Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 1-2 - Session CM1-2-TuA

Spatially-resolved and in situ Characterization of Thin Films, Coating and Engineered Surfaces I

Moderators: Damien Faurie, Université Sorbonne Paris Nord, France, **Naureen Ghafoor**, Linköping University, Sweden, **Aparna Saksena**, Max Planck Institute for Sustainable Materials, Germany

2:00pm **CM1-2-TuA-2 Advancements in XPS Depth Profiling using Femtosecond Laser Ablation (fs-LA) for Thin Film and Metal Oxide Surfaces**, ***James Lallo [james.lallo@thermofisher.com]***, Thermo Fisher Scientific, USA; *Tim Nunney, Robin Simposn,* Thermo Fisher Scientific, UK; *Mark Baker, Charlie Chandler,* University of Surrey, UK

XPS depth profiling is a widely employed analytical technique to determine the chemical composition of thin films, coatings and multi-layered structures, due to its ease of quantification, good sensitivity and chemical state information. Since the introduction of XPS as a surface analytical technique more than 50 years ago, depth profiles have been performed using ion beam sputtering. However, many organic and inorganic materials suffer from ion beam damage, resulting in incorrect chemical compositions to be recorded during the depth profile. This problem has been resolved for most polymers by using argon gas cluster ion beams (GCIBs), but the use of GCIBs does not solve the issue for inorganics. We have introduced a novel XPS system, Hypulse, that employs a femtosecond laser rather than an ion beam for XPS depth profiling purposes. This novel technique has shown the capability of eradicating chemical damage during XPS depth profiling for all initial inorganic, compound semiconductor and organic materials examined. The technique is also capable of profiling to much greater depths (several 10s microns) and is much faster than traditional ion beam sputter depth profiling. fs-LA XPS depth profile results will be shown for selected thin films, coatings, multilayers and oxidized surfaces and the outlook for this new technique discussed.

2:20pm **CM1-2-TuA-3 Sample Charging During X-Ray Photoelectron Spectroscopy Analyses of Thin Film Insulators: From Understanding to Solution**, ***Grzegorz (Greg) Greczynski [grzegorz.greczynski@liu.se]***, Linkoping University, Sweden **INVITED**

Sample charging during X-ray photoelectron spectroscopy (XPS) analyses of electrically insulating samples is a widely recognized challenge of this essential technique. If the electron loss caused by the photoelectric effect is not compensated due to specimens' poor electrical conductivity, the positive charge building up in the surface region results in an uncontrolled shift of detected core level peaks to higher binding energy (BE). This seriously complicates chemical bonding assignment, which is based on measured peak positions, and accounts for a large spread in reported core level BE values. In this talk a new method for charging elimination is presented. The solution is based on the *ex-situ* capping of insulating samples with a few nm thick metallic layers that have low affinity to oxygen. The application examples include several industry-relevant oxides. The versatility of the charging elimination is demonstrated for different oxides/cap combinations and air exposure times. Results of the follow-up study aiming at a better understanding of physics behind charging and its elimination are also discussed. Although these studies are based on thin films, the conclusions give insights into critical factors that govern charging phenomena in any other type of insulating samples.

3:00pm **CM1-2-TuA-5 Automated XPS/XAS Multiplet Fitting for Reproducible Orbital Covalency Extraction in Transition-Metal Systems**, ***Mariela Bravo-Sanchez [mariela.bravo@academicos.udg.mx]***, *Mario U. Delgado-Jaime, Tania E. Gonzalez-Robles,* Universidad de Guadalajara, Mexico **INVITED**

X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) are widely used to study the local electronic structure of transition-metal systems. However, extracting physically meaningful descriptors from these spectra is still challenging. In charge-transfer multiplet (CTM) analysis, which is required to reproduce the experimental data in highly covalent materials such as those based on molecular systems. However, the large number of parameters involved make it difficult to find a suitable solution and historically has taken several months to find a single fit under this approach.

In this work, we present an automated fitting framework for the joint analysis of XPS and XAS spectra to derive details of their electronic structure and to extract covalency. The approach treats spectral fitting as a constrained inverse problem and combines systematic parametric exploration with convergent search grids to identify stable regions of physically equivalent solutions. In this way, it becomes possible to obtain a more robust estimation of electronic parameters related to charge transfer and hybridisation.

The methodology is evaluated using thin films based on transition-metal phthalocyanines (Fe, Co, Mn, and Ni) as model systems. These materials are of great interest in the field of science materials, as they exhibit intriguing magnetic properties, but their origin has remained elusive. However, our approach has been effective in reproducing their XPS/XAS multiplet features, which are highly sensitive to metal–ligand covalency. Beyond achieving spectral agreement, the framework focuses on parameter stability, internal consistency between XPS and XAS, and the symmetry-based decomposition of orbital covalency as a relevant electronic descriptor.

This contribution is especially relevant for advanced characterisation workflows because it integrates spectroscopy, physics-based modelling, and automated data analysis into a reproducible pipeline. The proposed strategy can be extended to other transition-metal-containing materials, including engineered surfaces, where a reliable interpretation of XPS/XAS data is essential to understand structure–property relationships.

4:00pm **CM1-2-TuA-8 Is Platinum a Proton-Blocking Catalyst?**, ***Aparna Saksena [a.saksena@mpi-susmat.de]***, *Bingxin Li, Yujun Zhao, Manoj Prabhakar, Jörg Neugebauer, Mira Todorova, Dierk Raabe, Baptiste Gault, Yug Joshi,* Max-Planck-Institut for Sustainable Materials, Germany

Platinum, to date, is the most widely applied electrocatalyst for hydrogen evolution reaction (HER) in acidic media. It is assumed to be a proton-blocking catalyst with only surface-limited adsorption of the reaction intermediates. Here, we critically evaluate the bulk interaction of Pt with hydrogen (H), and its heavier isotope deuterium (D), by monitoring *operando* mass change of the Pt thin film electrode during galvanostatic heavy/water splitting by employing an electrochemical quartz crystal microbalance. Unexpectedly, we observe an irreversible temporal mass gain and a change in the reaction's overpotential, arising from diffusion of H/D into Pt, confirmed by atom probe tomography and thermal desorption spectroscopy. Sub-surface concentration of at least ca. 15 at. % of D in Pt was observed, diffusing down to a depth of more than 10 nm. Analytical description quantified the diffusion coefficient of D in Pt to be $(3.2\pm0.05)\times10^{-18}$ $cm^2 \cdot s^{-1}$. Density functional theory calculations supported the insertion of interstitial hydrogen as solid solution in Pt with a surface concentration of ca. 32 at.%. These findings challenge the existing credence of Pt-proton interaction being limited to the surface, prompting the expansion of the catalyst design strategies to account for property-modifying bulk diffusion of H/D in the Pt matrix.

4:20pm **CM1-2-TuA-9 Correlating Spectroscopic Ellipsometry Measurements in Imaging and Diffractive Modes**, *Md Rashedul Huqe, Yishu Foo, Kawshik Shikder, Yee Man Kwong, Zhang Yun, May Thawda Phoo,* ***Juan Antonio Zapien [apjazs@cityu.edu.hk]***, City University of Hong Kong

Non-imaging spectroscopic ellipsometry (SE) measurements provide extreme sensitivity on the fine details of subwavelength periodic samples and continue to be of importance because they are fast, contactless, and non-destructive. Such measurements, and corresponding modelling using Rigorous Coupled-Wave Analysis (RCWA), the Finite-Difference Time-Domain (FDTD) model, or the Finite Element Model (FEM), are done under the critical assumptions that i) the detected light includes only the zero-order specular reflection and ii) that the illumination area is sufficiently large to reasonably satisfy the ideal assumption of an infinite lattice. However, the increasing demand on photonic and plasmonic metamaterial applications provides fresh challenges for the SE strategies leading to renewed interest in imaging ellipsometry (IE). To date however, the use of IE for quantitative characterization of complex samples face significant challenges from experimental and modelling limitations when the aforementioned assumptions are not met. We recently proposed and build a dual-mode, imaging- and diffractive- spectroscopic ellipsometer to provide correlative and quantitative characterization of multiscale samples. We will discuss our current insights into the opportunities and challenges of this approach, including on-going efforts for the modelling and quantitative characterization of samples with complex structures.

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4:40pm **CM1-2-TuA-10 Machine Learning Assisted Structure-Property Relationships by Nanoindentation**, ***Ude Dirk Hangen* [ude.hangen@bruker.com]**, Bruker Nano GmbH, Germany; *Eric Hintsala, Bernhard Becker, Benjamin Stadnick, Kevin Schmalbach, Douglas Stauffer,* Bruker, Inc., USA

Nanoindentation can give a highly localized fingerprint of the materials elastic and plastic properties via the measured reduced modulus and hardness, respectively. Many thousands of indents can be done in a reasonable amount of time with modern instrumentation which can cover the sub-micron to mm-scale, allowing for structure-property relationships to be determined in complex heterogeneous materials. Machine learning can assist in this process in numerous ways, which will be discussed here. First, automatically identifying phases as regions of similar properties through clustering will be presented alongside a method to evaluate the uncertainty and bias of this approach.

Secondly, Bayesian optimization will also be employed to improve instrument efficiency in terms of placing indents in the most needed areas. Lastly, workflow improvements for the correlation of the indentation properties to co-located structural data will also be detailed.

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