Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Golden State Ballroom - Session CM-ThP

Advanced Characterization, Modelling and Data Science for Coatings and Thin Films Poster Session

CM-ThP-3 Temperature-Dependent Oxidation Mechanisms of Binary Nitride Compounds: A Molecular Dynamics Approach*, Sara Fazeli,* MS4ALL, France*; Edern Menou,* ***Marjorie Cavarroc [marjorie.cavarroc@safrangroup.com],*** SAFRAN, France*; Pascal Brault,* MS4ALL / GREMI, France

Binary nitride (XN) compounds represent an important class of advanced ceramic materials, increasingly recognized for their suitability in high-temperature applications such as aerospace components, turbine blades, and protective coatings. Transition metal nitrides such as titanium nitride (TiN) and zirconium nitride (ZrN) are especially noted for their outstanding hardness and resistance to corrosion. In addition, nitrides of non-transition metals, including carbon nitride (CN), silicon nitride (SiN), and boron nitride (BN), function as essential refractory materials due to their high stability under extreme temperatures and durability in harsh environments. The oxidation behavior of binary nitride materials is often a crucial factor in selecting materials for high-temperature use, as the oxidation resistance of a given XN phase depends on its capacity to form a stable, passivating oxide layer. It is worth noting that a distinct change in the oxidation mechanism is observed at high temperatures, which is attributed to phase transformations in the oxidation products. The insights gained from the oxidation behavior will facilitate the more efficient design and rapid discovery of XN phases that maintain optimal performance in oxidizing environments at elevated temperatures. In this study, we perform ReaxFF and COMB3-molecular dynamics (MD) simulations of the oxidation of binary nitride compounds XN (X = B, C, Si, Ti, and Zr) at four different temperatures (900 K, 1300 K, 1500 K, and 1700 K) to elucidate the mechanism of the oxidation states in the oxide layer.

At the lowest temperature, oxygen chemisorption occurred on the binary compounds without significant surface oxidation. In contrast, at higher temperatures, the amount of O_2 adsorbed increased steadily, particularly for transition metal nitrides. High oxygen coverage at elevated temperatures may lead to structural reconstructions of the surface. This study provides valuable insights into the oxidation mechanisms, helping researchers identify strategies to form stable, protective oxide layers, which enhance corrosion resistance and broaden the industrial applications of high-temperature materials, paving the way for the development of other binary nitride compounds.

CM-ThP-4 Simulating Mode-I Crack Opening Process in Transition Metal Diborides via Machine-Learning Interatomic Potentials*,* ***Shuyao Lin [shuyao.lin@tuwien.ac.at],*** TU Wien, Institute of Materials Science and Technology, Austria*; Zhuo Chen, Zaoli Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; Lars Hultman,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; Paul Mayrhofer, Nikola Koutna,* TU Wien, Institute of Materials Science and Technology, Austria*; Davide Sangiovanni,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

The critical stress-intensity factor K_{IC} and fracture strength σ_f define the fracture resistance of brittle ceramics. However, their experimental measurement is challenging and provides limited atomic-scale insight into crack tip behavior. In this work, we overcome these limitations by offering atomic-scale information on crack growth while evaluating fracture toughnesses and fracture strengths via machine-learning-assisted simulations. Transition metal diborides (TMB_2:s) serve as a case study, with a focus on understanding the Mode-I crack opening response across six distinct orientations within 2 different phases (α and ω). Molecular statics and dynamics calculations were used to systematically test model sizes and thicknesses, ensuring efficient simulations and accurate extrapolation of macroscale mechanical properties via constitutive scaling laws. By incorporating the phase-dependent and anisotropic mechanical properties of the α-phase TMB_2:s, the observed phenomena, as revealed through strain distribution and bond distances, align closely with those well-studied ceramics such as nitrides, offering insights into the fracture mechanisms within realistic deformation environments via atomistic level perspective. Furthermore, while α- and ω-WB_2 exhibits minimal phase dependence in deformation plasticity strength, as supported by both theoretical and experimental results, the fracture strength, as determined through the defective model, demonstrates a significant variation. The results show that the K_{IC} varies across different orientations and phases within the group IV, V, and VII TMB_2:s, correlating with their respective tensile and shear strengths.

CM-ThP-6 Correlative XPS & SEM Analysis for NMC and Na-Ion Battery Cathode Material Surface Composition*,* ***James Lallo [james.lallo@thermofisher.com],*** Thermo Fisher Scientific, UK, USA*; Nannan Shi, Albert Ge,* Thermo Fisher Scientific, UK, China*; Tim Nunney,* Thermo Fisher Scientific, UK

Advanced energy storage has become increasingly vital in many fields, from transportation, to defence, to everyday connectivity. This has led to a growing market demand and development for lithium-ion battery storage solutions.High-tech products such as smartphones, tablets, drones, and electric vehicles all rely on compact, powerful energy storage, with lithium-ion batteries being an essential component. Lithium battery primarily consist of cathode, anode, electrolyte, and separator materials. In lithium battery material research, how to comprehensively characterize and analyse battery materials, and how to use this characterization information to further improve battery material performance has become the focus of current researchers.This poster uses LiNixCoyMn(1-x-y)O2 (NCM)/LiCoO2 [NMC] composite cathode and Sodium Ion Fe/Mg cathode materials as examples. We employee a combination of Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS) characterization techniques to conduct a comprehensive analysis of the composite cathode materials. This approach yields rich sample information, helping researchers quickly evaluate and study any battery cathode materials.

The workflow combines scanning electron microscopy (SEM) [Thermo Scientific AXIA Chemisem] and X-ray photoelectron spectroscopy (XPS) [Thermo Scientific Nexsa G2 & ESCALAB QXi] into a correlated process, enabling the same regions of interest to be investigated; providing both high-resolution imaging and surface analysis from the same positions, even when collected using separate tools.

While SEM can easily visualize 2D materials, these layers are typically too thin to be easily characterized with the analytics commonly present on the microscope such as energy dispersive X-ray (EDX) analysis. XPS, meanwhile, cannot easily resolve surface structures at the required resolution, but can clearly detect what material is present at the surface, and quantify any chemical changes that might have occurred. XPS instrumentation typically also incorporates additional analytical techniques, such as an in-situ Raman spectrometer that is coincident with the XPS analysis position, which can be used to obtain further information.

CM-ThP-7 Optimizing Combinatorial Materials Discovery with Active Learning: A Case Study in the Quaternary System Ni-Pd-Pt-Ru for the Oxygen Evolution Reaction*,* ***Felix Thelen [felix.thelen@ruhr-uni-bochum.de],*** *Rico Zehl, Ridha Zerdoumi, Jan Lukas Bürgel, Wolfgang Schuhmann, Alfred Ludwig,* Ruhr University Bochum, Germany

Steering through the multidimensional search space of compositionally complex solid solutions towards desired materials properties makes the use of efficient research methods mandatory [1]. Combinatorial materials science offers rapid fabrication, e.g. magnetron sputtering, and high-throughput characterization methods. Still, improvements to materials exploration cycles are necessary, since combinatorial methods are also suffering from the curse of dimensionality. At the scale of multinary systems, planning follow-up experiments based on already acquired data is economically feasible only through the use of machine learning techniques [2].

In this study, we comprehensively explored the quaternary composition space of Ni-Pd-Pt-Ru for electrocatalytic applications with a streamlined discovery workflow. Enabling a fast synthesis, the fabrication of the materials libraries was performed by magnetron co-sputtering, and all libraries were subsequently characterized by energy-dispersive X-ray spectroscopy and X-ray diffraction. Guiding through the composition space, an active learning algorithm was used in an optimization cycle, which balances exploration and exploitation through the expected improvement acquisition function. The libraries were characterized electrochemically by an automated electrochemical scanning droplet cell setup [3] for the oxygen evolution reaction.

Six materials libraries were enough to find the global activity optimum in the system. The findings of six additional libraries are used to validate the activity trend. Our approach illustrates the potential of ML-driven optimization frameworks in accelerating the identification of promising multinary materials and underscors the value of integrating ML with high-throughput synthesis and characterization techniques in modern materials science.

References:

[1] Banko, L., Krysiak, O. A., Pedersen, J. K., Xiao, B., Savan, A., Löffler, T., Baha, S., Rossmeisl, J., Schuhmann, W. and Ludwig, A. (2022) 'Unravelling composition-activity-stability trends in high entropy alloy electrocatalysts by using a data-guided combinatorial synthesis strategy and computational modelling', Advanced Energy Materials, vol. 12, no. 8.

[2] Ludwig, A. (2019) 'Discovery of new materials using combinatorial synthesis and high-throughput characterization of thin-film materials libraries combined with computational methods', npj Computational Materials, vol. 5, no. 1.

[3] Sliozberg, K., Schäfer, D., Erichsen, T., Meyer, R., Khare, C., Ludwig, A. and Schuhmann, W. (2015), 'High-throughput screening of thin-film semiconductor material libraries I: system development and case study for Ti-W-O.' ChemSusChem, vol. 8, no. 7.

CM-ThP-8 High-Throughput Aging Studies of Vapor-Deposited Perovskite Thin-Films Using Precise Automated Characterization and Machine Learning-Assisted Analysis*, Alexander Wieczorek,* ***Sebastian Siol [sebastian.siol@empa.ch]****,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

High-throughput experimentation (HTE) is increasingly being employed to accelerate metal halide perovskite (MHP) semiconductor thin-film development.[1] As of now, most approaches focus on solution-based deposition methods. To address the need for scalable and fabrication approaches, vapor-based deposition methods are gaining popularity.[2] However, durability concerns remain a major obstacle for large-scale deployment.[3] This motivates high-throughput stability studies of vapor-deposited MHP thin films. Combinatorial materials science is perfectly suited to address this challenge, specifically for time-consuming degradation studies where parallelization of experiments is key.[4] Using vapor deposition techniques, large parameter spaces can be covered on single substrates, whereas automated characterization and data analysis facilitate rapid properties screening.[5]

In this work, we present a comprehensive workflow for the aging of thin-film MHPs which includes structural, optical and chemical characterization.[6] To mitigate ambient degradation during characterization or transfers, we employ a complete inert-gas workflow. Furthermore, we perform a rapid *in-situ* screening of the transmission and reflectance under accelerated aging conditions. The samples are exposed to 85 °C and 1 kW m^{-2} white light bias, probing intrinsic material degradation in an accelerated fashion. With a temperature variation of ±1 °C and light intensity variation of <2% across combinatorial libraries, meaningful combinatorial stability screening is enabled. Automated characterizations of the structural properties yield deep insights into the aging process, extending and validating insights from changes in the optical transmission. We further demonstrate how these data sets can be used to better understand changes in the optical properties for highly scattering thin-films using machine learning assisted analysis. Furthermore, the workflow can be combined with high-throughput surface characterization techniques that our group previously demonstrated as a novel tool for accelerated materials discovery and optimization.

As a case study, we investigate the effect of residual precursors on the stability of two-step deposited MHP thin films grown on vapor-deposited templates. This workflow further allows to screen compositional spaces of libraries grown from completely vapor-based deposition methods.

References:

[1]Ahmadi et al. *Joule* **2021**, *5*, 2797.

[2]Guesnay et al. *ACS Photonics* **2023**, *10*, 3087.

[3]Siegler et al. *ACS Energy Lett.* **2022**, *7*, 1728.

[4]Sun et al. *Matter* **2021**, *4*, 1305.

[5]Gregoire et al. *Nat. Synth.* **2023**, *2*, 493.

[6]Wieczorek et al. *J. Mater. Chem. A* **2024**, *12*, 7025.

CM-ThP-9 Advanced Depth Profiling of Thin Films Using Angle-Resolved XPS/HAXPES*, Jennifer Mann, Norb Biderman, Kateryna Artyushkova,* ***Anthony Graziano [agraziano@phi.com]****,* Physical Electronics, USA

X-ray photoelectron spectroscopy (XPS) is a powerful technique for non-destructive analysis of the chemical composition of thin layers and interfaces. Angle-resolved XPS (AR-XPS) has traditionally been used with Al Kα (1486.6 eV) X-ray beams to determine non-destructively determine layer thicknesses up to 5-10 nm below the surface. Recent advancements in AR-XPS, including the integration of Cr Kα (5414.8 eV) hard X-ray photoelectron spectroscopy (HAXPES), have extended capability to 15-30 nm below the surface.

PHI's *Strata*PHI analysis software has been developed to reconstruct quantitative, non-destructive depth profiles from angle-dependent and single-angle photoelectron spectra. The latest version of *Strata*PHI combines Al Kα and Cr Kα XPS and HAXPES data within a single depth profile, enhancing the analytical information extracted from various depths.

Modern microelectronics devices contain thin films with different properties and purposes. Chips are often comprised of conducting films that form the interconnect layers as well as dielectric films that provide electrical insulation. In multilayer stacks, buried interfaces and subsurface layers are often beyond the analysis depth of traditional XPS. The information depth enabled by combined XPS and Cr Kα HAXPES is particularly useful for analyzing these types of materials.

This poster will discuss the principles behind AR-XPS and HAXPES, the new features of *Strata*PHI, and show some recent applications of the combination of these advanced methods to non-destructively probe thin films relevant to microelectronics.

CM-ThP-14 Thickness Quantification of Coatings as Part of the Rietveld Analysis of X-Ray Diffraction Data*,* ***Thomas Degen [thomas.degen@panalytical.com]****, Detlef Beckers, Mustapha Sadki, Nicholas Norberg,* Malvern Panalytical B.V., Netherlands*; Namsoo Shin,* Deep Solution Inc., Republic of Korea

For the in-line absolute thickness analysis of FeZn layers on galvanized steel we developed a Rietveld [1] based, full-pattern fitting method that fits a general layered structural model to a measured XRD Scan. The fitted model then delivers both the absolute layer thicknesses as well as the chemical composition of the layers and other key information like unit cell sizes, size/strain, and texture related information for all phases of the model. The method is implemented in the Malvern Panalytical software package HighScore Plus [2] V5.2.

The layer thickness modelling is based on the variable and increasing absorption of X-rays in the layers with different chemistry and thickness. Basically, by integrating over all beam paths, we accumulate the reduction in intensity of the total beam. Each layer adds a new absorption term with its own linear absorption coefficient. The method is theoretically correct, still in practice we need to know the packing factor and density of each layer. To solve that, we introduced an instrument dependent (alignment, tube aging etc) calibration factor for each layer. These calibration factors are determined from a dedicated data set, where many samples are characterized using multiple methods like SEM, wet analysis etc. In this presentation we show some data and analysis of about one year of continuous online analysis.

The initial fit model comprises:

1. Initial/expected thickness values, for all the phases
2. Calibration factors for all phases determined based on analyzed knowns
3. Intensity calibration factor to counteract tube aging
4. Atomic phase models, typically taken from structural databases

Output after fit:

1. Absolute thickness for all as layer marked phases
2. All other fit model parameters, like unit cells, size/strain information, texture index and more
3. Quality of fit indicators, Chi-Square, R_{wp} etc.

[1] H.M. Rietveld, *A profile refinement method for nuclear and magnetic structures*, J. Appl. Cryst. (1969), **2**, 65-71.

[2] T. Degen, M. Sadki, E. Bron, U. König & G. Nénert, *The HighScore Suite*, *Powder Diffr*. Vol. **29**, (2014), 13-18.

CM-ThP-17 Finding Optimal Catalysts for Methane Pyrolysis: DFT and AIMD Modelling and Simulation*, Martin Matas,* ***David Holec [david.holec@unileoben.ac.at]****,* Montanuniversität Leoben, Austria

Methane pyrolysis is its heat decomposition into carbon and hydrogen without emitting carbon dioxide. However, the operating temperatures are too high for large-scale hydrogen production by catalyst-free methane pyrolysis. Therefore, finding catalysts, lowering the operating temperatures and making methane pyrolysis economically and environmentally viable, is an important goal. We employ two theoretical approaches to the search for suitable catalysts. First, we combine the Sabatier principle and microkinetic modelling with density-functional theory to describe the adsorption of C and H atoms and intermediate methane-pyrolysis molecules on single-element metal catalyst surfaces. The results show, e.g., that the adsorption gets stronger with decreasing the catalyst d-block group number. Notably, various operating temperatures and methane/hydrogen partial pressures require various optimal catalysts. Second, we use ab-initio molecular dynamics to observe the molecule reactions in the vicinity of metals relevant to the liquid-metal bubble-column reactors. We examine the effect of element choice and alloying on the reaction rates and trajectories. Again, their dependence on the combination of temperature and catalyst material was proven. Collectively, our results show that the reaction parameters and catalyst choice have to be carefully matched. Therefore, our contribution establishes the foundation for large-scale studies of catalyst surfaces, alloy compositions, or material classes.

CM-ThP-18 Transverse and Longitudinal Elastic Characterization of Thin-Films Using Picosecond Acoustics*, Asma Chargui,* CNRS-IEMN, France*; Nicolas Martin,* IEMN-FEMTO, France*; Gabriel Ferro,* Université de Lyon, France*; **Arnaud Devos [arnaud.devos@iemn.fr]**,* CNRS-IEMN, France

Picosecond acoustics refers to ultra-high-frequency acoustics that produce hypersound (far beyond ultrasound), which is of course no longer heard, but which is very useful for measuring the properties of thin films and other nanostructures. The technique first saw the light of day in the 1980s[1], and since then has become as popular in the academic world as it is in industry, where it is used to control microprocessors on production lines. To access the world of hyper or “nanosounds”, there are no microphones or transducers, just laser light delivered in extremely brief flashes, femtosecond pulses. A femtosecond optical pulse excites a short acoustic pulse inside the sample and another optical pulse is used to monitor acoustic propagation and reflections. But this technique has an intrinsic limitation: only certain acoustic waves are accessible, namely longitudinal waves. And this is a problem, because elasticity is governed by several constants which require the measurement of speed of sound of several types of wave. Previous work has shown that it is sometimes possible to get around this limitation[2], but always in specific sample configurations. In particular, it was impossible to generalize to thin-film samples on silicon, THE basic geometry for applications, so these attempts were in vain. In this work, by using a thin metallic layer deposited in inclined columns, we have shown that any transparent layer on silicon can be characterized in terms of longitudinal and transverse waves. The inclined layer acts as a mixed longitudinal/transverse emitter when subjected to the laser, and the picosecond acoustic technique gain a new dimension. Although the study was initially dedicated to transparent thin films, such as silica, aluminum nitride and silicon carbide[3], the process is now being extended to non-transparent layers, such as metallic layers.

References:[1] C. Thomsen, J. Strait, Z. Vardeny, H. J. Maris, J. Tauc, J. J. Hauser, Phys. Rev. Lett. 53, 989–92 (1984).[2] T. Pezeril, Opt. Laser Technol. 83, 177 (2016).[3] A. Chargui, N. Martin, G. Ferro, and A. Devos, Appl. Phys. Lett. 125, 192202 (2024) https://doi.org/10.1063/5.0228331

Author Index

Bold page numbers indicate presenter