove box. HCl-treated InP wafers were then loaded in the pARXPS chamber without exposure to the air. A successful deoxidation of InP surfaces has been evidenced after this treatment in previous work [1]. This study compares pARXPS results for InP (100) treated in HCl, with various concentrations and times, and then stored under N₂ or exposed to the air (see fig. 1a,b). The evolution of surface species as a function of storage time (under 16 mbar of N₂) or air exposure time has been monitored accurately to compare reoxidation kinetics (see fig. 1a,b).

A slight shoulder variation was observed in the P 2p spectra of HCl-treated InP surfaces (see fig. 1c,d), indicating an additional spectral contribution (see fig. 1e). Some previous studies have evidenced the possibility of —P—H component contribution [2], whereas other contributions relate —P—Cl environments in these experimental conditions [3]. Based on additional TXRF measurements, we support the hypothesis of —P—Cl bonds at the InP surfaces post-treatment. Furthermore, the —P—Cl components ratio was found to be inversely proportional to that of InP surface oxides during storage post-treatment (see fig. 1a,b).

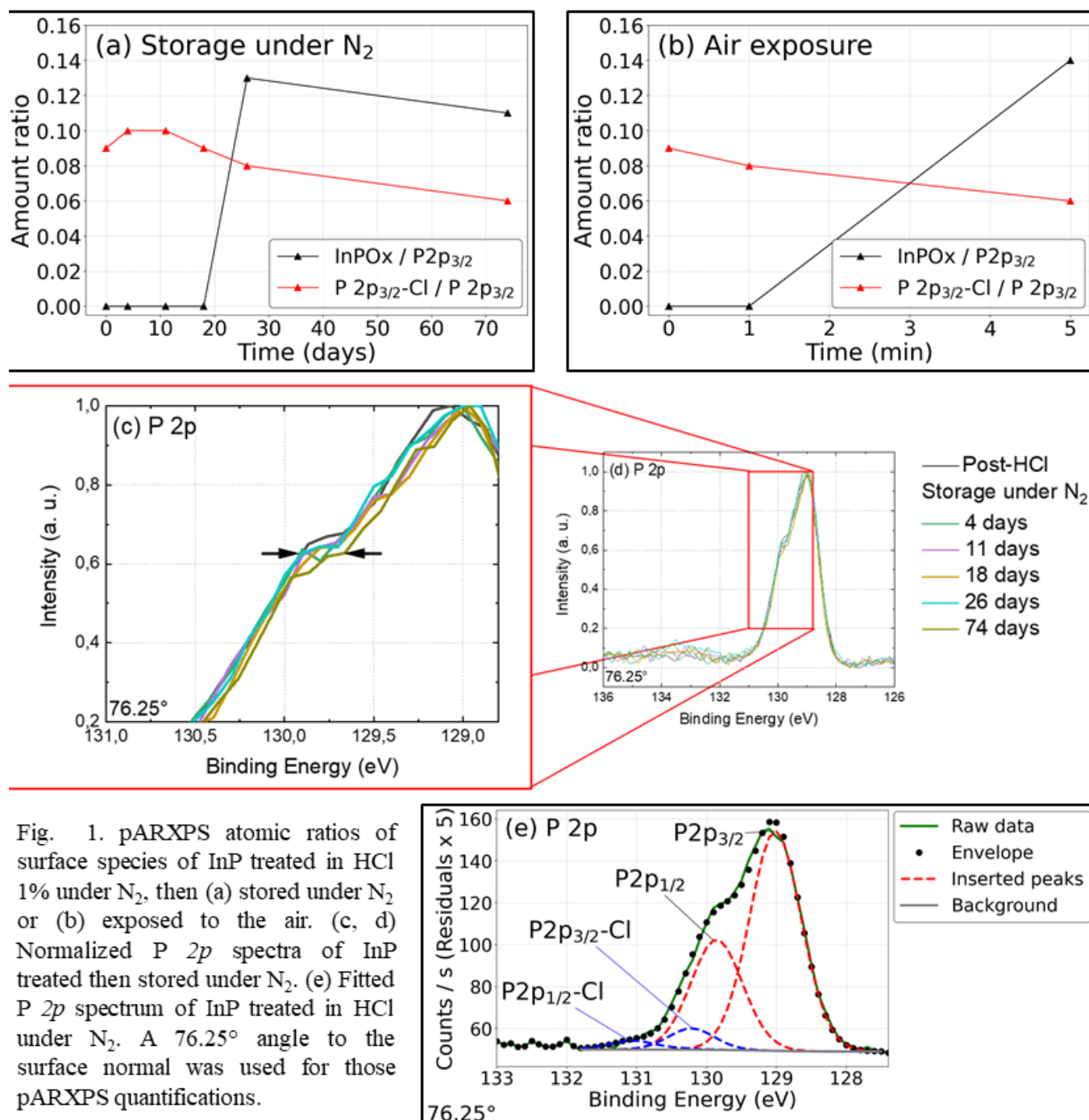
The presentation will highlight and discuss the experimental protocol, the spectral fitting model and the pARXPS results obtained during this study, along with perspectives on the wet chemical functionalization of InP surfaces.

Acknowledgments: The authors wish to acknowledge financial support for this work from CEA-Leti, and the RENATECH network coordinated by CNRS.

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- [3] L. Santinacci *et al.*, *J. Electrochem. Soc.*, vol. 165, n° 4, p. H3131-H3137, 2018, doi: 10.1149/2.0181804jes.

Keywords: III-V Compound Semiconductor, InP, HCl, pARXPS, quasi-insitu



Nondestructive Analysis of $\text{Al}_2\text{O}_3/\text{SiO}_x/\text{Si}$ Passivation Layers for Photovoltaics Using Angle-Resolved HAXPES Techniques

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$\text{Si}/\text{SiO}_x/\text{Al}_2\text{O}_3$ stacks are widely investigated in advanced semiconductor devices due to their balanced interface quality, electrical reliability, and process compatibility. In such structures, device performance is not solely determined by the moderate high-k dielectric, but is strongly influenced by the interfacial SiO_x layer, whose thickness and chemical states are highly sensitive to annealing conditions. Variations in this interfacial SiO_x layer can lead to noticeable changes in leakage current, dark current, and threshold voltage stability. Therefore, understanding how annealing affects the chemical state and thickness evolution of the SiO_x layer is critical for optimizing device reliability and electrical performance. In practical device structures, the Al_2O_3 layer is typically deposited thicker than 15 nm to suppress tunneling leakage and prevent annealing-induced local defects from directly impacting the Si substrate. However, such thicknesses limit the ability of conventional laboratory XPS for probing the buried SiO_x and Si layers. While sputter depth profiling is an alternative, ion bombardment may alter the interfacial chemistry, making it less suitable for tracking intrinsic thermal evolution. In this work, we investigated the layer thickness of $\text{Si}/\text{SiO}_x/\text{Al}_2\text{O}_3$ stacks subjected to different post-annealing treatment using angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and angle-resolved hard-X-ray photoelectron spectroscopy (AR-HAXPES). Both techniques revealed that an increase in SiO_x thickness with increasing annealing temperatures. AR-HAXPES provides a more reliable evaluation of the buried layer thickness due to its enhanced probing depth and the absence of sputter-induced damage. Furthermore, in situ heating combined with HAXPES was employed to directly monitor temperature-dependent chemical-state evolution at the $\text{Si}/\text{SiO}_x/\text{Al}_2\text{O}_3$ interface without interruption or environmental exposure. This approach enables the captures of transient and non-equilibrium sub-oxide states that may be modified or eliminated during cooling and air exposure. In a result, AR-HAXPES and in situ heating combined with HAXPES demonstrate their capabilities to provide critical insight for optimizing annealing processes, interface passivation, and electrical performance in post-annealing processed semiconductor devices.

Keywords: AR-XPS, AR-HAXPES, HAXPES with in situ heating

Study of time-resolved photoemission dynamics in semiconductor materials for photovoltaic cells

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In order to improve solar cell efficiencies, steps such as photon absorption, electron-hole pair generation, charge carrier separation, transport, and collection should be better understood and controlled¹. In this context, the quality of the absorber material and the control of interfaces with charge transport layers, i.e., favorable band alignment and limited non-radiative recombination, are of primary interest.

In this work, we investigated the influence of doping types and surface chemistry on the surface photovoltage (SPV) of GaAs substrates. Indeed, laser illumination modifies the band bending at the surface, driving the system toward the "flat-band" regime. This band bending phenomenon is crucial to control band alignments, particularly at interfaces, where it directly influences solar cell performance². The associated SPV can be observed through shifts of photoemission peaks in binding energy. Figure 1 shows, for instance, the observed shift on the Ga 3d peak and the associated exponential increase of the SPV with laser power.

By this method, we compared several surface passivation strategies. In particular, surface deoxidation by immersion in H₂SO₄ leads to a slight modification of the surface composition. Sulfuration with (NH₄)₂S treatment showed promising results to passivate the surface, although this passivation appeared unstable over time³. In addition, surface functionalization via grafting of sulfur-containing molecules (alkanethiols) was explored, as these molecules are expected to provide more stable passivation than simple S-terminated surfaces⁴.

In a second step, the same systems were investigated under dynamic conditions using time-resolved photoemission spectroscopy (TRPES) at the TEMPO beamline of the SOLEIL synchrotron². This pump-probe approach enables direct observation of photoinduced carrier dynamics and the temporal evolution of the SPV. These measurements allow quantifying SPV evolution on microsecond timescales, in connection with carrier separation, trapping and recombination processes.

Furthermore, thanks to this unique setup, in which the laser is directly implemented within the ultrahigh-vacuum chamber of the XPS system and co-localized with the X-ray beam, we were able to correlate the obtained chemical information with photoluminescence (PL) spectroscopy, a sensitive tool to evaluate non-radiative recombination and electronic defects of surfaces/interfaces.

Acknowledgements: This work benefited from financial support from the PEPR TASE program (Minotaure Project, ANR-22-PETA-0015).

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Keywords: Photovoltaics, Time-resolved Photoemission, Semiconductors, Interfaces

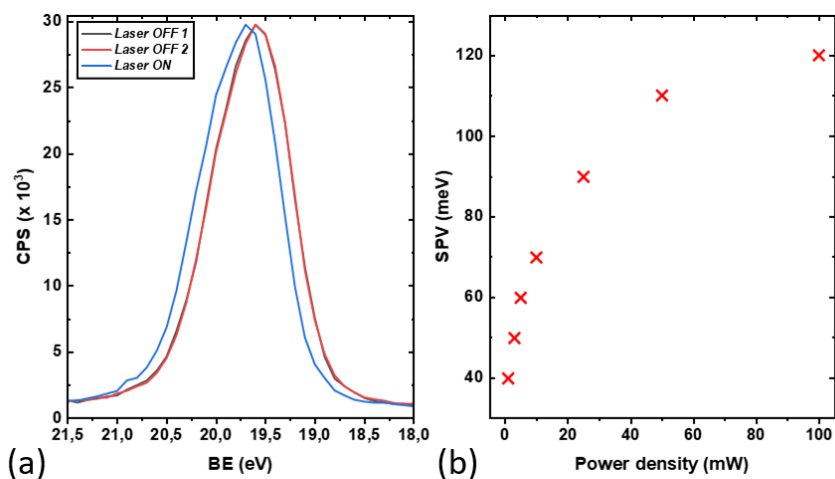


Figure 1 : (a) XPS spectra of Ga 3d for n-GaAs recorded before, during, and after laser illumination (laser OFF $\rightarrow$ ON $\rightarrow$ OFF). (b) SPV of the Ga 3d peak as a function of laser power.

Extended study of Metal / p-HgCdTe Interface combining HAXPES and ToF SIMS analysis

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P-type metal contacts on semiconductors remain a major technological challenge, particularly in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ (CMT), a benchmark material for cooled infrared detectors [1]. Experimentally, the number of defective pixels tends to rise, leading to performance degradation at higher operating temperatures [2]. One possible origin of this deterioration is attributed to non-ideal, Schottky-type behavior at the metal/p-type CMT interface. Interactions between metals and CMT were extensively studied by X-ray photoelectron spectroscopy in the 1990s [3], nevertheless, the contact formation mechanisms remain insufficiently understood. To further elucidate the processes governing this interface, we carried out a detailed physicochemical characterisation using a combination of Hard X-ray Photoelectron Spectroscopy (HAXPES) and depth-resolved analysis by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The objective was to gain deeper insight into both the formation of metal contacts on CMT and the interfacial reactivity as a function of the metal nature.

Thin (~ 10 nm) metal contacts were deposited on arsenic-doped p-type $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ ($x = 0.29$) with a carrier concentration of approximately $1 \times 10^{18} \text{ cm}^{-3}$. All contacts were fabricated using industrially representative and identical preliminary surface preparation protocols (dry plasma preparation and wet chemical etching) to ensure consistency. Various sputtered metals: gold, titanium and aluminium were investigated. The buried interface chemistry was examined to analyse interfacial chemistry including interdiffusion phenomena, oxidation processes, and interface state formation. Electronegative secondary ions were analyzed using a TOF-SIMS 5 instrument (IONTOF GmbH), operated with a Bi_3^+ primary ion beam for surface analysis and a low-energy Cs^+ sputter beam for depth profiling. Substrate elements were monitored to locate the interface and assess elemental composition. HAXPES spectra (Quantes, ULVAC-PHI), recorded with a $\text{Cr K}\alpha$ X-ray source, revealed the degree of oxidation.

These techniques are complementary and reveal interfaces with varying composition and extent depending on the deposited metal. The interface exhibits a tellurium-rich region characterized by the presence of an oxidized TeO_x -type interfacial layer with varying thickness. HAXPES spectra allow quantification of the extent of tellurium oxide formation (Figure 1). ToF-SIMS depth profiles enable monitoring of tellurium enrichment and mercury depletion near the interface, along with more or less pronounced interdiffusion of both the metal and tellurium (Figure 2). The interfacial oxide and tellurium excess could influence carrier transport and contribute to the non-ideal electrical behavior of these contacts.

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[1] DOI : [10.1007/s11664-008-0426-3](https://doi.org/10.1007/s11664-008-0426-3)

[2] DOI : [10.1117/12.2178954](https://doi.org/10.1117/12.2178954)

[3] DOI: [10.1088/0268-1242/9/9/021](https://doi.org/10.1088/0268-1242/9/9/021)

Keywords: HgCdTe, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Hard X-ray Photoelectron Spectroscopy (HAXPES), Metal/Semiconductor Interface, Schottky Contact

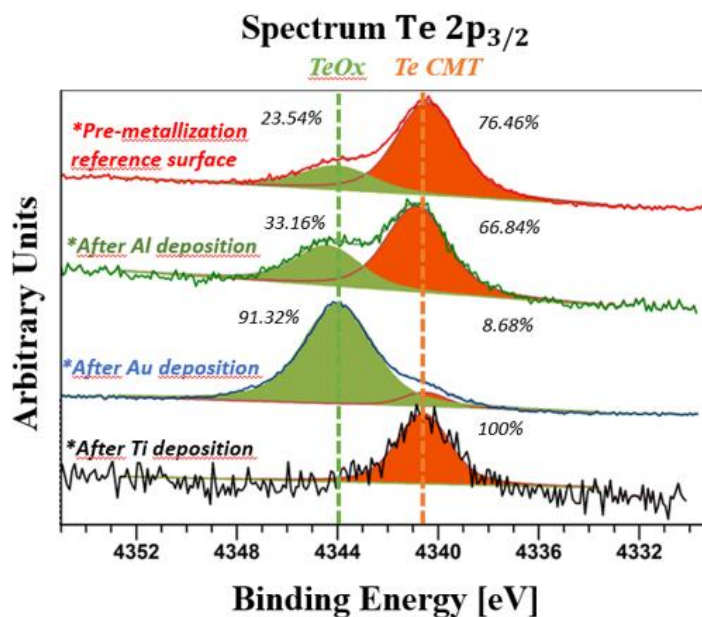


Figure 1: Evolution of the Te 2p spectrum before and after Al, Au, or Ti deposition

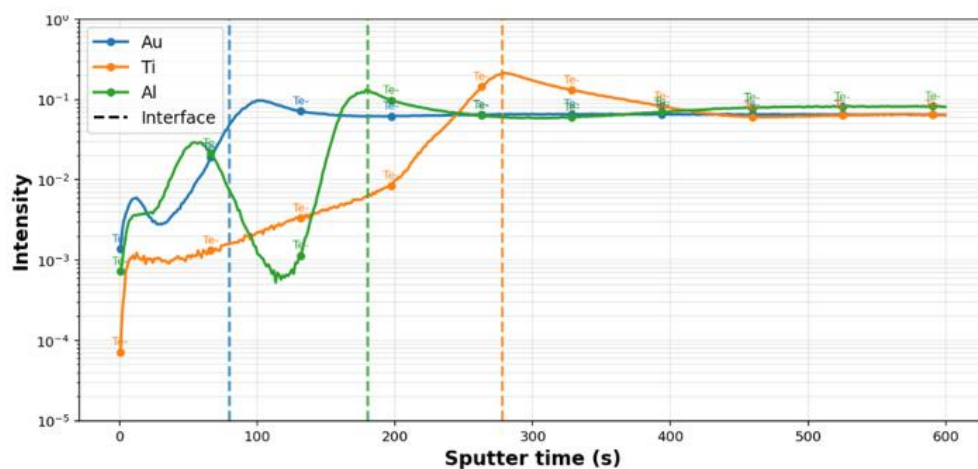


Figure 2: Comparison of the sputtering profiles for Al, Au and Ti on CMT

Enlarged chemical characterization of III-V material heterostructures for advanced communication devices

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The relentless pursuit of higher performance in optoelectronic devices and next-generation telecommunication systems (5G/6G) has placed III-V semiconductor heterostructures at the forefront of materials research. These materials, renowned for their exceptional electronic and optical properties, are critical for applications ranging from high-speed transistors to photonic integrated circuits. However, their performance is intrinsically linked to the atomic-scale composition and integrity of their surfaces and interfaces. Even minor deviations—such as unintended dopant segregation or interfacial diffusion—can significantly degrade device functionality. Thus, the development of advanced characterization techniques capable of probing these interfaces with high sensitivity and spatial resolution is paramount.

In this study, we focus on the chemical composition and interfacial behavior of heterostructures based on InP/GaAs_{0.51}Sb_{0.49}/InP stacks, as well as precise localization and quantification of dopants. We utilize a combination of advanced characterization techniques, namely time-of-flight secondary ion mass spectrometry (ToF-SIMS), magnetic sector SIMS and (M-SIMS) x-ray photoelectron spectroscopy XPS. Angle-resolved XPS (ARXPS) is employed to investigate the spatial distribution of Sb and As, revealing an undesired Sb segregation within the top InP layer, while confirming the absence of As diffusion. Completed with hard x-ray photoelectron spectroscopy (HAXPES), complementary depth-sensitive insights were collected, further validating the Sb segregation and making its quantification possible. These results were confirmed from different SIMS measurements, giving detailed in-depth location of matrix elements. In addition, taking benefit of its great sensitivity, M-SIMS helps to validate the correct doping level and restrained location of active regions.

The integration of ARXPS, HAXPES, ToF-SIMS, and magnetic sector SIMS establishes a powerful analytical framework for probing interfacial properties in III-V heterostructures. This multi-faceted approach not only enhances our understanding of segregation and diffusion mechanisms but also provides critical insights for optimizing material growth processes. Ultimately, such advancements are essential for unlocking the full potential of III-V materials in cutting-edge optoelectronic and telecommunication applications, where precision and reliability are non-negotiable.

Acknowledgments: This work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the "Recherche Technologique de Base" and "France 2030 – ANR-22-PEEL-0014" programs of the French National Research Agency (ANR). Part of it was supported by the LabEx MINOS under Contract No. ANR-10-LABX-0055.

Keywords: III-V heterostructures, ARXPS / HAXPES, SIMS, interfacial characterization, Sb segregation

High sensitivity, in situ analysis of hydrogen using dynamic SIMS

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Hydrogen is the most abundant element in the environment and can be incorporated into materials either intentionally—during processes such as epitaxy, annealing, ion implantation, or photolithography—or unintentionally through environmental exposure, including corrosion or hydration. Precise characterization of hydrogen distribution is therefore essential for designing semiconductor and functional materials with tailored properties, and for understanding the mechanisms that govern their performance and reliability.

Dynamic Secondary Ion Mass Spectrometry (SIMS) is one of the most sensitive and reliable techniques for quantifying and profiling hydrogen in solids. Its capability to combine extreme detection sensitivity with excellent depth and lateral resolution makes it a technique of choice for semiconductor materials analysis. SIMS is based on controlled sputtering of the sample by a focused primary ion beam, generating secondary ions that are collected and analyzed by a mass spectrometer. Dynamic SIMS, using high primary ion doses in combination with a magnetic-sector mass spectrometer, enables the highest sensitivity for hydrogen and other light elements.

CAMECA has developed several state-of-the-art magnetic-sector SIMS instruments optimized for different analytical needs.

The IMS 7f-Auto provides outstanding depth profiling performance with high automation and throughput. It enables detection of hydrogen at the ppm level and delivers accurate in-depth distributions from a few nanometers to tens of micrometers, making it highly suited for semiconductor process monitoring and advanced materials development.

The NanoSIMS-HR offers complementary capabilities with its unique combination of lateral resolution (down to 30 nm), high mass-resolving power, and seven-mass multicollection. These features allow high-resolution mapping of hydrogen and associated species, providing insight into nanoscale non-uniformities and local chemical environments within complex materials and device structures.

The insights gained from dynamic SIMS are crucial for advancing fundamental materials research and for supporting the development of next-generation semiconductor technologies. In this contribution, we present several application examples highlighting the role of dynamic SIMS in hydrogen analysis across different research domains, demonstrating how the technique continues to expand the boundaries of surface and interface characterization.

Keywords: Hydrogen, SIMS, profiling, mapping, characterization

Monitoring of Wafer Contamination in European Research Facilities: An Interlaboratory Field Study

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Modern micro- and nanoelectronic devices are developed in highly specialized cleanrooms. To accelerate and strengthen the innovation of the European microelectronics industry, it is necessary to bundle the professional and technical competencies of the European research institutes. To collaborate efficiently, these research institutes must be able to exchange wafers without spreading metallic contamination. Today, this risk is often checked with additional "witness wafers" that are processed and analyzed late in the project, which takes time and cleanroom capacity.

Within the PREVAIL project, the four largest European 300 mm research cleanrooms (Fraunhofer, CEA-Leti, imec and VTT) carried out an interlaboratory field study to determine whether their existing contamination monitoring data is reliable enough to be used instead of witness wafers. Therefore, one partner intentionally contaminated twelve wafers with Al (1×10^{12} at/cm²) and Cr, Cu, Fe, Ge, Mo, Ni, Ta, Ti (each element 1×10^{11} at/cm²). Each partner received three of these wafers and analyzed them with its standard methods: vapor phase decomposition coupled with inductively coupled plasma mass spectrometry (VPD-ICP-MS) and, if available, bevel VPD-ICP-MS and total reflection X-ray fluorescence (TXRF).

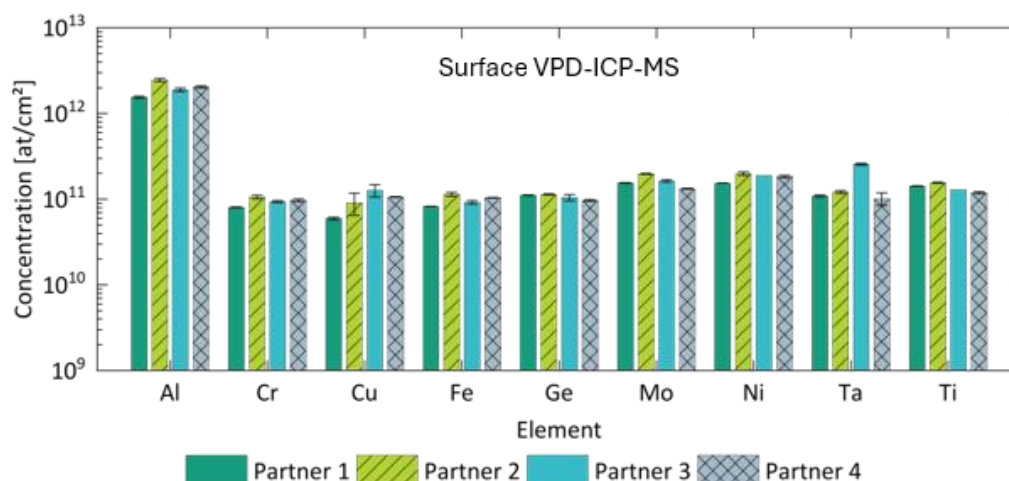
Despite using different tool set-ups, scan solution composition and (sub-)tool coupling, the laboratories achieved remarkably similar results. The precision within the laboratories was also excellent: for six elements, all partners achieved relative standard deviations below 5.5 % and for the remaining three elements below 30 %, which corresponds with the typical acceptance criteria. This demonstrates that the different VPD-ICP-MS setups are effectively equivalent for the assessment of risks during wafer exchange.

Bevel VPD-ICP-MS measurements systematically indicated higher contamination levels compared to the surface analysis, which can be explained by a mathematical discrepancy caused by the different surface areas. Any additional differences can be explained by increased deposition at the wafer edge during intentional contamination or by higher abrasion at the wafer edge during transportation.

TXRF tended to indicate lower concentrations and was limited by its detection limits for some elements. However, it remains attractive as a non-destructive, locally resolved technique when its detection limits match the required specifications.

Overall, the study shows that the interpretation of existing monitoring data can reliably replace witness wafers, enabling earlier planning of cleaning strategies, reducing cross-contamination risks and improving the utilization of costly research cleanroom infrastructure.

Keywords: contamination monitoring, semiconductor, 300 mm wafer, VPD-ICP-MS, TXRF



Wafer-Scale Metrology of buried layers by XPS/HAXPES and Multi-Energy Glancing-Angle XRF

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Precise wafer-scale metrology of thickness and composition in buried layers is critical for controlling process variability and ultimately ensuring the performance and reliability of nanoelectronic devices. While XPS/HAXPES enables thickness determination and elemental depth profiling in thin inorganic stacks, advanced XRF fab tools provide accurate quantification of elemental mass deposition.

This study reports on the assessment of XPS/HAXPES measurements performed at Al K α , Ag L α , and Cr K α on 300 mm wafers using a SPECS EnviroMETROS system, applied to high-k (HfO₂:ZrO₂) multilayer stacks for FeRAM applications [1] and to high-k/metal gate stacks for advanced nanoelectronics [2], using multi-energy glancing-incidence XRF [3] as a complementary metrology approach (Figure 1).

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doi:10.1109/IEDM50854.2024.10873378
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Keywords: HAXPES, Metrology, XRF, Semiconductor

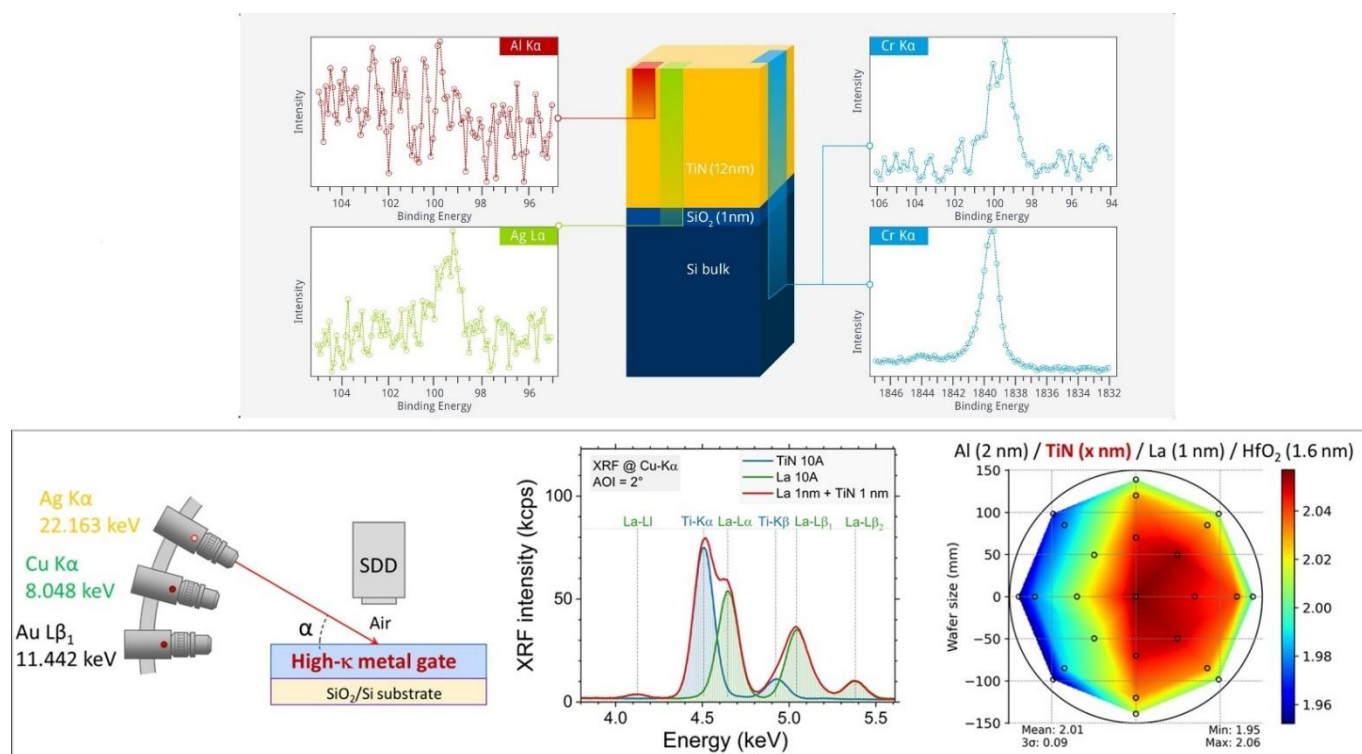


Figure 1: **top:** High-resolution Si 2p (and Si 1s) core-level spectra of a 12 nm thick TiN sample measured with Al K α , Ag L α , and Cr K α excitation; **bottom left:** Rigaku MFM310 ED-XRF instrument; **middle:** XRF spectra acquired using Cu K α excitation energies for the determination of La and Ti mass deposition in metal gate stacks; **right:** full map of XRF-deduced TiN thickness in a high-k-metal gate stack

Quantification of the reduction of sputter deposited vanadium oxide under XPS analysis conditions

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The various oxidation states of vanadium oxide provide a range of band gaps, conductivities and redox behaviour making them useful as active layers in electronic, optical and electrochemical devices.^[1] Vanadium oxide films have found applications from smart windows and batteries to neuromorphic devices.^[2,3] Reliable X-ray photoelectron spectroscopy (XPS) analysis of vanadium oxide films is complicated by X-ray beam and charge compensation induced changes in oxidation state, which can obscure the relevant intrinsic chemistry.^[4] There have been limited studies to quantitate the extent to which different conditions contribute to the reduction. In this work, sputter-deposited V_2O_5 films were characterized using monochromatic Al $K\alpha$ XPS with systematic variation of acquisition parameters to quantify X-ray and flood gun induced reduction. Time resolved spectra were used to establish quantitative dose-response relationships for the reduction under various analytical conditions. These results provide a protocol for artifact aware XPS measurement of multivalent vanadium oxides and establish guidelines for correlating XPS derived chemical states with the functional behaviour of vanadium oxide based memristive devices. Consideration will also be given to the processing conditions that the thin films will be exposed to for device fabrication and how these may impact the final oxidation state of the vanadium oxide in the functional memristor device.

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Keywords: vanadium oxide, XPS, reduction, memristor

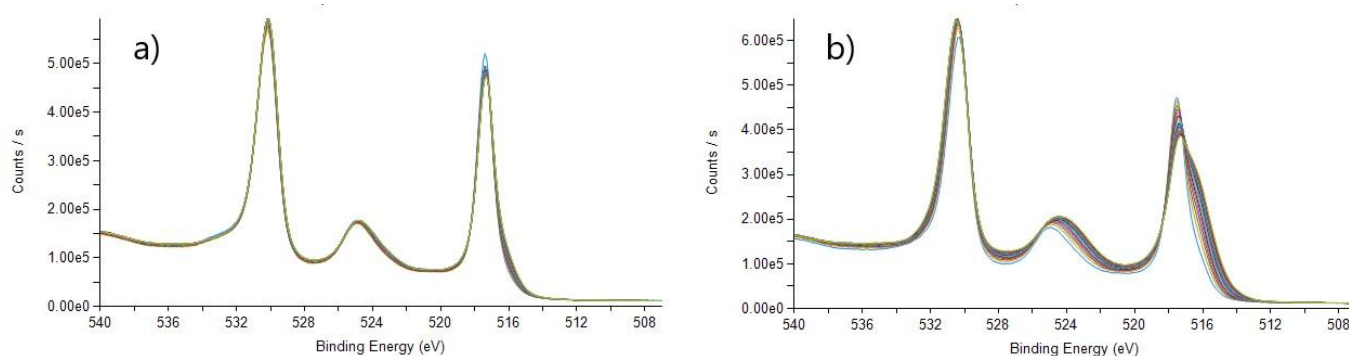


Figure 1: Time series showing reduction under a) X-ray exposure and b) both X-ray and charge compensation.

XPS study on β -aluminum-gallium oxide: composition, bandgap, and substrate dependence

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Beta-phase gallium oxide is a transparent, wide-bandgap semiconductor with a band gap of 4.85 eV [1], making it a promising candidate for applications in high-power devices and UV photodetectors. With its higher calculated breakdown field [2], β -gallium oxide is expected to outperform well-established materials such as silicon carbide and gallium nitride for high-power switching. To further enhance the high-power capabilities, as represented by the Baliga figure of merit, [3], an increase in the electric breakdown field, E_b , is required. A proven successful strategy is alloying with aluminum [4], which requires incorporating more than 25% to increase the BFOM above its initial value due to reduced electron mobility. Following a similar approach, we have grown thin films on a β -gallium oxide substrate by metal-organic vapor-phase epitaxy (MOVPE).

This work aims to explore the relationship between the chemical composition and electronic properties of β -($\text{Al}_x\text{Ga}_{1-x}$)₂O₃ ($0 < x < 0.4$) thin films, focusing on how different growth parameters and substrate miscuts influence these properties. First, it demonstrates that aluminum incorporation depends on the choice of substrate, suggesting a likely threshold at $x > 0.4$. The Al concentration has been measured by X-ray photoelectron spectroscopy (XPS) and compared with the Al content determined from changes in the lattice parameter as measured by X-ray diffraction (XRD). Additionally, the homogeneity of thin films has been investigated through XPS depth profiling obtained at different take-off angles, revealing varying aluminum contents at the sample surface. The samples were cross-checked against gallium oxide and aluminum oxide reference samples to confirm their stoichiometric composition and to rule out possible aluminum cluster segregation. Furthermore, carbon impurities, likely introduced by carbon-based precursors, were not detected by XPS, addressing a common problem in MOVPE growth. Additionally, the Auger parameter was studied, highlighting the well-defined binding states within the films. Furthermore, the band gap has also been determined by XPS via electron-loss analysis for thin films and compared with optical absorbance measurements on bulk crystals grown by the Czochralski method [4]. The surface was studied by atomic force microscopy (AFM) to assess surface morphology and roughness. Overall, our thin films exhibit excellent structural and chemical properties, thus bringing this film technology closer to application.

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Keywords: MOVPE, beta aluminum gallium oxide, epitaxy, bandgap

Growth of $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ nanodots droplet epitaxy on GaAs(111)A monitored by in situ XPS and ex situ microscopy

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Indium gallium nitride ($\text{In}_x\text{Ga}_{1-x}\text{N}$) quantum dots are of considerable interest for optoelectronic applications due to their tunable emission properties, which can be utilized in devices such as LEDs, lasers, photodetectors, and solar cells. In recent years, droplet epitaxy (DE) has emerged as a promising alternative to conventional growth techniques such as the Stranski–Krastanov mode. This DE method relies on a two-step process consisting of the self-assembly of group-III metallic ($\text{In}_x\text{Ga}_{1-x}$) droplets, followed by their crystallization through nitrogen incorporation as the group-V element.

In this work, we investigate the nitridation process of self-assembled Ga and $\text{In}_{0.3}\text{Ga}_{0.7}$ nanodroplets, with the aim of optimizing the growth of GaN [1] and $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ nanodots on GaAs(111)A substrates by DE. The growth process is monitored in situ using X-ray photoelectron spectroscopy (XPS) [2], combined with ex situ microscopy techniques, providing complementary qualitative and quantitative insights. The use of two X-ray sources and variable collection angles in XPS enables tuning of the probing depth and reveals possible in-depth diffusion of species during nitridation. These observations are further supported by chemical mapping performed using transmission electron microscopy. Finally, initiating nitridation at low temperature -leading to the formation of a nitride shell- followed by a gradual increase in substrate temperature up to 350°C, allows the growth of high-density ($> 10^{11} \text{ cm}^{-2}$) $\text{In}_{0.3}\text{Ga}_{0.7}\text{N}$ nanodots on GaAs(111)A with the zinc blende crystallinity.

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Keywords: InGaN nanodots, Droplet Epitaxy, In situ XPS

Surface and Bulk Characterisation of Organic Semiconductors Using X-ray and Ultraviolet photoemission spectroscopies

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Organic semiconductors continue to attract significant interest for their applicability in flexible, lightweight, and low-cost electronic devices. Their utility includes various organic electronic devices, including Organic Thin-Film Transistors (OTFTs), Organic Light-Emitting Diodes (OLEDs), Organic Photovoltaics (OPVs), and organic diodes. Their performance arises from charge transport via delocalized electronic states, a characteristic of their π -conjugated molecular structures.

Materials such as DNTT and CuPc operate as p-type semiconductors, while CuF₁₆Pc functions as an n-type analogue; furthermore, F₄TCNQ is widely employed as a high-electron-affinity dopant for enhancing p-type conductivity. Optimising device operation requires a detailed understanding of the semiconductor surface chemistry, interfacial energetics, and depth-dependent electronic structure.

In this work, we demonstrate an integrated characterisation methodology using a modern X-ray Photoelectron Spectroscopy (XPS) platform capable of both small-area measurements and 2-dimensional X-ray photoelectron imaging. These techniques enable quantitative analysis of chemical composition and electronic structure in both blanket films and printed semiconductor patterns, providing insight into interactions with substrates and templating/electrode layers. Ar_n⁺ cluster ion depth profiling reveals the evolution of chemical states and electronic properties throughout the film thickness. Ultraviolet Photoelectron Spectroscopy (UPS) is further employed to determine work functions and valence-level alignments, key parameters governing charge injection and transport. Together, this multimodal approach establishes a robust framework for probing interfacial phenomena and guiding the rational design of high-performance organic electronic devices.

Keywords: XPS, UPS, organic electronics, Ar cluster depth profile

A Digital Workflow for Sulfur 2p XPS Materials Analysis

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Sulfur 2p XPS helps to identify reduced and oxidised sulfur species in catalysts, metal sulfides, corrosion products, and energy materials. However, sulfur 2p spectra are still fitted and interpreted inconsistently across the literature [1]. Common problems include incorrect assignment of spin-orbit doublets, inconsistent peak widths, poor charge correction, and inadequate treatment of overlapping sulfur components [1]. These problems reduce reproducibility and can lead to incorrect chemical-state assignments. Manual curve fitting is particularly difficult for new XPS users and often produces inconsistent results. We have developed a digital workflow to make sulfur XPS analysis easier and more reproducible. The workflow reads XPS VAMAS or text files. It selects the S 2p region, applies optional charge correction by referencing the C 1s peak to 284.8 eV or by using a manual energy shift, subtracts a Shirley background, and fits the spectrum using constrained S 2p doublets with Casa-like Gaussian-Lorentzian mixed peak shapes, fixed spin-orbit splitting, and fixed area ratios. The fitted peaks are then compared with a sulfur reference library. The library includes sulfides, disulfides, elemental sulfur, sulfite, sulfate, thiosulfate, and organosulfur species.

The workflow also compares the full fitted curve with reference sulfur curves to suggest likely materials. It reports tied matches when the sulfur signal is not unique. This helps avoid over-interpretation. The method was tested on sulfide and oxidised sulfur samples, including MoS₂-, FeS-, and sulfate-containing spectra. It gives a practical path from raw XPS data to fitting, plots, and clearer interpretation.

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Keywords: XPS, Charge Correction, Material, curve fitting

Surfaces of porous materials

Sustainable carbon membranes made from lignin with autonomously formed pore structure

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Lignin is one of the most abundant bio-polymers (together with cellulose and chitin), which carries in the world of plants important structural, transport and protective functions. Being a by-product in the cellulose and paper industry, lignin is mostly burned in enormous quantities as fuel. Nevertheless, recent studies explore its promising potential as a raw material for the agricultural, food or pharmaceutical industry. Furthermore, lignin can be converted into various materials of high value, as e.g. carbon fibers or carbon black, by means of specific heat treatments and carbonization processes.

In this contribution a new routine for the fabrication of carbon membranes with a tailored porous structure was developed (illustrated in Fig. 1a) by means of carbonization of pure, sole lignin powder in an inert N₂ atmosphere, *i.e.* with no binder, additive or solvent needed. The prepared membranes were investigated in detail by various complementary analytical techniques comprising scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), Auger-electron spectroscopy (AES) and porosity characterization (Hg porosimetry as well as N₂ and CO₂ adsorption measurements). By optimizing the carbonization process it was revealed that the type of the lignin precursor (e.g. Kraft, Organosolv, alkali or soda lignin) as well as the specific conditions used during the carbonization step (temperature and annealing rate) dramatically affected the inner level of porosity and structure of the formed membrane. As illustrated in the electron micrographs shown in Fig. 1b, the morphology of the prepared carbon membranes comprised interconnected irregularly shaped powder grains, a network of partly sintered and molten grains, sponge like structures made of interconnected hollow spheres and bubbles. Chemical analysis revealed an interesting contrast between the bulk and surface composition of the carbonized membranes. While the bulk of the material showed enrichment in the C concentration with increasing carbonization temperature (determined by EDX and illustrated in Fig. 1c), which is in line with the desired conversion of the pristine organic bio-material into pure C material, the results from surface analysis showed the additional formation of an additional surface layer consisting mainly of Na₂CO₃ (determined by XPS and AES and also illustrated in Fig. 1c). Based on the obtained analytical results, the diverse observed processes and reactions, which occurred during the carbonization process of the lignin materials, will be discussed and summarized, also with respect to future applications, like sustainable bio-based advanced filter structures or novel electrode materials for sustainable energy storage.

Keywords: lignin, porous carbon structures, carbon membranes, carbonization process

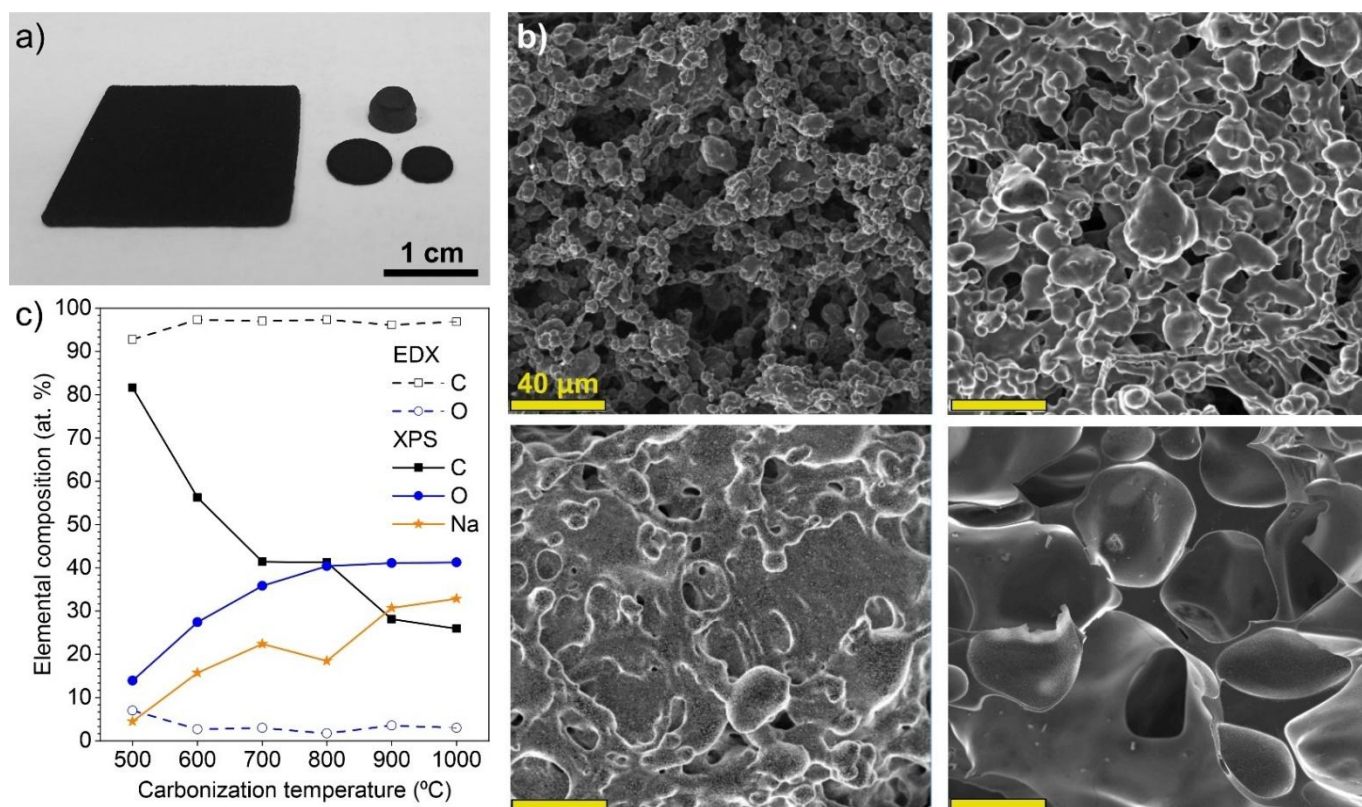


Figure 1. Optical appearance (a) and SE micrographs (b) of the carbon membranes and the elemental composition (EDX and XPS) as function of the carbonization temperature.

Fractographic Analysis of Al–Si High-Pressure Die Castings in Mega Casting Applications

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The rapid industrial adoption of high-pressure die casting (HPDC) to produce large, highly integrated aluminum components, commonly referred to as Mega-casting, has introduced new challenges related to defect tolerance, surface integrity, and structural reliability. The size and complexity of the tooling, combined with non-uniform thermal and flow conditions, can lead to heterogeneous distributions of defects including pores and oxide-related features, which play a decisive role in damage initiation and fracture. In parallel, the increasing use of recycled Al–Si alloys, driven by sustainability and cost considerations, raises critical questions regarding oxide formation, melt cleanliness, and porosity control in industrial-scale castings.

In this study, Al–Si high-pressure die casting samples were subjected to slow strain rate tensile tests at room temperature. The fracture surfaces after testing were investigated using optical microscopy (OM) and scanning electron microscopy (SEM) combined with surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The aim is to establish a correlation of defects and local chemistry with the tensile properties and fracture in Al–Si high-pressure die castings.

This contribution will demonstrate how the integration of advanced characterization techniques provides a comprehensive framework for investigating defect-controlled fracture in HPDC Al–Si alloys. The approach is particularly relevant for Mega-casting applications with increased recycled content, where defect tolerance and surface integrity are critical for ensuring structural performance and long-term reliability.

Keywords: Al–Si Alloy, HPDC, Mega-casting, Fractography, XPS and AES

Synthesis of mesoporous TiO₂ diphosphonate for 5-HMF production: From sol–gel nanoparticles to mesoporous catalyst

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Mesoporous metal phosphonates (PMPs) are hybrid organic-inorganic materials, formed through the interaction of metals oxide precursors and organophosphonic acids or esters. These materials combine tunable porosity with both Lewis and Brønsted acidity, making them promising heterogeneous catalysts. However, achieving controlled synthesis approaches to make these materials mesoporous, while also providing a controlled surface chemistry is challenging, as the coordination of phosphonate to metal oxides strongly depends on reaction conditions and hydrolysis behavior.[1]

Bharadwaj et.al in 2022, prepared tetraethyl propane 1,3-diylbis(phosphonate (TEPD) capped TiO₂ nanoparticles via a sol method [2]. By adapting the acid concentration, the TEPD (ester) hydrolysis degree and properties of the obtained stable sol could be regulated. Herein, we report the synthesis of a novel mesoporous titania – diphosphonates (PMP), derived from these partially hydrolyzed TiO₂ diphosphonate sols, via a hydrothermal method, using F127 as the structure directing agent (Fig. 1A).

The obtained mesoporous materials exhibit surface areas of 484-510 m²/g, pore sizes of 5.3-5.6 nm and pore volumes of 0.65-0.68 cm³/g (Fig. 1B). Advanced surface characterization techniques including XPS and ³¹P NMR were employed to probe phosphorus coordination, surface OH groups, and structural stability. Although the sol particles exhibited distinct differences in surface OH groups, FT-IR and XPS analyses revealed comparable surface chemistry among the resulting mesoporous materials, indicating that surface chemistry differentiation from the sol particles were not preserved during mesostructure formation.

The catalytic performance of both the sols and the corresponding PMPs was evaluated in the conversion of cellobiose to 5-hydroxymethylfurfural (5-HMF), a reaction requiring both Brønsted and Lewis acid sites. While the catalytic activity of the sols varied depending on the acid equivalents used during synthesis, all PMPs exhibited similar activity. Maximum conversions of 98% for the sols and 60% for the PMPs were achieved, comparable to literature benchmarks.[3]

Our study demonstrates the novel synthesis of mesoporous titania bisphosphonates and its potential and first time use as heterogeneous acid catalyst for 5-HMF synthesis.

Acknowledgements: FWO and F.R.S.-FNRS (Belgium) – Excellence of Science (EOS) program “PHOSPORE”

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Keywords: mesoporous titania diphosphonate, heterogeneous catalysis, Brønsted and Lewis acid sites

Investigating Cs-implanted graphite using dual-source XPS supported with DFT

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A sample of highly orientated pyrolytic graphite (HOPG) was implanted with Cs⁺ ions in order to study the effect on the graphite matrix and the chemical form of Cs once embedded. Cesium is a primary fission product in nuclear reactors and is known to be mobile within the graphite moderator at elevated temperatures and so studying and understanding its physio-chemical behaviour within a graphitic matrix is valuable. At an ion energy of 50 keV, the mean implantation depth was calculated to be ~22 nm, allowing for investigation with X-ray Photoelectron Spectroscopy, (XPS), where both a traditional Al K α X-ray source and a higher energy Ag L α source was used for an increased sampling depth deeper into the surface. Analysis found that there was a reduction of sp² C–C bonding with increasing implantation dose, resulting in a total loss of sp² character at ~6 atomic % Cs⁺. A striking increase in higher binding energy components (285.8–289.4 eV) in the C 1s spectra cannot be attributed solely to the presence of C–O species, instead indicating a dramatic re-ordering of the graphitic lattice to accommodate and neutralize the embedded Cs. XPS analysis indicates the formation of cesium carbonate within the graphitic material; this is reinforced by analysis of a Cs₂CO₃ reference sample. Additionally, thermodynamics equilibrium simulations, supported by simplified density functional theory (DFT) calculations, are performed, leading to strong agreement with the XPS findings; that is, the most stable form of Cs within the graphite matrix is expected to be cesium carbonate (Cs₂CO₃), which is in thermodynamic equilibrium with degraphitised HOPG and oxygenated degraphitised HOPG

Keywords: Dual Source XPS, Cesium implanted graphite, Ion induced damage, Fission products, sp²-sp³ ratio

Quantitative XPS Analysis of Electronic Inhomogeneous Samples

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X-ray photoelectron spectroscopy (XPS) provides comprehensive qualitative, quantitative, and chemical insights into the surface (5-10 nm) of materials. However, analyzing XPS data quantitatively is challenging due to the multiple parameters involved. One parameter that primarily influences quantitative analyses is the inelastic mean free path (IMFP) of photoelectrons. The IMFP depends on the material and electron energy. It can be measured for specific systems using elastic-peak electron spectroscopy and electron energy loss spectroscopy using a transmission electron microscope. [1] The well-established TPP-2M formula can also be used to calculate the IMFP for elements and compounds. [2] For most of the elements the IMFP of their oxides is very similar to the value of their metallic form. Other elements, however, exhibit a significant difference between their elemental/metallic and oxidic IMFPs, like La or Sr, as shown in Figure 1. For compounds, an average matrix with homogeneous composition is assumed regardless of the elements involved. For compounds consisting of elements with a significant difference between their oxidic and elemental IMFP (like perovskites), angle-resolved XPS (ARXPS) insights combined with various other quantitative techniques reveal conflicting information regarding the quantification of these compounds. Thus, a different approach is necessary when dealing with these kinds of compounds. Using a combination of elemental and oxidic IMFPs for compounds may be more appropriate.

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Keywords: Quantitative XPS, IMFP, ARXPS

Adsorbate-Selective Diffusion Modulation in TMA-Modified ZIF-8

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Metal–organic frameworks (MOFs), particularly zeolitic imidazolate frameworks such as ZIF-8, are widely investigated for applications in molecular separations, sensing, and catalysis due to their tunable microporosity and favorable transport properties. ZIF-8 is especially attractive because its nominal pore aperture (~ 3.4 Å) and framework flexibility enable the transport of a broad range of guest molecules. However, achieving control over diffusion kinetics is challenging, especially while maintaining maximal adsorption capacity. Furthermore, mass transport in nanoporous materials directly affects their performance in applications, as seen in adsorption-based separations where diffusion kinetics limit the maximum production rate. Post-synthetic modification via a vapor-phase infiltration using trimethylaluminum (TMA) offers a promising strategy for tailoring the transport behaviour. However, fundamental insights into the TMA infiltration process, the resulting chemical states, and the compositional distribution throughout the porous layer remain limited, hampering a direct correlation between modification and mass transport in ZIF-8 thin films.

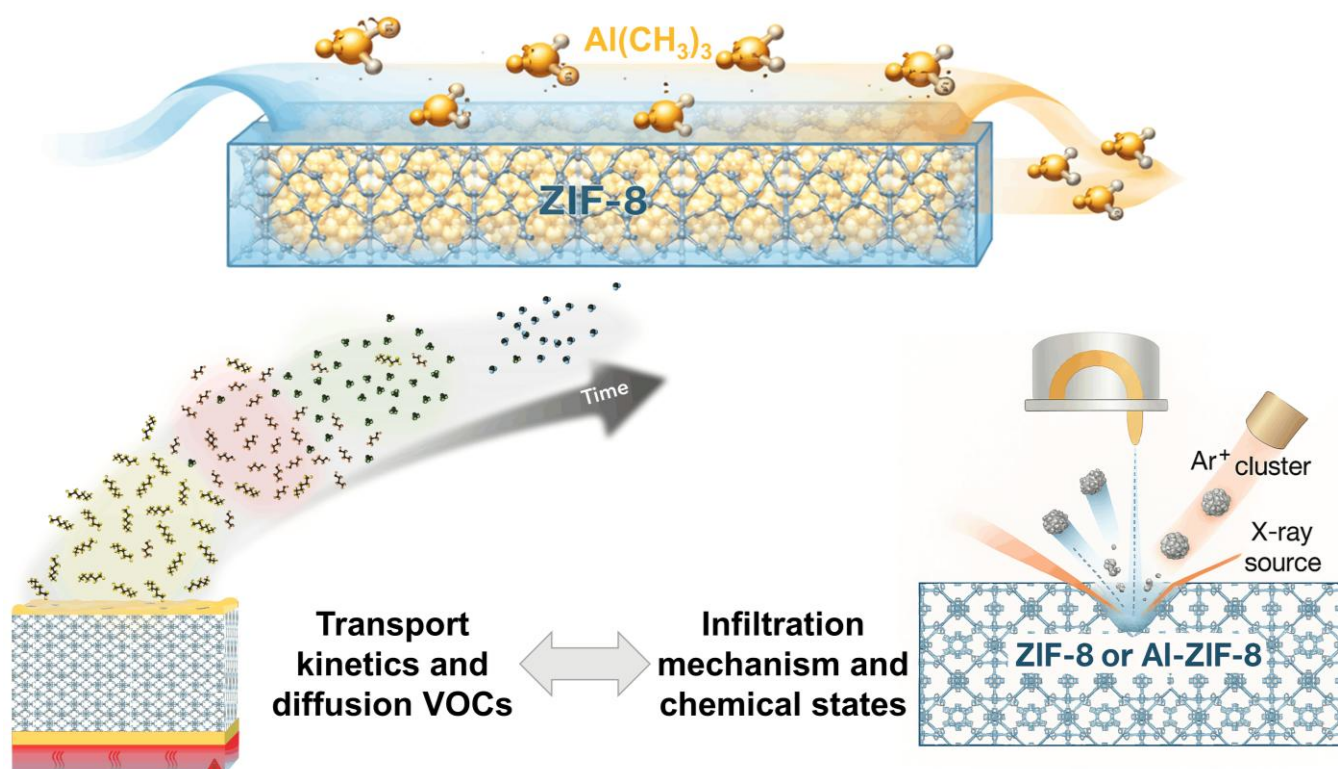
ZIF-8 thin films (300 nm) were treated with different TMA pulses in an ALD reactor and investigated via equilibrium uptake and diffusion measurements for various guest classes, including alcohols, ketones, and alkanes. Grazing-incidence XRD and quartz crystal microbalance (QCM) measurements confirmed that the framework remained intact, and equilibrium uptakes were unchanged across all guest molecules and TMA pulses, indicating a preserved pore accessibility and adsorption thermodynamics. In contrast, the transport kinetics were strongly affected as diffusion rates decreased by factors of 2 to 100, most prominently for non-polar molecules, which could be tuned via the number of TMA pulses.

Argon gas-cluster ion beam (GCIB)-XPS depth profiling revealed a gradual aluminum concentration front extending toward the ZIF-8/Si substrate interface with increasing TMA pulses. A non-stoichiometric exchange mechanism is observed, characterized by the absence of a 1:1 substitution of Zn by Al and the incorporation of an excess of aluminum within the film. Complementary TOF-SIMS depth profiling identified two aluminum states: an oxide or oxide-hydroxide phase near the surface and aluminum partly coordinated to imidazolate linkers in the bulk. This distribution suggests that TMA first infiltrates within the ZIF-8 surface to form an oxide-rich phase, while subsequent infiltration leads to partial incorporation of aluminum into the framework, modifying local coordination environments without disrupting crystallinity and porosity.

This study demonstrates how combining complementary characterization methods yields insights otherwise inaccessible. TMA modification enables decoupling of diffusion kinetics from equilibrium adsorption in ZIF-8, providing a pathway to tailor transport properties in MOF thin films for sensing applications.

Keywords: metal-organic frameworks, ZIF-8, transport diffusion, trimethylaluminum, post-synthetic vapor infiltration

Vapor phase infiltration TMA



Technique development and metrology

Evaluation of high-energy-resolution spectrum imaging by a fast hemi-spherical analyzer (f-HSA)

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Electron spectroscopies such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and reflection electron energy loss spectroscopy (REELS) are powerful techniques for surface and interface analysis because the electron detection depth is significantly shallower than that of X-rays in bulk analysis. A scanning Auger microscope (SAM), equipped with a focused electron probe and an electron analyzer, enables nanoscale electron spectroscopy. The lateral spatial resolution of SAM is on the order of nanometers, determined by the electron probe diameter, while the detection depth is also on the nanometer scale, defined by the inelastic mean free path of the detected electrons.

In recent years, we have reported measurement techniques and hardware developments aimed at high-throughput data acquisition for SAM [1–4]. Such high-speed capabilities are particularly advantageous for spectrum imaging of minute regions, as they reduce beam-induced damage and sample drift. Analysis of sub-micron-scale particles and electronic device failures critically requires a highly focused electron probe and efficient data acquisition.

In this study, we present an enhanced fast hemi-spherical analyzer (f-HSA) capable of spectrum acquisition with dwell times as short as 10 μ s, without inducing energy shifts or spectral shape distortion, as demonstrated in Figure 1. The working speed of the f-HSA is approximately 1,000 times faster than that of a conventional commercial SAM (JAMP-9510F, JEOL). We further improved the energy sweep algorithm of the f-HSA by adaptively varying the energy step of the detected electrons. Under the constant retarding ratio (CRR) mode, the energy resolution is proportional to the detected electron energy; therefore, increasing the energy step at higher kinetic energies effectively reduces the number of acquisition points while preserving spectral peaks and shapes. In addition, we implemented an image-based drift monitoring and correction function at every frame during spectrum imaging without additional acquisition overhead. This capability is particularly effective for fast measurements, as the correction interval scales with the frame rate. Fast data acquisition using the f-HSA expands the applicability of SAM to minute-area analysis and long-term measurements involving time-dependent changes.

Keywords: AES, SAM, spectrum imaging

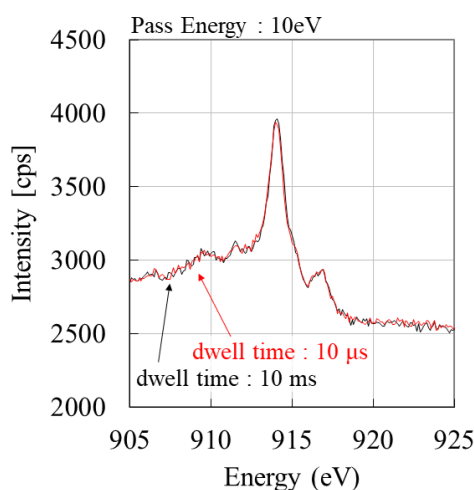


Fig. 1 Electron spectra of Cu KLL with f-HSA.

Multimodal Characterization of Polymer Surface Crystallinity using Scanning Helium Atom Microscopy and Cluster SIMS

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The optimisation of industrial polymer performance often relies on the precise control of interfacial and surface properties. Whilst traditional bulk characterisation methods such as X-ray Diffraction (XRD), Differential Scanning Calorimetry (DSC), and Vibrational Spectroscopy (FTIR/Raman) are well-established, they lack the surface specificity required to distinguish between crystalline and amorphous domains at the outermost atomic layers. This analytical gap hinders the development of advanced surface functionalities where molecular orientation and crystallinity are paramount.

Gas cluster ion beams (GCIBs) are highly versatile, having variable beam energy ranges and utilising a range of gas species. Such beam energies generate different fragmentation patterns when the bonding sites in the molecular structures are physically cleaved by varying beam energies. As an extreme example, very high beam energy generates elemental ions, but very low beam energy cannot sputter the surface therefore only backscattered ions of the beam are observed. In this work, we propose a novel Cluster SIMS approach which uses various cluster sizes of GCIBs to distinguish surface statuses regarding molecular formations or crystallinities. Preliminary Cluster SIMS results demonstrate that variations in surface morphology influence chemical bond scission energies, creating distinct fragmentation patterns that serve as "fingerprints" for specific structural states (e.g., crystalline vs. amorphous) in chemically identical polymer films.

To complement the structural data from the Cluster SIMS, we employ the Scanning Helium Atom Microscopy (SHeM) approach as a strictly non-destructive probe for these sensitive surfaces. By employing neutral, low thermal-energy helium atoms ($E < 50$ meV), SHeM achieves absolute surface sensitivity, scattering exclusively from the electron density of the topmost layer. Consequently, it enables not only scanning morphological analysis but also localised two-dimensional helium diffraction from micrometre-sized crystalline domains. Utilising diffraction contrast imaging allows visualisation of surface defects and structural changes with unprecedented sensitivity. Crystalline domains promote high-intensity specular reflection, whilst amorphous regions exhibit diffuse scattering. Therefore, SHeM may be used to image brittle, insulating, and organic surfaces without the beam-induced damage and charging effects problematic in scanning electron microscopy (SEM)[1].

This study shows an integrated multimodal approach, combining the high structural sensitivity of SHeM with chemical molecular information by Cluster SIMS. Our findings indicate that this methodology provides a comprehensive understanding of polymer surface crystallinity at the nanoscale, offering a robust pathway for optimising the next generation of high-performance surface-functionalized materials.

References:

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Keywords: Cluster SIMS, Scanning Helium Atom Microscopy (SHeM), Surface Crystallinity, Polymer, GCIB

Advances in Electron Spectroscopy for Characterizing GaN-Based HEMTs

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Gallium nitride (GaN) is a highly suitable material for the fabrication of high-performance integrated circuits designed to operate at high frequencies. In particular, GaN technology enables improvements in power levels, efficiency and compactness of HEMTs (High Electron Mobility Transistors), unlocking new functionalities for terrestrial and space telecommunication applications, in the military field (e.g., radars with active antennas for target detection) and the civilian field (e.g., 5G telecommunications).

Although HEMT-GaN technology now benefits from mature manufacturing processes, its full deployment is still hampered by electron trapping phenomena at critical interfaces (gate/barrier, passivation layers)¹. These traps, resulting from crystal dislocations, point defects, or unintentional impurity incorporation, cause structural (cavities) and chemical (interdiffusion, oxides) defects that play a key role in degrading the transistor's dynamic performance. Optimizing these next-generation devices therefore requires deciphering the correlations between electrical, chemical, and structural properties. Here we propose a correlative approach combining X-ray photoelectron spectroscopy (XPS), Auger spectroscopy (AES), and transmission electron microscopy (TEM), used in synergy to offer a new and complementary perspective on the origin of the electrical performance limitations and degradation of GaN HEMTs over time.

While Lab-XPS is not compatible with the direct analysis on device (micrometric spot), this technique has proven to bring accurate information for fabrication steps. A further limitation of conventional XPS (Al source) arises from the overlap between the N 1s photopeak and the Ga L₂M_{4,5}M_{4,5} Auger transition, which makes the determination of nitrogen content more challenging. To overcome this issue, we developed a detailed decomposition procedure based on the NLLS (Non-Linear Least Squares) method over an extended energy range encompassing both the Ga L₃M_{4,5}M_{4,5} and Ga L₂M_{4,5}M_{4,5} transitions. This method takes advantage of the twin-peak shape of these Auger features to accurately constrain the fitting parameters and will be illustrated on III-N compounds².

In parallel, we addressed the challenges associated with HEMT analysis by developing a methodology that enables Auger spectroscopy measurements directly on transistor cross-sections using our nano-probe system. To our knowledge, this innovative approach is unprecedented and has required the establishment of a dedicated protocol, including sample preparation by FIB, allowing complementary STEM-EDS analyses to be performed on equivalent samples.

Acknowledgements: The authors thanks DGA funding of GREAT project (2020 65 0049), SOITEC, UMS and FR SPE.

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2. K. Gaffar et al., J. Vac. Sci. technol. A 43, 043205 (2025)

Keywords: GaN technology, HEMT, multi-technique approach, electron spectroscopies, TEM

Intensity-energy response function of Al/Cr-K

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Aside its sensitivity to the chemical state of elements, photoemission is often used for determining material composition. Such a quantification relies on relative sensitivity factors (RSFs) involving a correction related the intensity-energy response of the used hemispherical spectrometer. Its determination was approached through a round-robin involving 13 instruments working with low (Al/Mg-K α) and high (Cr-K α) energy photon sources. An algorithm [1,2] based on the analysis of the inelastic background and the universal inelastic electron scattering cross sections (IESCS) was intensively tested against calibrated Al/Mg-K α instruments and calculated RSFs over the 15 core level peaks of coinage metals (Ag, Au, Cu). In both cases, the linear correlation within $\pm 10\%$, over two orders of magnitude in intensity and for kinetic energies ranging from ~ 400 to 1400 eV, showed the consistency of the proposed approach [2]. To do so, all the contributions to RSFs (e.g. non-dipolar terms in the photo-ionization cross section, elastic scattering effects, surface excitations, beam polarization by the monochromator) were critically reviewed and taken into account using the state-of-the-art modellings and databases. Strong variations were evidenced among instruments, regarding not only the response functions, but also the theoretical RSFs due to different measurement geometries. For the Cr-K α hard x-ray instruments for which calibration is not yet well-established, the same analysis was performed with a set of different materials (Al, Si, Ge, Fe, Co, Ni, Cu, Zn, Nb, Mo, Ag, W, Au). A $\pm 10\%$ satisfactory agreement against theoretical RSFs over 69 core levels spanning a large kinetic energy range (300–4000 eV) could be achieved with a common response function [2]. The analysis method was implemented into the recently distributed *IAP* package [3]. Its potential extension based on measured IESCS with reflection electron energy loss spectroscopy will be discussed. Despite limitations, this work opens interesting perspectives for a systematic calibration of photoemission instruments.

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Keywords: XPS/HAXPES, energy-intensity response, relative sensitivity factor, quantification

An interlaboratory study on a test material for the evaluation of area selection fidelity in small-area XPS measurements

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Small-area XPS is increasingly used for the evaluation of structures on surfaces but is missing a validated methodology for quality control [1]. Operators may thus be unable to determine if they use an incorrect field-of-view (FoV), such as sampling too large of an area, or a measurement position with an offset from the center of the structure. In such instances, electrons from the structure as well as electrons from the substrate would reach the detector [2]. To address this problem a test material was developed presenting two types of structure sets: Cr squares and Cr circles with lateral dimensions ranging from 300 to 5 μm embedded into an Au-coated substrate, see fig. 1. A metrological SEM was used to evaluate the artifact size and shape accuracy [3]. This test material is suitable for most beam sizes used in XPS for analysis of surface structures as small as 5 μm . Both a methodology and calibration artifacts are desired for improving and validating lateral resolution and area selection of XPS.

For the evaluation of the suitability of the test material and the measurement protocol a project under the auspices of VAMAS with 15 participating laboratories from all over the world measuring the dedicated XPS test material with their own instrumentation was organised. Within the VAMAS TWA 2 A47 project the test samples and measurement protocols were distributed by BAM to all participants. The participants were asked to measure all test structures with at least three different beam sizes. The results obtained are to be incorporated into the revision of ISO 18516 in ISO TC 201. Based on the measurement results, a workflow with an evaluation matrix for small-area XPS measurements is being developed to indicate when a measurement is accurate, adequate, or inaccurate.

Selected references:

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Keywords: Small-area XPS, test material, field-of-view, imaging

Developing a tiered approach to reviewing and reporting XPS data and results

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The purpose of this talk is to explore ways to address two seemingly different but related challenges with the quality of published XPS information. The first issue is the large discrepancy between information that ISO and ASTM standards require for reporting and the actual reporting (often lack of reporting) in the literature. A 2019 study noted that reporting of “required” parameters was as low as 10% but that the number of parameters required in standards was much greater than some journals expect or might allow. The need for adequate reporting is increased as AI and data archives need information to identify data of appropriate quality. The second issue is associated with peer review in papers where surface analysis is not the focus of the paper. Papers submitted by XPS users working on specific research areas are reviewed by experts in specific topics. These subject-matter experts may not have the expertise to adequately review the validity of reported XPS results. Thus, data in the literature may be flawed or without enough information to assess the quality of the results and reviewers may not have the knowledge to recognize the issue. Based on the nature of some of the data in the literature, some reviewers may not even look at the XPS data.

XPS can be applied in different ways for varying purposes and the needs for data reporting and therefore an appropriate review will depend on the nature of the use. Many of the standards focus on the requirement that the information be adequate to fully replicate the data. This results in reporting requirements that can be onerous and not fully relevant to many XPS uses. This talk explores the idea that a tiered approach might provide a useful guide for improving the reporting and reviewing of XPS data. One possible scheme involves three levels: i) Credibility Level – the data follows generally good practices and is adequate for the purpose used in the journal/report; ii) AI or Archive Level – the data and analysis are of good quality and with sufficient information about the instrument, the sample, the data and analysis so that the data is appropriate for data bases with relevant information about the context and purpose; iii) The Reference and/or Fully Repeatable Level – full information is provided that it would enable experts to fully replicate the experiments and the data reported is of “reference data” quality.

Keywords: XPS, Parameter reporting, Data reporting, review criteria

New methods for XPS depth profiling using femtosecond laser ablation

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XPS depth profiling remains one of the most widely used approaches for determining the chemical composition and electronic structure of thin films, coatings, and multilayer architectures, valued for its quantitative capability, sensitivity, and chemical state specificity. For more than five decades, depth resolution has relied predominantly on ion beam sputtering. However, ion-induced chemical damage continues to limit the accuracy of depth profiling across a wide range of organic and inorganic materials, often leading to preferential sputtering, reduction effects, and erroneous compositional data.

While argon gas cluster ion beams (GCIBs) have significantly mitigated damage in polymers and other organic systems, equivalent solutions for inorganic materials and compound semiconductors have remained elusive.

We present a newly developed XPS depth profiling platform that integrates a novel femtosecond laser ablation (fs-LA) approach, and a dual-mode ion source capable of both monatomic and gas cluster ion beam operation. Femtosecond laser ablation has been shown by Baker *et al* [1] to be a promising method for XPS depth profiling without inducing chemical state changes in the sample. By incorporating this capability with the established ion beam methods, depth profiling that is more representative of the true chemistry of the sample is possible across a broader spectrum of materials.

In addition to eliminating sputter-induced damage, fs-LA XPS depth profiling enables significantly increased profiling depths, reaching several tens of microns, while dramatically reducing analysis time compared to conventional sputter depth profiling methods.

This presentation will outline the critical experimental parameters governing fs-LA XPS implementation, including laser-material interaction considerations and optimization strategies for different material classes. Representative depth profile data from technologically relevant materials will be presented to highlight the transformative potential of this approach for advanced coatings, energy materials, and multilayer functional systems

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Keywords: XPS, Depth profiling, fs-laser ablation

Resolving Interface-Driven Properties in hybrid materials by Correlative XPS, AES and ToF-SIMS Analysis

Joachim Allouche (*Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux (IPREM) CNRS UPPA UMR 5254, Pau, France*)

In multifunctional hybrid nanomaterials, performance is governed by interfaces. Whether in core-shell nanoparticles, nanocomposite films, electrochemical stacks or bio-nano systems, the first few nanometers control reactivity, charge transfer, degradation pathways and biological interactions. Accessing these structurally and chemically complex interphases requires a correlative surface-analysis strategy combining chemical specificity, lateral resolution and controlled depth access.

We present an integrated methodology based on X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) coupled with Scanning Auger Microscopy (SAM), and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), supported by advanced cross-section preparation using focused ion beam and mechanical cross-polishing. XPS provides quantitative surface composition and chemical-state identification within the top 5–10 nm. AES/SAM enables elemental mapping with lateral resolution down to 5–10 nm, allowing single-particle and intergranular analysis. ToF-SIMS delivers molecular and fragment information from the outermost 1–2 nm, granting access to organic functionalities and interfacial reaction products.

This correlative workflow enables direct visualization of buried interfaces in core-shell and alloyed nanoparticles, revealing nanoscale elemental segregation and heterogeneity. In hybrid block copolymer/metal nanoparticle films, the combination of XPS and ToF-SIMS discriminates between grafted functionalities, polymer domains and inorganic phases, linking nanostructuration to surface chemistry. In battery electrode stacks, cross-sectional AES/SAM mapping identifies interfacial degradation products and elemental redistribution within particle aggregates, establishing direct correlations between interphase chemistry and electrochemical performance.

A distinctive contribution of this work concerns bio-nano interfaces, a domain where correlative surface analysis at the nanoscale remains scarce in the literature. By combining ToF-SIMS molecular imaging with AES elemental mapping and XPS chemical-state analysis, we resolve nanoparticle-bacteria interfaces at the single-cell level and monitor enzymatically induced surface transformations. This approach enables identification of surface chemical modifications triggered by microbial activity and provides direct evidence of interface generation during biodegradation processes.

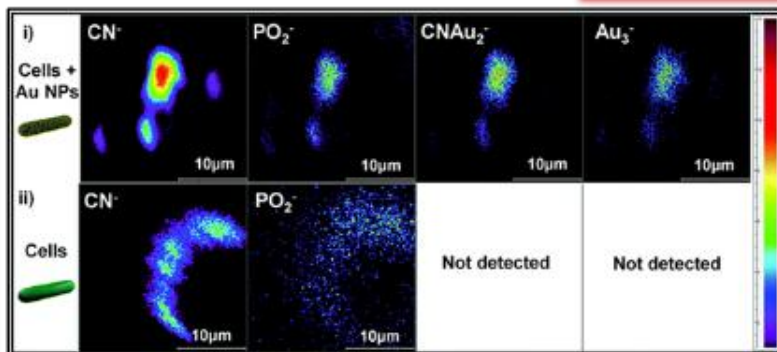
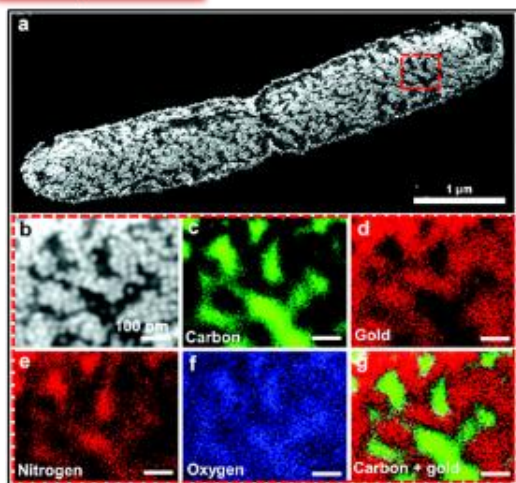
Beyond specific systems, the key outcome is methodological: controlled access to buried and reactive interfaces, multiscale spatial resolution, and depth-sensitive chemical-state analysis within a unified analytical framework. By positioning the interface as the central object of investigation, this multimodal strategy establishes a transferable surface-science toolbox for decoding structure-chemistry-property relationships in complex hybrid nanomaterials.

Keywords: multifunctional hybrid nanomaterials, XPS, AES, ToF-SIMS

AES/SAM

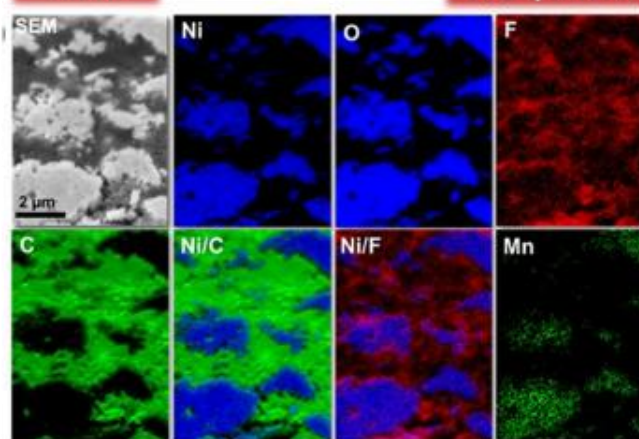
Bio-nano-interfaces

ToF-SIMS



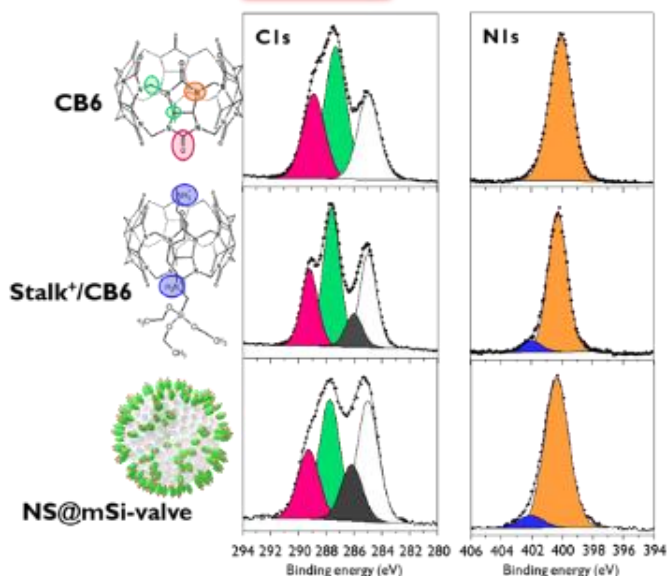
SEM

AES/SAM



Lithium Batteries

XPS



Core-shell nanoparticles

Surface techniques for interfaces characterization in hybrid materials

Non-Destructive Characterization of Film Thickness and Fractional Coverage Utilizing XPS and StrataPHI

Kateryna Artyushkova (Physical Electronics Inc, Chanhassen, USA), **Norb Biderman** (Physical Electronics Inc, Chanhassen, USA), **Amy Ferryman** (Physical Electronics Inc, Chanhassen, USA)

Atomic layer deposition (ALD) is widely used due to its precise deposition capabilities, allowing for the creation of very thin, conformal, and high-quality films on the nanometer scale. These films are ideal for applications requiring precise barrier layers, passivation layers, or protective coatings in complex geometries, particularly in microelectronics, sensors, and medical devices. ALD deposition of alumina offers several advantages, including uniform coating on complex 3D structures, precise thickness control, high purity, and suitability for sensitive substrates due to its low deposition temperature. The self-limiting behavior of ALD cycles allows for controllable film growth in which a homogenous film can be achieved at the lowest film thickness. To control the thickness in a range of few nanometers, it is important to understand the interaction between the reactants and substrate during the nucleation period, or the first few cycles. X-ray photoelectron spectroscopy (XPS) is a well-established technique for non-destructive analysis of the chemical composition of thin layers and interfaces. By analyzing a material at varying takeoff angles between the sample and analyzer, angle dependent XPS (ADXPS) can be utilized to probe the thickness and chemical composition of thin films without creating ion beam-induced damage associated with destructive sputter profiling. The spectral results obtained by ADXPS can be furthered evaluated by StrataPHI, a software product designed by Physical Electronics, to calculate not only the thickness of thin films but also provide an estimate of fractional coverage, which is of great importance for high-throughput metrology of thin-film structures. This presentation will highlight the benefits of utilizing angle dependent XPS in combination with StrataPHI modeling software to non-destructively characterize and simultaneously calculate the layer thickness and fractional coverage of a series of aluminum oxide films deposited on glass substrates throughout the nucleation period by the ALD process.

Keywords: ALD, thickness, coverage, XPS, HAXPES

Effect of ambient humidity on scanning electrochemical cell microscopy measurements

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Scanning electrochemical cell microscopy (SECCM) [1] is a state-of-the-art nanoelectrochemical technique for measuring and mapping of a variety of redox processes at interfaces with high resolution. Over the past decade, SECCM has become an important tool for studying heterogeneous electrochemical activity in a wide range of systems, including electrocatalytic materials, corrosion processes, and electrochemical energy storage systems [2-3]. By confining the electrochemical cell to a nanoscale liquid meniscus formed at the tip of an electrolyte-filled nanopipette, SECCM allows localized probing of surface reactivity while minimizing perturbation of the investigated interface.

SECCM usually relies on highly confined measurements inside of a small liquid droplet formed between an electrolyte-filled nanopipette, containing a quasi-reference counter electrode and a conductive substrate, that acts as a working electrode. This configuration is very advantageous as it is conceptually very simple and allows collection of localized information of local reactivity via faradaic current measurements at a constant or dynamically scanned potentials.

Despite the widespread application of SECCM, the influence of environmental conditions on measurements has received surprisingly little attention. In particular, the extremely small volume of the SECCM meniscus suggests that evaporation may occur rapidly under ambient conditions. Changes in evaporation rate are expected to strongly depend on relative humidity and may significantly affect electrolyte concentration, ionic speciation, local mass transport, and reaction kinetics within the droplet.

Here, we would like to draw the attention to a very important factor that remained ignored in SECCM experimentation – relative humidity. Small dimensions of the liquid droplet in SECCM suggest an enormous rate of evaporation that has profound effect on speciation, local kinetics, mass-transport and even chemistry of the processes in SECCM. We illustrate the influence of this parameter on SECCM in several example experiments and also with help of numerical simulations show that ignoring this parameter could lead to a completely erroneous interpretation of SECCM data.

These findings highlight the importance of environmental control in SECCM experiments and provide practical guidelines for improving the reproducibility and quantitative reliability of nanoscale electrochemical measurements.

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Keywords: Scanning electrochemical cell microscopy (SECCM), Relative humidity, Nanoscale electrochemistry, Electrochemical interfaces, Evaporation effects

On the Application of Ambient SKPFM for Surface Electrochemical Studies**Reynier Revilla** (*Materials and Chemistry, Vrije Universiteit Brussel, Brussels, Belgium*)

Scanning Kelvin Probe Force Microscopy (SKPFM) has become a widely used tool for assessing local surface potentials with sub-micrometric resolution. In corrosion and electrochemical research, it is frequently employed to infer relative nobility differences, micro-galvanic interactions, oxide film behaviour, and surface reactivity. However, the interpretation of Volta potential differences measured in air remains non-trivial and requires careful consideration of the underlying electrochemical and physicochemical phenomena.

This presentation discusses the application of ambient SKPFM to investigate surface electrochemical processes through selected case studies. First, the role of SKPFM in understanding micro-galvanic corrosion phenomena is addressed, highlighting key interpretation challenges and factors that may compromise data reliability. Second, a novel in situ methodology for monitoring the repassivation kinetics of aluminium in air is presented, demonstrating how time-resolved Volta potential measurements can provide insight into native oxide film growth. Third, the influence of controlled thermal oxide layers on hydrogen transport through steel surfaces is discussed, emphasising the importance of surface state in degradation phenomena. Finally, the direct correlation between local surface potential and electrochemical potential in $\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes is shown, illustrating the quantitative capabilities of SKPFM beyond corrosion systems.

Together, these examples demonstrate the versatility of ambient SKPFM as a powerful surface-sensitive technique for studying electrochemical phenomena across different material systems, while underlining the importance of rigorous interpretation and methodological standardisation.

Keywords: Scanning Kelvin Probe Force Microscopy, Surface electrochemistry, Micro-galvanic corrosion, Oxide film growth, Local potential mapping

Cryo-XPS Characterisation and Advancing Solution-Representative Analysis of Functional Nanoparticles

Liam Soomary (Kratos Analytical Ltd, Manchester, UK), **Simon Hutton** (Kratos Analytical Ltd, Manchester, UK), **Chris Blomfield** (Kratos Analytical Ltd, Manchester, UK)

A central aspect of nanoparticle design involves the precise control and thorough understanding of surface functionalisation. While structural characterisation is commonly achieved using methods such as Transmission Electron Cryomicroscopy (cryoTEM), obtaining robust quantitative information about *surface* chemistry continues to present significant challenges.

X-ray Photoelectron Spectroscopy (XPS) is widely regarded as a powerful method for quantitative surface analysis due to its strong sensitivity to elemental composition and chemical bonding environments. Nevertheless, the necessity of ultra-high vacuum (UHV) conditions can disrupt the native environment of many organic nanoparticle systems. Sample preparation by removal of solvent raises concerns regarding potential alterations in morphology and the integrity of surface-bound functional groups. Emerging cryogenic approaches to sample preparation for XPS analysis (cryo-XPS) have been developed to address these limitations. By rapidly vitrifying liquid samples, nanoparticles can be retained in a near-native state under UHV, thereby reducing preparation-induced artefacts and allowing interrogation of surface chemistry with minimal structural disturbance.

This talk explores the methodology and complementary strategies for studying nanoparticles in solution and emphasises the advantages of cryo-XPS for examining surface-functionalised systems. Focus is placed on polyethylene glycol (PEG)-modified nanoparticles, which are extensively employed in drug delivery and biomaterials applications. Using lipid nanoparticles as a representative case study, we demonstrate how careful optimisation of sample preparation, transfer, and analytical protocols can significantly enhance the reliability of quantitative surface characterisation of nanoparticle materials.

Keywords: cryo-XPS, nanoparticles, X-ray photoelectron spectroscopy

High Sensitivity Analysis of Reflection Electron Energy Loss Spectra Using Spectrum Image

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The miniaturization and increasing complexity of semiconductor devices have intensified the demand for analytical techniques capable of probing surface states with high spatial resolution. Conventional methods such as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have long been used for surface analysis; however, the versatility of large-aperture energy-dispersive X-ray spectroscopy (EDS) operated at low accelerating voltages has recently broadened its use. Although low-voltage EDS enables surface-sensitive elemental analysis, it suffers from limitations including significant peak overlap due to the predominance of outer-shell characteristic X-rays and restrictions on the applicable accelerating voltage required for efficient detection.

To address these challenges, the present study focuses on reflection electron energy loss spectroscopy (REELS) using low-energy incident electrons. REELS provides access to electronic structures, band gaps, unoccupied states, and surface-specific features such as hydrogen, lithium, and defect states through the analysis of energy losses of electrons reflected from the outermost surface. In particular, elastic scattering peaks exhibit subtle energy shifts and changes in full width at half maximum (FWHM) as a result of recoil effects that depend on the atomic composition of the sample [1]. Although recoil-induced spectral variations have been observed previously, extracting these differences in the form of spatial distributions has been difficult because their magnitude is extremely small, typically below 1 eV.

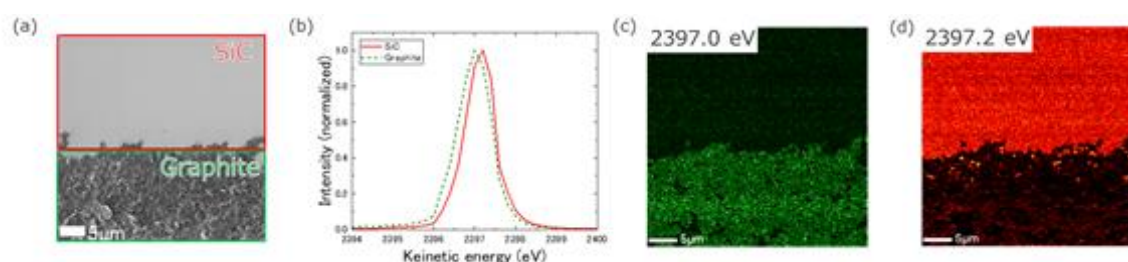
In this work, we demonstrate that Spectrum Image acquisition and analysis enable the extraction of recoil-induced peak shifts as spatial maps with sub-eV sensitivity [2]. A test sample consisting of colloidal graphite deposited on a SiC substrate was analyzed under the following conditions: accelerating voltage 2.4 kV, probe current 2 nA, pass energy 10 eV, energy step size with 0.2 eV. The elastic peak from the low-atomic-number graphite region showed a recoil-induced shift of approximately 0.2 eV relative to that of SiC, and this difference was successfully visualized as a two-dimensional distribution.

The proposed method offers a high-spatial-resolution, low-damage surface analysis technique that complements or surpasses low-voltage EDS for materials characterization. Its applicability to a wide range of materials systems highlights its potential as an advanced analytical tool for surface-sensitive investigations in materials science.

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Keywords: AES, Spectrum Image, REELS, elemental analysis



(a) Secondary electron image of the analysis area. (b) spectra extracted from the Spectrum Image (solid line: SiC region; dashed line: colloidal graphite region). (c) spatial map extracted at the 2397.0 eV peak and (d) spatial map extracted at the 2397.2 eV peak

Unveiling the Water/Solid Interface in Low-Carbon Cements through Cryo-XPS

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Concrete is the second most used substance by humanity, after water. Its production relies on Portland cement (PC), which contributes about 8% of global anthropogenic CO₂ emissions. Most of these emissions come from clinker, formed by the thermal decomposition of limestone: $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ ($T \approx 1450^\circ\text{C}$), releasing 0.8 tons of CO₂ per ton of clinker. A promising approach to reduce cement's carbon footprint is partially replacing clinker with supplementary cementitious materials (SCMs). Among these, calcined clays are particularly attractive, and cements containing them are already produced and used in some countries.¹

Considering that concrete hardening is driven by the hydration reactions of clinker in the presence of aggregates, studying the interactions at the water/calcined clay interface is essential to understand the hardening process of this type of low-carbon concrete. One particularly relevant interaction is the electrostatic interaction between clay particles and the ions present in water. Indeed, the hydration water in concrete has a high pH, meaning that the silanol (Si–OH) and aluminol (Al–OH) groups on the surface of calcined clay particles can become deprotonated. As a result, the particles carry a negative surface charge, which is balanced by cations present in the water.

In this contribution, a XPS study of the water/calcined clay interface is presented. To preserve the water/solid interface under ultrahigh vacuum conditions, we performed cryo-XPS experiments, in which the interface was rapidly frozen to prevent water crystallization and maintained in this state throughout the measurement process. We show that the results cannot be interpreted using simple methods based on the relative sensitivity factors (RSFs) of the analyzed core levels. Instead, we simulated the peak areas using SESSA software² with relatively simple models, given the complexity of the interface. Model optimization allowed us to calculate the surface charge density of the particles at different pH values, which agreed well with alternative measurements of the same parameter obtained by potentiometric titration. We thus demonstrate that the methodology developed—combining cryo-XPS experiments with SESSA simulations—is a more powerful approach than previous studies of inorganic water/solid interfaces using RSF-based cryo-XPS analysis.³

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Keywords: XPS, surface analysis, cryo-measurements, water interfaces, SESSA

Microscopic Origins of Surface Loss in Thin Silicon Nitride Membranes: A Multi-Technique Profiling Approach

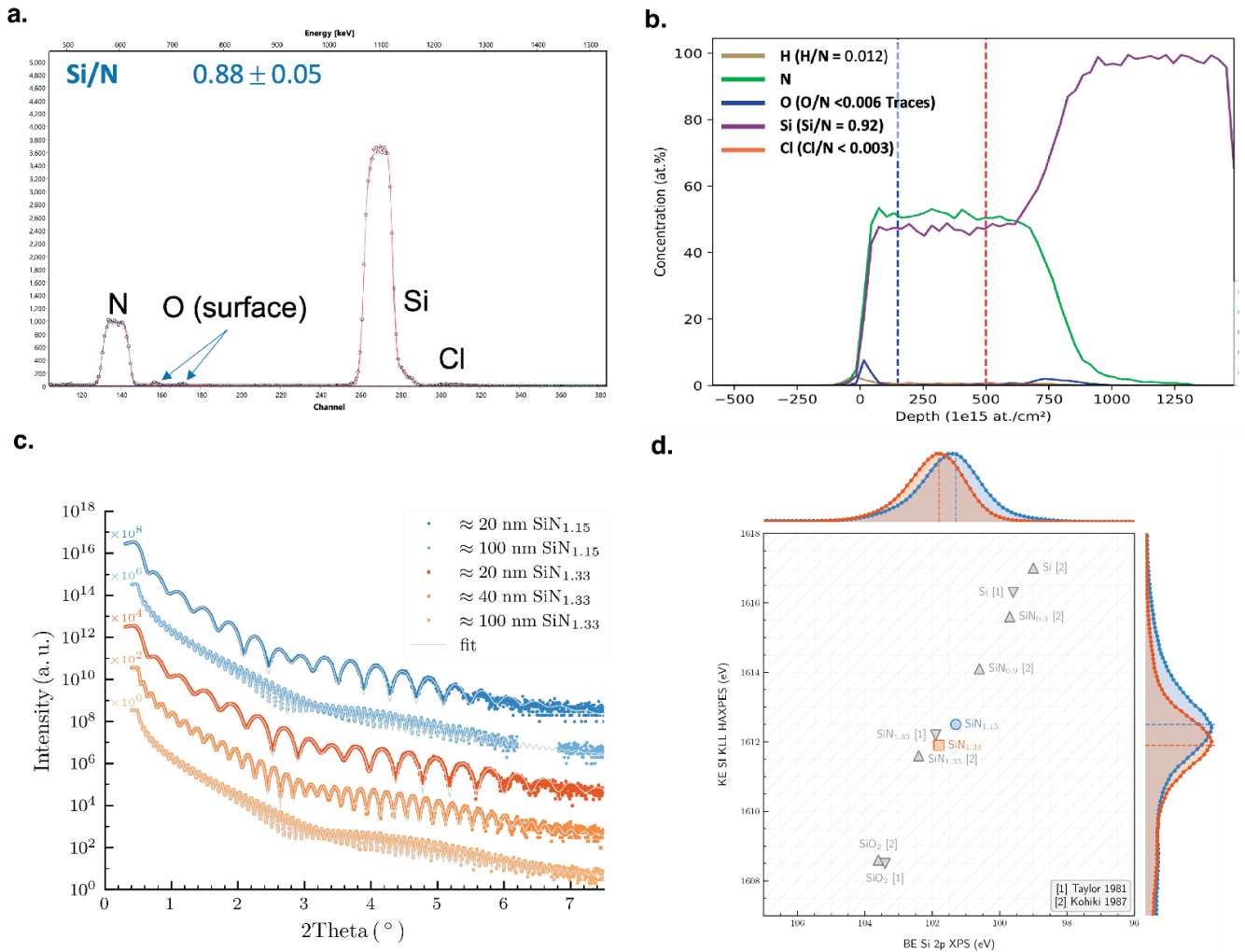
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High-stress silicon nitride (SiN) thin membranes are leading mechanical resonators for quantum optomechanics and sensing, combining low mass with exceptionally high-quality factors and $Q \cdot f$ products at room and cryogenic temperatures. For operation well in the quantum regime, further enhancement of their intrinsic (i.e., material related) quality factors is required. For the ultra-thin membranes, and the most sensitive ones, energy dissipation scales linearly with thickness and is therefore governed by surface loss, rendering the membrane surface the key bottleneck for Q -factor improvement. Despite this strong phenomenological evidence, a microscopic understanding of the origin and distribution of these loss channels is still lacking, largely due to the experimental challenge of performing accurate, quantitative and depth-resolved analysis on nanometre-scale membranes while preserving their mechanical integrity.

This contribution presents a technique-driven metrology framework that combines and adapts a suite of complementary methods to obtain a comprehensive microscopic picture of the surfaces and near-surface regions of SiN quantum-grade membranes. For quantitative elemental and light-species, i.e., H, depth profiling on the tens-of-nanometres scale, we employ ion beam analysis in the form of Rutherford Backscattering Spectrometry (RBS; Fig 1a) and Elastic Recoil Detection Analysis (ERDA; Fig 1b), exploiting their capability for absolute, model-traceable thickness and composition determination in complex thin-film stacks. X-ray reflectivity (XRR) and spectroscopic ellipsometry constrain film thickness, mass density, and optical constants and are jointly modelled with IBA data to reduce parameter degeneracy and improve accuracy (Fig 1c). The chemical states and depth-dependent bonding environments are probed via X-ray Photoelectron Spectroscopy (XPS) and Hard X-ray Photoelectron Spectroscopy (HAXPES), extending sensitivity from the topmost surface into the buried SiN bulk (Fig 1d). Infrared nanomechanical photothermal sensing allow us to extend our understanding of the chemical states to light-species, e.g., H, which is not accessible by XPS and HAXPES. Employing Electron paramagnetic resonance (EPR) on samples of different thickness and stoichiometries, allows us to quantify paramagnetic defect centres and determine their distribution across the membrane. Paramagnetic defect centres are potential microscopic loss channels in high- Q resonators.

By carefully tuning and cross-calibrating these techniques—originally optimized for more conventional thin-film systems—we establish an integrated metrology platform tailored to free-standing, ultra-thin SiN membranes. The resulting dataset directly links elemental composition, bonding configuration, defect populations, optical properties and density to regimes known to be surface-loss-limited, thereby providing the experimental groundwork needed to rationally engineer surfaces and interfaces for next-generation, ultra-low-dissipation mechanical resonators in the quantum regime.

Keywords: XPS/HAXPES, Ion Beam Analysis, X-ray reflectivity, Electron paramagnetic resonance, Photothermal nanomechanical IR spectroscopy



Applications of Spectrum Imaging Using a Fast Hemispherical Analyzer (f HSA)

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Scanning electron microscope (SEM) equipped with an electron spectrometer enable compositional and chemical-state analyses by Auger electron spectroscopy (AES) and reflection electron energy loss spectroscopy (REELS). In recent years, we have reported various measurement techniques and applications based on spectrum imaging schemes [1–4]. To further improve data-acquisition throughput, we developed a fast hemispherical analyzer (f-HSA) system, thereby accelerating both spectral acquisition and spectrum-imaging measurements. In this presentation, we introduce representative AES measurement examples obtained using the spectrum imaging capability of the f-HSA.

As a demonstration, we show an extension of the high-speed measurement capability to depth-resolved spectrum imaging (Depth-SI) by combining continuous spectrum-imaging acquisition with Ar-ion etching. Depth-SI constructs a multi-dimensional data cube that incorporates not only the lateral (X–Y) information but also the depth (Z) dimension, allowing retrospective extraction of local spectra from arbitrary positions and depths. Figure 1 presents Depth-SI results acquired from a MOS device structure. The SEM and AES measurements were operated at 30 kV with a probe current of approximately 20 nA. Ar-ion etching was performed at 3 kV for 50 cycles. Owing to the increased throughput, Depth-SI data can now be acquired efficiently within a reasonable time, enabling reconstruction of three-dimensional elemental distributions. The reconstructed 3D elemental distributions clearly visualize, for example, carbon located between Si_3N_4 regions, SiO_2 regions embedded in Si, and the spatial distribution of WSi_2 . A key feature of the proposed approach is that, in addition to 3D visualization, local spectra can be directly inspected, ensuring that map contrasts are grounded in the actual spectroscopic signals. The ability to visualize three-dimensional elemental distributions—including depth information—in near-surface thin layers highlights the utility of the method. These capabilities are expected to open new application areas that leverage the inherent surface sensitivity of electron spectroscopy.

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Keywords: AES, SAM, SEM

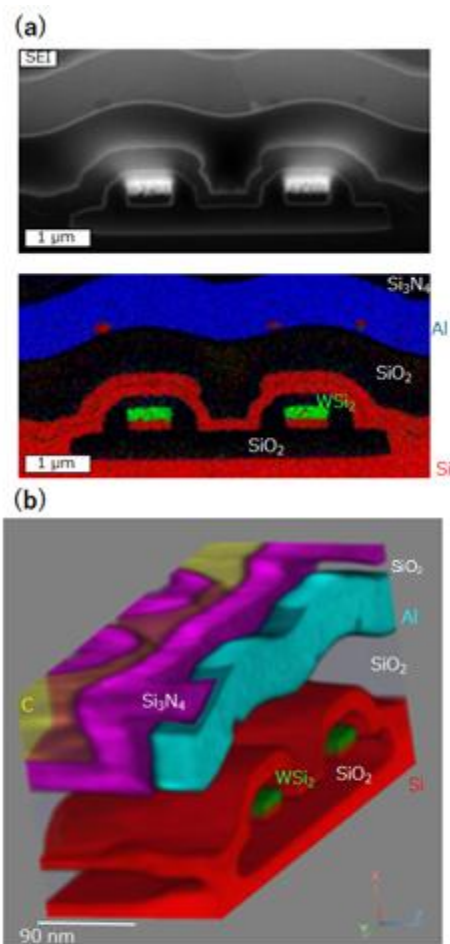


Fig. 1 (a) Cross-sectional SE image of a MOS device sample and AES maps obtained by spectrum imaging; (b) three-dimensional elemental distributions reconstructed from the Depth-SI dataset. Note that the SiO₂ regions are rendered with reduced opacity (lower contrast) in (b).

A combined Hyperspectral Imaging – Multivariate Analysis approach to surface analysis

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Multimodal analytical approaches are widely employed in various scientific disciplines to obtain complementary chemical and structural information from complex materials systems. However, particularly in surface analytics, multimodal/hyperspectral imaging has been used only in very specific cases, so far.

In this contribution, we present a hyperspectral data-fusion approach that enables the combined analysis of multiple ultra-high vacuum (UHV) surface-sensitive techniques within a single multivariate framework.

Hyperspectral imaging datasets were acquired using four partially complementary UHV-based surface analysis methods: X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Auger-Meitner Electron Spectroscopy (AMES), and low-energy Energy-Dispersive X-ray Spectroscopy (EDX). All measurements were performed on identical surface areas and subsequently spatially co-registered with high positional accuracy. Relative elemental distribution maps obtained by XPS, AMES, and EDX, together with mass-resolved ion images from SIMS, were assembled into a unified hyperspectral data cube. Principal Component Analysis (PCA) was then applied to the combined dataset to identify correlated chemical and compositional variations across the different techniques.

The approach is demonstrated using a technologically relevant failure-analysis case study on industrially produced nickel surfaces exhibiting non-wetted regions following a soldering process. Reliable identification of the chemical origins of de-wetting is essential for reducing failure rates and improving long-term process stability. In addition, we show the application of the Hyperspectral Imaging/Multivariate Analysis approach in a tribology application using MXenes. Attention was paid to minimizing beam-induced modifications of the surface, with acquisition parameters chosen to preserve the native surface stoichiometry throughout the multimodal measurement sequence.

Overall, this work establishes hyperspectral data fusion as a robust strategy for integrated surface analysis. The presented methodology enables more sensitive detection of lateral and interfacial chemical variations and might be applicable to many complex materials systems studied by complementary surface-sensitive techniques.

Keywords: Hyperspectral Imaging, Multivariate Analysis, Failure Analysis, Tribology

Operando ORP-EIS/ATR-FTIR for Real-Time Monitoring of Interfacial Degradation of Coatings Under Cathodic Polarization

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The combination of barrier coatings and cathodic protection (CP) represents a widely adopted strategy for mitigating corrosion in buried metallic structures. However, cathodic reactions induced by CP can generate reaction products that compromise coating's adhesion, leading to a phenomenon known as cathodic delamination. This process is recognized as the primary degradation mechanism for organic coatings on submerged steel substrates. Understanding the mechanisms underlying cathodic delamination, as well as exploring effective mitigation approaches, is crucial for the development of advanced protective systems with enhanced resistance to cathodic disbondment.

The diffusion of water, oxygen, and ions plays a critical role in the kinetics of cathodic protection (CP) systems as they are necessary for cathodic reactions. Understanding and monitoring these diffusion processes are fundamental because they directly influence the rate and mechanism of delamination [1]. In our research group we have developed a methodology based on the application of odd random phase electrochemical impedance spectroscopy (ORP-EIS) to differentiate between the diffusion of water and ions [2–4]. In this methodology, a two-layer electrical equivalent circuit (EEC) is used to monitor the movement of ions ingress front across the thickness of the coating. Furthermore, the time of arrival of the ions at the buried interface was calculated and verified with in situ ATR-FTIR measurements in Kretschmann geometry [4,5].

In this work, the aim is to employ this methodology to unravel the influence of cathodic polarization on the dual diffusion kinetics of water and ions in the organic coatings. The innovation of this work lays in presenting operando ORP-EIS, integrated with ATR-FTIR to monitor electrolyte diffusion and the real-time chemical and electrochemical phenomena occurring in the buried interface, during cathodic polarization. In Operando ORP-EIS technique, ORP-EIS will be performed during polarization, which is a nonlinear and non-stationary process, by superimposing a multisine AC perturbation signal on the polarization DC potential [6].

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Keywords: ATR-FTIR, Operando ORP-EIS, Cathodic polarization, interfacial disbondment

Multimodal Submicron IR microscopy for Comprehensive Materials Characterization

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High-resolution chemical imaging of surfaces and interfaces is critical for understanding heterogeneous materials, thin films, polymers, and functional coatings. Infrared (IR) and Raman microscopies are widely used, but each has inherent limitations. Conventional IR microscopy is diffraction-limited, yielding lateral resolution typically around 10–20 μm , while Raman microscopy suffers from weak scattering cross-sections, resulting in low signal sensitivity and long acquisition times. Consequently, both techniques have limited applicability for small, (sub-)micron features or complex substrates.

Here, we present Optical Photothermal Infrared (O-PTIR) spectroscopy, which overcomes these constraints by detecting IR absorption via a visible probe measuring photothermal effects. The technique enables non-contact, reflection-mode measurements with submicron spatial resolution defined by the visible wavelength rather than the IR excitation.

O-PTIR provides submicron IR chemical mapping with spectral fidelity comparable to conventional FTIR transmission or ATR measurements. Simultaneous Raman spectroscopy can be acquired from the same location, delivering correlative vibrational information without sample transfer or modification. Integration with fluorescence imaging further accelerates region-of-interest selection and improves measurement efficiency. The technique is compatible with a broad range of materials, including polymer blends, thin films, and particulate contaminants.

Representative applications will be highlighted to illustrate the versatility of O-PTIR: mapping polymer phase separation at submicron scales, identifying multi-layered coatings and particulate contamination on glass and metallic surfaces, and characterizing chemical heterogeneity in microstructured or functional thin films. Its robust multimodal capabilities, high spatial and chemical resolution, and adaptable measurement conditions establish O-PTIR as a powerful tool for surface and interface analysis across materials science, cultural heritage, and related fields.

By achieving submicron spatial resolution, high chemical sensitivity, and simultaneous multimodal measurements, O-PTIR significantly outperforms existing microscopy methods, enabling detailed surface and interface characterization that was previously inaccessible with traditional vibrational techniques.

Keywords: Optical Photothermal Infrared Spectroscopy (O-PTIR), Multimodal Vibrational Spectroscopy, Submicron Chemical Mapping, Surface and Interface Analysis

Disentangling Beam-Induced Artefacts in Chemically Amplified Resist ToF-SIMS and Orbitrap™-SIMS Depth Profiling

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Photolithography is a patterning technique central to semiconductor manufacturing which relies on photosensitive thin films called photoresists. One of the most used photoresist types is Chemically Amplified Resist, composed of a copolymer matrix containing molecular additives. The achievement of sub-20 nm feature sizes in advanced lithography is hindered by nanoscale inhomogeneities in the distribution of these additives. Characterizing these variations and understanding their origins requires characterization tools capable of identifying molecular species and their spatial distribution within the film at the nanometre scale.

ToF-SIMS and Orbitrap™-SIMS currently provide the most suitable capabilities, offering molecular depth profiling with ~5 nm resolution. Both techniques use Gas Cluster Ion Beams (GCIB) to sputter organic material with minimal damage. In most ToF-SIMS systems, an Ar GCIB performs erosion between static LMIG analysis cycles, whereas Orbitrap™-SIMS uses a single Ar GCIB beam in dynamic mode. As a result, the primary-ion conditions for secondary-ion generation differ. Orbitrap™-SIMS asset lies in its mass resolution, providing accurate chemical identification whereas ToF-SIMS spectra of photoresist suffer from mass interference between multiples overlapping molecular fragments.¹

Many studies have highlighted the merit of Orbitrap™-SIMS high mass resolution, yet beam-sample interactions have received little attention. Recent reports suggest that using Ar GCIB as a single dynamic beam in Orbitrap™-SIMS enhance depth resolution and reduce chemical damage.^{1,2} However, when Ar GCIB is applied as an analysis beam in ToF-SIMS, beam-induced artefacts emerge, differing between static and dynamic sputtering.^{3,4} These discrepancies have not been addressed yet.

In this work, we first demonstrate how such artefacts would affect depth profiles on organic photoresist films with thicknesses varying between 30 and 90nm. We compare data taken on two ToF-SIMS dual-beam configurations: (1) LMIG (static analysis) + GCIB erosion, and (2) GCIB (static analysis) + GCIB erosion, and an Orbitrap-SIMS with a single Ar GCIB beam. This comparison allows to disentangle the respective contributions of GCIB-related analysis artefacts from dynamic sputtering conditions to the observed depth-profile distortions in organic photoresist films. This is a stepping stone towards clarifying the link between analysis conditions and their impact on the collected data, preventing erroneous data interpretation.

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Keywords: ToF-SIMS, Orbitrap-SIMS, Photoresist, Ar GCIB, depth profiles

Study of ion transmission in OrbiSIMS to detect molecular structure

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Orbitrap secondary ion mass spectrometry analysis (OrbiSIMS) [1] is performed on an instrument that uses a hybrid approach combining the high mass resolution of an Orbitrap analyser with the speed and high spatial resolution of a time-of-flight (ToF) analyser. This approach has been growing in popularity in a wide range of applications in life sciences and materials science.

For ion transfer in OrbiSIMS, the sample is biased by a target voltage V_T necessary to match the acceptance window of the Orbitrap.[2] It has been shown that controlling this parameter gives OrbiSIMS the ability to separate molecules based on their dissociation patterns which are related to molecular structure. Leveraged this phenomenon analytically took OrbiSIMS beyond the limitations of the m/z scale and spatially resolved the signal of structural isomeric trisaccharides [3].

This project aims to expand the method and apply it to isomer mixtures, searching for a quantitative measure that demonstrates the relative concentrations of the mixtures as well as their spatial relationship. The preliminary studies on ion transmission are of trisaccharides; systematically varying the target voltage and studying transmission of molecular ions and their fragments for OrbiSIMS. The next step will be to apply this method to the ion transmission of fatty acids which are building blocks of lipids. The ability to spatially resolve isomeric biomolecules in mixtures using SIMS could be transformative as these types of molecules play important biological roles.

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Keywords: OrbiSIMS, mass spectrometry, imaging

Correlative XPS and SEM/EBSD with Cluster Ion Etching for Enhanced Surface Preparation

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Correlative imaging and surface analysis (CISA) provides a powerful framework for comprehensive materials characterisation by integrating complementary analytical techniques within a unified workflow. In this work, we demonstrate the application of a correlative approach combining X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD), and Raman spectroscopy, supported by cluster ion etching for enhanced surface preparation.

Two case studies highlight the capabilities of this methodology. First, single-crystal MoS₂ flakes on silicon were analysed using combined XPS, Raman, and SEM. Spatially resolved XPS revealed distinct molybdenum chemical states, including sulphide and oxidised species, while Raman spectroscopy identified variations in layer thickness. Correlation with SEM imaging confirmed differences in flake morphology and density, linking structural variation with increased oxidation in multilayer regions. Second, a low-alloy, high-carbon steel sample was investigated using correlative XPS and EBSD. XPS line scans quantified iron oxidation states and oxide thickness variations across the sample, while EBSD mapping—enhanced by cluster ion etching—provided high-quality phase and orientation information, confirming a mixed austenite–martensite microstructure.

These results demonstrate that a multi-technique, correlative approach is essential for capturing both chemical and structural complexity in advanced materials. The CISA workflow enables seamless navigation between instruments while maintaining precise regions of interest, significantly improving analytical depth and confidence.

Keywords: XPS, EBSD, Correlative, Workflow, Raman

Use of XPS-CREM for detecting hydration-driven changes in the electrical conductivity of $\text{La}_2\text{Ce}_2\text{O}_7$ thin films

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Chemically Resolved Electrical Measurements (CREM)¹ harnesses the charging-like effects in X-ray Photoelectron Spectroscopy (XPS) to extract sample's electrical properties. Here, we apply CREM to investigate a novel proton-conducting material made of hydrated $\text{La}_2\text{Ce}_2\text{O}_7$.² Conventional electrical measurements show that the activation energy for conductance decreases from ~ 1.07 eV in the as-deposited film to ~ 0.7 eV after hydration. We attribute this reduction to a change in the dominant transport carriers: electron conduction via oxygen vacancies in the as-deposited film and proton conduction in the hydrated film.

As temperature decreases from 473 to 360 K, both films become less conductive; however, hydrated $\text{La}_2\text{Ce}_2\text{O}_7$ exhibits weaker temperature dependence: At 360 K, its conductance is approximately five times higher than that of the as-deposited film. Measurements below this temperature failed, because the films become too resistive for conventional measurements, preventing reliable room-temperature characterization.

To overcome this limitation, we employed CREM within the XPS chamber to evaluate conductivity at room temperature under ultra-high vacuum. In brief, CREM modulates the electron flood gun while simultaneously measure (1) the net current through the sample and (2) the shifts in core-level binding energies, reflecting resistive potential drops. The ratio of current changes over energy shifts, provides an effective film's perpendicular conductivity.¹ CREM measurements (see figure) revealed that, at room temperature, hydrated $\text{La}_2\text{Ce}_2\text{O}_7$ was roughly three orders of magnitude more conductive than the as-deposited film, consistent with the expected exponential dependence on activation energy. Although XPS cannot directly detect hydrogen, the sustained high conductivity under vacuum supports stable proton incorporation within the lattice.

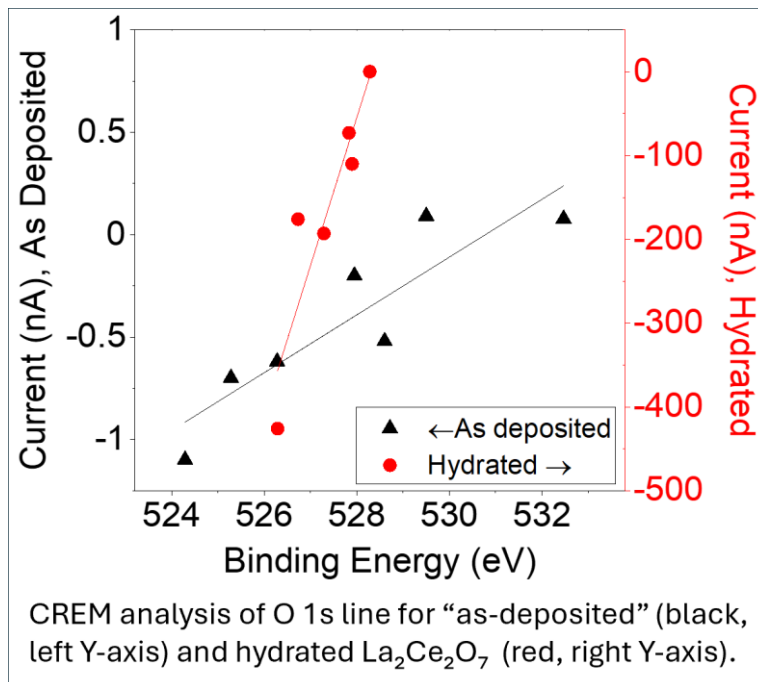
To directly probe proton transport, we deposited proton-sensitive WO_3 , which turns from transparent to opaque upon proton insertion (H_xWO_3), accompanied by reduction of W(VI) to W(V). Devices comprising ITO/ $\text{La}_2\text{Ce}_2\text{O}_7$ / WO_3 exhibited bias-induced coloration only when $\text{La}_2\text{Ce}_2\text{O}_7$ was hydrated. Furthermore, CREM-driven proton injection revealed a significant shoulder of reduced-tungsten in the W 4f line, characteristic of W(V), only when the underlying $\text{La}_2\text{Ce}_2\text{O}_7$ was hydrated. These results confirm proton-mediated transport.

The presentation will outline the CREM methodology and its application to study of $\text{La}_2\text{Ce}_2\text{O}_7$ and $(\text{H}_x)\text{WO}_3$

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Keywords: CREM, XPS, proton conductor, $\text{La}_2\text{Ce}_2\text{O}_7$, WO_3



X-Ray Photon Electron Spectroscopy degradation study on insulating samples

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XPS measurement can cause chemical degradation of samples [1]. This degradation makes it difficult to directly access at surface characterisation, but slow degradation allows original data to be extracted from both the initial and degraded states. This is particular relevant when dealing with insulating samples since neutralization using an electron source is often mandatory to get proper measurement. However, this flow gun may also induce damage and deciphering its impact from the X-ray beam damage is crucial in order to finally optimize measurement conditions.

In this work, we first performed measurements on cellulose using monochromatic Al K α and monochromatic Ag L α . As a first approximation, we showed that the degradation is mainly due to the photon flux and not to the neutralizer. Then we also characterize the variation of the degradation rate with the Ag source compare to Al source with the same resolution and spectrum intensity.

In a second step, based on the previous step, the surface chemistry of heterogeneous thin films of iron oxalate complexed by propylene glycol was characterized. We performed the measurement of the iron sample at room temperature and at 163 K. Using the PCA projection [2], and linear least square fit. [3,4] we achieved to extract the non-degraded component and the degraded one Fig. [1].[MR1] .. [MR2] Two iron chemical environments and 3 carbon chemical states were identified after data treatment. Cooling these iron samples reduces X-ray degradation by a factor of about 5 meaning that information on the pristine sample could be extracted.

Keywords: XPS, Iron, Degradation

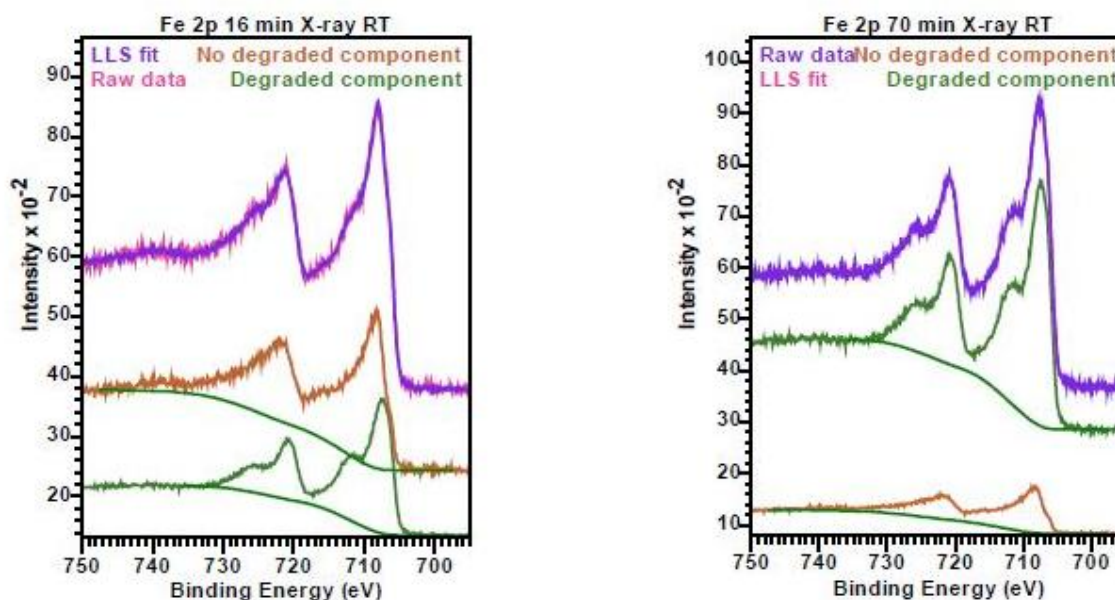


Fig 1: Iron Fe 2p peak modeling after exposure to X-ray (300W) and neutralizer for 16 (left hand side), 70 minutes (right hand side)

Combined XPS and HAXPES for Overlay Analysis

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The use of photoemission spectroscopy for analysis of layered systems is a well-established, reliable, and precise technique. The measurement of silicon oxide layers on silicon was one of the first standards developed under ISO for photoemission spectroscopies¹, and BIPM key comparisons have demonstrated that XPS is the most accurate technique for measurement of planar overlayers on the <10 nm scale². Likewise, studies have shown the strength of XPS measurement of coatings on a variety of structures, including micro/nanoparticulate materials³.

HAXPES instrumentation, with its greater information depths and broader energy range, improves this capability by allowing measurement of thicker overlayers. In addition, this larger information depth results in a corresponding slight reduction in surface sensitivity, thus reducing susceptibility to any inhomogeneity in coating thickness. By taking account of these differences, HAXPES measurements can thus be used in tandem with traditional XPS to provide additional information about coating thickness and variability, improving measurement accuracy. The challenge of how to combine information from different X-ray energies requires attention.

Here we outline methods to combine information and demonstrate the improvements provided by HAXPES when measuring coating thicknesses for samples with heterogeneous coatings, as well as a method for removing the influence of damaged overlayers from spectra e.g. as produced during ion beam sputtering.

Examples of typical coating thickness measurement using both XPS and HAXPES are shown for simple planar silicon oxide films as a model system. The same methods are also demonstrated and compared for some more complex nanoparticle systems with silica coatings on either iron oxide nanoparticles or lanthanide-based up-conversion nanoparticles.

Additionally, we show a method by which both techniques can be combined for flat systems with rough or inconsistent coatings to obtain more accurate results than can be achieved by XPS or HAXPES alone. These methods and the advantages of HAXPES for measurements of coatings and overlayers are discussed in the context of the development of future standards for HAXPES under ISO.

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3. doi:10.1021/acs.jpcc.6b06713.

Keywords: XPS, nanoparticles, coatings, overlayers, thickness

Hard X-ray photoelectron spectroscopy with photon energy up to 40 keV for characterization of deeply buried interfaces

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Hard X-ray photoelectron spectroscopy (HAXPES) is a powerful technique for investigating the chemical and electronic states of bulk materials and buried interfaces non-destructively, thanks to its significant probing depth. However, the typical probing depth of conventional HAXPES (up to 10 keV) is often insufficient for examining complex multi-layered structures, such as the semiconductor devices or electrochemical energy storage materials like battery electrodes. In these practical applications, the regions of interest are often buried under layers exceeding several tens of nanometers. Such limitations frequently necessitate destructive sample preparation, including the thinning or removal of electrodes and insulators, which may alter the intrinsic chemical or electronic states at the critical interfaces. To overcome these challenges and achieve a much larger probing depth, we have developed a high-energy HAXPES (HE-HAXPES) system utilizing photon energies up to 40 keV. This system is implemented by combining a conventional hemispherical electron energy analyzer with an applied bias voltage to the sample [1]. The capability of this system was demonstrated using a 200-nm-thick SiO₂ film on Si substrate. Figure 1 shows the Si 1s spectra measured at excitation energies ranging from 10 to 40 keV. At a photon energy of 10 keV, no signal originating from the Si substrate was detected, indicating that the probing depth was insufficient to reach the buried interface. In contrast, at 20 keV, a weak signal assigned to the bulk Si substrate began to appear around a binding energy of 1840 eV. Furthermore, at 30 and 40 keV, the Si substrate signals were clearly observed with increasing intensity. These results clearly demonstrate that the probing depth increases as a function of the excitation X-ray energy, enabling the non-destructive observation of regions deeper than 200 nm. However, it was also observed that the energy resolution significantly degrades at these higher excitation energies. We recognize this as a critical technical challenge, and further improvements in the optics and experimental setup are required to achieve higher precision for detailed electronic structure analysis. Nevertheless, the HE-HAXPES system excited up to 40 keV serves as a promising tool for providing genuine insights into the electronic states of deeply buried functional layers in a wide range of materials. We will also discuss the application of this method to other functional materials and its future outlook.

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Keywords: Hard X-ray photoelectron spectroscopy, HAXPES, High energy

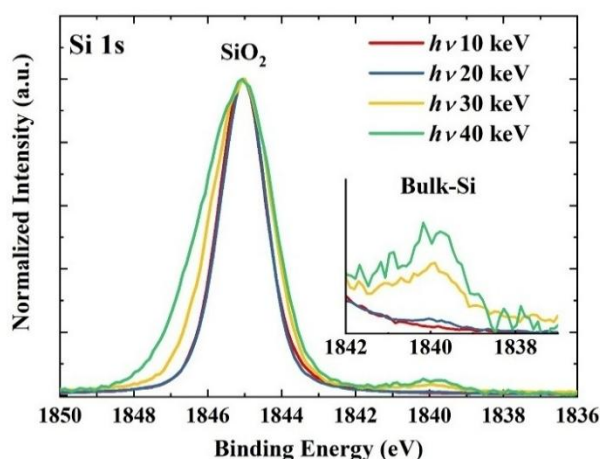


Figure 1: Fig. 1. Si 1s spectra of a 200-nm-thick SiO₂ film on a Si substrate measured at excitation energies ranging from 10 to 40 keV.

Quantification challenges of binary compounds using Hard X-ray Photoemission Spectroscopy (HAXPES)

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Hard X-ray photoelectron spectroscopy (HAXPES) extends the probing depth of conventional laboratory XPS and enables access to the chemistry of buried elements. This gain in information depth, however, also makes quantitative analysis more challenging, since peak intensities become increasingly sensitive to photon-energy-dependent photoionization cross sections, (in)elastic electron transport, experimental geometry and analyzer transmission [1,2]. Recent literature has therefore emphasized that reliable HAXPES quantification requires careful treatment of both the inelastic background and the relative sensitivity factors used for composition calculations [1,2,5].

In this work, these challenges are investigated on simple homogeneous binary compounds involving light and heavy elements, with potential relevance to material families such as sulfides (e.g., MoS₂, WS₂), nitrides (e.g., GaN, TaN, NbN), and oxides (e.g., SiO₂, TiO₂). The study examines how the inelastic background influences peak-area determination in the hard X-ray regime, where energy-loss contributions become more pronounced and can significantly affect the intensity assigned to the main photoemission line [3,4]. Peculiar attention is paid to the Tougaard background treatment, as it provides a physically meaningful framework for describing inelastic-loss contributions at high kinetic energy. The effect of the sensitivity-factor formalism is also examined through a comparison between experimental and theoretical RSFs [5].

The objective is to contribute to the development of a more robust and broadly applicable workflow for HAXPES quantification by clarifying how background treatment and sensitivity-factor formalisms influence the reliability, consistency, and physical meaning of composition measurements.

Acknowledgement: This work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the “Recherche Technologique de Base” and “France 2030 – ANR-22-PEEL-0014” programs of the French National Research Agency (ANR).

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Keywords: HAXPES, Quantification, Relative sensitivity factors, Tougaard background

When HAXPES gets vertical: sidewall-specific lab-scale analysis of GaN LED pixels after plasma etching

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The manufacture of pixels in gallium nitride (GaN)-based micro light-emitting diodes (LEDs) involves a plasma etching step, which results in material degradation at the pixel edges. This is particularly critical for small pixels and leads to a loss in the electro-optical efficiency of the GaN pixels. To address this issue, the development of etching processes generating lower material degradation is necessary [1]. Thus, in order to qualify the etchings, it becomes essential to characterise the sidewalls of GaN patterned pixels. To this end, we applied variable angle detection XPS/HAXPES on micron-scale patterns in the form of a set of arrays with different inter-pixel separation at a constant analysis angle. The method exploits the shadowing created by neighbouring patterns [2] when the photoelectron take-off angle is matched with variable inter-pixel separation of two different pixel arrays. In HAXPES, two crucial advantages serve our goal of a reliable analysis of the sidewall chemistry, namely the suppression of the overlap between Ga Auger and nitrogen core lines, on the one hand. And on the other hand, the higher sensitivity to chlorine residues from the plasma enabled by the strong Cl 1s lines previously not accessible in XPS. As a side-result, the determination by XPS of the valence band maximum confirms the presence of plasma-induced defects in the GaN band gap, leading to non-radiative recombination of electron-hole pairs in the material thereby reducing its electro-optical efficiency at the pixel periphery.

Acknowledgments: *This work, carried out on the Platform for Nanocharacterisation (PFNC), was supported by the "Recherche Technologique de Base" and "France 2030 – ANR-22-PEEL-0014" programs of the French National Research Agency (ANR).*

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Keywords: Gallium nitride, HAXPES, Etching, Sidewall

Multi-Dimensional Electron Energy Spectroscopy: Rapid Scan Auger Electron Spectroscopy Development for Next Generation

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Auger electron spectroscopy (AES) is a well-established analysis method enables elemental analysis as small as 100 nm² with analysis depth of less than 10 nm. It also provides high-spatial resolution elemental mapping on the top surface with the high-spatial resolution of several nanometers. However, conventional AES generally requires long acquisition time of more than 5 minutes needed to obtain a survey wide-range spectrum, approximately 10 minutes acquisition time for one elemental map with better signal-to-noise ratio. We have been developing *Spectrum Image* (SI) method for AES since 2016 and reported its potential capability and applications [1-4]. The SI method provides a spatial Auger map that includes a wide range electron energy spectrum in cube data format, allowing spectra to be extracted from any area and intensity maps to be generated by post-processing. By improving the acquisition sequence and a new intensity-correction method for the electron analyzer, the acquisition time of SI method has been significantly reduced. For example, acquisition of a 256 x 256 pixel SI dataset with a wide energy range of 30 to 2000eV requires approximately 5 hours. Its performance is achieved about 40 times as fast as a conventional acquisition method of AES. However, it was difficult to meet analyst's requirement in terms of the sample throughput with even the SI method.

We started a new project to develop next-generation Auger instrument to acquire cube data quickly by SI method since around 2020 and the first unit was completed in March 2026. With newly designed hardware and software to SI method, the acquisition speed was improved remarkably. It is possible to acquire a spectrum-image dataset for 256 x 256 pixels with wide energy range spectrum of 30 to 2000eV in approximately 1 minute. In this report, we will describe the general features of it and demonstrate some applications of the SI method. Moreover, SI-based depth profile data which includes elemental information with three dimensions will be introduced as an advanced application.

Keywords: AES, Surface, Electron Spectroscopy, Spectrum Image, MDEES

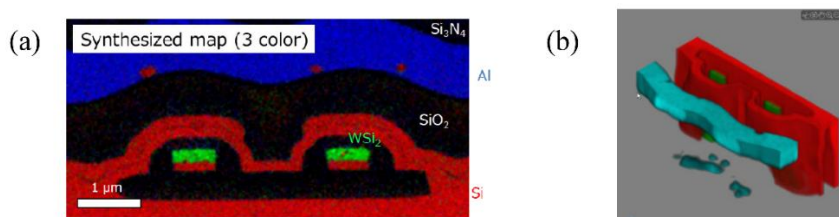


Fig 1. A MOS transistor sample cut by FIB was analyzed by SI method. (30 kV, 20 nA, 256x192 pixels)

(a) Synthesized map of nitrogen, silicon and tungsten acquired by SI method.

(b) 3D view image of nitrogen, silicon and tungsten acquired by SI depth profile method.

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Thin films and coatings

ALD Cr₂O₃ layers for corrosion protection of Al alloys: an XPS, ToF-SIMS and electrochemical study

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Aluminium alloys must be protected against corrosion and to this end oxide layers are currently used. They consist primarily of Cr(III) and Zr (IV) conversion coatings, replacing Cr (VI) that is now banned by REACH regulations in Europe. In this work we explored the protective effect of pure chromium oxide (Cr(III) layers deposited by atomic layer deposition (ALD) and investigated by a combination of XPS and ToF-SIMS analysis before and after corrosion tests.

Chromium oxide ALD layers have been deposited on aluminium AA 2024 alloy (widely used in the aeronautic industry) with different layer thicknesses, and characterized by XPS and ToF-SIMS. It was found that a dense and uniform chromium oxide layer covers both the aluminium matrix and the copper-rich intermetallic particles present in this alloy. Corrosion tests have been conducted by exposing the alloy to an alkaline KOH solution, selected because it is chemically aggressive for aluminium oxide. Additional electrochemical measurements were performed.

The alloy covered by a 50 nm thick ALD layer shows very good resistance to corrosion. However localized corrosion (pitting) is still observed at a few defective sites. The details of the localized corrosion mechanisms, investigated by 2D chemical imaging and 3D reconstruction using ToF-SIMS, will be discussed as well as the way to optimize the layer for improved corrosion resistance.

Keywords: ALD, Thin Oxide Layers, Aluminium alloy, Corrosion, XPS, ToF-SIMS

Surface and Interface Characterization of ALD-Grown Ultrathin Oxides on Hybrid Perovskites by XPS and HAXPES

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Hybrid perovskites have emerged as highly promising materials for photovoltaic applications due to their low fabrication cost and remarkable power conversion efficiencies. However, their long-term stability and sensitivity to environmental exposure remain major obstacles to large-scale deployment. There is currently no consensus in the literature, and the strategies reported for improving the stability of perovskite-based solar cells consist either of improving the active layer stability itself or of including ultrathin adjacent layers between the charge transport layers and the perovskite (molecular surface modifiers or oxides).

The choice of deposition technique for these adjacent layers and their nature is of course essential for maintaining the integrity of the perovskite layer, but they also play a key role in the efficiency of charge carrier extraction. In this work, ultrathin oxide layers (SnOx and TiOx) are grown on the metal halide perovskite surface using Atomic Layer Deposition (ALD), with a focus on the determination of interfacial interactions. Although ALD enables the deposition of highly conformal and homogeneous layers, precise deposition conditions must be established in order to avoid altering the perovskite layer.

The originality of this work lies in the detailed investigation of the impact of the ALD process on the perovskite surface, starting from the interaction between the precursors and the perovskite prior to oxide growth. This approach provides valuable insight into the physicochemical phenomena occurring at the perovskite/oxide interface, which are usually studied only after the oxide layer has been deposited. The chemical instability of hybrid perovskite layers also makes surface and interface characterization particularly challenging, especially when using X-ray Photoelectron Spectroscopy (XPS), where beam damage and ionic sputtering effects can alter the material.

For this reason, this study also investigates strategies to identify and minimize degradation during characterization. Three complementary approaches are employed. First, surface-sensitive XPS measurements are performed on perovskite surfaces exposed to selected ALD precursors. Then, thin (around 10–15 nm) and ultrathin (around 5 nm) ALD layers are considered, allowing comparison of the perovskite/oxide interface chemistry obtained with and without sputtering. Hard X-ray Photoelectron Spectroscopy (HAXPES) measurements at 2 and 6 keV performed at a synchrotron facility are correlated with laboratory XPS experiments (Al k-alpha source, 1.5 keV) to assess the consistency of the results obtained, providing insights into reliable surface and interface characterization approaches for hybrid perovskite systems.

Keywords: ALD, Perovskite, XPS, HAXPES

Study of the densification of TiO₂ film deposited by atmospheric dielectric barrier discharge plasma

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Titanium dioxide (TiO₂) is a widely spread material used in various applications such as in biomedical, paint or even energy. This semiconductor has a moderate bandgap of 3.2 eV which makes it an appreciate photoactive material. Industrially, most TiO₂ films are synthesized with low pressure processes as it gives better control on the process parameter and films with good purity. To reduce electrical consumption [1], researchers investigate film deposition at atmospheric pressure and that leads to new challenges [2] such as an increased deposition rate. This results in the rapid formation of an uncontrolled microstructure. Most of the films deposited at atmospheric pressure reported a characteristic cauliflower-like structure [3, 4]. We recently reported that the choice of plasma gas could highly impact the deposition rate of the film and therefore also modify the microstructure [4]. The present study investigates the impact of deposition parameters such as plasma gas, substrate temperature and precursor flux, to densify TiO₂ layer. The deposited layers are characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Diffuse reflectance spectroscopy (DRS), water contact angle (WCA) and X-ray photoelectron spectroscopy (XPS). This multi-technique characterization approach allows us to correlate the coating structure and properties with the plasma deposition parameters.

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Keywords: Dense layer, Atmospheric pressure, Dielectric barrier discharge, Cauliflower-like structure, Plasma crystallization

Contact Electrification at Silica-Gold Interface in Ultra-High Vacuum

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Contact electrification, or contact-separation electrification, is a fundamental physical process involving electrical, mechanical, and chemical interactions when two solid surfaces come into contact. This phenomenon is crucial for various applications including microelectronics, tribology, surface science, and nanotechnology, where interface properties directly affect device performance and material behavior. At the interface, an exchange of electrons, ions, and neutral species can occur due to differences in chemical potential, elastic modulus, and chemical reactivity, introducing complexity and uncertainty into the contact process [1]. The silica-gold ($\text{SiO}_2\text{-Au}$) interface particularly exhibits considerable measurement uncertainty due to the complex interplay between surface chemistry and experimental conditions [2].

To elucidate this process, we investigate interface interactions using atomic force microscopy (AFM) and surface composition by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS), both under ultra-high vacuum ($\sim 10^{-10}$ mbar) conditions. Prior to the contact-separation measurement, we ensured the cleanliness of the gold surface by sputtering a gas cluster ion beam (GCIB) composed of 1,500-atom argon clusters to effectively remove surface contaminants. Contact-separation experiments were performed using a ball shaped cantilever tip (diameter: 10.2 μm) made of SiO_2 contacted with an Au surface using contact-mode AFM. Force-distance curves demonstrate significant energy dissipation for a range of different applied force conditions. The energy dissipation consistently increases across consecutive contact-separation cycles, which is attributed to irreversible localized physical and chemical modifications at the interface that do not spontaneously recover. This suggests that the Au surface itself undergoes plastic deformation or structural rearrangement at the contact points under the applied force. ToF-SIMS analysis of the contact points reveals distinct changes in the surface composition, with characteristic fragments of SiCH_3 and SiC_3H_9 corresponding to dimethylsiloxane molecules adsorbed on the SiO_2 surfaces which is likely due to contaminations transferred from the cantilever contact to the Au substrate. Additionally, enhanced Au signal intensities in ToF-SIMS are observed at the contact points compared to the intensity of the clean gold, indicating localized surface deformation caused by mechanical manipulation and high electrostatic potential differences generated at the contact interfaces [2]. This investigation provides mechanistic insights into the contact-separation processes, elucidating the interplay between interface interactions and surface compositional modifications during repetitive contact cycles.

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Keywords: Contact electrification, Triboelectricity, atomic force microscopy, time-of-flight secondary ion mass spectrometry

Rapid thermal annealing of amorphous GeSe₂-Bi₂Se₃ thin films and waveguides

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Radio-frequency (RF) magnetron co-sputtering was used to deposit amorphous Ge-Bi-Se thin films from GeSe₂-Bi₂Se₃ targets. This study explores the effect of rapid thermal annealing (RTA) on as-deposited films under different annealing conditions to investigate the influence of annealing temperature and duration on their structural, optical and morphological properties. The RTA was performed by varying the annealing temperature from 200 to 325 °C, with annealing times of 10 s, 30 s, and 60 s. Systematic characterisation of as-deposited and annealed thin films was performed using variable-angle spectroscopic ellipsometry (VASE), XRD, AFM, EDS and SEM techniques. Optical studies revealed that thin films retain their refractive index and bandgap energy, ensuring their optical stability upon annealing at the highest temperature and for the longest duration. Morphological studies revealed that the annealed films were of high quality, with no cracking or degradation, and that the films maintained their amorphous nature regardless of annealing temperature or duration.

Waveguides were fabricated following RTA studies on the thin films to evaluate their stability upon rapid thermal annealing. Results show a reduction in roughness upon annealing, while no noticeable deformation or degradation of the waveguide structure under different annealing conditions.

Overall, this work confirms the optical and structural stability of Ge-Bi-Se chalcogenide thin films/waveguides and demonstrates their potential as a promising material for photonic and waveguide applications that need precise control of optical, structural, compositional and morphological properties.

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Keywords: Rapid thermal annealing (RTA), Ge-Bi-Se, Thin films, RF magnetron co-sputtering, Waveguides

Fabricating High quality superconducting NbN thin film by radio frequency reactive magnetron sputtering

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Niobium nitride (NbN) is a technologically important superconductor which is widely used in superconducting electronics, Josephson junctions, and terahertz detectors due to its relatively high superconducting transition temperature ($T_C \approx 17$ K) and large superconducting energy gap. However, achieving high-quality NbN thin films typically requires ultrahigh-vacuum environments, lattice-matched substrates, or elevated growth temperatures, which complicates scalable multilayer device fabrication.^[1–3] Here we demonstrate the growth of high-quality NbN thin films that are deposited at room temperature on native-oxide-covered Si(100) substrates in a high-vacuum chamber (base pressure in 10^{-6} mbar) using reactive radio frequency (RF) magnetron sputtering. In this regard, a systematic study is carried out by varying a range of process parameters and then characterizing their detailed microstructure and correlating with the T_C values. Moreover, the film stoichiometry, defect concentration, crystallographic orientation and oxygen content are found to play a crucial role on the T_C of the NbN film. Additionally, an oxygen-gettering strategy prior to deposition is carried out in this high vacuum chamber to bring down the oxygen content in the NbN film, which could be correlated with the reported high quality NbN thin film using an UHV-based sputter deposition chamber.

The X-ray Photoelectron Spectroscopy (XPS) analysis indicates higher deposition rate further suppressing oxygen uptake during the film deposition, thereby resulting in reduced Nb–O bonding within the film (~ 5 at. %). Grazing-incidence X-ray diffraction (GI-XRD) confirms the formation of cubic δ -NbN with the (111) peak located at $\sim 35.8^\circ$. In contrast, nitrogen-deficient films exhibit a pronounced shift of this peak to 36.4° , indicating lattice contraction and the loss of superconductivity. Films deposited under the optimized process conditions exhibit metallic transport behaviour typical of sputtered NbN films, with a residual resistivity ratio (RRR) of 1.2 and a maximum superconducting transition temperature of $T_C = 13.7$ K measured using a cryogen-free measurement system (CFMS). These results demonstrate optimized process control enabling high T_C NbN film deposition at room temperature in a simple high-vacuum environment, thereby providing a scalable route for superconducting device fabrication on silicon substrates.

Keywords: XPS depth profiling, NbN thin films, Superconductivity, Residual oxygen incorporation, Reactive sputtering

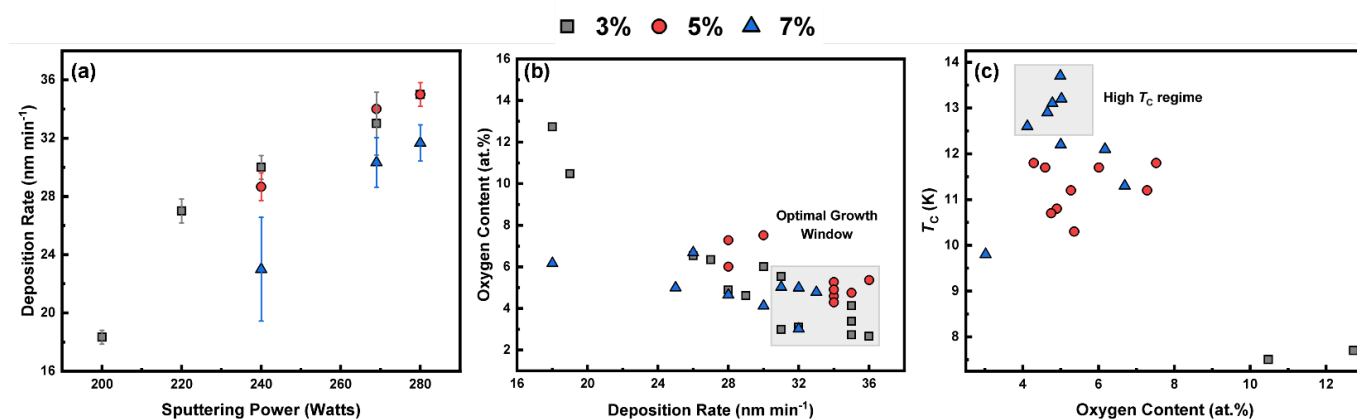


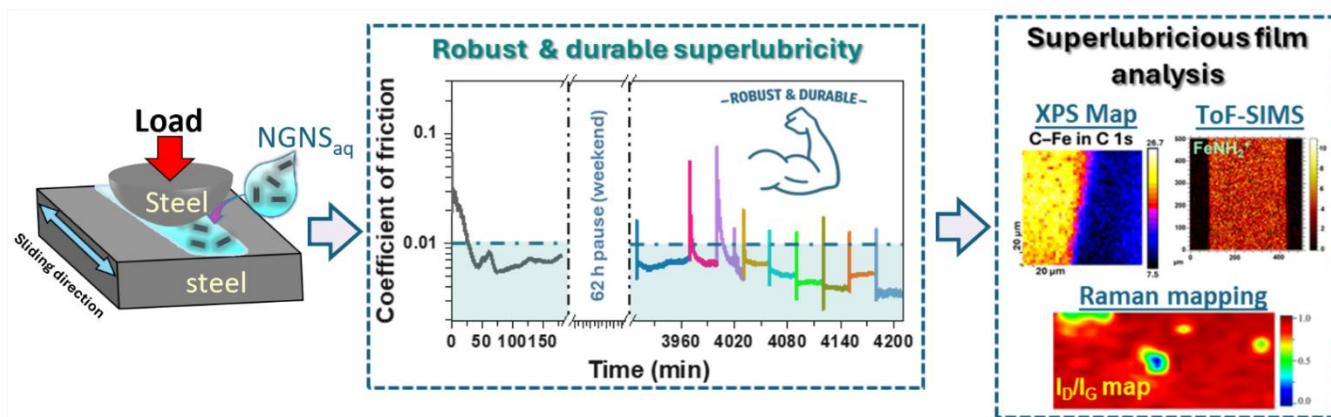
Figure 1: (a) Deposition rate as a function of RF sputtering power for films grown under different nitrogen fractions (3%, 5%, and 7% N₂). (b) Oxygen content obtained from depth-profile XPS plotted as a function of deposition rate. (c) T_C as a function of oxygen content. Films with lower oxygen concentration exhibit higher T_C , defining a high T_C regime (shaded region).

Chemisorption-driven superlubricity on engineering steel enabled by nitrogen-doped graphene nanosheets

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Macroscale superlubricity presents a promising strategy to reduce frictional losses and enhance the durability of mechanical systems. However, achieving robust and long-lasting superlubricity in aqueous-lubricated metallic systems remains a key challenge, particularly under high contact pressures, due to limited understanding of interfacial mechanisms. In this work, we report a novel lubrication mechanism enabled by nitrogen-doped graphene nanosheets (NGNS) in aqueous glycerol, which promotes the formation of a robust and durable tribochemical film that induces stable macroscale superlubricity in steel/steel sliding pairs. To assess robustness under realistic conditions, we designed a dedicated long-term and intermittent start-stop testing protocol, demonstrating that the in situ-generated film can effectively adapt to dynamic contact conditions. Superlubricity was observed in a boundary lubrication regime with an average coefficient of friction of ~ 0.006 , while yielding extremely low wear-rates on the order of $10^{-9} \text{ mm}^3/\text{Nm}$. Mechanistic investigations reveal that the friction is primarily attributed to the chemisorptive adsorption of NGNS onto the worn steel surface, as evidenced by the in-situ formation of $\text{Fe-N}_x\text{-C}_y$ moieties. These moieties have abundant active sites that enhance the subsequent anionic adsorption of pyrrolic-rich NGNS. Simultaneously, shear-induced exfoliation of nanosheets leads to the formation of an amorphous graphitic film, which further stabilizes the superlubricity state. This work provides new insights into chemisorptive interfacial interactions and the functional characteristics of NGNS in achieving robust aqueous superlubricity, highlighting NGNS-based lubricants as a promising pathway toward energy-efficient, environmentally friendly lubrication solutions for demanding industrial applications.

Keywords: Superlubricity, N-doped graphene, Tribochemistry, Chemisorption, Carbon neutrality



XPS Depth Profiling of Multilayer Stacks using Femtosecond Laser Ablation (fs-LA)

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Multilayer stacks of different materials are commonly employed across a wide range of technical fields. XPS depth profiling of multilayers has been investigated previously using traditional ion beam sputtering techniques, with rotation of the sample during etching increasing the depth resolution. With the recent introduction of femtosecond laser ablation (fs-LA) as a novel depth profiling method, it is important to optimise the analytical approach to enhance depth resolution. A femtosecond laser with a 1030 nm peak wavelength, pulse length of 160 fs and top-hat optical beam shaper has been employed to perform the XPS depth profiles. Results will be shown for different classes of material using analytical set-ups with and without laser polarisation rotation and sample rotation. Discussion of the results will consider the origins of crater roughening in fs-LA depth profiling, influence of top-hat uniformity, material related effects and describe the best analytical approach for optimisation of depth resolution.

Keywords: XPS, Depth Profiling, Femtosecond Laser Ablation, Multilayers

An influence of flux on reflow melting of the tinned steel

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Approximately a third of world tin production is used for packaging tinplate [1]. The tin reflow process is used to transform the matte appearance of as-electroplated tin layer to bright finish typical of reflowed tinplate and to produce a thin FeSn₂ alloy layer at the interface, thereby improving corrosion resistance.

Prior to the reflow-melting, an aqueous flux solution containing benzoic and sulfuric acids is sprayed to both sides [2]. The strip is then dried leaving a solid flux residue distributed uniformly over the surface. The purpose of flux is to limit the growth of tin oxides/hydroxides and to lower the surface tension of molten tin. The flux causes also a grain refinement during solidification; also dysmorphism: a lack of crystal orientation, causing the surface to acquire more or less amorphous properties. When the strip is reflow-melted at 240°C, an alloy is formed while the unreacted tin is flowing into a uniform surface. The strip is then quenched in water causing the tin to solidify to a very finely-divided crystalline structure i.e. crystal growth is suppressed and “freeze” as a shiny surface without irregularities. Subsequently, the flow-melted tinplate is passivated by dipping into the Cr-based solution.

Recently, one of Tata Steel customers had an issue with a yellowish staining of tinplate upon the curing of a transparent lacquer layer. Typically, the yellow staining of tin is attributed to thick SnO layer (>30 nm) which was in contrary to the oxide thickness of 7 nm found within the stains. This staining, within the central part of the strip, resembles a fluid pattern elongated in rolling direction of few centimetres wide and 30–100 centimetres long. This evidence would suggest a relation to the production process and fluid nature.

A thorough XPS and HR-SEM/EDX study of stained and non-stained surfaces, followed by production trials, revealed a relation between the staining and excessive flux concentration. According to our findings the excess of the flux increases the microroughness of the flow melted tin surface, and therefore promotes the iron diffusion during the flow-melting and, later, inhomogeneous Cr passivation which results in 3–4 nm thicker Fe-Sn mixed oxide, that caused the staining. The combination of surface characterisation and production trials enabled us to tune the flux concentration within the right pH-window and therefore guarantee the excellent surface quality of the product.

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Keywords: tinplate, reflow-melting, surface engineering, surface characterisation, staining

Interfacial Oxidation-State Control in ALD-Based CeO_x/WO_3 Heterostructures

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The self-limiting nature of atomic layer deposition (ALD) enables the fabrication of chemically uniform layers with precise thickness control and conformality. These qualities, along with their compatibility with complementary metal-oxide semiconductor (CMOS) technology, make ALD an excellent method for preparing ultrathin deposits and fabricating miniaturized devices. However, changes in surface chemistry during the first cycles, in addition to interactions with the underlying substrate, result in the formation of an interface region that, in ultrathin deposits below 10 nanometer thickness and on the order of their Debye length, will likely influence material properties, potentially differing from those of the bulk material.

Among metal-oxide candidates for gas sensing, tungsten oxide shows resistive and optical responses towards exposure to H_2 . However, single metal oxides typically require operation at high temperatures. One approach to increase the sensitivity is the formation of metal oxide heterostructure: for example, $\text{CeO}_2/\text{SnO}_2$ and $\text{CeO}_2/\text{In}_2\text{O}_3$ heterostructures have shown the emergence of additional active sites and thus increased oxygen adsorption at the interface [1,2]. This improvement is related to ceria's excellent redox properties, even at low temperatures, which enable it to readily switch between the Ce^{3+} and Ce^{4+} oxidation states and to act as an oxygen storage material. Here, we study interface formation in CeO_x/WO_3 heterostructures, which are shown to exhibit unique hydrogen-sensing properties that are strongly influenced by the interface.

We have grown cerium oxide by ALD on thick tungsten oxide films deposited by thermal evaporation using the $\text{Ce}(\text{dpmg})_3$ precursor and ozone. Using operando spectroscopic ellipsometry and in-situ X-ray photoelectron spectroscopy (XPS), we observe a gradual transition from a pure Ce^{3+} oxidation state in the initial ALD cycles to Ce^{4+} with increasing film thickness under steady growth conditions (see Fig. 1a)). This allows us to adjust the oxidation state by varying the thickness of the deposited film, highlighting the important role of the interface in ultrathin films. Changes in the ceria oxidation state are linked to alterations in the chemistry of the carbon- and nitrogen-containing precursor residues (see Fig. 1b)-c)). In addition, we have explored the oxidizability and reducibility of CeO_x/WO_3 heterostructures with varying ceria film thickness, correlating these insights with gas-sensing measurements. This bottom-up approach allows the use of ALD as an interface engineering tool to fine-tune the gas-sensing performance of miniaturized devices.

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Keywords: ALD, XPS, Spectroscopic Ellipsometry, CeO_2 , WO_3

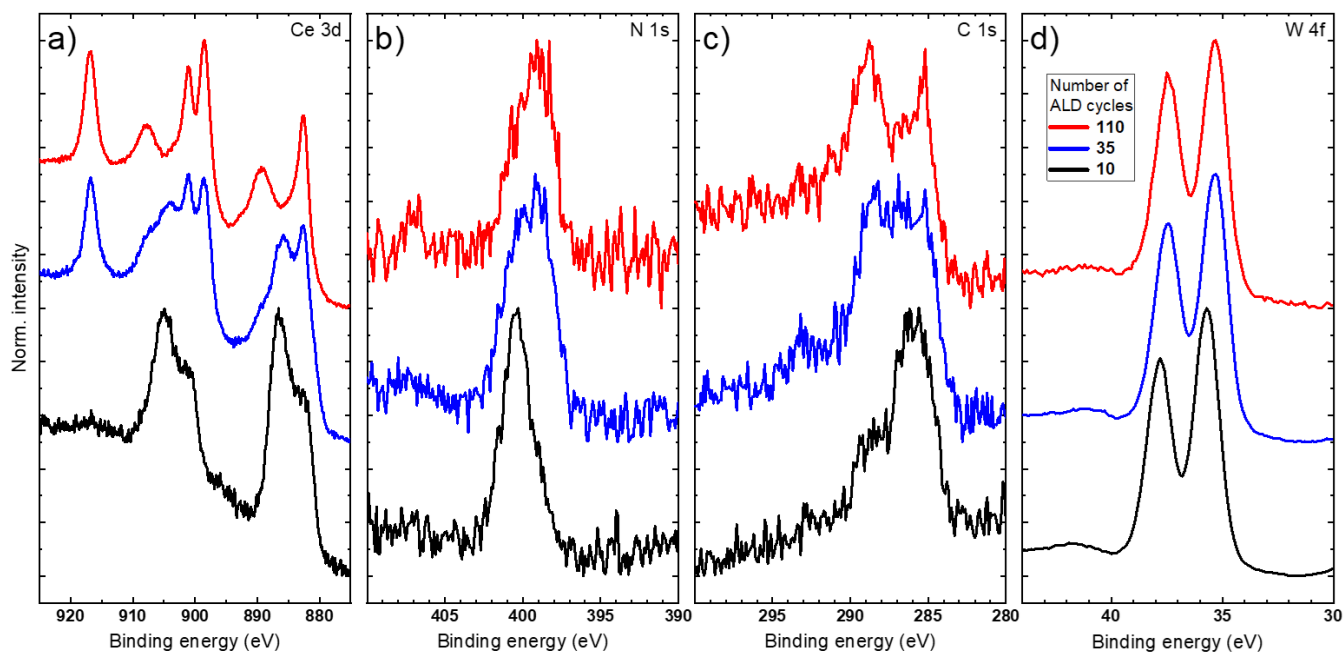


Fig. 1 a) Ce 3d XPS spectra, b) N 1s XPS spectra, c) C 1s XPS spectra, and d) W 4f XPS spectra for 10, 35 and 110 ALD cycles of CeO_x/WO_3 .

Determining oxidation state via Auger line shape analysis: Defect engineering of ALD-SnO_x films for ambient H₂ sensing

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Hydrogen (H₂) will play an important role in future energy systems, but its widespread adoption is hindered by safety concerns stemming from its high diffusivity, broad explosive range, and low ignition energy. To address these issues, simple, scalable, and inexpensive H₂ sensors that operate at low temperatures are required. Metal oxide gas sensors, e.g., based on tin oxide (SnO_x), are established for H₂ sensing but still require further improvements to enable low-temperature operation without noble-metal functionalization. Targeted enhancement of structural and chemical defects offers a potential pathway to improve the performance of pristine metal oxides. In this work, we present a comprehensive investigation of defect engineering of ultra-thin SnO_x films grown by atomic layer deposition (ALD), a deposition method that enables facile scalability and excellent thickness control for H₂ gas sensing applications.

By combining in-situ X-ray photoelectron spectroscopy (XPS) and operando spectroscopic ellipsometry, we have correlated the evolution of surface chemistry and film thickness with defect concentration. Sample morphology is assessed using inelastic peak shape analysis with the QUASES software, showing excellent agreement with ellipsometry measurements. We also introduce a straightforward linear combination approach for determining the Sn cation oxidation state based on analysis of the Sn MNN Auger line (Fig. 1a, b). Interestingly, the highest amount of defect-related Sn²⁺ species is observed for samples prepared with a highly oxidizing co-reactant, and is associated with the incorporation of precursor-related impurities into the film. Correlating near-ambient-pressure XPS and functional sensor test measurements demonstrates room-temperature H₂ sensing with ultra-thin SnO_x films (Fig. 1c) and reveals a distinct relationship between defect concentration and enhanced sensor performance. Overall, Sn MNN line-shape analysis provides a depth probe comparable to the Debye length of SnO_x (i.e., the length scale relevant for ultrasensitive gas sensing), offers complementary insights to the established Wagner plot, and avoids issues arising from the interpretation of Sn 3d spectra of close-to-amorphous SnO_x. These results highlight the potential of defect engineering to enhance sensor performance and showcase how in-depth Auger line-shape analysis enables the correlation of surface chemistry with sensor performance.

Keywords: Atomic Layer deposition, Gas sensing, Auger line, Tin oxide, QUASES

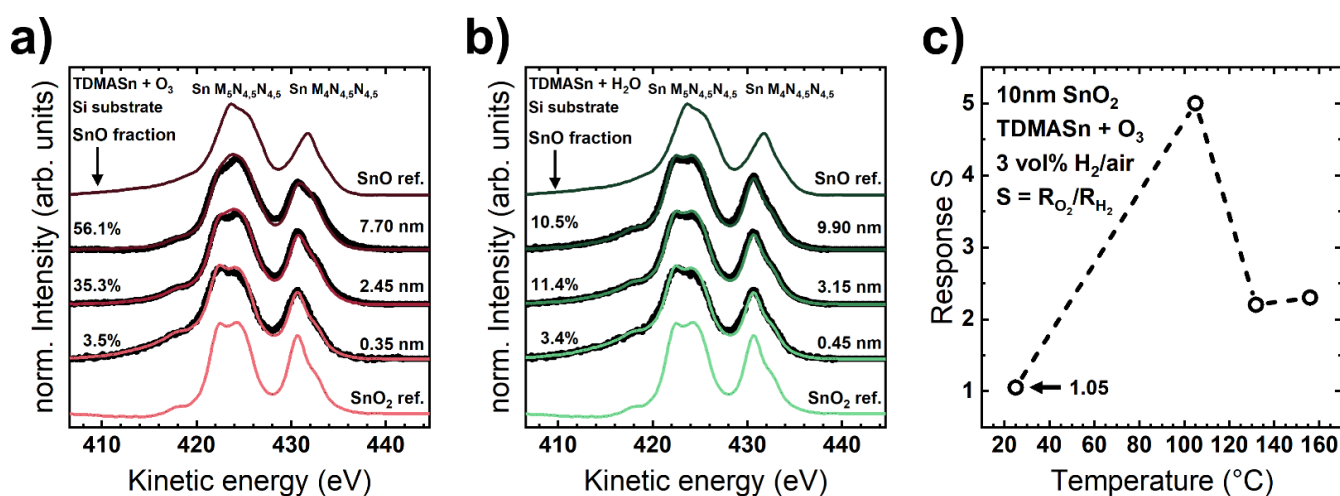


Fig. 1 Fits of Sn MNN Auger spectra of ALD-SnO_x grown with a) O₃ and b) H₂O as co-reactant on Si substrates. c) Response of 10 nm ALD-SnO_x grown with O₃ on interdigitated electrodes against 3 vol. % H₂ at different temperatures.

Correlative surface analytics of ultrathin Ti-based conversion layers on pretreated hot-dip galvanized steel

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The investigation of environmentally friendly Ti and Zr based conversion coatings on hot-dip galvanised steel gained significant scientific interest as the exact mechanism of corrosive degradation in industrial grade material is not yet fully understood. [1-2]

After alkaline cleaning and pretreatment of skin-passed zinc (Z) and zinc-magnesium-aluminium (ZM) steel surfaces with transition metal fluoridic acids a thin elusive conversion layer is formed, which dictates adhesion of subsequently applied coatings and long-term corrosion resistance. [2] The local accumulation or depletion of specific elements in this nanometer thick conversion layers is a result of prevailing processing conditions and plays a major role in the longevity of the material. [3] Due to the complex and heterogeneous nature of the formed layer structure, a correlative approach in surface analytics has to be pursued for a proper description, as presented in this study.

In detail, surface analytics by X-ray photoelectron spectroscopy (XPS) in combination with depth profiling by argon ion sputtering, shows the formation of nanometer thin surface layers followed by a mixed oxide structure depending upon the underlying substrate material and pretreatment conditions. Newly, complementary information is obtained by depth profiling using less degrading argon ion cluster sputtering coupled with helium ion scattering spectroscopy (ISS), which is found to significantly increase the depth resolution to monoatomic scale for the topmost nanometers and, consequently, yields a more differentiated view on the composition of the surface layer structure. Finally, Auger electron spectroscopy (AES), in combination with scanning electron microscopy (SEM) and ultra-high vacuum energy dispersive X-ray spectroscopy (UHV-EDX), complements this correlative approach by adding nanometer lateral resolution and highlighting the heterogeneous nature of the surface of skin-passed Z/ZM coated steel. AES directly shows the close relationship between topography and resulting distribution of pretreatment specific domains. Key elements such as titanium and fluorine are successfully mapped using AES despite their low surface concentrations resulting from the applied coating weights of only few mg/m².

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Keywords: auger electron spectroscopy, ion scattering spectroscopy, depth profiling, titanium conversion coatings, hot-dip-galvanised steel

Analysis of superhydrophobic biopolymer coatings through combination of green chemistry and laser texturing

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The development of superhydrophobic soft bio-based polymer layers is gaining momentum and essential for their application in protective coatings, as industries shift toward environmentally benign materials and surface-engineering strategies. The integration of green chemistry with laser surface texturing offers a powerful and sustainable route to fabricate superhydrophobic biopolymer and nanocellulose-based coatings. Reviews highlight the environmental advantages of laser methods that avoid fluorination or silanization, demonstrating their ability to generate micro/nanostructures achieving high contact angles and low sliding angles while avoiding hazardous materials. Green chemistries enable the use of renewable feedstocks such as cellulose, nanocellulose, and bio-based additives such as natural waxes, while laser-based top-down micro/nanopatterning provides precise, non-contact control over hierarchical roughness essential for superhydrophobic behavior. Recent work demonstrates that femtosecond laser patterning dramatically enhances water repellence of spray-coated hydrophobic nanocellulose coatings in combination with the design of surface patterns with island-like geometries. In parallel, the bio-based epoxy coatings with different grades of natural wax additives can be patterned through femtosecond laser texturing for increase in water contact angles and reduction of contact angle hysteresis. Experimental results confirm the direct influence of laser-generated hierarchical patterns on hydrophobic performance. The coatings are characterized by combination of chemical and topographical techniques at different length scales. Analysis through analytical models further validate that the wetting behaviour follows a theoretical Cassie-Baxter transition, although the heterogeneous nature of their composition. Developed surfaces are promising for replacement of PFAS substances in coatings for packaging materials and wood industry.

Keywords: coating, bio-based, superhydrophobic, texturing, wetting

Fluorinated Silane Layers on SiO₂: Surface Coverage and Thermal Stability Probed by Combined LEIS and XPS

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Self-assembled monolayers (SAMs) of fluorinated silanes represent ultrathin coatings that control surface energy, chemical stability, and interfacial properties in thin-film and coating technologies. In this work, fluorinated silane layers based on two molecules with different chain lengths (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (TDFOTS) and (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane (HDFTS), see figure, were deposited on native oxide-terminated silicon substrates using an experimentally simple liquid-phase sandwich deposition method. However, the layer's parameters must be controlled.

The surface coverage, composition, and thermal stability of the prepared films were investigated using a combination of Low Energy Ion Scattering (LEIS) and X-ray Photoelectron Spectroscopy (XPS), supported by spectroscopic ellipsometry and Scanning Electron Microscopy (SEM) scans. LEIS, owing to its extreme surface sensitivity and mass selectivity, provides direct information about the outermost atomic layer and surface elemental termination. The measurements confirmed that the fluorinated silanes form closed, fluorine-terminated surfaces, effectively shielding the underlying SiO₂ substrate, which was detected only as a weak background signal. Temperature-dependent LEIS measurements performed during in situ annealing up to 700 °C revealed a gradual decrease in the fluorine signal at lower temperatures, corresponding to the desorption of weakly bound species. Above approximately 500 °C, the signal stabilises, indicating the presence of a strongly bound fraction of the fluorinated layer. A surface concentration is evaluated using the Teflon reference [1]. At higher temperatures, increasing silicon and oxygen signals, with ratios characteristic of SiO₂, reflect partial exposure of the substrate.

XPS analysis provided complementary chemical information from the near-surface region, confirming the presence of fluorinated carbon species and supporting the thickness estimation based on C1s/Si2p signal ratio and plasmon loss signal next to Si2p and 2s signals. Ellipsometry measurements further corroborated the thickness changes induced by thermal treatment.

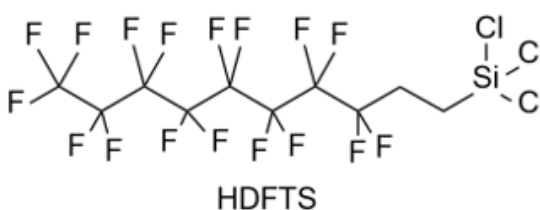
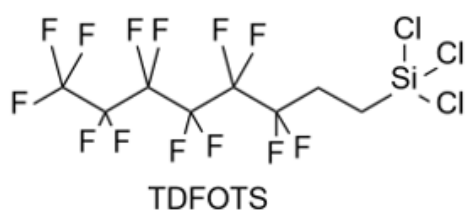
The combined use of LEIS and XPS thus represents a powerful approach for the characterisation of ultrathin fluorinated coatings, enabling a detailed understanding of surface termination, chemical structure, and thermal stability, which are critical for the design and optimisation of advanced thin film systems.

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Keywords: self-assembled monolayers, fluorinated silanes, surface chemistry, LEIS, XPS



Effect of C5 insulating coatings on the fatigue performance of adhesively bonded electrical steel stacks

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Adhesive bonding of stacked electrical steel laminations is essential for next-generation electric machines, offering gains in electromagnetic efficiency and structural reliability compared with welding or mechanical interlocking. Achieving long-term durability requires robust interfacial adherence between the adhesive and the insulation varnish on the steel substrate, particularly under thermomechanical and environmental loads representative of service. Dot-bonding with acrylate resins is a new approach for manufacturing electrical steel stacks. Hence, the main objective of this study was to evaluate the mechanical performance of dot-bonded electrical steel laminates under service-relevant conditions using a fracture-mechanics framework.

Electrical steel sheets were coated with commercially available acidic and alkaline C5 insulating coatings and cured at a peak metal temperature of 280°C. Double cantilever beam (DCB) specimens were fabricated by stacking the coated sheets, inserting a silver leaf as a well-defined crack starter, and adding reinforcement sheets. The assembly was dot-bonded with a commercially available, peroxide-crosslinking acrylic adhesive and cured at 200°C for 30 minutes. Environmental cyclic fatigue tests in air were conducted in a temperature range from 23 to 90°C.

Both, the strain-energy release rate in the threshold regime (G_{th}), which is of relevance for a design of no crack growth, and the debonding rate in the stable crack-growth regime were temperature dependent. For example, G_{th} , increased with temperature, rising from 12.8 to 21.1 J/m² for the alkaline C5 coating and from 9.7 to 14.5 J/m² for the acidic C5 coating. For the alkaline coating, both the stable crack-growth rate and the Paris exponent increased with temperature, whereas the acidic coating did not exhibit such a clear trend. X-ray photoelectron spectroscopy (XPS) of the fractured surfaces revealed a layer thickness of the insulating coatings and the dot-bonding adhesive in the range of 1 µm. Due to the high fraction of inorganic fillers in insulating coatings, the crack was propagating alternately in the insulating layer.

Environmental fatigue testing proved to be a sensitive approach for a service-relevant assessment of the durability of dot-bonded electrical steel sheets. Future work will aim to establish structure-property relationships by varying the insulating coating or the adhesive and by testing at elevated temperatures and/or in different heat carrier fluids.

Keywords: environmental fatigue tests, electrical steel stacks, C5 insulating coatings, acrylate adhesive

Van der Waals interactions as driving forces in interphase formation of polymer thin films

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Polymer materials are known for their weak intersegment interactions and conformational energy barriers on the order of k_bT . Consequently, the conformation of chain segments can be altered at low energetic cost without compromising the cohesion of the solid. This is often referred to as flat energy landscape, a characteristic property of polymers which is in stark contrast with other solid materials that form lattices leading to distinct minima in their energy landscape.

The flat energy landscape of polymers becomes relevant when they interface with other materials, as in the case of thin polymer films on a substrate. In the absence of strong interactions such as chemical or electrostatic interactions, the attraction between the two materials is governed by van der Waals interaction, an electrodynamic effect. As a dynamic phenomenon, the van der Waals attraction depends on the electron density and resonance of the electrodynamic spectrum of the interfacing materials. However, for polymer materials with a flat energy landscape, electrodynamic interactions with an interfacing material can be enough to alter the polymer's conformation, adjusting its electrodynamic profile to approximate the profile of its interfacing neighbour and thereby increasing the interfacial adhesion.

We believe that this is the dominant mechanism of the formation of a polymer interphase, causing other additional changes of physical properties, which the interphase is known for, such as the change of glass transition temperature (T_g) or change of mechanical properties. Here, we propose a direct observation of the van der Waals properties of polymeric thin films measured relative to an atomic force microscope (AFM) probe. This observable is additionally correlated with the mechanical properties of the thin film, also measured by AFM force distance curves (FDC). Using this method, we observed the effect of varying the van der Waals interaction between the substrate and thin (30, 65 and 120 nm) films of poly (n-butyl methacrylate) (PnBMA). This has given us insight into the formation mechanism of polymer interphases, which contributes to a general understanding of the phenomenon.

Keywords: Atomic force microscopy, nanomechanical, adhesion, van der Waals, polymer thin films

XPS characterization of artificial saliva droplets on common substrates: the role of surfactants

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The investigation of adsorption phenomena of proteins at specific surfaces has several implications including pathogen viability and transmission on solid substrates [1], cleaning strategies in industrial contexts [2]. The rational design and optimization of anti-fouling treatments can be dictated for example by the protein-surface binding affinity and packing density as model systems [3]. Therefore, it could be particularly critical to evaluate the possible orientation, unfolding, restructuring of proteinaceous components when in contact with inanimate surfaces, also in combination with peculiar species such as surfactants, cleaning products or antimicrobial materials.

In previous works, it was envisaged that the evaporation kinetics and aerosol microdroplet deposition of artificial saliva (a mixture of mucin, inorganic salts, nutrients) could play a role in virus transmission and inactivation on surfaces [1]. Fluorescence atomic force microscopy microscopies demonstrated the role of surface roughness, chemical nature of the substrate, and topography [1]. However, the role of surfactants, which mimic basic examples of cleaning formulations, when in contact with mucin has not been addressed.

We have previously used X-ray photoelectron spectroscopy (XPS) to investigate protein orientation/modification in different scenarios [4-5], also correlating mass spectrometric information relevant to protein possible modification/unfolding [6]. In this communication, we report the XPS characterization of model droplets deposited on different substrates of common use (plastics, glass, etc.) demonstrating the distinctive behavior of each surfactant depending on their chemistry. We have studied four systems: linear alkylbenzene sulfonate (LAS), sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and benzalkonium chloride (BAC). In particular, anionic species seem to screen proteinaceous components tending to segregate at the top. Mass spectrometry and morphological results are also provided to support the findings.

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Keywords: antimicrobial coatings, XPS, protein, touching surfaces, topography

XPS and Hydrogen Permeation Analyses of Nanostructured Multilayer Coatings

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Hydrogen is a promising clean energy carrier, especially when produced as “green hydrogen” via renewable-powered electrolysis, offering a sustainable alternative to fossil fuels. Nevertheless, its storage and management remain challenging due to hydrogen embrittlement in high-strength steels, which can lead to degradation, leakage, or failure. To address this, metallic coatings as W and Ni-P alloys are being explored as effective hydrogen permeation barriers (HPBs). These materials exhibit lower hydrogen diffusion coefficients compared to steel [<https://doi.org/10.3390/coatings15040365>] making them appealing candidates for enhancing safety and efficiency of hydrogen storage systems. Ongoing research and development efforts are focused on optimising HPBs, including innovations in nanostructured multilayer coatings that promise better performances.

High-purity iron foils (100 µm, 50 × 50 mm) were used as substrates and three micrometre-thick coating series were deposited and tested. The performance and the efficiency of these coatings was assessed employing an analytical methodology [<https://doi.org/10.3390/coatings15040442>] that combines in-situ electrochemical measurements with ex-situ surface analysis. XPS was employed [[https://doi: 10.1116/6.0003733](https://doi.org/10.1116/6.0003733)] to ensure reproducible surface preparation, using a Thermo Fisher Scientific Theta Probe spectrometer operated at base pressures below 5×10^{-7} Pa. Spectra were acquired with monochromatic Al K α radiation (1486.6 eV), and the energy scale was calibrated according to ISO 15472:2010. Curve fitting was performed using CasaXPS following iterative Shirley background subtraction. The investigation revealed that the native oxy-hydroxide layer, consisting of Fe(II)ox, Fe(III)ox, and FeOOH, had a thickness of 5.4(0.1) nm, in addition to an organic layer of 3.0(0.1) nm.

HP tests were carried out utilizing a Devanathan–Stachurski cell, where 0.1 M HCl solution with 0.2 g/dm³ As₂O₃ was employed in the charging side to inhibit hydrogen recombination, while 0.1 M NaOH was used in the detection side. The effective hydrogen diffusion coefficient of the 100 µm iron substrate was $D_{\text{eff}} 3.4(0.3) \times 10^{-12}$ m²/s, while coated samples exhibited D_{eff} values roughly an order of magnitude lower.

The discussion will highlight two pivotal aspects of HPBs evaluation: first, the critical role of surface preparation on the detection side, which ensures stable passivation in 0.1 M NaOH and yielding reliable hydrogen detection currents; and second, the use of a bilayer coating–substrate model to extract the true diffusion coefficient of the HPB film D_f . The best coatings achieved D_f values on the order of 10^{-16} m²/s, demonstrating excellent HPB performance and confirming the strong potential of these proprietary nanostructured multilayer coatings in advancing hydrogen storage technology.

Keywords: Hydrogen permeation barrier (HPB), Nanostructured Multilayer Coatings, X-ray photoelectron spectroscopy, Iron substrate, Hydrogen embrittlement

Thermal stability of engineered Al oxide layers on an AM Al-Fe-Zr alloy

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The global transition toward net zero emissions is accelerating the adoption of technologies with more demanding operating conditions, thereby increasing the need for aluminum alloys capable of withstanding increasingly harsh environments, in particular temperatures above 200 °C. Conventional age-hardenable aluminum alloys, such as the 5000 and 6000 series, are proving insufficient in meeting these requirements in terms of temperature stability and surface integrity.

A recently developed Al-Fe-Zr alloy for additive manufacturing (AM) has gained attention due to its improved high-temperature performance and superior thermal conductivity compared to commonly used AM AlSi10Mg. Nevertheless, AM-specific challenges, i.e. surface quality variations, porosity, and limited hardness, remain barriers for their implementation. Part of those can be overcome by using electrochemical surface treatment, like anodizing, as a surface finish.

This study investigates different engineered Al oxide layers, produced by barrier and porous anodizing processes, and assesses their stability under thermal aging at temperatures above 200 °C. A comprehensive microstructural analysis combined with structural and electrochemical characterization was conducted to evaluate their high-temperature behavior and the corresponding changes in oxide chemistry and structure. The effect of surface pre-treatments was also investigated to correlate initial surface roughness with the growth of anodic barrier(-like) Al oxides, as well as the subsequent porous oxide growth rates.

The thermal stability of the anodic Al oxide layers was compared to Al₂O₃ layers deposited by atomic layer deposition (ALD).

These findings provide new insights into surface treatment strategies for AM Al components exposed to harsh environments.

Keywords: electrochemical surface treatment, Atomic Layer Deposition (ALD), thermal stability, surface modification, engineered Al oxides

How Sub-nm Binary Oxide Overlayers Shape Surface Dipoles, Thermochemical Stability & Morphology of (La,Sr)CoO_{3-δ}

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Modifying the surfaces of mixed ionic and electronic conductors (MIECs) has attracted attention as a strategy to enhance oxygen-exchange reaction kinetics and to attenuate surface degradation.[1,2] This study investigates the high-temperature stability and cation segregation behavior of La_{0.6}Sr_{0.4}CoO_{3-δ} (LSC) thin films modified with ~0.5 nm CaO (basic) and SnO₂ (acidic) overlayers after annealing at 800 °C. The results reveal that the electronic nature of the surface oxide—particularly its acidity—affects secondary ion (SI) formation. Changes in SI intensities originate from variations in surface composition (at the Oxide|LSC interface) and the formation of near-surface electrostatic dipoles.[3,4] Combining Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), X-ray Photoelectron Spectroscopy (XPS), Secondary Electron Microscopy (SEM)/Energy Dispersive X-ray Analysis (EDX), and Auger-Meitner Electron Spectroscopy (AMES), we provide a comprehensive picture of surface and sub-surface changes, segregation, inter-diffusion, and secondary phase formation.[5] Sr enrichment during high-temperature annealing occurs at the surface regardless of the overlayer. However, variations in surface morphology arise, depending on the surface acidity, which is modulated by the different oxide overlayer. This correlation is fundamental for the formation of secondary phases and for determining the impact of acidic gas-phase impurities. Further, these findings suggest that surface modifications cannot actively prevent Sr segregation at high temperatures, leading to complex surface dynamics and significantly altering the processes of secondary-phase formation induced by Sr segregation. These results give new insights into sub-nanometer-scale material interactions and offer perspectives for enhancing MIEC stability in SOFC/SOEC applications.

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Keywords: Mixed ionic electronic conductors, Cation segregation, Thin films, Surface chemistry, Thermal degradation

Layer-by-layer growth of copper-based SURMOFs on functionalized SiO₂: a comprehensive surface characterization study

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Metal–organic frameworks (MOFs) are porous coordination polymers assembled from organic linkers and metal or metal-cluster nodes. Renowned for their high surface area, structural tunability, chemical versatility, and stability, MOFs have attracted considerable attention for applications in gas storage and separation, catalysis, and sensing. For integration into advanced devices, however, MOFs, typically synthesized as powders, must be immobilized onto solid supports in a controlled and robust manner.

Layer-by-layer growth represents a powerful strategy for anchoring MOFs onto surfaces, enabling the fabrication of well-defined and tunable surface-supported frameworks (sur-MOFs). In this work, we investigate the stepwise growth of a copper-based MOF on thermally grown SiO₂ substrates pre-functionalized with a zirconium phosphate interlayer. This model system provides a reproducible and technologically relevant platform for studying interfacial processes during MOF assembly.

A comprehensive physico-chemical characterization was carried out after each deposition step. Time-of-flight secondary ion mass spectrometry enabled molecular-level analysis of surface composition and interfacial chemistry, while X-ray photoelectron spectroscopy provided semi-quantitative elemental and chemical-state information. In addition, atomic force microscopy was employed to monitor surface morphology and growth evolution.

The combined surface-sensitive analytical approach allows detailed insight into the mechanisms governing sur-MOF formation, interfacial bonding, and layer homogeneity.

The results demonstrate controlled growth on a well-defined oxide substrate and establish a robust methodology for engineering functionalized nanostructures, with potential applications in environmental protection and renewable energy technologies.

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Keywords: SURMOFS, Surface modification, Layer-by-layer growth, Tof-SIMS

From Oxide Dissolution to SAMs: Mechanistic Insights into NHC Adsorption on Naturally Oxidized Copper

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In recent years, the development of organic inhibitors for metal corrosion protection has attracted growing interest. Among these, N-heterocyclic carbenes (NHCs), renowned for their strong affinity with metals and electronic stability, have emerged as promising candidates for forming self-assembled monolayers (SAMs) on metallic surfaces, particularly on gold and copper. However, the literature shows that many factors influence NHC adsorption, including molecular structure, substrate nature, deposition method, and parameters such as exposure time, suggesting that kinetic effects also play a major role. Moreover, under working conditions, copper is oxidized, adding complexity to the understanding of NHC-copper interaction. As a result, the adsorption mechanism on naturally oxidized copper remains poorly understood.

This study investigates the mechanism and kinetics of adsorption of Bisdodecylimidazolium bromide (I^{C12}) by liquid-phase (10^{-2} M in ethanol) on naturally oxidized copper (Cu_2O , 2.5 nm) under controlled atmosphere (Ar glovebox). The combination of X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) measurement reveals a complete dissolution of the native oxide layer within 2 h of exposure to I^{C12} , followed by adsorption of the intact molecule onto metallic copper between 2 and 18 h. Adsorption occurs via a C–Cu bond, indicating the imidazolium deprotonation to a carben adduct, with two distinct modes: direct adsorption accounting for 15% of the surface coverage and complex formation ($(I^{C12})_2-Cu$) covering 85%. Quantitative analysis indicates progressive film densification and alkyl chain alignment over 18 h, suggesting self-organization of the organic layer over time. Surface characterization further reveals co-adsorption of the NHC and bromide counter-ion. A complementary study of the counter-ion effect on copper provides insight into the reaction mechanism. The results shows that bromide ions promotes oxide layer dissolution during immersion, effectively acting as a pre-treatment that enables subsequent NHC adsorption onto metallic copper substrate. Finally, after 18 h of immersion, the resulting film reaches a I^{C12} molecular density of 2.2 molecules/nm² and a thickness of 1.4 nm, consistent with an upright adsorption mode where the alkyl chains are tilted by 35° relative to the surface normal. As a first test of the density and inertness of the film obtained, surfaces treated for long immersion time (>4h) present a strong limitation to the reoxidation after air exposure, unlike untreated metallic copper, confirming the formation of a dense I^{C12} protective layer.

This study provides new mechanistic insights into the adsorption dynamics of NHCs on oxidized copper, underscoring the critical role of counter-ions and kinetic effects in film formation.

Keywords: N-Heterocyclic Carbene, Self-Assembled Monolayer, Copper, Oxide, Adsorption

A complementary approach to the interfacial studies between organosolv lignin and aluminium oxide

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In this study, the interfacial interactions between aluminium oxide and organosolv lignin are investigated using X-ray photoelectron spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) in Kretschmann geometry (KG) in a complementary approach. This approach provides information on the elemental composition and the formation of bonds at the interface.¹ The aim is to understand and optimize the interactions between lignin and aluminium in order to optimize the performance of lignin-based coatings. These coatings offer a sustainable alternative to the traditional coatings which often contain hazardous components that pose a risk to both health and the environment.² Organosolv lignin was selected because it is highly pure and sulphur-free and aluminium was selected as the substrate due to its tuneable and stable oxide layer.^{3,4}

XPS and ToF-SIMS analyses of aluminium oxide with a thin layer of lignin revealed hydrogen and ionic bonding are the primary bonding mechanisms, as seen by the increase in alcohol and carboxylate functions at the interface. ATR-FTIR-KG produced an in-situ image of the dynamic character of the interface. Initially, the carboxylate and hydroxyl regions confirmed the results obtained with XPS and ToF-SIMS. However, after 24 hours, water started to accumulate at the interface, which decreased the number of hydrogen and ionic bonds and simultaneously lead to a growth in the aluminium oxide layer. These findings provide critical insight into the interactions between lignin and aluminium and open the door for further interfacial and corrosion studies.

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Keywords: Lignin, Interfacial studies, Aluminium, coatings

The role of topcoat curing on the adhesion of UV-cured primers

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Coil coatings are a highly demanding class of protective coatings that are applied to a metallic substrate prior to being formed into the end product. The coating systems must be able to withstand significant mechanical deformations during the forming processes. Conventionally, coil coating formulations are organic solvent-based and require energy-intensive gas-powered thermal ovens to incinerate the solvents and cure the coatings, resulting in high energy usage, CO₂ equivalent and volatile organic compound (VOC) emissions. In light of environmental and net-zero targets, alternative curing technologies that significantly reduce energy consumption and associated carbon emissions, must be investigated.

A solution is radiation curing technology, where an electron beam (EB) or photons such as ultraviolet (UV) are used to initiate the crosslinking reaction and cure the coatings, rather than thermal energy. The energy is focused on curing the coating and can be completed at ambient temperatures using electricity which significantly reduces the energy consumption. The radiation-cured coatings are also organic-solvent free eliminating VOC emissions.

As the coil coating industry begins to transition to radiation curing, implementation of the technology is following two routes. Some investigate fully radiation-cured primer and topcoat systems, whereas others implement "hybrid" systems that pair radiation-cured coatings with conventional solvent-borne layers to enable faster adoption.

Field trials have shown the adhesion performance for UV-primed coil coating systems vary depending on the topcoat curing process. Samples containing a UV-cured primer with a conventional solvent-borne topcoat show improved adhesion compared to a fully radiation-cured system. The hypothesis is that the thermal curing step provides the time and energy to allow migration of minor components in the formulation compared to the almost instantaneous curing process for radiation curing. In particular, the thermal curing step may allow the migration of the phosphoric-acid based adhesion promoter to the primer-substrate interface and hence improve adhesion.

In this work a series of four UV primer systems with differing levels of adhesion promoter were investigated to evaluate the above hypothesis. Standard coil coating mechanical tests were employed to determine the adhesion performance of each system and XPS and ToF-SIMS were utilised to understand the chemical phenomenon behind the differences in performance. To probe interface chemistry, these methods were used in combination with ultra-low angle microtomy (ULAM) and femtosecond laser ablation (fs-LA) XPS.

Initial results indicate that the thermal curing step leads to migration of the adhesion promoter towards the primer-substrate interface, leading to the improved adhesion.

Keywords: Adhesion, Coil coatings, Radiation curing, XPS, ToF-SIMS

POSTERS

Biomaterials engineering and analysis

Industrial Batch Processing of Self-Assembled Monolayers for Biosensor Chip Functionalization

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Wafer-scale surface functionalization of CMOS compatible biosensor chips is essential for high-performance biomolecular sensing. Chemical vapor deposition (CVD) of silane-based self-assembled monolayers (SAMs) is a promising approach because it is compatible with batch processing and substantially reduces chemical consumption compared with liquid-phase deposition. However, vapor-phase SAM deposition has mainly been explored at laboratory scale and typically after chip fabrication, with limited evidence of scalability and reproducibility in industrial manufacturing environments.

Here, we investigate optimized vapor-phase deposition of azidosilane SAMs by batch processing on 200 mm silicon wafers using an industrial MVD300® deposition system (KLA Corporation). The resulting surfaces were comprehensively characterized by film thickness measurements, water contact angle analysis, infrared spectroscopy, and particle contamination analysis. Azidosilane SAMs were selected because their azide functional groups enable efficient immobilization of target biomolecules via click chemistry, making them highly attractive for biosensor applications.

Silicon wafer substrates were first activated by in situ oxygen plasma within the MVD300® process chamber and subsequently functionalized through reaction with vaporized azidosilane and water precursors. The influence of deposition parameters on SAM properties was systematically evaluated using complementary characterization techniques. The optimized batch process was then assessed for within-wafer (WIW) and wafer-to-wafer (WTW) uniformity.

The deposited SAMs exhibited highly uniform thicknesses of 0.4 ± 0.1 nm and water contact angles of $53 \pm 5^\circ$, with comparable standard deviations for WIW and WTW distributions. Infrared spectroscopy revealed a characteristic azide absorption peak at 2100 cm^{-1} , directly reflecting the surface density of azide functional groups. Peak intensities showed relative standard deviations (RSDs) of 7–13% for WIW and 10–20% for WTW distributions. Importantly, the process demonstrated high reproducibility, with average infrared peak intensities across three independent batch runs varying by less than 3% RSD. In addition, SAM deposition introduced only 14 ± 5 particles (>250 nm diameter) per wafer, indicating negligible formation of undesirable silane-polymerization aggregates.

Together, these results demonstrate that highly uniform and reproducible SAM coatings can be achieved at wafer scale using CVD processes compatible with CMOS manufacturing environments. This approach supports the large-scale manufacturing of affordable biosensor chips pre-functionalized for biomolecular sensing applications.

Keywords: chemical vapor deposition, self-assembled monolayer, surface functionalization, biomolecule, wafer-scale

Electrogravimetric analysis of chondrocyte-laden electrospun polymer-hydroxyapatite scaffolds using EQCM

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Electrospun scaffolds combining biopolymers and hydroxyapatite (HAp) are widely explored for cartilage tissue engineering; however, their electrochemical and electrogravimetric responses in the presence of cells remain poorly understood. In this study, electrospun membranes composed of sodium alginate, collagen and polycaprolactone were cultured with mesenchymal cells (Lonza/PT-5025) under chondrogenic differentiation conditions for 7, 10 and 14 days and modified with different HAp compounds. (1) micrometric-(μ HAp), (2) nanometric-(nHAp), (3) functionalized nanometric-(nHAp_f) and (4) natural-decellularized bovine condyle to produce a hydroxiapatite-lilke compound-(NKB). The electrochemical behavior of the cell-laden membranes was investigated by cyclic voltammetry coupled with electrochemical quartz crystal microbalance (CV-EQCM) after cell culture, using distilled water as measurement media. The electrochemical examination was complemented with alcian blue staining, and immunohistochemical staining of Sox-9, Colagen 2A and Aggrecan to confirm terminal chondrogenic differentiation. All membranes exhibited pseudocapacitive voltammetric profiles, with significant differences in cathodic charge depending on HAp structure. The cathodic charge increased in the following order: μ HAp<NKB<nHAp<nHAp_f. EQCM measurements revealed distinct electrogravimetric responses among the formulations. μ HAp and nHAp membranes showed negative frequency shifts during cathodic polarizations (-8.63 and -16.65 Hz), whereas NKB and nHAp_f systems exhibited positive frequency excursions, with a pronounced response for nHAp_f sample (+147.54 Hz) and a moderate shift for NKB membrane (+27.8 Hz). Reversibility analysis indicated that the μ HAp membrane displayed the highest recovery (~82%) while NKB and nHAp_f systems showed limited recovery and significant post-cycle drift. Alcian Blue staining was positive for μ HAp, nHAp, nHAp_f and NKB membranes after 10 and 14 days, and was stronger in the nHAp_f and NKB conditions. At 10 and 14 days, the cells on the NKB scaffolds formed robust clusters and structures characteristic of chondroid matrix. Staining for Sox-9, Aggrecan, and COL2A, expression was more intense in the nHAp_f and NKB scaffolds, confirming chondrogenic differentiation. In contrast, expression was low or almost undetectable in μ HAp, nHAp at all times examined. These results indicate that the physicochemical properties of HAp directly affect cellular behavior and matrix formation during culture, and that the type of HAp incorporated into the scaffold significantly influences the cellular response. These findings demonstrate that HAp structure and surface functionalization strongly modulate the electrochemical and electro-mechanical response of chondrocyte-like-laden electrospun membrane. In particular, functionalized systems induced larger and less reversibles electrogravimetric responses, suggesting stronger interfacial interactions and enhanced structural rearrangement within the biological composite layer.

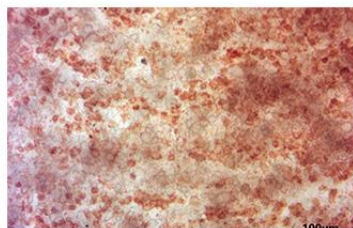
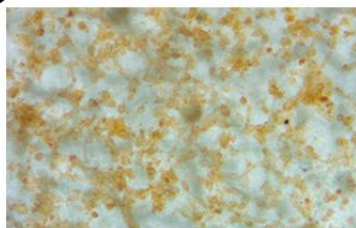
Acknowledgments: P. González- Alva acknowledge UNAM-PAPIIT-IN204124 for the financial support of this work.

Keywords: EQCM, hidroxyapatite structure, electrospun membranes, biological assays, mesenchymal stem cells

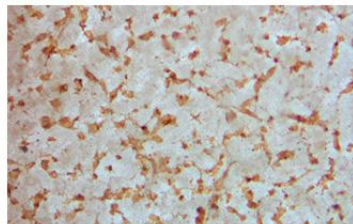
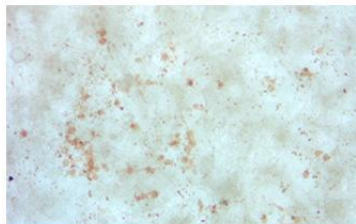
Sox-9

μHap

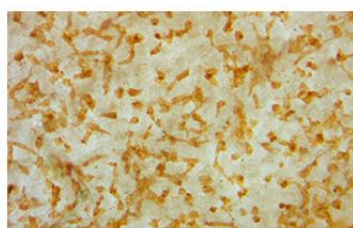
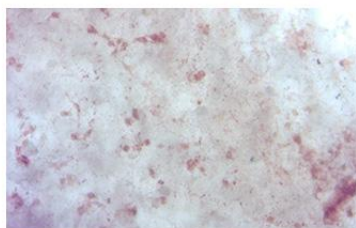
NKB



Aggrecan



Col2A



Secondary ion yield enhancement for lipids in frozen hydrated lymphoma tissue samples using Cryo-H₂O-GCIB-SIMS

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The enhancement of secondary ion yields (SI-yields) for lipids by combining frozen-hydrated sample handling and H₂O gas cluster ion beams (GCIBs) was investigated in lymphoma tissue sections. Using an Ionoptika J105 time-of-flight secondary ion mass spectrometry instrument equipped with a 40 keV GCIB, H₂O and CO₂ gas clusters with E/n (kinetic energy per atomic mass for the cluster) ranging between 0.09 and 0.15 eV were compared on frozen-hydrated and freeze-dried tissue sections. Here we present and discuss the benefit of H₂O GCIB and the effects of cryogenic analysis on secondary ion yields and depth profiling on frozen-hydrated tissue sections.

The results showed that SI-yields for intact lipids increased while fragmentation decreased with decreasing E/n for H₂O and CO₂ GCIBs. At similar E/n, the H₂O-GCIB had significantly higher SI-yields and reduced fragmentation, but a very similar sputter rate when compared to the CO₂ GCIB. Tissue sections analysed under frozen-hydrated conditions had higher and general SI-yields for organic molecules and sputter rates compared to freeze-dried samples. Depth profiling combined with atomic force microscopy measurements highlighted that freeze-drying altered the sample condition, significantly reducing the sputter rate and secondary ion yields.

Keywords: GCIB-SIMS, Frozen-hydrated, biological samples, Cryogenic analysis, Depth profiling

Catalysis

CO oxidation on size-selected Pt clusters on TiO₂ and SnO₂: metal–support interaction and size effect studied by NAP-XPS

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Nobel metal nanoparticles supported on metal-oxide surfaces show a high catalytic activity in a variety of reactions. In particular, deposited size-selected clusters represent a unique class of materials that offer a high tunability of chemical properties with high efficiency of material utilization. For this contribution two different cluster sizes, Pt₁₃ and Pt₄₀, supported on two technologically relevant supports, TiO₂ and SnO₂, were studied for CO oxidation under atmospheric and near-ambient pressure conditions [1]. Both, cluster size and support material, directly influenced the catalytic activity, with Pt₄₀/TiO₂ showing the best performance. In situ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) was used to identify changes in the Pt oxidation state under reaction conditions, revealing that a higher metallicity promotes catalytic activity. However, the activity is not solely determined by the final Pt oxidation state, which rather evolves from a combination of strong metal-support interactions and size-dependent effects. Especially in the case of Pt supported on SnO₂ ex situ XPS and ion scattering spectroscopy (ISS) measurements suggested a SnO₂ overgrowth leading to enhanced chemical stability and sintering resistance of the Pt clusters. At the same time, the overgrowth limits the access of the reactants to the active Pt sites, ultimately leading to lower catalytic activity of Pt_n/SnO₂ compared to Pt_n/TiO₂ catalysts.

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Keywords: CO oxidation, NAP-XPS, Pt cluster

Towards greener titanium phosphonate catalysts for 5-HMF: influence of HCl concentration and diphosphonate structure

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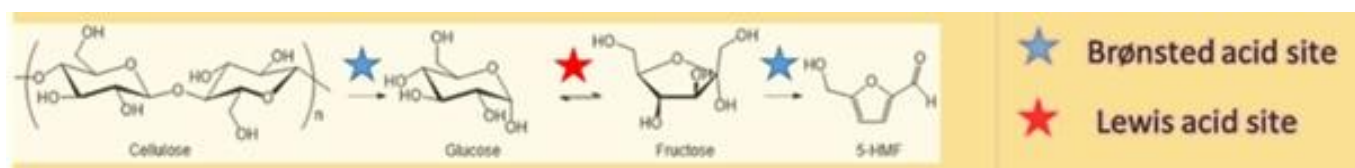
Porous metal phosphonates (PMPs) are hybrid materials formed from metal precursors and organophosphonic acids or esters. They combine high surface areas, often exceeding $300 \text{ m}^2 \text{ g}^{-1}$, with notable chemical stability over a wide pH range and thermal stability typically above 200°C . Among the different classes of PMPs, this project focuses on (meso)porous titanium phosphonates and their application as heterogeneous catalysts for biomass conversion, specifically for the production of 5-hydroxymethylfurfural (5-HMF).

Despite their potential, the controlled synthesis of (meso)porous PMPs remains challenging, mainly due to the strong and rapid interaction between phosphonate groups and metal oxide units, in this case Ti(IV) centers. Therefore, precise control over precursor reactivity, hydrolysis, condensation, and network formation is required. In this work, phosphonic acid moieties are introduced through the in situ hydrolysis of tetraethyl propylene-1,3-diphosphonate (TEPD), aiming to avoid rapid precipitation and promote the controlled assembly of hybrid porous networks.

A greener synthetic route was explored by replacing conventional organic solvent-based titanium phosphonate syntheses with fully aqueous conditions, using titanium(IV) bis(ammonium lactato)dihydroxide (TiBALDH) as a water-soluble titanium precursor. The effect of hydrochloric acid concentration on the synthesis was investigated and identified as a key parameter controlling the properties and catalytic performance of the resulting materials. In addition, the influence of the organic bridging group in the diphosphonate precursor on the structural and catalytic properties of the materials was studied using tetraethyl p-xylylenediphosphonate (TEXD) and tetraethyl 1,4-phenylenediphosphonate (TEPhD). This comparison provides insight into the role of linker flexibility, steric bulk, and rigidity, with TEPD representing a flexible aliphatic linker, TEXD a bulkier semi-rigid linker, and TEPhD a rigid aromatic linker.

The changes in properties of (meso)porous titanium phosphonates, induced by altering the acid concentration and the diphosphonate precursor, were evaluated towards their impact on performance in 5-HMF production. This reaction proceeds through three steps: hydrolysis of cellulose-derived substrates, glucose–fructose isomerization, and fructose dehydration, requiring a suitable balance of Brønsted and Lewis acid sites. Robust and tunable titanium phosphonate catalysts may therefore offer an attractive alternative to homogeneous mineral acids and conventional heterogeneous catalysts, which often suffer from corrosion, waste-management issues, leaching, deactivation, or limited tunability.

Keywords: PorousMaterials, TitaniumPhosphonates, HeterogeneousCatalysis, BiomassValorisation, 5-HMF

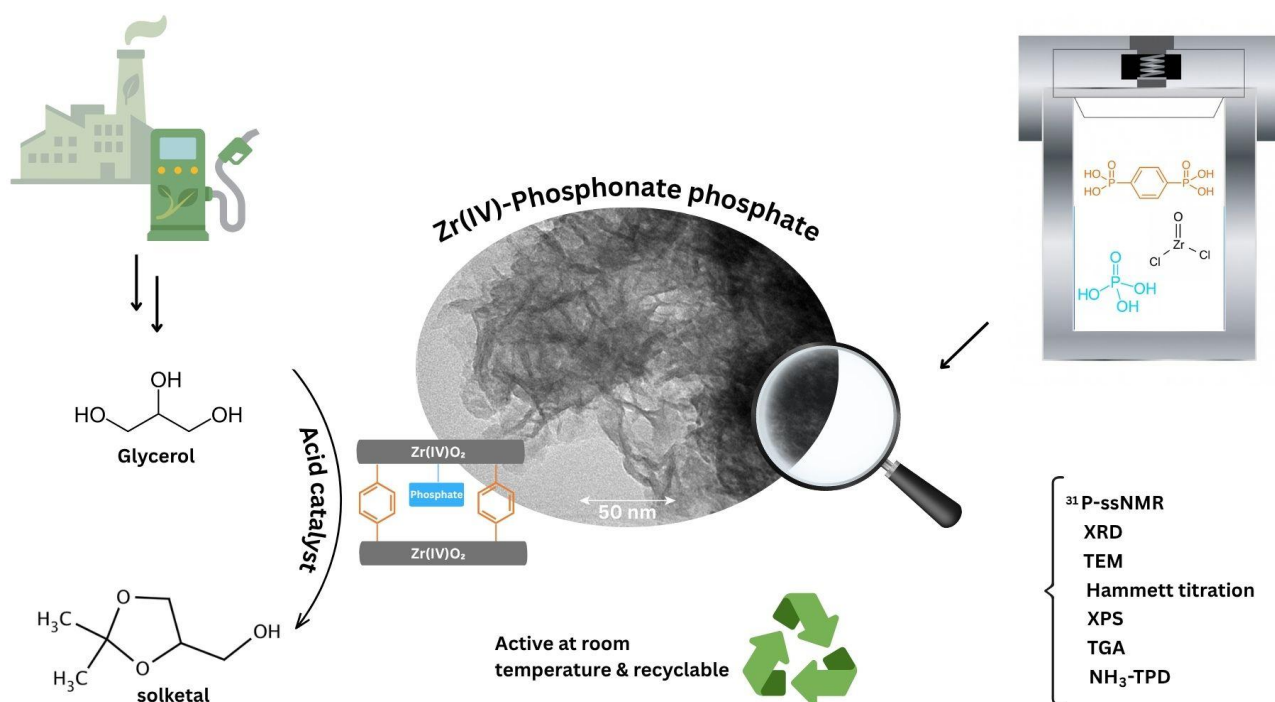


Zirconium (IV) layered phosphonate-phosphate as catalysts for the valorization of glycerol

Nahal Ghanemnia (University of Hasselt, Hasselt, Belgium), **Nahal Ghanemnia** (UHasselt, Hasselt, Belgium)

The valorisation of glycerol, a large-volume byproduct of biodiesel production, remains a key challenge for the bio-refinery sector. Among the available strategies, its acetalisation with acetone offers a sustainable route to produce solketal, a valuable fuel additive. The feasibility of this valorisation route is, however, largely dependent on the continuous research towards highly performant, stable catalysts with carefully designed acidic sites. In this work, hybrid porous zirconium phosphonate-phosphate materials were synthesised and evaluated as recyclable heterogeneous catalysts. The acidity was systematically investigated using Hammett indicators, supported by solid-state ^{31}P NMR, XPS, and ammonia TPD analyses. Their structural and thermal stability was also assessed. The incorporation of phosphate groups was found to be essential to provide sufficient Brønsted acidity and enhance the long-term stability of the catalysts, as evidenced by their successful recyclability during multiple catalytic runs. In addition, yields of 85%, with a selectivity of 98% can be reported in optimal conditions, and the catalyst was even found to offer very promising conversions at room temperature.

Keywords: biomass valorization, hybrid acid catalysts, metal phosphonate phosphates, hybrid porous materials



Acidity-Activity Relationships in Metal-Doped Silica Catalysts Probed by ^{31}P Solid-State NMR

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The development of a circular economy relies on catalytic processes converting renewable feedstocks and waste into value-added chemicals. Representative examples include the valorization of glycerol, the upgrading of biomass-derived platform molecules, and the utilization of CO_2 . [1] Despite involving different substrates and reaction pathways, these transformations are strongly influenced by the acidic properties of the catalysts, particularly the nature, strength, and ratio between Lewis (L) and Brønsted (B) acid sites. The limitations of conventional homogeneous acids, such as corrosion, catalyst recovery, and environmental concerns, have driven the development of heterogeneous solid acids. A wide variety of acid materials have been explored, including zeolites, heteropolyacids, metal-organic frameworks (MOFs), carbon nanomaterials, and silica-based solids. Among them, silica-based catalysts are especially attractive because their acidic properties can be tailored through incorporation of different metal cations into the framework. [2] Understanding catalyst acidity is essential for establishing structure-activity relationships and optimizing catalytic performance. In this context, solid-state nuclear magnetic resonance (ssNMR) spectroscopy has emerged as a powerful technique for probing heterogeneous acid sites. When combined with suitable probe molecules, ssNMR enables investigation of the nature, strength, and distribution of Lewis and Brønsted acid sites at the molecular level. In particular, trimethylphosphine (TMP) is employed due to its sensitivity toward different acidic environments and the favorable NMR properties of the ^{31}P nucleus (100% natural abundance). [3] In this work, a series of metal(IV)-doped silica materials was synthesized via a sol-gel route and used as a model system to investigate acidity-activity relationships. Hollow silica nanospheres and nanotubes containing Ti^{4+} , Zr^{4+} , or Hf^{4+} were prepared with different Si/M ratios to tune their acidic properties (Figure 1). The materials were characterized by complementary physicochemical techniques, with particular emphasis on ^{31}P TMP-ssNMR. The proposed methodology is broadly applicable to heterogeneous acid catalysts. In some cases, however, TMP is not suitable; for example, in phosphorus-containing materials, signal overlap may occur. Alternative probes, such as ^{13}C -enriched acetone, can then be employed to avoid spectral interferences. This makes probe-assisted ssNMR a valuable tool for characterization and catalyst design.

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Keywords: TMP, ssNMR, Heterogeneous Catalysis, Acid active sites, Lewis-Brønsted Ratio

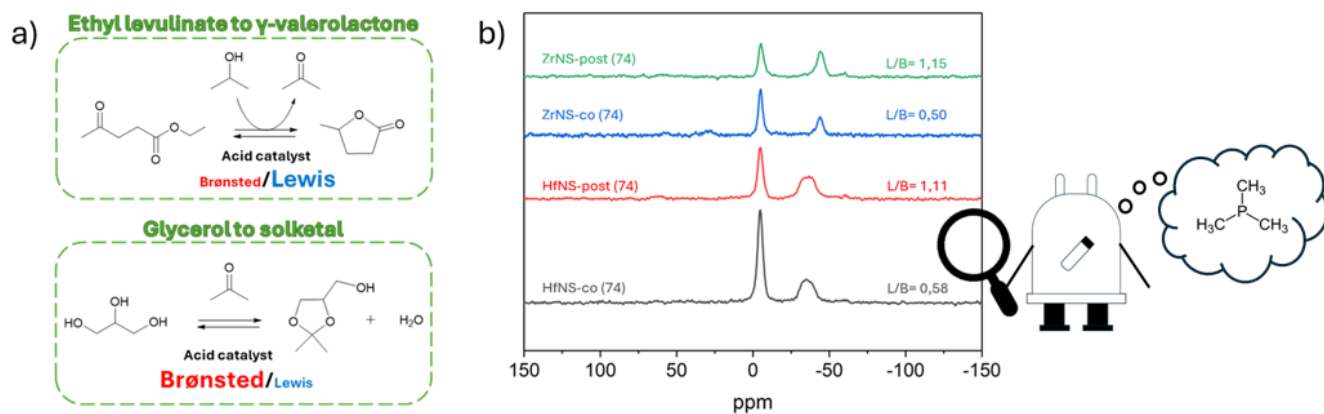


Figure 1. a) The two reactions studied. b) ^{31}P -ssNMR spectra of TMP adsorbed on a series of sample.

Chemical Mapping of Sub-Monolayer Oxygen Species on Acid Treated HOPG Surfaces Through Photo-Induced Force Microscopy

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Carbon is widely used as a support for heterogeneous catalysts because of their relatively low cost, high surface area and the ease with which precious metals can be reclaimed from the support at the end of the catalyst's active life [1]. In most cases, these carbons are acid washed, before the adsorption of the active component. The wash serves two purposes; it removes unwanted inorganic contaminants present in the carbon; and it introduces oxygenated functionalities that modify the behaviour of the carbon towards the adsorption of the active component and the reaction solvent [2].

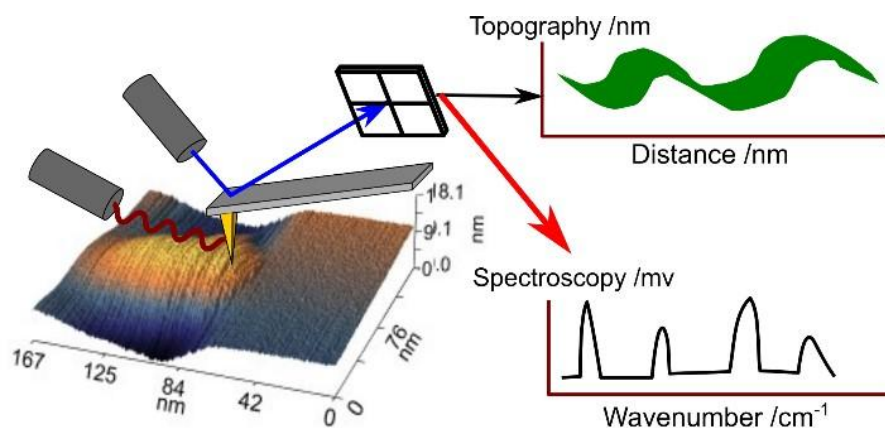
Our previous work using HOPG as a model carbon substrate has shown HCl and HNO₃ have a significant impact on the surface topography through intrusion by the acid into the graphite, causing weakening and breakage of the interplanar bonds [3]. Chemical derivatisation studies via XPS, has shown that depending on the acid, the surface forms hydroxyl, carbonyl and nitrate containing functions, however, to date the location of these features, especially with relation to the protrusions are unknown [4].

Herein, we present the first Photo-Induced Force Microscopy (PiFM) studies of acid treated HOPG surfaces allowing the unambiguous correlation of surface topography with sub-monolayer oxygen functionalities through chemically distinct vibrational spectra, supported by XPS and computational measurements.

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Keywords: PiFM, Carbon, Catalysis, XPS, Oxidation



Vibrational spectroscopy at 5 nm resolution

Surface analysis of anion exchange membranes after operation in a water electrolysis cell

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Green hydrogen, obtained through electrolysis processes, constitutes a viable alternative to both traditional energy vectors (fossil fuels, methane) and reducing agents in numerous industrial processes. This transition is justified by its high calorific value per unit mass and its capacity to minimize negative environmental impacts, such as CO₂ emissions into the atmosphere derived from industrial and energy-related processes. Moreover, there are relevant geopolitical reasons that support advancing toward a new paradigm based on hydrogen, progressively replacing fossil fuels with the purpose of reducing Europe's energy dependence.

Low temperature anion exchange membrane water electrolysis (AEMWE) is an emerging technology for the production of green hydrogen. This technology does not present limitations associated with the cost and availability of catalysts (as it is not based on the use of critical raw materials such as platinum group metals) and operates with aqueous solutions containing low electrolyte concentrations, which provides greater process stability and overall durability of its components. Figure 1 shows a simplified diagram of the elements of an AEMWE cell along with the processes that take place during its operation.

A key element of this technology is the anion exchange membrane that separates the anode and cathode compartments in the cell. It acts as water diffusion layer and solid polymer electrolyte that conducts hydroxide ions (OH⁻) under application of polarization voltage while physically separating the produced hydrogen and oxygen gases at the cathode and anode side of the cell, respectively. It is well known that the durability of these membranes is a critical issue to scale-up this technology to industrial applications. Understanding the processes at the catalyst/membrane interface is of paramount importance for the development of high-performance and durable devices.

In this work, we present a preliminary study using XPS and 2D TOF-SIMS analysis of the evolution of the species at the surface of anion exchange membranes before and after operation. It is observed a clear evolution of a uniform 2D distribution of species at the surface of the membrane before use to clear preferential enrichment of species and radicals at specific regions of the membrane in tight contact with the catalysts (CL) deposited on the porous transport layer (PTL) supports after operation. We will correlate the observed behavior with the electrochemical performance of the cell.

Keywords: TOF-SIMS, Water electrolysis, Anion Exchange Membrane, Green Hydrogen

Activity versus Stability in Porous Metal Phosphonates: Insights from Glycerol Conversion to Solketal

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Glycerol is one of the main by-products of the biodiesel industry and is abundantly available on the market. This versatile molecule can be converted into cyclic acetals, such as solketal (Figure 1), through an acetalization reaction. The synthesis of solketal is characterized by high atom economy and a potentially low E-factor.¹ Moreover, solketal can be used as a green solvent and biofuel additive, thus contributing to the development of a circular economy. To enhance the conversion of glycerol into solketal, the use of an acid catalyst is required. Both Lewis and Brønsted acid sites play a key role in achieving high catalytic efficiency,² and for this reason in this work four novel porous Zr(IV)- and Ti(IV)-based metal phosphonates (PMPs) were investigated as heterogeneous catalysts.

On the one hand, two Zr(IV) materials exhibiting a layered structure were prepared, in which zirconia layers are interconnected either by both a linker (1,4-phenylenediphosphonic acid) and a spacer (phosphoric acid) or solely by the linker. On the other hand, two Ti(IV) materials constituted by amorphous porous metal phosphonates were synthesized through the controlled hydrolysis and condensation of tetraethyl propylene diphosphonate (TEPD) and titanium butoxide, either in the presence or absence of the surfactant F127 as a templating agent, giving amorphous porous metal phosphonates. All the synthesized solids display high specific surface areas (300–400 m² g⁻¹) and remain thermally stable up to 300 °C.

Preliminary catalytic tests revealed that all materials are active toward solketal synthesis. Hot filtration and recycling experiments were performed to assess catalyst stability. Interestingly, the most active catalysts proved to be the least stable ones, highlighting an important aspect of catalyst evaluation: intrinsic activity alone is not sufficient, whereas stability and reusability over consecutive cycles are crucial parameters. Two of the investigated catalysts, namely the Zr(IV)-layered PMP embedding both linker and spacer and the Ti(IV) -PMP synthesized in the presence of F127, showed no leaching of active species and were recyclable for several consecutive cycles. Therefore, porous metal phosphonates can be considered promising catalysts for the conversion of glycerol into solketal, being also competitive in terms of performance with similar catalytic systems previously reported in the literature.

Keywords: Glycerol valorization, Porous metal phosphonates, Heterogeneous catalysis

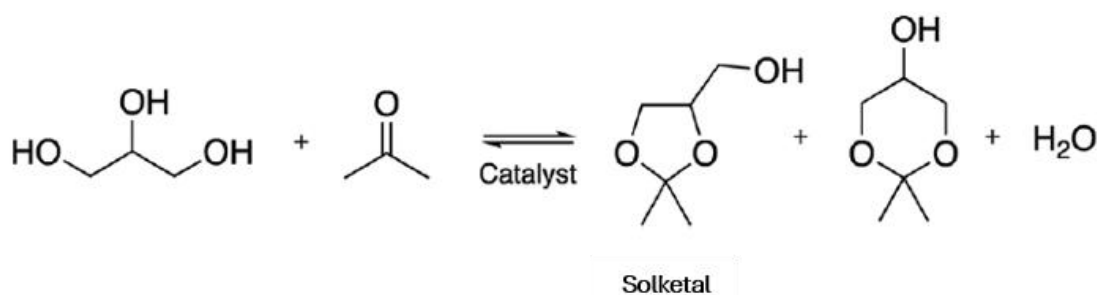


Figure 1. Conversion of glycerol into solketal.

Synthesis of carbon-based bifunctional Lewis/Brønsted acid catalysts for 5-HMF production from cellobiose

Alessia Tonelli (IMCN/MOST, UCLouvain, Louvain la Neuve, Belgium)

Lignocellulosic biomass has been recognized as a promising renewable resource for the production of a number of key commodity chemicals. Among the possible products that can be obtained by upgrading its cellulose component, 5-hydroxymethylfurfural (5-HMF) is a high added-value platform chemical that can be valorized. Transforming cellulose into 5-HMF requires three steps involving hydrolysis of the biomass, isomerization of the attained glucose into fructose, and the subsequent dehydration of the latter into 5-HMF [1] (Figure 1). Therefore, there is a strong interest in developing bifunctional catalysts presenting both Brønsted and Lewis acid sites for favoring this multi-step transformation in one pot. In addition, the use of a carbon solid support can provide superior mechanical and chemical resistance to the water and O-rich media provided by such a feedstock, along with tunable textural and surface properties.

In the present work, mesoporous aluminosilicate patches [2-3] have been grafted on the surface of a carbon support (activated carbon powder, fraction < 50µm) together with benzyl sulfonic moieties [4] to provide both Lewis and Brønsted acid sites, respectively, to the same solid. To study the elemental composition and microstructural features achieved, SEM/EDX, TEM (Figure 1), and XPS analyses have been performed. Nitrogen physisorption was used to confirm the mesoporous nature of the catalysts, while Boehm titration and ³¹P MAS NMR with PMe₃ probe were applied to investigate their acidity and confirm the presence of both Brønsted and Lewis sites in the final material. The activity of the synthesized bifunctional catalysts and that of their corresponding monofunctional counterparts (sulfonated carbon and aluminosilicate patched carbons) was compared for the upgrading of cellobiose to 5-HMF. A proximity effect was found when the two acidic sites are combined onto the same substrate, facilitating the overall conversion of the sugars involved. A maximal yield of 37% of 5-HMF was attained after 23 h with catalyst I4@BATEOS/SO₃H in a THF:mQ water system at 423 K. No significant traces of side products were observed after 23 hours, indicating the high selectivity of the catalyst for the targeted transformations.

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Keywords: 5-Hydroxymethylfurfural, Biorefinery, Bifunctional catalysts, Heterogenous acid catalysts

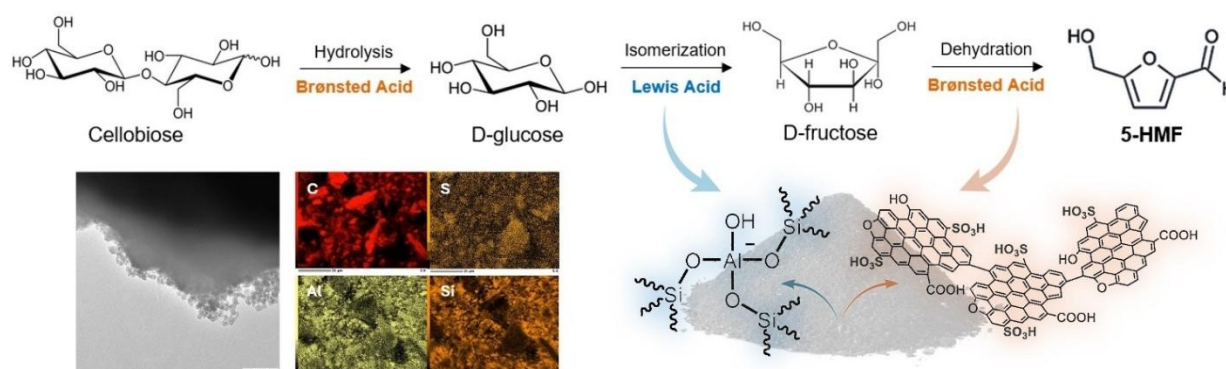


Figure 1: Synthesis of 5-hydroxymethylfurfural (5-HMF) from cellobiose mediated by Brønsted (benzyl sulfonic moieties) and Lewis (aluminosilicate patches) acid sites co-located at the surface of an activated carbon support. On the left side, a TEM image of the attained oxide patches and the corresponding SEM-EDX maps are provided.

Design of sulfonated-silica based acid catalysts for biomass valorization

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The depletion of fossil resources is driving industries to seek more sustainable and environmentally friendly alternatives. Among the available options, biomass and its derivatives have emerged as promising chemical platforms to produce value-added products.

For instance, glycerol, a major by-product of biodiesel production, can be converted into solketal through an acid-catalyzed acetalization reaction [1]. As solketal is a valuable fuel additive, this transformation contributes to a circular economy approach, aligning with sustainability goals. Another example is the conversion of cellulose (or model carbohydrates such as cellobiose) into 5-hydroxymethylfurfural (HMF), a key platform molecule that serves as a precursor for a wide range of bio-based chemicals traditionally derived from petroleum [2].

Despite the differences in substrate complexity and reaction pathways, both transformations rely mainly on the catalytic activity of Brønsted acid sites [3, 2], highlighting the importance of designing efficient solid acid catalysts for biomass valorization. In this work, dendritic silica nanoparticles (DSNP) used as catalytic supports were functionalized with sulfonic acid moieties (via 3-(trihydroxysilyl) propane-1-sulfonic acid, TPS), to catalyze both reactions (Figure 1).

The grafting efficiency and structural properties of the material were assessed using a combination of characterization techniques, including transmission electron microscopy (TEM), nitrogen physisorption, X-ray photoelectron spectroscopy (XPS), and solid-state magic angle spinning nuclear magnetic resonance (SS-MAS NMR). Both ^{13}C and ^{29}Si NMR spectra were performed under cross-polarization (CP) and direct-excitation (DE) conditions.

The acidic properties of the functionalized materials were further investigated using trimethylphosphine (TMP) as a molecular probe in solid-state ^{31}P MAS NMR experiments [3]. Depending on the type of acid site, TMP can either be protonated on Brønsted sites or coordinate to Lewis acid sites, leading to distinct chemical shifts in the ^{31}P NMR spectra [3]. This methodology provides valuable insights into the relationship between acidity and catalytic performance. The predominance of Brønsted acid sites (Figure 2) correlates with the high catalytic efficiency observed for both reactions, highlighting the suitability of these materials for acid-catalyzed conversions.

Keywords: Heterogeneous catalysis, Biomass, Mesoporous silica, Solid state NMR, Acidity assessment

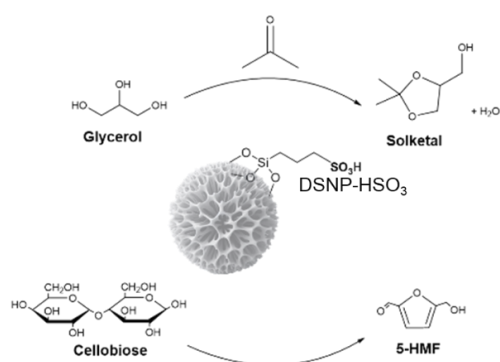


Figure 1. Schematic representation of the two catalytic reactions.

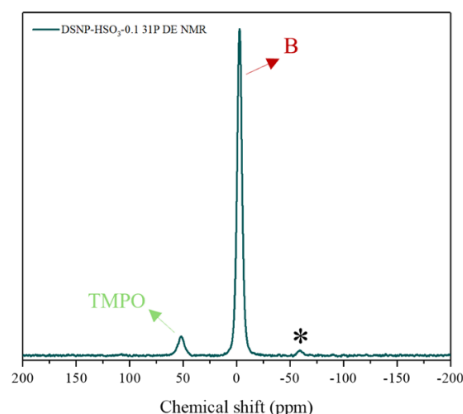


Figure 2. ^{31}P NMR spectrum: acidity assessment

Designing Spatially Heterogeneous Catalyst Surfaces for Accelerated Screening of Alkaline Water Splitting by SECCM

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Understanding how surface structure influences catalytic activity is essential for accelerating the development of efficient water splitting electrodes. Scanning Electrochemical Cell Microscopy (SECCM) enables localized electrochemical measurements with micrometer-scale resolution, allowing catalytic activity to be mapped directly across heterogeneous surfaces. When combined with identical-location EDS and EBSD analysis, spatial variations in activity can be correlated with grain orientation, surface oxidation state, and local composition. This approach transforms intrinsic surface heterogeneity into a powerful screening tool.

Recent methodological advances have improved the stability and reliability of SECCM measurements in alkaline environments. However, systematic strategies to deliberately engineer spatially heterogeneous catalyst surfaces remain limited. Since SECCM extracts the most information from samples exhibiting broad local variability, rational sample design becomes a key factor in maximizing screening efficiency. Here, we demonstrate how such model systems enable accelerated identification of structure-activity relationships, thereby guiding the design of next-generation alkaline water splitting electrodes.

Keywords: SECCM, Alkaline Water Splitting, High-throughput

Mechanistic Insights into Phenol Hydrodeoxygenation via Precisely Engineered Metal–Acid Bifunctional Catalysts

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The depletion of fossil fuels and increasing environmental challenges have accelerated the development of renewable energy conversion technologies. Fast pyrolysis of biomass followed by upgrading of bio-oil offers an effective pathway to produce sustainable liquid fuels; however, the high concentration of phenolic compounds derived from lignin significantly reduces the stability and storage performance of bio-oil. Catalytic hydrodeoxygenation (HDO) enables efficient removal of phenolics to generate high-quality fuels such as cyclohexane, but conventional sulfide and noble-metal catalysts often suffer from limited activity and harsh operating requirements.

Metal–acid bifunctional catalysts provide a promising solution due to the synergistic action between metal sites for hydrogenation and acid sites for dehydration and C–O bond cleavage. Yet, the spatial matching rules, cooperation mechanisms, and reaction pathways governing metal–acid synergy in phenol HDO remain insufficiently understood. In this study, metal-supported ZrO_2 catalysts (M/ZrO_2) are rationally designed by tailoring acidity, metal dispersion, and metal–acid proximity to achieve highly efficient phenol conversion under mild conditions.

To elucidate the structure–performance relationship, essential structural characterization is combined with key in-situ spectroscopic monitoring to track reaction intermediates and active-site evolution. Kinetic analyses and DFT calculations further identify rate-determining steps and clarify how metal–acid cooperation facilitates C–O bond activation and deoxygenation selectivity.

This integrated experimental and theoretical investigation establishes a fundamental structure–effect correlation for metal–acid bifunctional porous catalysts in phenol HDO. The findings provide scientific guidance for developing next-generation, highly active and selective catalysts for bio-oil upgrading and broader biomass-to-fuel applications.

Keywords: Phenol Hydrodeoxygenation, Bifunctional catalysts, Metal-acid site balance, Structure-activity relationship

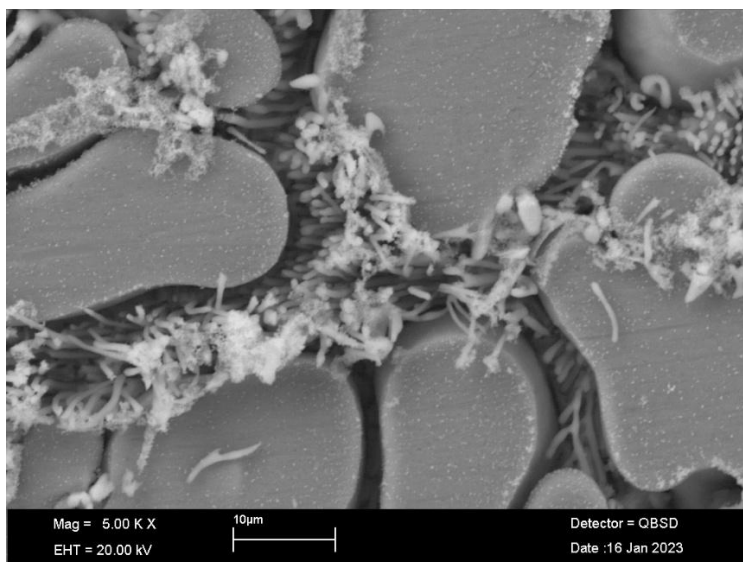
Corrosion

Microstructural modification of a Al-12Zn-12Mg-xCu anode to promote galvanic corrosion in the as-cast condition

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Aluminum-based sacrificial anodes used for cathodic protection in marine environments typically rely on Al-Zn-Mg systems and often require toxic activators, such as Indium or Mercury, to prevent surface passivation. This work investigates the development of a modified 7xxx series alloy (Al-12Zn-12Mg) by evaluating the influence of Cu additions (1, 2, and 3 wt.%) to tailor the morphology and distribution of the τ -Al₂Mg₃Zn₃ phase, promoting active galvanic dissolution in the as-cast condition. The alloys were produced via gravity casting in metallic molds, and microstructural characterization focused on the interdendritic regions using SEM-EDS. As shown in Fig. 1, the as-cast microstructure consists of an interdendritic eutectic network of τ -phase whiskers and fine τ precipitates dispersed within the α -Al matrix. The electrochemical response was evaluated through Open Circuit Potential (OCP) monitoring and potentiodynamic polarization (Tafel) in simulated seawater. Results showed that Cu additions significantly influenced the phase assembly, where OCP measurements indicated a trend towards more positive corrosion potential values as Cu content increased, confirming the establishment of localized cathodic sites. However, the excessive growth of the eutectic region creates bigger internal galvanic couples that promote passivation mechanisms that reduce the anode's ability to provide effective electron transfer to the protected structure. While Tafel analysis indicated higher corrosion current densities (I_{corr}) for 2 wt.% and 3 wt.% Cu alloys, this accelerated kinetic activity resulted in intensified localized attack rather than homogenous oxidation. The 1% Cu alloy exhibited the highest electrochemical efficiency (36.4%) due to a more favorable distribution of intermetallic phases. Conversely, higher Cu concentrations triggered excessive microsegregation of τ particles, leading to severe grain detachment and reducing efficiency to 26.4% and 32.5%. These findings suggest that while Cu acts as a microstructural activator, future heat treatments are required to redistribute Cu into fine τ precipitates to prevent premature grain loss to enhance the sacrificial performance. The as-cast condition shows limited electrochemical efficiency to act as an effective sacrificial anode.

Keywords: Sacrificial anodes, 7xxx series alloys, intermetallic phases, Grain detachment, SEM-EDS



Data analysis

UNIFIT 2027 – Improved Spectrum Processing, Analysis and Presentation Software for XPS, AES, XAS, RAMAN Spectroscopy

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UNIFIT is an established processing, analysis and presentation software for XPS, AES, XAS and RAMAN spectroscopy data. The improved features of the newest version are presented.

The advanced peak fit of XPS data using the Shirley and different Tougaard-background models is demonstrated. The calculated background functions and Inelastic Scattering Electron Cross Sections are shown. The improved determination of the analyser transmission function is demonstrated.

As an example for the improved handling of AES data of O KLL, the complex analysis of a SAM (Scanning Auger Microanalysis) measurement and the corresponding SEM (Scanning Electron Microscopy) image are shown.

A combined XAS and XPS analysis of the Ti L Edge and Ti 2p peak demonstrates the advantage of the peak fit of correlated XAS and XPS spectra. The results of the peak fit of the XPS data can successfully be used for the modelling of the XAS spectral background.

Using an example of RAMAN-micro analysis of a solar cell silicon wafer, the differences of the results with and without peak fit of the RAMAN data are shown. Additionally, the advanced spike correction integrated in the Unifit software is demonstrated. The spikes of a RAMAN measurement, caused using cosmic radiation, are removed successfully.

Keywords: UNIFIT analysis software, Tougaard background, data reduction, XPS, transmission function

Quantitative Ce 3d XPS analysis in cerium oxide: background effects, fitting strategies, and comparison to theory

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The XPS fit of the Ce 3d region in CeO₂ and Ce₂O₃ oxides has been crucial in characterizing catalysts for various processes, including automotive exhaust treatment in three-way catalysts, hydrogen production via thermochemical water splitting, methane reforming, the water-gas shift reaction, oxidation of volatile organic compounds, and CO₂ conversion. In all cases, the relative amounts of Ce³⁺ and Ce⁴⁺ cations—directly related to the concentration of oxygen vacancies—are directly linked to catalyst performance. Therefore, XPS has become a standard tool for determining the chemical oxidation state of cerium cations across many fields, most of which are not fully familiar with the details of XPS analysis. This has led to the spread of poor-quality XPS fitting routines that often ignore basic physical constraints and overlook the efforts of the experimental and theoretical XPS communities over the past few decades to develop more accurate, physically meaningful fit models [1].

Here, we discuss three approaches for Ce³⁺/Ce⁴⁺ quantification in detail: XPS peak fitting, linear combination fitting of Ce₂O₃ and CeO₂ reference spectra, and factor analysis. In the first case, we account for background correction when Al K α , the most extensively employed anode, is used, extracting the Ce MNN Auger signal that partially overlaps with the Ce 3d region around 915 eV [2]. We also compare our fit model with the theoretical work of Kotani [3] and the experimental models developed by Romeo [4] and Skala [5], showing that a proper background correction can affect the absolute value of the extracted Ce³⁺/Ce⁴⁺ ratio and the associated error. The advantages and disadvantages of the linear combination and factor analysis methods are discussed, demonstrating their usefulness in situations requiring quantitative, robust routine analysis. For comparison purposes, the XPS fit of the O 1s regions to effectively extract the Ce³⁺/Ce⁴⁺ ratio is also compared to the Ce 3d results.

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Keywords: Ceria, Background, XPS fitting, Factor analysis, Linear combination

Estimating peak fitting errors in XPS: Influence of line shape, mixing parameter, and noise on measurement uncertainty

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Accurate quantification of X-ray photoelectron spectra is crucial for reliable and reproducible surface analysis. Peak fitting is a central aspect of this workflow for both novice users and experienced analysts, yet the treatment of fit uncertainties and the influence of fit model parameters remains largely unclear. A number of different line shapes have been used to generate synthetic peak envelopes for XPS fitting routines, including the mathematically convenient Gaussian-Lorentzian sum and product functions, as well as the physics-based Voigt profile. The differences in line shape among these functions have been discussed by several authors [1-3], along with the influence of the so-called mixing parameter on their line shapes. However, a comprehensive assessment of the errors in parameters determined from peak fitting with different line shapes and mixing parameters has not been presented to date, limiting the comparability of fit models across different line shapes.

To further the understanding of the influence of line shape and mixing parameter, and to provide first-time users of the technique with reasonable estimates of the errors associated with their fitted model, we present a comprehensive discussion of these error sources. Using synthetic spectra similar to those of Conny & Powell [4], we assess the suitability of the numerically-calculated covariance matrix for estimating errors in fit parameters, and compare it with error estimates based on statistical and modeling considerations using Poisson statistics and the χ^2 value, respectively. In addition, the influence of signal-to-noise ratio, peak overlap, and background inclusion on the fit is presented, along with practical guidelines for error estimation. Finally, the effect of smoothing on error estimation has been studied for spectra exhibiting low signal-to-noise ratios. These investigations show that the overall uncertainties are largely governed by the error estimates of the fit model rather than by statistical errors, as further shown by the application of this methodology to selected experimental spectra.

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Keywords: Peak fitting, Error estimation, Covariance matrix, Fit uncertainty

Structural and chemical degradation of DNTT-based OTFTs under UV exposure studied by GIXD and tender XAS measurements

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Organic thin-film transistors (OTFTs) are attractive for low-temperature and printable electronics, yet their electrical performance often degrades under UV illumination. To disentangle crystallographic and chemical contributions to this degradation, we studied DNTT based OTFTs before and after UV exposure using grazing-incidence X-ray diffraction (GIXD) and X-ray absorption spectroscopy (XAS) measurements.

GIXD at SPring-8 BL19B2 (12.40 keV, incidence angle 0.12°, PILATUS 300K) showed that diffraction peak profile and crystal orientational features were essentially unchanged after UV exposure, indicating negligible impact on lattice parameters and crystal orientation in the crystalline domains. In contrast, S K-edge XAS spectra measured at SAGA-LS BL11 under Helium at atmospheric pressure (2.47 keV; fluorescence and conversion-electron yield) revealed a clear modification of the sulfur chemical state. Comparison with a Na_2SO_4 reference suggests the emergence of oxidized sulfur species induced by UV irradiation. Angle-dependent XANES demonstrated that the newly appeared oxidized feature exhibits little orientation dependence, suggesting formation of a disordered, non-crystalline oxide-like component.

These results show that UV degradation proceeds primarily via photo-oxidation at sulfur sites while preserving the overall crystalline framework. The combined GI-XRD and tender XAFS approach provides a robust pathway to correlate structural integrity and chemical transformation in OTFT degradation processes.

Keywords: Organic thin film transistor, X-ray diffraction, X-ray absorption spectroscopy

Glasses, Ceramics, and Oxides

Lutetium sulphide powders studied by X-ray photoelectron spectroscopy

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Rare-earth sesquisulfides with general formula RE_2S_3 represent a promising class of materials for optical and optoelectronic applications due to their wide transparency range, high refractive index and good chemical stability. In particular, Lu_2S_3 is a low-phonon chalcogenide host suitable for rare-earth doping and mid-infrared photonic applications [1]. Recent work has demonstrated the first successful growth of Lu_2S_3 single crystals by the micro-pulling-down technique and revealed their interesting spectroscopic properties, including luminescence transitions spanning from the visible to the mid-infrared spectral range [2]. However, the electronic structure and surface chemistry of these materials remains largely unexplored. In this work, the surface composition and electronic structure of lutetium sulphide were investigated using X-ray photoelectron spectroscopy (XPS). Several reference powders were prepared to distinguish between lutetium bonding environments corresponding to S–Lu–S, S–Lu–O and O–Lu–O configurations. These references were subsequently used to evaluate the quality and composition of a Lu_2S_3 crystal. The XPS analysis confirmed that lutetium in the crystal is predominantly present in the Lu^{3+} oxidation state, while sulphur occurs mainly in the S–Lu–S bonding configuration with minor contributions from oxidized surface species. The results demonstrate that XPS is a powerful tool for probing the electronic structure of Lu_2S_3 -based materials and enables reliable identification of different lutetium or sulphur bonding configurations, which is essential for interpreting electron-related processes occurring in the system.

Keywords: Lutetium sulphide, Lutetium oxide, crystal growth, micro-pulling-down technique, XPS

In Situ NAP XPS of Hydrogen Driven Reduction in PtCoO₂: Impact of Organic Surface Functionalisation

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For over two decades, Cu has been the primary material for interconnect applications in the back end of line (BEOL) of integrated circuits. However, as the exponential reduction in feature size of microchips predicted by Moore's law continues, interconnect lines and vias are expected to reach sub-10 nm dimensions in the coming years. At these critical dimensions, the line resistance of copper will no longer meet performance requirements [1]. Delafossite oxides, in particular PtCoO₂, show significant promise as alternative interconnect materials due to their highly anisotropic electronic structure and exceptionally low in-plane resistivity, with bulk values as low as 2.1 μΩ cm [2-4].

Despite these promising electronic properties, delafossite oxides also present integration challenges, including their high susceptibility to reduction under forming gas or other reducing atmospheres. Oxygen loss leads to the formation of metallic Pt-Co alloys with substantially higher resistivity. As PtCoO₂ is expected to encounter reducing conditions during standard device fabrication steps such as forming gas annealing (FGA), developing strategies to protect the oxide surface is essential.

To address this, a range of organic self-assembling monolayers (SAMs) and small-molecule inhibitors (SMIs) were investigated for their ability to passivate PtCoO₂ against reduction. Successful assembly of each SAM/SMI was confirmed via immersion-based deposition followed by water contact angle measurements exceeding 85°, compared to ~35° for the untreated surface.

Using real-time near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and near-edge X-ray absorption spectroscopy (NEXAFS) during in-situ hydrogen annealing up to 450 °C, we tracked the chemical evolution of both the molecular layers and the underlying oxide. The spectroscopic data reveal distinct differences in thermal stability and interfacial behaviour across the passivation schemes, enabling us to identify the onset of reduction and monitor its progression. These insights highlight the complex interplay between surface functionalisation and redox stability, offering guidance for future development of effective passivation strategies for delafossite-based interconnects.

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Keywords: Delafossite Oxides, Organic Passivation, NAP-XPS, Hydrogen Reduction

Surface analysis of a mixed oxide phase of Chromium(VI) and Molybdenum(VI) supported on Yttria-Stabilized Zirconia

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New Advanced Technical Fuels (ATF²) containing chromium are being developed to enhance nuclear reactor safety under accident conditions [1]. Chromium chemistry is matter of concern because chromium in the +VI oxidation state is toxic and/or carcinogenic to plants, animals, and humans [2]. Consequently, the transport of chromium in association with volatile fission products such as iodine, caesium, and molybdenum, in case of nuclear plant accident has emerged as a new issue. During investigations of this topic, evidence for a mixed chromium molybdate species was identified.

Gas phase chromium reactivity in presence of molybdenum was investigated in a high temperature environment. After vaporization of Cr₂O₃ and MoO₃ in a controlled atmosphere, the chromium and molybdenum vapors are transported in a thermal gradient from 1550°C down to 150°C. In this thermal gradient, they can react in gas phase, agglomerate or deposit on the yttria-stabilized zirconia (YSZ¹) surface of the experimental tube. Deposition of a mixed oxide composed of chromium and molybdenum has been firstly identified by EDX analyses below 400°C.

A combination of analytical techniques, including XPS, TOF-SIMS, grazing incidence XRD, Raman spectroscopy, IR spectroscopy, SEM, and EDX, was employed to investigate the chemical composition of the resulting deposit. The corresponding EDX bulk analyses indicate a Cr/Mo molar ratio ranging from 1 to 2 which differs from the XPS surface analysis where a Cr/Mo atomic ratio equal to 6.7 is found. XPS analyses also reveal the simultaneous presence of chromium (III), chromium(VI) and molybdenum(VI) in the deposit. The presence of two doublet peaks with low binding energy separation in the Mo 3d spectrum may show the existence of the two chemical environment for Molybdenum, one of them being a chromium molybdate. The presence of mixed species is also consistent with thorough evaluation of oxygen to metals ratio. Moreover, ToF-SIMS analyses revealed the presence of ionic clusters associated with a mixed chromium–molybdenum oxide. The analysis of a mechanical mixture of chromium and molybdenum oxides ruled out the possibility that these signals arise from recombination phenomena. Raman analyses, performed to evidence the mixed compound, were challenging as the laser induction beam is degrading the sample in real time, even at low laser power due to the instability and volatility of chromium (VI). However, Raman analyses show a homogeneous Cr(VI) compound extending from the deposit surface down to the YSZ support surface.

References:

YSZ¹ : Yttria Stabilized Zirconia

ATF² : Advanced Technical Fuels

Keywords: Mixed oxide, Chromium (VI), Molybdenum (VI), XPS, ToF-SIMS

Impact of water molecules on the near-subsurface region of lead chromate PbCrO_4 mineral

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Lead chromate PbCrO_4 is a mineral commonly found in nature under the name crocoite. It has a monoclinic crystal structure, which is more stable than orthorhombic under normal conditions, and is a semiconductor with an energy gap of approximately 2 eV.

The preliminary investigation of electronic properties characterization of material were executed with used to synchrotron radiation. The base of electronic structure of PbCrO_4 was thoroughly investigated for two types of surfaces of the studied mineral – broken in situ and ex situ. Occupied states were investigated using standard photoemission spectroscopy (PES), while unoccupied states were investigated using X-ray absorption spectroscopy (XAS).

The influence of water molecules on subsurface layer were studies in electronic structure as well as crystallographic and surface topography analysis. The impact of water molecules revealed change the stoichiometry of PbO sublattice in PbCrO_4 mineral. The observed changes in stoichiometry and consequently the chemical decomposition of the surface layers have been investigated by surface-sensitive methods such as X-ray photon spectroscopy (XPS) and time of flight-secondary ion mass spectroscopy (ToF-SIMS). Information about the dynamics “leaching of lead” from lead chromate has been obtained based on the observation the changes of surface topography (AFM microscope). Structural changes of crystalline powders treated water was obtained based on the x-ray diffraction (XRD) research.

The obtained results give the questions for the potential used the surface of this material, e.g. in the photocatalytic process of the decomposition water.

Keywords: lead chromate, subsurface region, electronic structure, chemical decomposition, photocatalysis

TOF-SIMS ^2H Isotope Distribution Analysis of Mechanically Induced Cracks in Soda-Lime Glass

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Numerous studies and experiments have demonstrated the significant influence of water and humidity on crack growth in various types of glass [1] [2] [3]. It is well-known that water can accelerate crack propagation when the glass is under mechanical stress, while in stress-free glass it may induce healing-like effects at the crack tip. However, the underlying mechanisms governing these processes are not yet fully understood. Here, we investigate water-glass interactions at cracks in soda-lime silica glass using high-resolution Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

Cracks were generated via Vickers indentation and conventional glass cutting, and subsequently, exposed to ambient conditions, heavy water ($^2\text{H}_2\text{O}$), or deionized water to simulate weathering. ToF-SIMS (IONTOF M6 Plus, equipped with FIB) enabled elemental mapping of ^1H and ^2H , revealing species distributions at crack interfaces and at FIB-cut cross-sections.

Our findings provide new insights into the role of hydrogen mobility in glass cracks, potentially improving the understanding of crack propagation and healing mechanisms at the sub-micrometer scale.

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Keywords: glass, ToF-SIMS, crack propagation in glass, hydrogen mobility in glass cracks

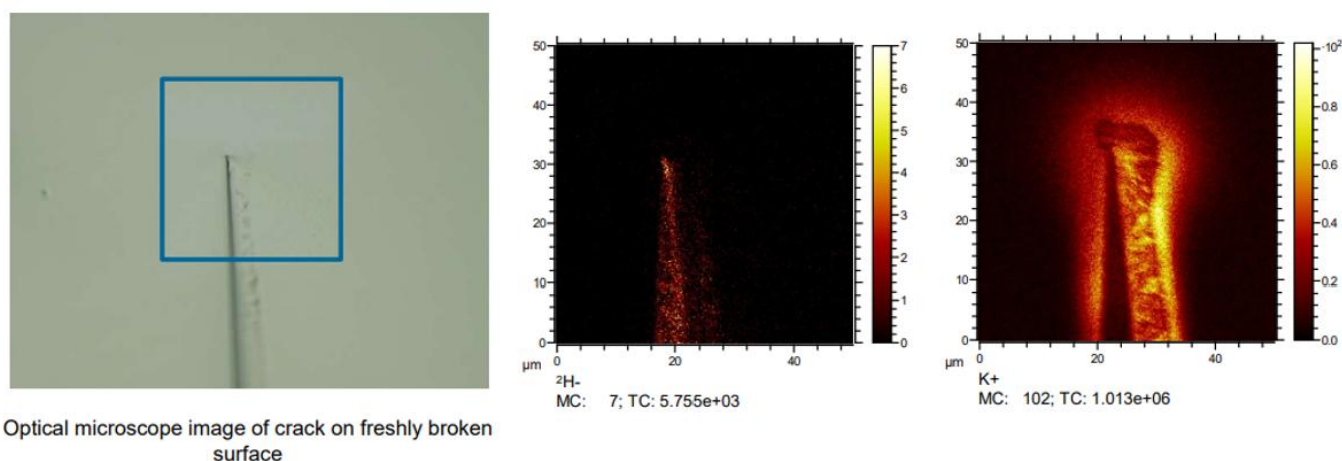


Figure 1: Detailed view of crack in soda-lime glass with ToF-SIMS elemental maps of $^2\text{H}^+$ and K^+ showing signal intensity distribution in and around the crack

***In-situ* and near ambient pressure analysis**

Near Ambient Pressure-X-ray Photoemission study of Water-GaAs interface

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Gallium arsenide (GaAs) stands out as a promising candidate for high-performance photocatalysis due to its favorable band edge positions, optimal band energies, and excellent charge transport properties [1]. However, the use of GaAs as a photoelectrode material is hindered by the high wafer cost, corrosion susceptibility, and the substantial overpotential required to initiate water splitting.

Since photoelectrochemical processes occur in aqueous electrolytes, understanding the nature of water interactions with semiconductor surfaces is of paramount importance. To elucidate the chemistry of the water/GaAs interface under realistic conditions, we investigated interfacial interactions using Near-Ambient XPS (NAXPS). Experiments were conducted at room temperature under water exposure, as well as under combined water exposure and red-laser illumination (671 nm). The pressure in the spectrometer analysis chamber was maintained at 2 mbar in continuous-flow mode. Recent studies have demonstrated that unintentionally doped GaAs thin films grown on bare silicon wafers achieve high photoelectrochemical performance [2]. Therefore, two types of photocathodes; with and without Pt catalyst; were examined: Zn-doped (10^{16} cm^{-3}) p-type GaAs wafers and 1 μm -thick unintentionally doped GaAs layers grown via molecular beam epitaxy (MBE) on p-doped silicon substrates. Native oxides on the GaAs surfaces were not removed prior to XPS measurements to ensure that the semiconductor surfaces of the photoelectrodes were studied under realistic conditions. Consequently, water molecules primarily interacted with the oxide layers present on the GaAs surfaces.

Our findings reveal that bare GaAs wafers and epitaxial GaAs layers exhibit markedly distinct surface compositions. These differences significantly influence the interaction of water with the electrode surface, thereby affecting the evolution of surface composition. Finally, we demonstrate that the surface photovoltage (SPV) response under illumination indicates p-type doping in the GaAs epilayer. The SPV magnitude varies not only with the nature of the GaAs samples but also with the presence or absence of a Pt catalyst, with the highest SPV effect observed for the GaAs/Si:Pt sample.

This research is supported by the “France 2030” French National Research Agency NAUTILUS Project (ANR-22-PEHY-0013) and the French National EQUIPEX+ NANOFUTUR program (ANR-21-ESRE-0012)

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Keywords: III-V semiconductor, NAXPS, photocatalysis, GaAs

In situ and operando APXPS study of hafniconic MLD

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Molecular Layer Deposition (MLD) extends Atomic Layer Deposition (ALD) by enabling the growth of hybrid organic-inorganic thin films through sequential, self-limiting surface reactions. By incorporating organic precursors into ALD-type processes, MLD provides access to materials with tuneable chemical functionality while maintaining the precise thickness control, conformality, and scalability of conventional ALD (cf. Fig. 1). Such hybrid materials are of increasing interest for applications requiring tailored mechanical, electronic, or chemical properties.

Understanding MLD surface chemistry, particularly during nucleation and low-temperature growth, remains a key challenge. Here, MLD processes are investigated using a dedicated ALD/MLD reactor cell integrated with ambient pressure X-ray photoelectron spectroscopy (APXPS) setup at the SPECIES beamline of the MAX IV Laboratory (Lund, Sweden)¹. This setup enables time-resolved *in situ* observation of surface reactions under near-realistic growth conditions.

As a model system, hafniconic² growth on silicon substrates is studied using alternating exposures of tetrakis (dimethylamido)hafnium (TDMAHf) and ethylene glycol (EG) at 100 °C. The deposition process involves precursor adsorption, nucleation, and saturation, which can be followed in real time using APXPS. The presence of N 1s and Hf 4f signals at the beginning of the measurement originates from prior TDMAHf exposure, indicating a pre-saturated surface due to preceding MLD experiments in the same cell. Upon introduction of ethylene glycol, the N 1s signal disappears, consistent with removal of -NMe₂ ligands and formation of Hf-O-C bonds (cf. Fig. 2). Shifts in Hf 4f and C 1s toward higher binding energy and O 1s toward lower binding energy reflect changes in the local chemical environment, consistent with hybrid film formation. The C 1s position supports the presence of intact ethylene linkers.

These results highlight the capability of *in situ* APXPS to resolve MLD reaction mechanisms under realistic conditions, providing insight into surface chemistry pathways relevant for hybrid thin film growth.

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Keywords: Molecular layer deposition (MLD), APXPS, XPS, *in situ*, time-resolved

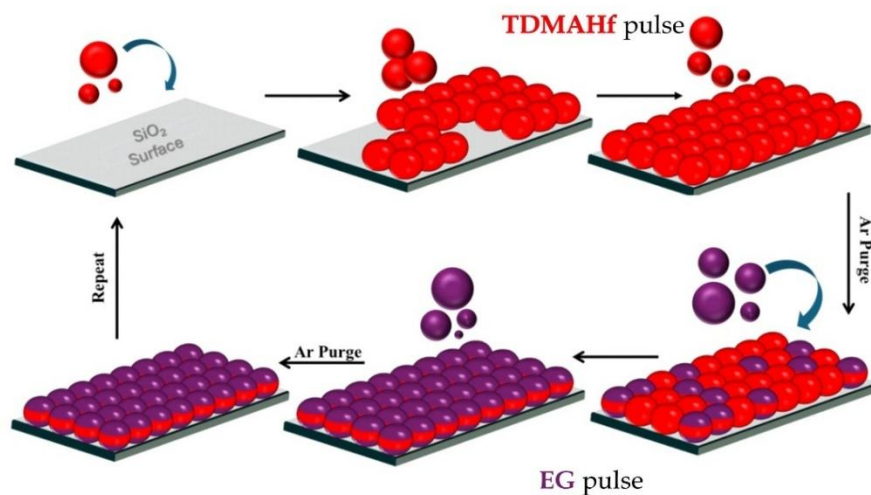


Figure 1: Graphical representation of sequential deposition of MLD process.

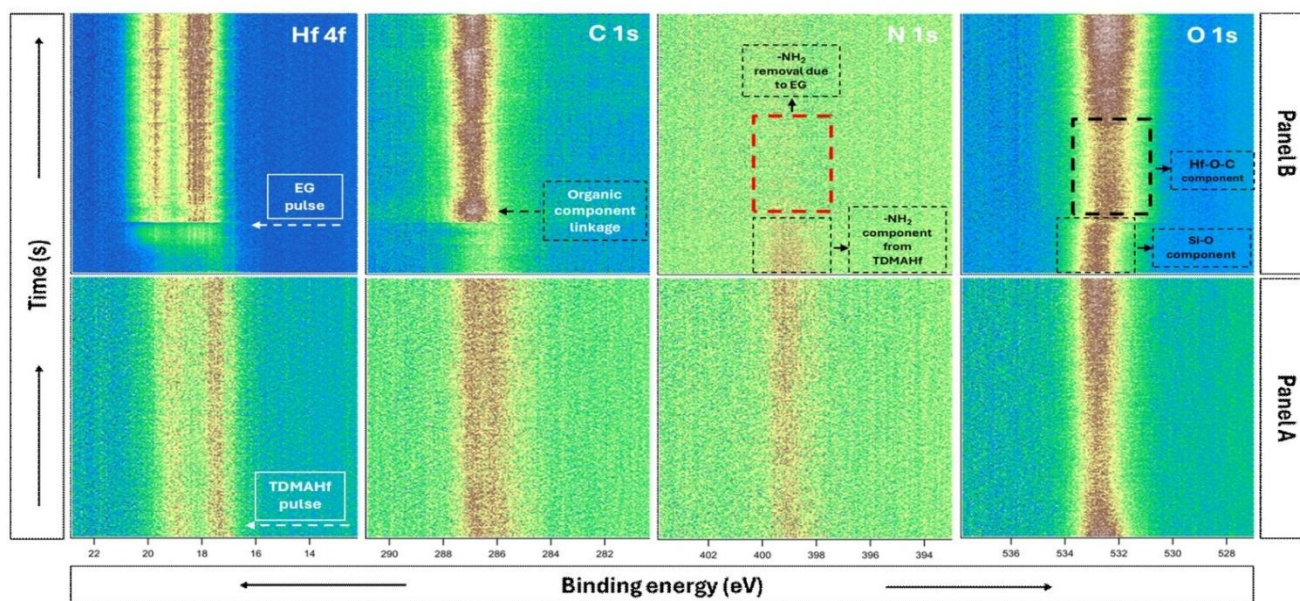


Figure 2: Time-resolved snapshots of core-levels during the MLD deposition process. **Panel A** shows the TDMAHf half-cycle. **Panel B** shows the core-levels after the ethylene glycol (EG) pulse.

NAP-XPS – new end station at SOLARIS synchrotron

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Ambient pressure X-ray photoelectron spectroscopy is a well-established technique for probing the electronic and chemical structure of interfaces between solids, gases, and liquids. Since its development in the early 1970s, the method has become a cornerstone of catalysis and surface science research. A new system dedicated to near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) has recently been installed at the SOLARIS facility. The instrument is designed for investigations of solid-gas interfaces under controlled conditions and will ultimately serve as the end station of the PHELIIX beamline.

The heart of the system is a high-pressure cell combined with a differentially pumped hemispherical electron energy analyser, enabling measurements in gaseous atmospheres up to 30 mbar, with simultaneous sample annealing up to 950 °C using laser heating. Up to four different gases, or user-defined mixtures, can be dosed into the cell. The inlet and outlet gas composition can be continuously controlled and monitored using a quadrupole mass spectrometer.

Additionally, the system is equipped with a cryogenic manipulator, allowing standard XPS experiments to be performed. The sample can be cooled down to 20 K and heated up to 1400 K.

Currently, the system is operated using a laboratory X-ray source with an Al/Mg anode, while integration with the PHELIIX beamline, which will provide synchrotron radiation capabilities, is planned for the end of 2027.

Acknowledgements: *The work is supported under the Polish Ministry of Science and Higher Education project: "Support for research and development with the use of research infrastructure of the National Synchrotron Radiation Centre SOLARIS" under contract nr 1/SOL/2021/2. The construction of NAP-XPS is financed by the Polish Ministry of Science and Higher Education (7428/IA/SP/2023).*

Keywords: solid-gas interface, X-ray, ambient pressure, XPS

Machine learning in surface science

Evaluation of lubricant dispersibility in films using non-negative matrix factorization (NMF) and Voronoi tessellation

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Steel sheets are often provided with films or coatings to enhance their properties, and laminated steel sheets are one such example. In laminated steel sheets, lubricants are sometimes incorporated into the surface resin layer to improve formability. Achieving this effect requires appropriate dispersion of the lubricants; therefore, it is essential to characterize their distribution and evaluate their dispersibility.

To analyze the distribution of organic lubricants, techniques such as Raman spectroscopy and Fourier-transform infrared spectroscopy (FT-IR) are effective. In this study, mapping measurements of Raman spectroscopy were performed to visualize the lubricant distribution. However, Raman spectroscopy is susceptible to noise, and signals from small lubricant particles are often ambiguous, making their identification difficult.

To address this issue, spectral processing using non-negative matrix factorization (NMF) [1, 2] was applied to separate Raman spectra and enhance the clarity of the lubricant distribution. Because NMF imposes non-negativity constraints on both components and scores, it tends to yield sparse representations and enables extraction of more essential information. The maps obtained by NMF successfully captured smaller lubricant particles compared with conventional intensity ratio map.

Furthermore, the dispersibility was quantitatively evaluated by applying Voronoi tessellation to the identified lubricant distribution. In two-dimensional Voronoi tessellation, space is partitioned by perpendicular bisectors between neighboring points, and the partitioned regions are called Voronoi polygons. The area of each polygon reflects the distance between adjacent points, and the dispersibility can be evaluated by calculating the variance of these areas.

This method enables identification of particle positions from noisy spectral maps and provides a quantitative evaluation of dispersibility, demonstrating its applicability to a wide range of similar analytical problems.

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Keywords: Spectral map, Spectral processing, Non-negative matrix factorization, Voronoi tessellation, Steel

Beyond Ridge Patterns: ToF-SIMS and Machine Learning for Chemically Augmented Fingerprint Analysis in Forensics

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Fingermarks are residues left by an unknown donor's finger on a surface, and represent one of the most well-established forms of forensic evidence. Traditionally, they are treated as mere optical features and exploited for biometric identification through comparison of ridge patterns. However, this approach often fails in real-case scenario, when partial, smeared or aged fingermarks are not sufficient for identification of the offender. Moreover, standard forensic approaches neglect the rich wealth of chemicals embedded within fingermark secretions, consisting of complex mixtures of endogenous compounds characteristic of the individual (lipids, amino acids, metabolites), as well as exogenous substances from personal care products, pharmaceuticals, or environmental contact with illicit substances such as explosives or drugs [1]. Accessing this molecular layer transforms fingermarks from purely morphological identifiers into chemically informative traces, potentially enhancing suspect identification.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is uniquely suited for this purpose, combining extreme surface sensitivity, high mass resolution and sub-micrometre spatial resolution under static conditions, thus preserving ridge morphology while enabling label-free molecular detection [2,3]. However, ToF-SIMS generates intrinsically high-dimensional datasets, producing large spectral data that rapidly scale when multiple donors, substrates and contaminant classes are considered [4].

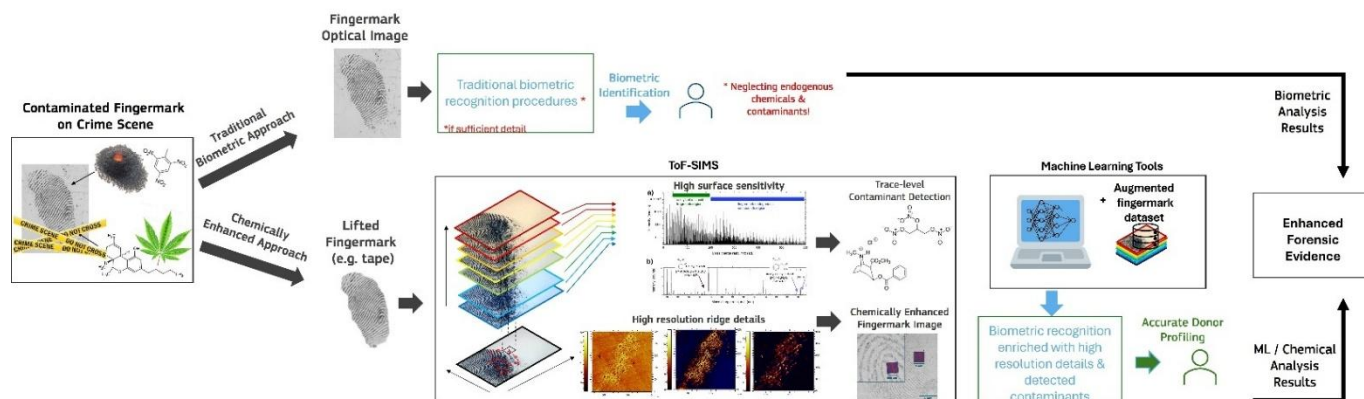
In this work, we created a ToF-SIMS database of fingermarks from multiple donors, including fingermarks from fingers intentionally contaminated with substances of interest to European law enforcement agencies (i.e. illegal drugs, explosives). Measurements were first performed on glass substrates, subsequently on forensic tape, then on fingermarks lifted with forensic tape, to mimic realistic casework conditions (Fig.1). The resulting measurements produce a large, complex spectroscopic dataset that cannot be reliably interpreted manually. To be able to extract meaningful information, we explore a tailored machine learning workflow: dimensionality reduction through Principal Component Analysis enables variance-driven spectral exploration, Random Forest classifiers support contaminant class discrimination, and non-linear embedding (t-SNE) facilitates the visualization of chemically distinct clusters.

Overall, by coupling high-resolution ToF-SIMS surface analysis with machine learning strategies, this work positions ToF-SIMS as a powerful tool for chemically enhanced forensic biometrics. Our approach has the potential to provide additional investigation leads where the traditional biometric recognition workflows prove insufficient, aiming to transform advanced surface analysis combined with machine learning into operational forensic practice.

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Keywords: ToF-SIMS, fingermarks, forensic science, illegal drugs, explosives



Metals

Quantification of Zn/Fe intermetallic phases on top of steel

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Hot-dip galvanized steel undergoes a post annealing process after leaving the molten zinc bath and passing the air knives but before touching the first roll in order to grow specific Zn/Fe intermetallic phases. This so called galvannealing step can improve weldability and paintability. The preferred Zn/Fe intermetallic phase is a hexagonal δ -phase. Unwanted phases are pure Zn (η -phase) and the brittle ζ -phase (monoclinic FeZn_{13}).

Some companies are defining tests via X-ray diffraction before accepting galvannealed steel sheets for use in their car production. These X-ray diffraction tests are not always reliable since the peaks of the different Zn/Fe-phases overlap in the 2θ diagrams because the lattice constants of the intermetallic Zn/Fe phases are multiples of each other. Furthermore, the lattice constants change slightly with different Fe concentration. Also, the texture of the Zn/Fe phases plays a role in quantification.

Therefore, I present a new approach in quantification of Zn/Fe phases. First step is a preparation with Ar^+ -ions in which the sample is cooled to -100°C . By this process a nearly flat cross section surface is created and further analyzed via scanning electron microscopy.

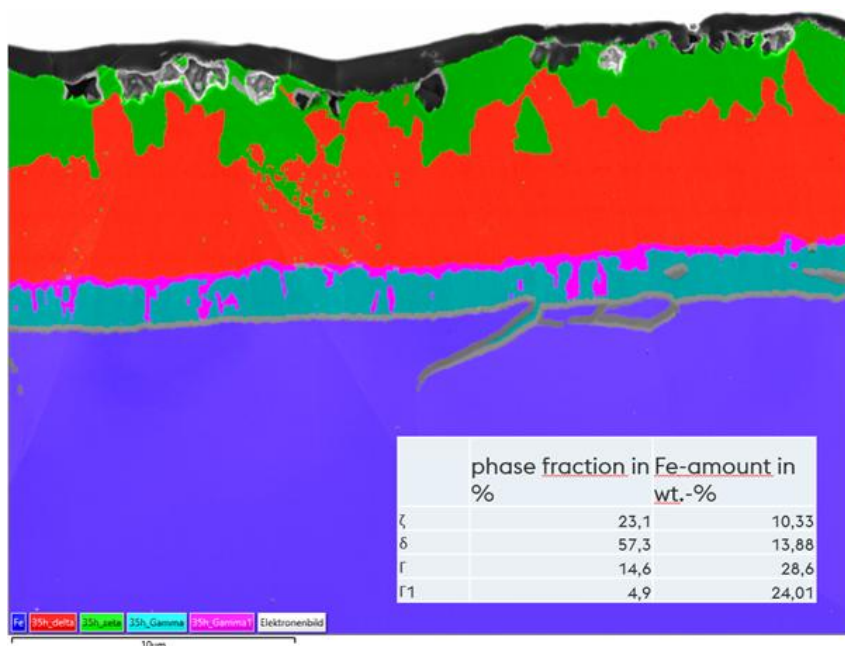
I tried to measure these surfaces with EBSD and finally identify the Zn/Fe phases via the package "map sweeper" in the "Aztec crystal" software from Oxford Instruments. The results were not satisfactory.

The solution for the quantification of the phases is by measuring the cross section sample surface with 5kV primary energy EDX. The evaluation is done via AutoPhaseMap, a principal component analysis tool (PCA) in the Aztec software. The phases are separated by their chemical composition. An example of an electrogalvanized steel sheet after heating in an oven for 35h at 200°C is shown below. One can determine the phase fraction and the chemical composition of each phase simultaneously.

In a small study, I compared the phase fractions of different electrogalvanized test samples after heating them in an oven between 3 and 72 hours with PCA, XRD Rietveld and XRD Toyota method.

In order to test the reliability and to demonstrate the possibilities of this PCA method, I analyzed additional samples with Zn/Fe phases.

Keywords: Zn/Fe intermetallic phases, quantification, EDX



DIC based surface analysis to characterize material behavior for polymer coated steel sheets

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Junyong Park (Production Engineering Research Institute, LG Electronics Inc., Pyeongtaek, Korea)

This study is concerned with characterization of material behavior of polymer coated steel sheets based on the surface analysis with digital image correlation (DIC) systems. Target materials were determined with galvanized mild steel sheets (0.6 mm thick) coated by powder base polymer or vinyl layers (under 50 μm thick). The surface roughness and the consistency of the coating were firstly evaluated by using optical surface analyzing machines to understand basic information. To characterize the material behavior, tensile tests were designed with dog-bone shaped samples following the ASTM E8M standard. The digital image correlation method was employed to measure the strain field on the surface of the materials. Because the speckle patterns must be generated on the surface of sample, there exists the possibility to obtain unreliable strain data due to the delamination of the coated layer from the base metal. To resolve this issue, an experimental approach with the DIC systems was proposed considering the coating type. Both in-situ and ex-situ analyses were carried out to identify the delamination of the coating. The effect of coating type on the material behavior especially for the stress-strain relation was evaluated regarding the role of polymer coating and its delamination during the tensile test. Details of changes in material behavior for the polymer coated steel sheets were discussed with various surface analyzing observations.

Keywords: Surface analysis, Polymer coated metal, Material behavior, Digital image correlation (DIC), Stress-strain curve

Visualization of Grains and Grain Boundaries in Zinc Foils Using ToF-SIMS Imaging Mode

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Zinc is an essential component of the steel industry. Galvanization is a process that protects materials from corrosion. The mechanical and corrosion-protective properties of the zinc coating are contingent on its microstructure, particularly grain size and grain boundaries. Consequently, a thorough microstructural examination of the zinc surface is imperative to enhance comprehension of these properties[1].

This study demonstrates the visualisation of grain and grain boundaries in pure zinc foils using the Imaging Mode of the IONTOF ToF-SIMS M6+. The measurements were performed using Bi⁺ primary ions in both positive and negative detector modes, with the secondary ions Zn⁺/Zn⁻, ZnO⁻, and ZnOH⁻ used for imaging. Fields of view ranging from 300 µm down to a few µm were examined, with a lateral resolution of approximately 100 nm. This enabled both overview images of the grain structure and high-resolution depictions of individual grains and grain boundaries as shown in Figure 1b. Despite the comparatively low yield of secondary zinc ions in the ToF-SIMS analysis, the grain structure could be imaged, which allows for further investigation of the samples[2].

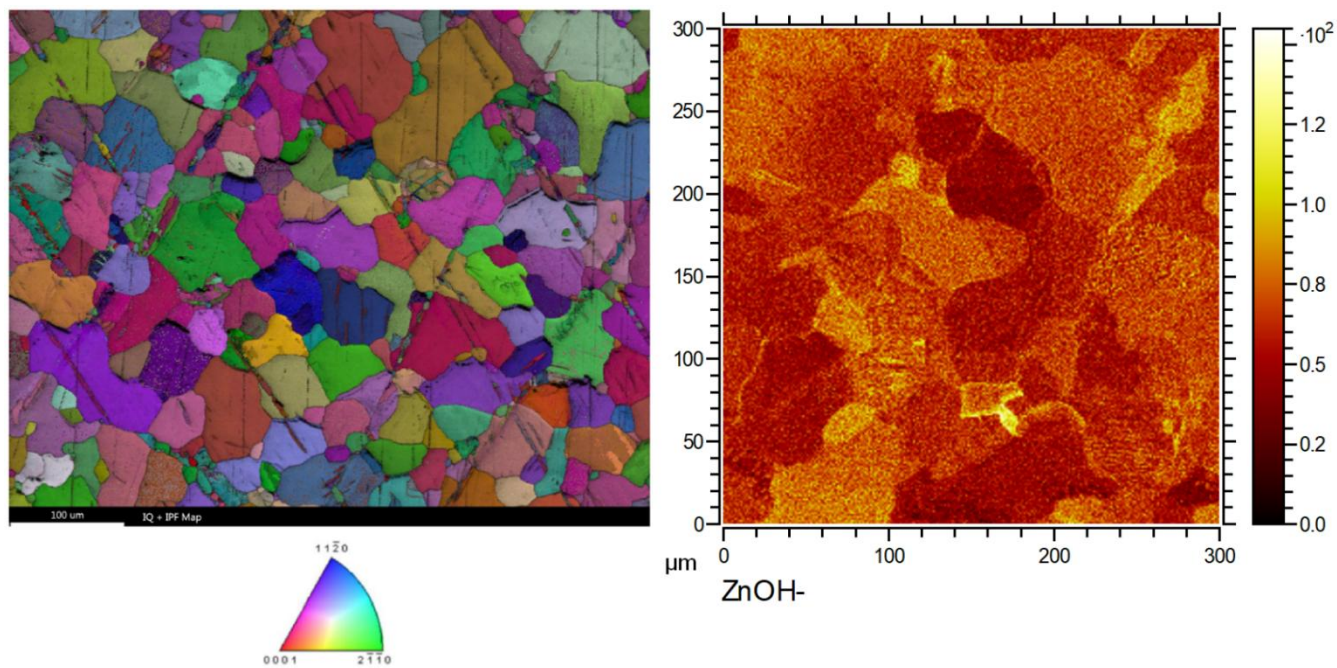
To obtain samples with varying, precisely adjustable grain sizes, the zinc foils were subjected to a process of heat treatment. Temperatures between 100 and 350 °C, which are below the melting point of zinc (420 °C), were applied for one hour each. This treatment makes it possible to systematically investigate the influence of grain size on the imaged structure[3].

In order to verify the grain structures imaged using ToF-SIMS, the samples were additionally characterised using scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) (See Figure 1a). A comparison of the methods confirms the consistency of the ToF-SIMS images with established microstructural reference methods. Taken together, these results establish the basis for further ToF-SIMS investigations of galvanized steels and contribute to a more profound understanding of the interaction between microstructure and corrosion protection.

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Keywords: ToF-SIMS, EBSD, Zinc, grain



Operando XPS Investigation of Interphase Formation at the $\text{In}/(\text{InLi})_x|\text{Li}_6\text{PS}_5\text{Cl}$ Interface in Solid-State Batteries

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Alloy anodes such as $\text{In}/(\text{InLi})_x$ are widely used as counter and reference electrodes in solid-state battery (SSB) research. Their elevated redox potential (0.62 V vs. Li^+/Li) is commonly assumed to suppress degradation of sulfide solid electrolytes, yet direct spectroscopic evidence for the chemical nature of the evolving interphase remains scarce and partly contradictory. Here, we employ operando X-ray photoelectron spectroscopy (XPS) to track interphase formation at the $\text{Li}_6\text{PS}_5\text{Cl}$ (LPSCI)| $\text{In}/(\text{InLi})_x$ interface under electrochemical bias, complemented by coulometric titration time analysis (CTTA) to quantify the associated charge consumption.

CTTA reveals that charge consumed at the LPSCI| $\text{In}/(\text{InLi})_x$ interface (0.62 V vs. Li^+/Li) is comparable to that at the $\text{Li}| \text{LPSCI}$ interface (0 V vs. Li^+/Li), challenging the assumption that higher potentials inherently limit interphase growth. Control experiments using the more stable $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) electrolyte allow decoupling of electrolyte decomposition from competing lithium uptake into the indium bulk. The data demonstrate that interfacial charge consumption is governed not only by electrode potential, but also by microstructure-related factors including effective contact area, lithium redistribution into the metal bulk, and native oxide layers.

For operando XPS, a composite working electrode (LPSCI/In) was employed to ensure electronic percolation while maintaining XPS accessibility to the reacting interface. A stepwise constant-current/constant-voltage protocol was applied directly inside a PHI VersaProbe IV spectrometer. Five measurement positions were monitored to account for the spatial heterogeneity of the composite geometry. Binding-energy calibration combined adventitious carbon referencing with correction for the applied working-electrode potential to address electrostatic shifts of insulating interphase products.

Already at 0.8 V vs. $\text{In}/(\text{InLi})_x$, a clear Li_2S signal emerges in the S 2p spectrum, intensifying upon further polarization. Simultaneously, the In 3d_{5/2} spectra reveal progressive reduction of the native In_2O_3 passivation layer, accompanied by Li_2O formation as identified in the O 1s region. Notably, neither In_2S_3 nor InCl_x species were detected — in contrast to previous ex situ reports — suggesting that earlier assignments may have been complicated by the presence of In_2O_3 . Upon repolarization, partial reversibility of both Li_2S and Li_2O formation is observed, indicating that the interphase is not entirely kinetically frozen.

These findings demonstrate that operando XPS can resolve the chemical evolution of interphase products at buried solid–solid interfaces under realistic electrochemical conditions. The results highlight Li_2S and Li_2O as the dominant interphase constituents and underscore the often-overlooked role of native metal oxide layers in defining interphase chemistry at alloy anodes in SSBs.

Keywords: energy materials, solid-state batteries, solid electrolyte interphase, alloy anode, lithium

Nanomaterials and nanostructuring

Advanced Microscopy as a Quantitative Analysis Method for (Nano)Particle Number Concentration in Liquid Suspension

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Beside the measurement of particle size and shape distribution, accurate determination of particle number concentration is essential for many applications¹. Widely used methods for the measurement of particle number concentration, such as MADLS, SAXS, sPLCP-MS, rely on material specific input parameters, modelling assumptions, or calibration strategies, which contribute to measurement uncertainty, making absolute quantification challenging and limiting direct metrological traceability². In the framework of the European project Concensus (<https://www.bam.de/Content/EN/Projects/Concensus/Concensus.html>), a dedicated counting-by-imaging approach is being studied to determine (nano)particle number concentration using imaging methods.

Imaging methods are well established for characterising the size and shape of (nano)particles with ISO standards in place: ISO 21363:2020 for TEM and ISO 19749:2021 for SEM. However, no corresponding standard operating procedures exist for the measurement of (nano)particle number concentration using imaging methods.

Avoiding artifacts arising from conventional drop-casting from liquid suspension is a challenging task³, however, some solutions have been partly found^{4,5}. This work presents a proof-of-principle study for determining the particle number concentration using SEM by employing a special sample preparation procedure. This allows the deposition of isolated particles within a small, localised spot on the substrate for further imaging⁶.

In the first stage, relatively simple materials, Ag and Pd nanoparticles, with monodisperse size distribution have been tested, with future project work increasing particle complexity to include other material types. The performance of our approach has been assessed by comparing the results with concentrations measured with MADLS. The results from both methods for both types of samples are in the same order of magnitude, i.e. 10^{11} particles/mL, which demonstrate the strong potential of SEM combined with dedicated sample preparation as a powerful method for the number metrology of (nano)particles. Further optimisation of this approach which is independent of material-type and theoretical assumptions will enable an automated workflow making imaging an accurate, fast, easy and standard method for quality assurance.

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Keywords: (nano)particle number concentration, sample preparation, Scanning Electron Microscopy

Synthesis and characterization of ZnTe nanoparticles for highly efficient chemical reduction

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The increasing concentration of carbon dioxide in the atmosphere is one of the most pressing environmental challenges and requires immediate attention. One promising approach to lowering CO₂ levels is the development of catalysts, capable of reducing carbon dioxide through photocatalytic processes, and then, possibly, reusing it as fuel or for other applications. Zinc telluride (ZnTe) can be considered a promising material for the photocatalytic reduction of carbon dioxide, where the crucial feature is the possibility of tuning the electronic properties of the material at the nanoscale size. Like CdSe[1], ZnTe has a tendency to form magic-size clusters, which are more stable than others as well as have specific optical properties. In this project, ZnTe was synthesized in the form of nanoparticles. With the synthetic protocols developed ZnTe nanoparticles with a size distribution between 2 to 7 nm were obtained. The analysis of the synthesized nanoparticles was conducted with XRD, Transmission Electron Microscopy (TEM), X-Ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (TOF – SIMS), and others. The TOF-SIMS characterization of the ZnTe nanoparticles required various types of nanoparticle thin-film preparation, which finally allowed the chemical composition of the clusters to be confirmed, as well as the chemical signal of ligands connected to the nanoparticles. The thermal stability of the used ligands has been analyzed with SIMS thermally-programmed desorption spectroscopy.

It is important to note that conventional nanoparticle synthesis methods often rely on hazardous solvents and reagents, contributing to environmental pollution. To address this issue, we are also exploring more sustainable synthetic strategies, including water-based approaches, which seek to reduce environmental impact while maintaining high material quality and functionality.

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Keywords: nanoparticles, Zinc telluride, Nanoparticle ligand stability, Secondary Ion Mass Spectrometry

Physicochemical characterisation of iron oxides and hydroxides applied as food additive E 172

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Within the European Union, iron oxides and hydroxides with specifications defined in Commission Regulation No 231/2012 are allowed as food additive E 172 in numerous food categories. This work examined the intrinsic properties of twelve commercially available pristine E 172 materials, using multiple techniques. Based on material colour, phase and particle shape, four main forms were identified by electron microscopy and X-ray diffraction: red spheroidal (octahedral) hematite ($\alpha\text{-Fe}_2\text{O}_3$); red elongated (rod-like) hematite ($\alpha\text{-Fe}_2\text{O}_3$); yellow elongated (rod-like) goethite ($\alpha\text{-FeO(OH)}$); and black spheroidal (cubic) magnetite (Fe_3O_4). These forms correspond with the three substances defined in the EC specifications, and two morphologies for red E 172 depending on the production process. Raman spectroscopy and X-ray photoelectron spectroscopy identified maghemite ($\gamma\text{-Fe}_2\text{O}_3$) as the dominant phase at the surface of magnetite (Fe_3O_4) particles, possibly due to a weathering process. Median values of the minimum Feret diameter distributions of the constituent particles obtained by quantitative EM analysis varied from 72 to 170 nm, depending on the E 172 form. Since for black E 172, the instability of the dispersion limits the representativity of the quantitative particle size measurement, two sampling approaches were compared. Time-of-Flight Secondary Ions Mass Spectrometry allowed to cluster and separate the different forms, based on differences in their surface chemistry and the presence of contaminants at trace level. Impurity levels measured by inductively coupled plasma mass spectrometry and optical emission spectrometry were under the limits defined in the EC specification. The results provide insight into the distinct iron oxide and hydroxide forms that are applied as E 172, and address current data gaps on physicochemical characterization.

Keywords: Iron oxides, Food additive, XPS, ToF SIMS, Physicochemical characterization

Synthesis and Characterization of 2D Mo-based Dichalcogenides for Advanced Optoelectronics

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Here, we present a comprehensive overview of the structural, optical and electrical properties of Mo-based transition metal dichalcogenides (TMDCs), specifically MoS₂ and MoSe₂, synthesized via different approaches. While MoS₂ was grown using conventional chemical vapor deposition (CVD), MoSe₂ was synthesized through a novel hybrid liquid-precursor approach integrated with a thermal assisted conversion (TAC) process. By utilizing a spin-coated aqueous molybdenum solution followed by selenization in an atmospheric-pressure CVD reactor, we achieved precise control over the morphology and crystallinity of the resulting MoSe₂ flakes. The quality of the synthesized layers was rigorously evaluated using a multi-analytical approach:

Raman Spectroscopy: Confirmed characteristic vibrational modes (Mo-S and Mo-Se bonds). Analysis of peak shifts and intensity variations provided insights into strain effects, interlayer interactions, and defect density.

TEM & AFM: High-resolution TEM confirmed a well-defined hexagonal crystalline structure and layer uniformity. AFM imaging further validated the surface morphology and low roughness, ensuring high-quality interfaces.

XPS: Verified the elemental composition, stoichiometry, and chemical purity, confirming the absence of unwanted oxidation states.

Furthermore, the study emphasizes the role of the dielectric environment and interface quality, which are crucial for maintaining high carrier mobility and minimizing charge scattering in 2D materials. The results demonstrate that the synthesis routes offer tunable electronic and optical properties, making these 2D materials excellent candidates for high-performance photodetectors and sensing devices in future optoelectronic and nanotechnological applications.

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Keywords: nanomaterials, dichalcogenides, characterization

Electrosynthesis of Zinc-based inorganic antimicrobials and their XPS characterization

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Antimicrobial zinc oxide or zinc-based insoluble salts can be electrochemically synthesized in galvanostatic conditions by selecting proper electrolytic media and choosing suitable stabilizers, as reported by our research group [1-3]. This approach makes use of low impact chemicals, is highly scalable and gives structures with different morphologies and sizes in high yield. For example, elongated ZnO structures have been prepared in NaHCO₃ solution added with asymmetric tetraalkylammonium salts to drive their preferential growth in one direction, followed by a calcination step [2]. Their efficacy as antibacterial/antiviral materials have been proven [1-2]. Antibacterial calcium hydroxyzincate has been synthesized by a one-step approach combining the anode electrolysis and a precipitation method [3]. Zinc phosphate (ZP) microparticles have been also electrosynthesized in dihydrogen phosphate solution containing sodium-4-polystyrene sulfonate as stabilizer.

More recently, our interest has moved towards the application of experimental design to the electrochemical route for defining optimum parameters [4]. Chemometric tools applied to the electrochemical synthesis have been underexplored so far. The central composite design (CCD) allows for efficient estimation of main effects and interactions.

In this contribution, ZP development will be illustrated emphasizing the advantages of electrochemical sol-gel routes. The versatility of this strategy will be further demonstrated, and cases of study will be discussed corroborating our findings by spectroscopic and morphological data. Moreover, the implementation of ZP into alginate films will be presented together with X-ray photoelectron spectroscopy (XPS) surface characterization.

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Keywords: nanoantimicrobials, electrochemical sol-gel, Auger parameter, bionanocomposites, self-standing films

Isorecticular Expansion in Porous Aluminum(III) Phosphonates: From Synthesis to Structure–Property Relationships

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Carboxylate-based Metal-organic frameworks (MOFs) are well-established classes of materials that feature precise control over properties such as specific surface area, porosity, composition, and thermal or chemical stability¹. Phosphonate-based MOFs remain comparatively underexplored despite their potential for high chemical and thermal stability.² Their targeted synthesis is challenging because phosphonic acids exhibit diverse coordination modes, often leading to complex framework formation and making isorecticular expansion difficult to control.³

Here, we report the synthesis, high-throughput optimization, and structural characterization of the novel porous phosphonate MOFs M-CAU-67 ($M = \text{Al, Ga}$), prepared from the ditopic linker *N, N'*-4,4'-bipiperidine-bis(methylenephosphonic acid). Single-crystal and powder X-ray diffraction show that CAU-67 is isorecticular to MIL-91⁴, but with an expanded framework architecture and pronounced guest-responsive flexibility (Figure 1). Temperature- and humidity-dependent PXRD, gas and vapor sorption, and solid-state NMR spectroscopy reveal reversible structural changes associated with water uptake, hydrogen-bond rearrangements, and changes in the local coordination environment. DFT simulations support the local framework connectivity and hydrogen-bonding motifs, and the experimentally observed structural changes. By combining diffraction, spectroscopy, sorption analysis, and computational modeling, this work provides a detailed structure-property picture of M-CAU-67 and demonstrates the potential of integrated experimental-theoretical approaches for understanding dynamic behavior in porous metal phosphonates.

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Keywords: Metal-organic framework, Metal phosphonates, Porosity, Isorecticular Chemistry

Surface Characterization of PLA Composite Films Reinforced with Micro- and Nano-crystalline Cellulose

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Growing environmental concerns associated with petroleum-based polymers have increased the demand for sustainable and biodegradable alternatives in engineering applications. Poly(lactic acid) (PLA) has emerged as one of the most promising biodegradable polymers due to its renewability, biocompatibility, and relatively good processability. However, its relatively low toughness, limited ductility, and sensitivity to environmental conditions restrict its widespread use in structural and load-bearing applications. Reinforcement of PLA with natural fillers represents a promising approach to improve its performance while maintaining its biodegradable nature.

Cellulose, the most abundant natural biopolymer, has attracted significant attention as a reinforcing material for polymer composites because of its low density, high specific strength, biodegradability, and renewability. Microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) promote interfacial interactions with polymer matrices due to their high aspect ratio and the presence of surface hydroxyl groups. Moreover, the recovery of cellulose from textile or other types of waste offers an environmentally friendly strategy that supports circular economy principles and sustainable material development [1,2].

In this study, thin composite films based on PLA reinforced with MCC, obtained from cotton-based textile waste through chemical processing, and commercial NCC were produced and their surface characteristics were investigated. PLA/MCC and PLA/NCC composite films containing different filler loadings (1, 3, 5, and 10 wt%) were prepared using a solution mixing and casting method.

Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) were employed to examine the surface morphology, the film roughness and the dispersion of cellulose particles within the PLA matrix. X-ray Photoelectron Spectroscopy (XPS) was performed to analyse the surface chemical composition. In addition, Fourier Transform Infrared Spectroscopy (FTIR) was used to identify functional groups and to explore potential chemical interactions between the polymer matrix and the reinforcing phases.

The results obtained from these complementary surface characterization techniques provide a deeper understanding of the interfacial behaviour and surface properties of PLA composites reinforced with micro- and nanocrystalline cellulose. This study aims to contribute to the development of sustainable polymer composite materials derived from renewable resources and textile waste, with potential applications in environmentally friendly engineering components.

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Keywords: Poly(lactic acid), Cellulose-reinforced composites, Micro an Nanocrystalline cellulose, Surface chemistry, XPS analysis

Reduction of graphene oxide with hydrogen plasma

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Reduction of graphene oxide is an alternative method for synthesizing graphene, enabling scalable production. Graphene oxide contains many oxygen functional groups, especially hydroxyl and epoxy groups, as well as carboxyl groups, which need to be removed. By removing oxygen-containing functional groups, graphene's intrinsic properties can be partially restored. Therefore, graphene oxide paper was treated in a low-pressure radio-frequency discharge created in hydrogen gas. The reduction kinetics at different plasma treatment times were investigated by optical emission spectroscopy (OES), whereas surface chemical changes were analyzed by X-ray photoelectron spectroscopy (XPS). The results showed an abrupt reduction of graphene oxide in a few tenths of a second. In 0.5 s of treatment, the initial oxygen concentration of approximately 30 at.% dropped to approximately 10 at.%. With further treatment, the oxygen concentration dropped to just 6 at.%. This small amount of remaining oxygen can also be attributed to partial re-oxidation upon exposure to ambient air. Consistent with the XPS results, a strong OH signal appeared in the OES spectra within the first few tenths of a second of treatment, indicating that hydrogen atoms from the plasma reacted with oxygen in graphene oxide, leading to the formation of OH groups, which were desorbed from the surface. Based on OES and XPS results, it can be concluded that GO samples are successfully reduced in hydrogen plasma.

Keywords: graphene oxide, reduction, plasma treatment, graphene-based nanomaterials, oxygen functional group removal

Semiconductor materials

Study of p-i-n solar cells based on InGaN/GaN Heterojunction

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III-N semiconductor materials have recently attracted significant interest for optoelectronic devices, including telecommunications lasers, optical fibres, LEDs, and photodiodes. Various types of GaN-based photodetectors have been developed, including PIN and Schottky barrier photodetectors, solar-blind ultraviolet photodetector focal-plane arrays, and UV avalanche photodiodes.

For more accurate results and an optimal configuration, optical properties and physical models—such as Fermi-Dirac statistics, Auger and Shockley-Read-Hall recombination, as well as doping- and temperature-dependent mobility models—were taken into account in our simulations. To demonstrate the impact of this technology on solar cell efficiency, as well as the benefits gained for the photovoltaic and renewable energy sectors, we conducted a detailed study of the InGaN/GaN heterojunction photovoltaic cell. This study focused on its structure, characteristics, and physico-technological parameters. We compared it with other structures based on different InGaN/GaN and Al-GaN/GaN alloys, aiming to achieve maximum efficiency and demonstrate its value for photovoltaics. The proposed structure, based on the InGaN/GaN heterojunction, is a promising candidate for high-efficiency solar cells. Overall, the obtained results confirm that InGaN materials represent the best choice in the field of photovoltaics.

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Keywords: InGaN/GaN, Heterostructure, Solar cells, Simulations, Photovoltaic

Translated from the original French version using automated translation tools.

The effect of surface treatment on the SiC-metal band alignment studied by in-situ XPS of ultrathin metal layers

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Silicon carbide (SiC) is a promising semiconductor for high-power electronics due to its wide bandgap of 3.26 eV. However, this large bandgap causes poor alignment between the work functions of both n-type and p-type SiC and commonly used contacting metals. As a result, a substantial Schottky barrier height (SBH) forms at the as-deposited metal/SiC interface, preventing ohmic contact formation. Thermal annealing is typically required to form an ohmic contact, but the underlying mechanisms remain unclear.

In this study, we investigate the interface between SiC and quasi in-situ sputtered ultrathin metal films using non-destructive X-ray photoelectron spectroscopy (XPS). SiC surface cleaning methods were first evaluated by XPS, followed by quasi in-situ sputtering of 3–5 nm metal layers and UHV transfer back to the XPS chamber for interface analysis. This workflow enables high-precision characterization of surface preparation routines and their influence on contact formation.

The measured Si2p and C1s core-level binding energies of the buried SiC substrate directly reveal the SBH. In addition, thermal annealing of the ultrathin metal layers allows in-situ observation of interphase formation and barrier lowering. We find a strong correlation between the cleaning method and the resulting band alignment. Pure wet-chemical cleaning and sputter cleaning both introduce interfacial states from impurities or lattice damage, leading to Fermi-level pinning and higher SBH values. In contrast, low-energy, low-pressure hydrogen plasma cleaning significantly reduces interface state density and yields the lowest SBH.

These results highlight the critical importance of controlled SiC surface preparation for achieving low-resistance ohmic contacts. The atomistic insights provided here support improved contact engineering strategies, enabling reduced contact resistance and enhanced device performance and reliability. The XPS-based approach demonstrated in this work further offers a robust in-situ validation tool for optimizing SiC surface treatments

Keywords: SiC, Metal-Semiconductor Contact, Schottky Barrier Height, Fermi Level Pinning (FLP), Band Alignment

Surfaces of porous materials

Tunable Metal-Organic Coordination Network at the Liquid-Solid Interface

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Single layered metal–organic coordination networks (MOCNs) are gaining attention thanks to their unique electronic and magnetic properties. The presence of coordinatively unsaturated metal sites within their structures provides additional binding locations for substrates in catalytic processes. Consequently, MOCNs fabricated on solid surfaces are emerging as promising candidates for use in solution-based heterogeneous applications. The bottom-up synthesis of such surface-supported MOCNs requires a rigorous design by utilizing two-dimensional (2D) crystal engineering. However, a comprehensive description of the factors governing their synthesis at the liquid–solid interface is still missing, resulting in only a few reported examples. In this work, we use scanning tunneling microscopy (STM) at the liquid–solid interface to reveal the effect of the choice of solvent, concentration, and temperature on the structure of a surface-supported MOCN constituted by a tritopic ligand containing pyridyl moieties and *trans*-protected Pd(II) cations. Co-ordination was confirmed by XPS and quantitative analysis of the network's crystallinity is presented. Furthermore, the impact of the synthetic pathway is investigated and a qualitative description of the growth mechanism is provided. Finally, the porosity of the extended honeycomb network is examined by studying the adsorption of guest molecules in its pores. Reprinted (adapted) with permission from J. Am. Chem. Soc. 2025, 147, 9, 7682–7693. Copyright 2025 American Chemical Society.

Keywords: MOF, 2D, STM, XPS

Spatially resolved surface characterization of grafted Nickel catalysts inside nanochannels

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Mesoporous anodic aluminum oxide (AAO) membranes functionalized with α -diimine Nickel(II) complexes have recently been explored as nanoscale chemical reactors, enabling confined-space polymerization of polyethylene with enhanced control over its microstructural features [1]. A key factor influencing the resulting structure–property relationship of the polymer is the spatial distribution of Ni catalysts within the membrane's one-dimensional nanochannels. Although responsive nanochannels are widely applied as biosensing platforms, methods for quantifying molecular surface concentrations inside such confined channels remain scarce in the literature.

Using X-ray photoelectron spectroscopy (XPS), we examined the covalent attachment of single-atom Ni catalyst molecules to both the outer and inner surfaces of AAO membranes via the functional linker trimethylaluminum. Moreover, we analyzed and quantified how the catalyst is distributed and how its absolute surface concentration varies inside and along the nanochannels throughout the membrane. By applying experimental intensity ratios of layer (Ni, see left side of Figure depicting a Ni 2p XPS scan for a treated AAO membrane) to substrate (Al) atoms, absolute catalyst loadings can be determined. Up to 0.6 catalyst molecules/nm² were detected in the central region of the nanochannels. This value corresponds to roughly 80% of the maximum monolayer surface coverage of 0.73 catalyst molecules/nm² measured on the flat membrane surface outside the pores.

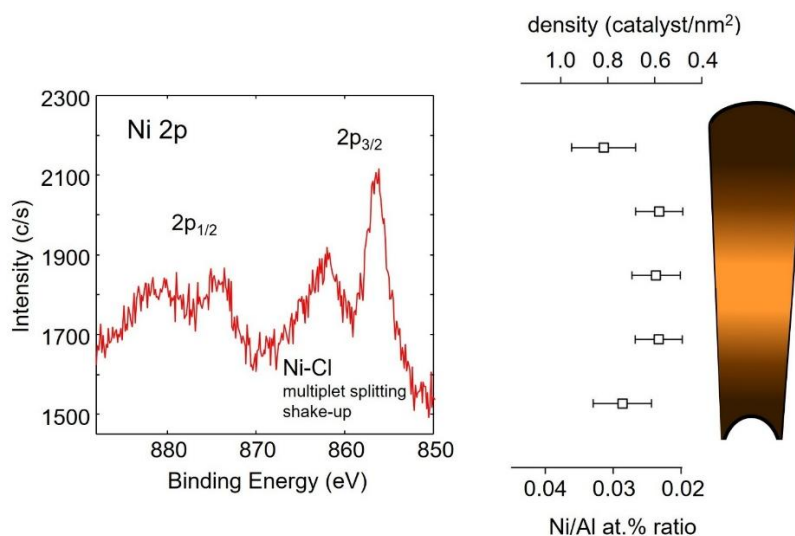
This study not only shows that functional catalysts can be successfully grafted within the confined environment of nanochannels but also provides a quantitative assessment of their surface concentrations. We observed catalyst density gradients along the nanopores (see right side of Figure depicting catalyst surface concentration at distinct positions across the nanochannels). Such quantitative spatial mapping establishes a basis for designing nanochannel reactors with tailored catalyst distributions.

Acknowledgements: We gratefully acknowledge financial support by Subitex (2020-2025).

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Keywords: surface functionalization, mesoporous anodic aluminum oxide, distribution inside nanochannels, molecular surface quantification



Growth and Physico-Chemical Characterization of Layer-by-Layer Cu-BTC Sur-MOF Thin Films for Organic Pollutant Removal

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To address the increasing demand for efficient water purification technologies, this work explores the fabrication of surface-anchored Metal–Organic Framework (Sur-MOF) thin films designed for the removal of organic contaminants from aqueous environments.

The Sur-MOF was prepared via a wet Layer-by-Layer deposition method using copper ions as coordination centers and 1,3,5-benzenetricarboxylate (BTC) as the organic linker. The resulting porous architecture and large surface area make these films promising candidates for adsorption-based applications. Their performance was evaluated using Rhodamine B (RhB), a representative dye pollutant commonly present in textile effluents.

Structural, morphological and compositional properties were investigated through UV–Vis spectroscopy, AFM and ToF-SIMS analyses. These techniques enabled correlation of film growth (controlled by the number of deposition cycles) with adsorption efficiency and exposure time. Regeneration and dye desorption experiments were also conducted to determine the operational stability and reusability of the material.

Overall, the results demonstrate that Sur-MOF thin films represent a promising and adaptable platform for sustainable water remediation and selective pollutant removal.

Acknowledgments: *This work is partially funded by the project PRIDE (MASE Prog. n. RSH2A_000037 – CUP: F57G25000320006).*

Keywords: Metal–Organic Framework (MOF), ToF-SIMS, Rhodamine B (RhB), Water remediation

Technique development and metrology

A High-Energy-Resolution Approach to AMES for Chemical State Identification at the Sub-micron Scale

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Auger (Meitner) Electron Spectroscopy (AMES) was widely used in surface science for rapid, non-destructive elemental analysis of the topmost atomic layers with lateral resolutions better than 10 nm. However, its application to chemical state analysis declined due to limited spectral resolution (typically 0.3–0.6% $\Delta E/E$), which prevented reliable detection of small bonding-induced chemical shifts.

However, state-of-the-art AMES instruments allow measurements with a high-energy-resolution option (HERO), enhancing AMES energy resolution down to 0.05% ($\Delta E/E$). This improvement is achieved by applying a controlled sample bias voltage combined with a retarding lens system to decelerate emitted electrons prior to energy analysis.

To elucidate the benefit of HERO in detail, AMES peak fingerprints for a defined set of elements in different chemical environments were acquired at varying resolutions. Systematic trends in full width at half maximum (FWHM) and relative peak intensity were evaluated. Distinct chemical states were successfully resolved for multiple elements. Measurement conditions were optimized to maintain practical acquisition times while preserving lateral resolution for chemical state mapping. In addition, a practical guide for this technique, highlighting its advantages and limitations when compared to more widely used techniques (e.g. XPS), was developed.

The achieved resolution represents a significant advancement in AMES performance and may reopen the technique for chemical state analysis while retaining the benefit of high lateral resolution.

Keywords: Auger Electron Spectroscopy, High Resolution, Chemical State Analysis, Lateral Resolution, Element Mapping

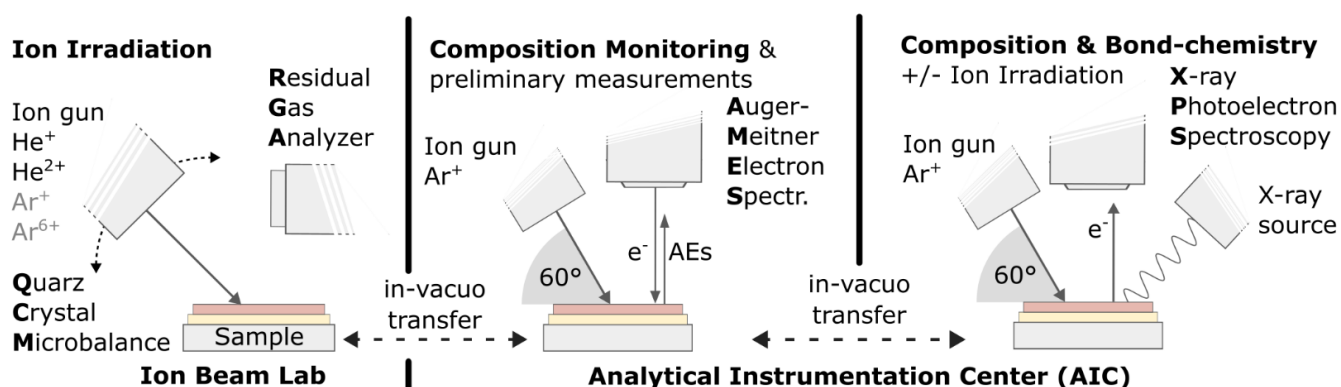
Combined AMES and XPS Analysis of In-Vacuum Transferred Solar Wind Irradiated Minerals

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Solar wind ion sputtering is one of the driving forces of creating the tenuous atmospheres observed around airless bodies such as asteroids, Mercury, and the Moon. The solar wind consists of approximately 96% protons (H^+), 4% alpha particles (He^{2+}) and other multiply charged ions in the per mill range (e.g., C^{4+} , O^{6+} , Ne^{7+}). The multiply charged species, albeit low in concentration, are expected to still significantly affect the sputtering process, since their stored potential energy is known to enhance sputter yields. For example, He^{2+} yields are about 1.5 times larger than those of He^+ , resulting in the 4% He^{2+} fraction contributing 40% of the solar wind yields. The sputtering process on representative samples, such as minerals and regolith, has been extensively investigated using quartz crystal microbalances (QCMs) to determine total mass yields. However, recent work has shown that existing sputtering models misrepresent parts of the sputtering process. While some models can reproduce total mass yields, they fail to capture the surface response and/or the angular distribution of the sputtered material. To discriminate between competing models, complementary data on the sputtered particles but also the irradiated surface is needed. We hereby propose a methodology to obtain surface-specific information, focusing on the multiply charged species in the solar wind.

The Analytical Instrumentation Center (AIC) of the TU Wien is equipped with a PHI 710 Auger-Meitner Electron Spectrometer (AMES), a PHI Versaprobe III X-ray Photoelectron Spectrometer (XPS), and a vacuum suitcase, which allows in-vacuum transfers from and to the AIC. The Ion Beam Facility of the Institute of Applied Physics (IAP) is equipped with a source that is capable of producing the desired multiply charged ions at typical solar wind energies of 1 keV/amu. The irradiated samples are transferred in a vacuum suitcase to the AIC to prevent the re-oxidation. The AMES will be used to determine the progress in surface composition changes before being transferred to the XPS to obtain surface composition and chemistry information. The high surface sensitivity of AMES allows obtaining qualitative surface compositions to investigate the sputter-induced atom-removal process that takes place in the uppermost atom layers. For quantitative data, Relative Sensitivity Factors are obtained through measurements with pure mineral samples are performed. We present challenges and opportunities associated with this approach and invite feedback and aspiration for potential applications beyond space research.

Keywords: AMES, XPS, Ion sputtering, Space weathering, Solar wind



European Metrology project SMURFnano: Standardized measurements of surface functionalities on nanoparticles

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Surface functionalization is a key process step in the manufacturing of engineered nanomaterials (NMs) and largely controls NM stability, reactivity, and performance in applications such as diagnostics, catalysis, sensing, and energy technologies. However, robust and standardized analytical workflows for quantifying NM surface chemistry and coatings are still missing, limiting process control and regulatory confidence. [1]

The SMURFnano consortium, which consists of 7 partners from Metrology Institutes, 3 academic partners, and 2 companies, addresses these challenges by systematically developing and validating quantitative methods for the surface characterization of core and core/shell NMs, including sample preparation workflows. Methods used for measuring surface functionalities and surface shell thicknesses include advanced chemical analysis techniques such as X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS), traceable and quantitative NMR (qNMR) as well as simpler optical and electrochemical methods for quality control in production processes and stability monitoring. [2,3]

Method validation is achieved through international interlaboratory comparisons (ILCs), enabling harmonized procedures, uncertainty evaluation, and cross-laboratory comparability. The resulting protocols, reference data, and test materials will provide a solid foundation for standardized measurements of NM surface chemistry. SMURFnano directly supports standardization activities within ISO, IEC, and OECD and follows the European Commission's "Putting (more) Science into Standards" initiative, strengthening the link between chemical process engineering and nanomaterial regulation.

Current activities of the SMURFNano project are focused on three inter-laboratory comparison studies:

VAMAS Project 19: *Analysis of total functional group content on aminated silica nanoparticles using quantitative NMR (qNMR)*; VAMAS Nanoparticle Populations – Technical Work Area 34,

VAMAS Project A51: *Analysis of the amount of surface functional groups on silica nanoparticles using XPS and SIMS*, VAMAS Surface Chemical Analysis – Technical Work Area 2,

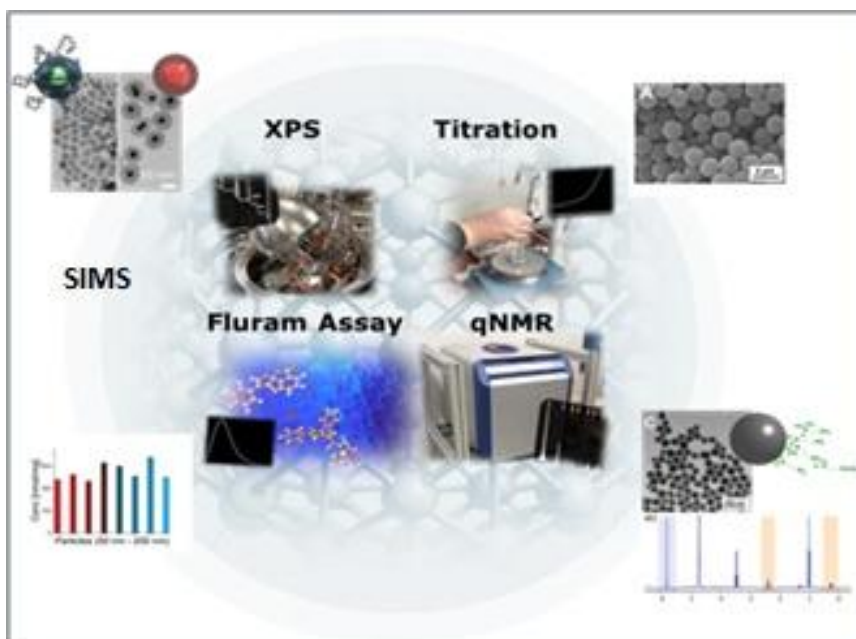
VAMAS TWA 2 A50: *Analysis of the shell thickness of core@shell nanoparticles by XPS, HAXPES, and SIMS* on a set of Au/SiO₂ systems with 3 shell thicknesses and 1 lanthanide core/shell LnNP system.

We gratefully acknowledge funding from the European Partnership on Metrology project 23NRM02 SMURFnano, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States, and contributions from partners from Istituto Nazionale di Ricerca Metrologica (INRiM), Italy, LGC Limited, UK, PTB, Germany, FU Berlin, Germany, and PolyAn GmbH, Gerlin.

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3. I. Tavernaro et al., *Nano Adv* **2025**, 7, 6888

Keywords: core/shell nanoparticles, functional group analysis, inter-laboratory comparison, XPS, SIMS, qNMR, surface modification



Evolving STXM Capabilities at the DEMETER Beamline of the SOLARIS Synchrotron for Nanoscale Characterization

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The STXM (Scanning Transmission X-Ray Microscope) end-station at the DEMETER beamline of the SOLARIS synchrotron provides a versatile platform for nanoscale chemical imaging and spectroscopy. DEMETER delivers tunable soft X-ray radiation across the 100–2000 eV range using an elliptically polarizing undulator, enabling element-specific contrast and nanoscale characterization of diverse materials. The STXM microscope achieves spatial resolution of about 20 nm and enables hyperspectral imaging through energy-resolved image stacks, allowing detailed chemical mapping essential for studying nanomaterials and engineered interfaces.

Recent developments significantly enhance the station's capabilities. A ptychography mode, currently being implemented, is expected to improve spatial resolution below 5 nm [1], offering a powerful tool for probing complex nanostructures with quantitative phase contrast. The integration of environmental cells enables *in situ* measurements, including studies under controlled atmosphere (inert gas) or during electrochemical processes [2], broadening the range of materials and phenomena that can be investigated. Additionally, partial fluorescence detection expands analytical sensitivity, complementing transmission measurements and enables imaging samples too thick for transmission mode.

Together, these developments strengthen DEMETER's role in both nanomaterials research and technique development. The combination of high-resolution STXM imaging, emerging ptychographic capabilities, flexible sample environments, and multimodal detection makes the end-station a valuable platform for advancing nanoscale metrology and exploring the structure–function relationships in modern materials.

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Acknowledgments: "Research at the National Synchrotron Radiation Centre SOLARIS is supported by the Ministry of Science and Higher Education, Poland, under contract no. 1/SOL/2021/2."

Keywords: STXM, Ptychography, Soft X-ray microscopy, Nanoscale imaging, XAS

Integrated UHV Platforms for Thin Film Growth and In-Vacuo Surface Analysis

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Modern surface science increasingly requires experimental platforms that combine material synthesis with high-resolution surface characterization under controlled environments. Integrated ultra-high vacuum (UHV) systems enabling direct transfer between preparation and analysis chambers provide powerful tools for studying dynamic surface processes during thin film growth and interface formation.

In this work we present advanced modular UHV platforms designed for integrated thin-film synthesis and surface analysis. The systems combine high-resolution X-ray photoelectron spectroscopy (XPS) with thin-film deposition techniques such as atomic layer deposition (ALD), magnetron sputtering and thermal processing within a single vacuum environment. Such architecture enables in-vacuo analysis of surfaces and interfaces without atmospheric exposure, allowing direct investigation of chemical states and electronic structure during material growth and processing.

The capabilities of these platforms are demonstrated through recent studies of functional thin-film materials. XPS investigations of ALD-grown hafnium–titanium oxide selective contacts revealed detailed information on oxidation states and interfacial chemistry relevant for silicon photovoltaic devices [1]. Surface-sensitive spectroscopy was also used to investigate silicon clathrate films integrated with NiOx-based selective contacts, providing insight into band alignment and sodium incorporation in the clathrate framework [2].

Additional studies include investigations of ALD-grown nickel sulfide thin films for electrochemical energy applications [3] and superconducting niobium carbonitride thin films for emerging quantum technologies [4]. Finally, in-vacuo studies of area-selective ALD processes highlight the importance of surface chemistry in controlling nucleation and film growth on oxide surfaces [5].

These results demonstrate how integrated deposition–analysis platforms enable systematic investigation of surface reactions, interface formation and growth mechanisms in advanced functional materials.

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Keywords: Ultra-high vacuum systems, X-ray photoelectron spectroscopy (XPS), Atomic layer deposition (ALD), In-vacuo surface analysis

Theoretical modeling of surfaces and interfaces

Beyond the kinetic nucleation theory: spatial organisation of self-assembled InGa nanodroplets

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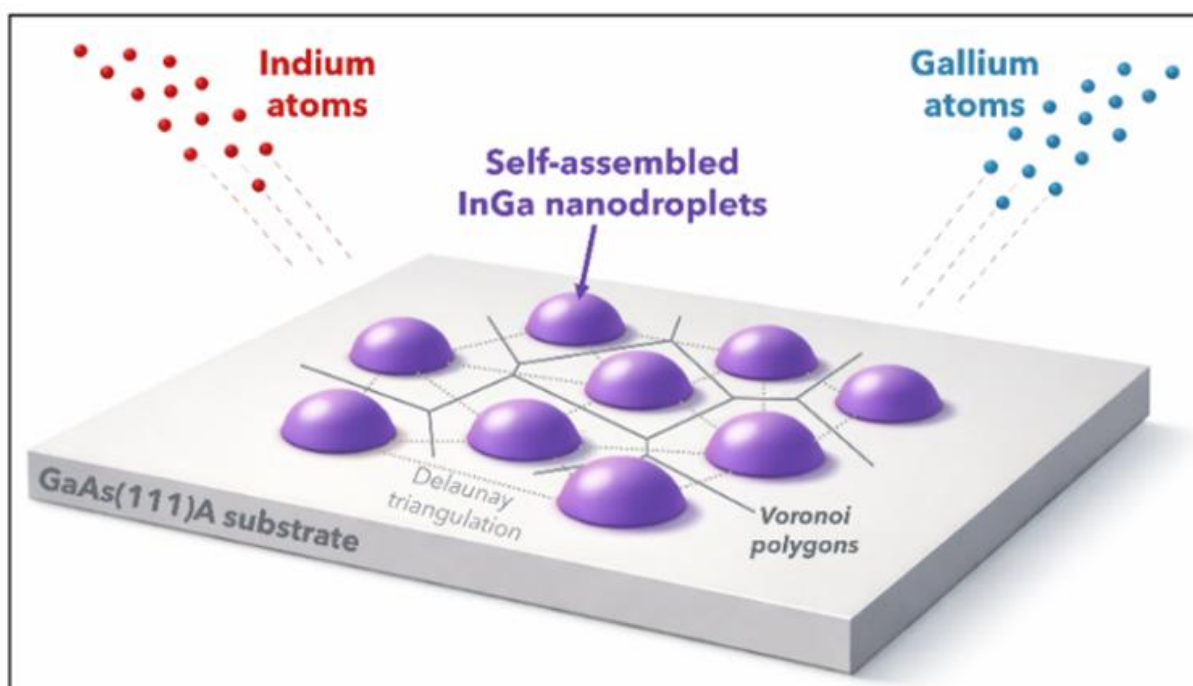
Indium-gallium based semiconductors (InGaAs, InGaN) and their nanostructures such as nanodots (ND) have attracted considerable interest for optoelectronic applications. Recently, the *droplet epitaxy* (DE) technique emerged as a promising technique to grow ND. This two-step process involves the self-assembly of group- metallic droplets ($\text{In}_x\text{Ga}_{1-x}$) followed by the incorporation of a group- element (N or As). Controlling the initial stage of droplet self-assembly is therefore a key challenge for achieving high-density and high-crystalline-quality nanodots.

We report a comprehensive study of the self-assembly of binary $\text{In}_x\text{Ga}_{1-x}$ nanodroplets on GaAs(111)A surfaces, by systematically varying both substrate temperature and indium composition. Experimentally, the In and Ga compositions were estimated using electronic spectroscopies (REELS and XPS [1]). In this work, we propose to combine droplet density measurements (SEM) with advanced statistical analyses of spatial distributions (based on Voronoi tessellation and Delaunay triangulation). Thus, we aim at going beyond the kinetic nucleation theory framework for the understanding of the underlying nucleation mechanisms. Our results reveal that a very important feature has been so far neglected in studies of droplet epitaxy: the elastic deformation of the substrate induced by liquid droplets. These findings provide new insights into nucleation processes and establish a solid foundation for optimizing the growth of high-density InGa-based quantum dots.

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Keywords: self-assembled InGa nanodroplets, droplet epitaxy, kinetic nucleation theory



Simulation of Corrosive Processes at Electrified Interfaces by Ab Initio Molecular Dynamics

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Ab Initio Molecular Dynamics (MD) provides valuable insights in dynamic processes at solid liquid interfaces on the electronic level. However, electrified interfaces have been inaccessible due to the interaction of charged systems with the periodic images. The recently developed thermopotentiostat [1] enables the use of electric fields across a solid/liquid interface by a computational electrode. This electrode consists of a fixed layer of Ne atoms, which confines the water, and provides a compensating charge to keep the cell charge-neutral. The thermopotentiostat acts in a similar way as a classical MD thermostat, updating the charge of the Ne atoms after every MD step to drive the potential difference towards a desired value on average. The electronic minimization cycle then redistributes the charge, leading to a corresponding counter charge on the electrode surface. The opposite charges lead to a realistic field distribution across the interface, allowing the study of dynamic processes under the influence of electric fields. This is for example expressed in a preferential orientation of the dipole vector of the water molecules, which align with the applied electric field. We apply this method to a Zn surface in contact with a water layer to study structural changes in the water structure evolution of H at the interface in anodic and cathodic conditions.

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Keywords: DFT, Solid/liquid interface, Molecular Dynamics, Electrochemistry

Local inverse inelastic mean free path for interface excitation determination

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We calculated a local inverse inelastic mean free path (local-IIMFP) for electrons crossing a vacuum/SiO₂ interface and a SiO₂/Si interface, considering various incident electron energies and crossing angles [1]. With these data, we conducted reflection electron energy loss spectroscopy (REELS) Monte Carlo (MC) simulations with electron energies between 500 and 2000 eV for three samples consisting of a film of SiO₂, with thickness of 1.2, 2.1, or 100 nm, deposited on a Si substrate. In parallel, we perform REELS measurements in the same conditions. The agreement between simulated and experimental spectra is very good in a range of energy loss of 50 eV [2]. In particular, both results show an energy loss peak at about 8 eV, which is a clear signature of the SiO₂/Si interface effect. We thus demonstrated the validity of the local-IIMFP model.

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Keywords: interface excitation, multilayer, position-dependent inverse inelastic mean free path, REELS

Thin films and coatings

Atmospheric Plasma Jet-Assisted Surface Engineering of Glass Fibres for Improved Fibre–Matrix Interfaces

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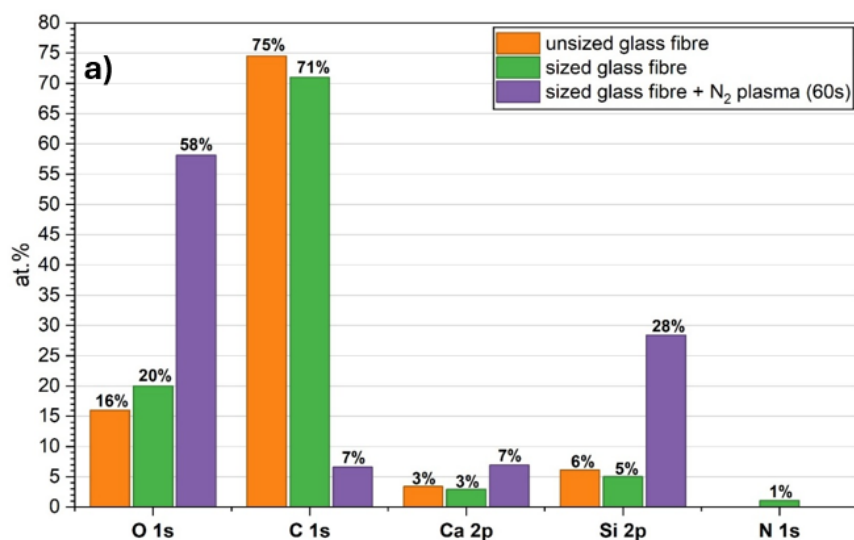
Atmospheric pressure plasma jets (APPJ) are increasingly applied for surface engineering of metals and polymers, enabling solvent-free cleaning, activation, and thin-film deposition under conditions compatible with inline processing. This is particularly relevant for glass fibres (GFs) [1] used as reinforcement in polymer composites, where sizing properties strongly influence the interfacial interactions and directly impact the mechanical performance and durability of the composite [2]. In this study, the modification of unsized and sized E-glass fibres (E-GFs) using a commercially available APPJ system (TIGRES CAT600) was investigated, with a focus on surface and interface characterization. First, sized E-GFs were treated with a nitrogen plasma to examine plasma-induced cleaning and etching of the original sizing. X-ray photoelectron spectroscopy (XPS) analysis revealed a substantial decrease in carbon and increased silicon and oxygen concentrations, indicating partial removal and modification of the organic sizing layer. In a second approach, unsized E-GFs were subjected to plasma cleaning and activation followed by dip-coating in a 3 wt.% solution of (3-mercaptopropyl)trimethoxysilane (MPTMS) prepared in a water/ethanol mixture (80/20 wt.%). Successful MPTMS deposition on the fibre surface was confirmed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) through characteristic vibrational bands associated with MPTMS. To evaluate MPTMS functionalization effects on fibre–matrix adhesion, single fibre pull-out tests were conducted using PA6 as the matrix material. The MPTMS-coated fibres exhibited a significantly higher interfacial shear strength (IFSS) of approximately 13 MPa compared to both the commercially sized (~9 MPa) and unsized reference fibres (~8.5 MPa). This is further supported by a reduction in critical fibre length for the MPTMS-treated samples (~1.2 mm vs. ~1.6 mm for the references), which indicates a more efficient load transfer across the fibre–matrix interface. These findings demonstrate that plasma activation followed by MPTMS dip-coating effectively improves interfacial bonding between glass fibre and polymer matrix, even in the absence of a commercial sizing. Ongoing work explores the substitution of the dip-coating step with aerosol-assisted atmospheric pressure plasma deposition to achieve integrated cleaning, activation, and coating in a single solvent-free process.

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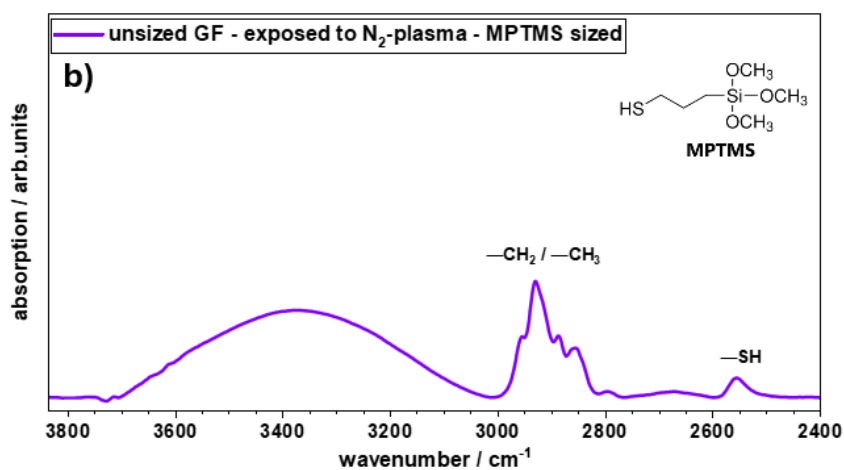
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Keywords: Atmospheric pressure plasma jet (APPJ), Glass fibre surface modification, Silane functionalization, Interfacial shear strength (IFSS), Fibre–matrix adhesion



a) Surface chemical composition of unsized, sized, and nitrogen plasma-treated glass fibres determined by XPS, showing atomic concentrations (at.%)



b) DRIFTS data of unsized glass fibres following plasma treatment and subsequent dip-coating with MPTMS.

Surface and Interface Investigation of Amorphous Nb₂O₅ ISFET layers using ToF-SIMS, XPS and XRD

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A complementary study of ToF-SIMS and XPS for metal oxide stacks used in ion-sensitive field-effect transistors (ISFETs) is minimal in literature, where defect-free interfaces yield better ISFET performance. This study focuses on the composition and elemental distribution throughout stacks of 30 nm amorphous Nb₂O₅ (a-Nb₂O₅) on 55 nm SiO₂, with Si as the substrate. Aside from pH sensing on ISFETs [1], Nb₂O₅ has other important uses such as in optics [2] and in non-volatile memory [3].

After radio frequency sputtering thin films from a Nb₂O₅ target, followed by three separate oxygen annealing treatments described in C. Beale et al [1], XRD shows the layers are amorphous, and surface XPS shows the presence of Nb⁵⁺ which has not been reduced. In ToF-SIMS, The Cs⁺ primary ion was used instead of O₂⁺ to minimize the adverse effects on depth profile quality, such as beam-induced chemical changes and roughening as well as oxygen ion implantation [4]. In addition, a low Cs⁺ primary ion energy beam at 500 eV was used to minimize profile broadening effects. Depth profiling ToF-SIMS shows that ⁹³Nb⁻ and NbO⁻ can be found in the gate oxide (SiO₂), indicating either that the Nb species are distributed for a wider range for samples heated at a lower temperature for a shorter time (400 °C for 2 h), or that interface defects with this annealing treatment lead to profile broadening with respect to the other two annealing treatments (400 °C for 10 h or 425 °C for 2 h). Results suggest that the broadening could be attributed to oxygen defects that have a direct effect on the sputter yield, or to roughening and mixing induced by the sputter conditions.

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Keywords: ToF-SIMS, XPS, XRD, Nb₂O₅, ISFET

Morphological changes of SiC nanostructures on Si substrate grown under UHV conditions

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Direct growth of Mo-based carbides on technologically relevant substrates such as silicon offers an alternative pathway toward scalable device integration. However, direct deposition involves complex interactions between Mo, Si, and carbon at elevated temperatures. Understanding the influence parameters such as temperature, deposition time, and carbon precursor is therefore essential. According to the strong tendency of C atoms to bond with Si rather than Mo, the formation of SiC on Si substrates can hinder the deposition of Mo₂C by consuming available carbon. This work aims to provide a pathway to overcome this limitation by pre-saturating the Si substrate through exposure to C₂H₄ gas under UHV conditions. The reaction temperature was kept constant, while the growth time was changed to monitor the surface morphological variation and to determine the optimal condition for achieving maximum surface coverage with minimal roughness of SiC layer. Despite these efforts, the lattice mismatch between the Si and SiC prevents the formation of a uniform continuous film. Surface study was carried out using AFM and SEM measurements. The images and extracted quantified data reveal that increasing deposition time leads to a higher density and height of SiC islands, while their lateral size decreases. The results show that after approximately 100 minutes of C₂H₄ exposure, the SiC islands almost approaches full coverage, as further confirmed by XPS measurements by the saturation behavior of Si and Si–C deconvoluted peaks.

Keywords: SiC nanostructure, UHV growth, Surface morphological change, Si substrate

Interface analysis and adhesion of tetravinylsilane plasma polymer films on polypropylene

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Polymeric materials used in packaging applications require effective barrier films that prevent the permeation of small molecules. Thin organosilicon coatings deposited by plasma-enhanced chemical vapour deposition (PECVD) are widely used to improve these barrier properties and represent a more environmentally friendly alternative to wet chemical processes. (de los Arcos et al. 2024a; de los Arcos et al. 2024b) However, recent studies suggest that adhesion of such ultrathin layers can differ for polymeric recyclates, motivating the search for new deposition strategies. (Müller et al. 2025; Kleines et al. 2022) In this work, we investigate tetravinylsilane (TVS) as an alternative precursor to the commonly used hexamethyldisiloxane (HMDSO).

The interface chemistry and morphology of plasma-polymerized TVS films were examined by Fourier-transformed infrared spectroscopy under grazing incidence (IRRAS), XPS, ellipsometry, and AFM. Self-assembled organothiol monolayers on gold were employed as a reference system for polypropylene (PP) to study interfacial reactions and film growth. The FTIR-spectroscopic results show that the plasma deposition of TVS does not degrade the underlying organic surface and leads to covalent C-C interfacial bond formation. These findings demonstrate that TVS plasma polymer layers can serve as effective adhesion-promoting interlayers for plasma-deposited barrier films.

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Keywords: Tetravinylsilane, PECVD, interface analysis

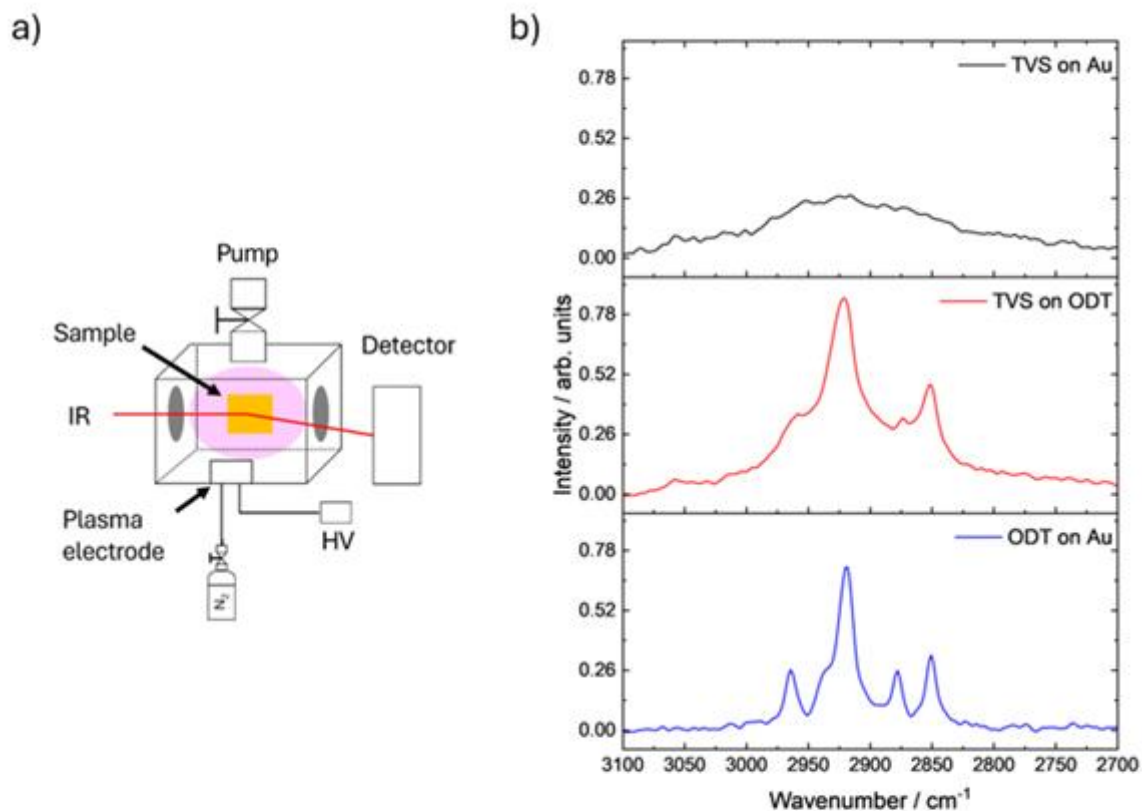


Figure 1: a) Schematic representation of the PM-IRRAS cell setup, with the plasma source and electrode for in-situ measurements. b) PM-IRRAS spectra of ultrathin TVS films deposited on an Au substrate (black, top), ODT-coated Au substrate (red, middle) and the ODT-coated Au substrate without TVS coating (blue, bottom). The spectral region between 3100 and 2700 cm^{-1} is shown, with clearly visible CH_2 vibrational modes.

Surface and Electrochemical characterization of SiN thin films deposited on Ni-based alloys using RF-M sputtering

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The acidic fluids and changes in the mouth environment promote tooth decay leading to the application of dental restorations to recover the functionality and aesthetics [1]. Among these, fixed dental prostheses are widely fabricated using Ni-Cr-Mo alloys since their good mechanical properties and corrosion resistance. They are also widely used in developing nations due to economic reasons [1]. Nickel compounds can be released from the metallic surface through corrosion of the implant by saliva and can lead to a local toxic attack. Also, the surface properties of the metals strongly influence the tissue interface and contribute to success or failure of the implant since modifies the osseointegration [2]. Then, some alternatives to increase the corrosion resistance are needed.

In this study a Ni Cr Mo alloy (VeraSoft) was cut into rods of 12 mm in diameter and 3 mm in thickness. The samples were polished and coated with SiN thin films using a lab-made magnetron RF sputtering equipment at 60 W and 300°C. The samples were electrochemically characterized (PDP, EIS) using PBS solution at 37°C for 400 hours. Surface characterization techniques (SEM-EDS, XRD, XPS) were also applied. The results show that NiCrMo coupons have a dendritic microstructure with micro Vickers hardness values of 501 HV1. The elemental composition indicates the presence of Ni, Cr, Mo, Al, Be and C. On the other hand, the SiN thin film grows following the Volmer-Weber growth model. The corrosion characterization (Fig. 1) indicates that SiN decreases the icorr by one order of magnitude. The EIS results show that the application of the SiN thin film increases the stability of the system over the testing time and increases the impedance modulus by at least one order of magnitude.

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- [2] <https://doi.org/10.3390/app122412814>

Keywords: thin films, sputtering, corrosion, implants, SiN

Secondary Ion Mass Spectrometry in Automotive Coatings: New Analytical Approaches

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Coating layer systems play an essential role in the automotive industry due to their protective, decorative, and other functional properties. In this study, new analytical approaches in the field of secondary ion mass spectrometry are being tested for their applicability to solving analytical problems in the coating industry. For this, one part is the detection and identification of contaminants in various pigments using principal component analysis of ToF-SIMS data. The second part includes imaging of a cross-section of a multi-layer coating system using Hybrid SIMS to identify the components of different layers and elucidate the presence of unknown molecular species.

Keywords: Coatings, Hybrid-SIMS, PCA, Orbitrap-SIMS, Cross-section

Structural control of CZA catalysts by Al vapor deposition

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Background: Cu-ZnO-Al (CZA) catalysts synthesized via electroless plating on zinc- aluminum alloy (ZDC2) plates exhibit a unique two-dimensional (2D) planar ZnO morphology, distinct from that of conventional catalysts. However, the lack of fundamental understanding of regarding their formation mechanisms has hindered precise control over their synthesis and catalytic performance. Preliminary studies have suggested that Al within the substrate plays a pivotal role in this process.

Objective: This study aimed to achieve precise control over CZA catalyst formation by modulating the surface conditions. Specifically, we investigated the influence of varying surface Al concentrations on copper (Cu) deposition behavior and the resulting crystal morphology.

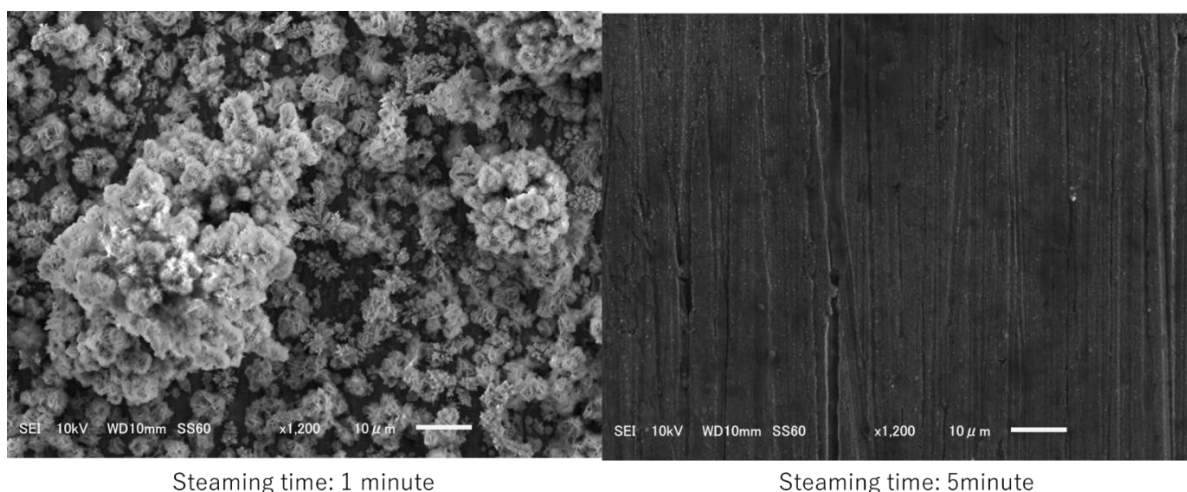
Methods: ZDC2 plates (2 cm square) were used as substrates. Al was vacuum-deposited onto one-half of each substrate to create comparative regions. The Al amount of Al was controlled by the deposition time (1 and 5 minutes), yielding concentrations of 28.06 at% and 69.31 at%, respectively. The samples were then instantaneously immersed in a 25% aqueous copper sulfate solution. The resulting morphologies were characterized using electron microscopy and energy-dispersive X-ray spectroscopy over a defined area of 8502.2145.

Results: 2D planar ZnO growth was observed in all the samples, but the precipitation density varied significantly with the Al concentration. At 1-minute deposition (28.06 at%), a high density of ZnO was observed not only on the protrusions but also within the gaps. Conversely, at 5-minute deposition (69.31 %), the precipitation density decreased compared with that at the at%), the precipitation density decreased compared to the 1- minute condition, indicating an optimal Al concentration for maximizing catalyst growth.

Discussion: The formation mechanism is attributed to the synergistic effect of physical fracturing and electrochemical localization. During immersion, the oxidation of the Al thin film into causes volume expansion. This expansion, combined with thermal stress from the deposition process, induces micro-fractures in the Al layer. Electrons released during Al oxidation are concentrated at these fractures, creating localized galvanic cells that attract and reduce Cu $2+$ ions. These micro-scale Cu clusters act as templates for the subsequent 2D ZnO growth. The decreased density of at 69.31 at% suggests that an excessively thick Al layer prevents substrate exposure by suppressing film rupture.

Conclusion: Our findings demonstrate that the synergistic effects of Al oxidation and physical stress are essential for morphological control. This insight provides a novel methodology for designing high-performance catalysts by tuning the thickness and thermal history of deposited metal films.

Keywords: ZDC2, Aluminum vapor deposition, Zinc crystals grown in a two-dimensional manner



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