

# Monday Morning, May 12, 2025

## Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

### Room Town & Country C - Session CM4-1-MoM

#### Simulations, Machine Learning and Data Science for Materials Design and Discovery I

Moderator: Davide G. Sangiovanni, Linköping University, Sweden

10:00am **CM4-1-MoM-1 Crystal Symmetry Determination in Electron Diffraction Using Machine Learning**, Kevin Kaufmann [kevin.kaufmann@oerlikon.com], Oerlikon Metco, USA **INVITED**

The recent adoption by the general public of artificial intelligence (AI) tools such as ChatGPT has reinvigorated research into AI applied to material science. Deep learning, a subset of AI, allows computer systems to autonomously learn patterns in data and construct efficient decision rules for tasks including classification, regression, or segmentation. In material analysis, these tools have primarily been applied to techniques requiring analysis of data collected in the form of images. Electron backscatter diffraction (EBSD) is one such technique benefitting from these recent efforts to improve material analysis by leveraging deep neural networks. Within the last decade, advancements in EBSD equipment have enabled the capture of high-definition diffraction patterns at rates exceeding 3,000 Hz. This creates significant opportunities for increasing the amount of information that can be ascertained from a sample, as well as opens the door for training data intensive deep neural networks.

Deep neural network-based classification of the diffraction patterns is motivated by Hough-based EBSD's susceptibility to structural misclassification; a failure mode that modern EBSD can encounter even when the researcher has complete knowledge of the sample prior to beginning analysis. While several methods to improve phase-differentiation have been proposed, each still requires pre-selection of phases and additional data (e.g. chemistry or simulated diffraction patterns) to be available. In contrast, deep neural network-based methods have demonstrated effective phase differentiation and identification of phases to the space group level without the need for further information. The deep learning approach to EBSD diffraction pattern analysis is capable of these more advanced analyses because it uses all information in the image when assessing a diffraction pattern, whereas traditional Hough-based EBSD pattern analysis discards a significant amount of information.

To promote adoption of AI tools, it must be determined if and when it is prone to error. To test the ideal operating conditions, the deep neural network model is trained using diffraction patterns captured with a fixed geometry and SEM settings, and a parametric study is performed to develop an understanding of model performance as several of the most common EBSD operating conditions are varied. Each time one parameter is varied, the diffraction patterns are re-collected, and the CNN used to reassess the space group identification. Ultimately, the model is found to retain a high classification accuracy even with significant changes to the diffraction conditions.

11:00am **CM4-1-MoM-4 Predicting Segregation Behaviour in Polycrystalline Materials: A Case Study of P in Fe**, Amin Reiners-Sakic, Christoph Dösinger, Alexander Reichmann, Ronald Schnitzer, Lorenz Romaner, David Holec [david.holec@unileoben.ac.at], Montanuniversität Leoben, Austria

The segregation of solutes to grain boundaries has a significant impact on material behaviour, particularly with regard to its mechanical properties and microstructural evolution. Computational tools have previously been employed to investigate this phenomenon, although the majority of studies are limited to coincidence site lattice (CSL) symmetrical boundaries. A methodology incorporating geometries associated with general grain boundaries, as observed in polycrystals, has recently been employed to investigate the substitutional segregation of phosphorus in iron. In this study, we further develop this approach to include interstitial sites. The model of polycrystalline bcc Fe comprises approximately  $7 \times 10^5$  atoms distributed across 12 grains of  $\sim 8 \text{ nm}^3$  total volume. Of these, approximately  $1 \times 10^5$  are substitutional segregation sites. In addition, approximately 1.2 million interstitial sites have been identified. The full segregation spectra for all of the aforementioned sites have been investigated using interatomic potentials in conjunction with state-of-the-art machine-learning techniques. The results demonstrate that phosphorus segregates to both site types, with a lower mean segregation energy for substitutional sites in comparison to interstitial sites. However, due to the higher number of interstitial sites, the total number of sites with

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comparable segregation energies to substitutional sites is significantly greater. By incorporating both segregation distributions, we can accurately predict P enrichment at different concentrations and temperatures, in agreement with experimental data. To validate this approach, we applied it also to Ni and H, showing that Ni segregates, albeit moderately, only to substitutional sites, while H segregates exclusively to interstitial sites, in line with existing literature.

11:20am **CM4-1-MoM-5 Machine Learning Prediction of Work Functions for No, No<sub>2</sub>, Co, Co<sub>2</sub>, and H<sub>2</sub>S Gas Molecules Adsorbed on ZnGa<sub>2</sub>O<sub>4</sub>(111) Surfaces**, Po-Liang Liu [pliu@dragon.nchu.edu.tw], Hsiang-Yu Hsieh, Chao-Cheng Shen, National Chung Hsing University, Taiwan

Zinc gallium oxide is a metal oxide gas sensing layer with exceptional thermal and chemical stability, capable of detecting gases such as NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, and H<sub>2</sub>S. The work function of Zinc gallium oxide can be assessed through first-principles calculations based on Density Functional Theory, which allows for the prediction of the sensor's sensitivity. Although Density Functional Theory provides accurate computational results, its high computational cost and time requirements limit its applicability for large-scale surface screening. This study used a database based on a density functional theory-based zinc gallium oxide sensor model. We developed an automated workflow using Python programming to extract crystal structure features as input for the machine learning model. The processed and filtered input features were employed to predict the work function of the sensor model, achieving a mean absolute percentage error below 6% in the prediction results. This study presents a trained machine-learning model interface that allows users to input crystal structure files for the rapid and accurate evaluation of the work function of Zinc gallium oxide sensors.

## Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

### Room Town & Country C - Session CM4-2-MoA

## Simulations, Machine Learning and Data Science for Materials Design and Discovery II

Moderator: Po-Liang Liu, National Chung Hsing University, Taiwan

1:40pm **CM4-2-MoA-1 Computational Approach to Probing Hydrogen in Atomic Layer-Deposited Barrier Coatings**, *Vladyslav Turlo, Simon Gramatte [simon.gramatte@empa.ch]*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

INVITED

The energy transition of our society requires an improved fundamental understanding of the chemical interaction of H with oxide materials, such as oxide membranes for H-purification, oxides for photocatalytic water splitting, and passivated oxides on steel. In particular, the effect of H impurities on the barrier properties of oxide layers grown by Atomic Layer Deposition (ALD) is of great scientific and technological interest, since hydrogen permeation barriers fabricated by ALD are broadly applied to address specific challenges for transport, handling, and storage of H, as well as for electronics, catalysis and gas sensing. However, resolving tiny changes in local chemical bonding states and structure of e.g. amorphous alumina oxides, as induced by H impurities originating from the ALD deposition process, still poses huge challenges for modern analytical tools up to date.

Here, the effect of hydrogen on the local chemical bonding states and structures of amorphous ALD alumina films is disclosed by predicting Auger parameter shifts, as measured by XPS/HAXPES, using a combination of atomistic and electrostatic modeling. First of all, it is demonstrated that a conventional melt quenching simulation procedure is not applicable for generating representative amorphous oxide structures with different H contents and densities, as observed in the experiment. Instead, a novel approach is proposed for simulating amorphous H-containing oxide structures by annealing reconstructed, highly defective crystalline hydroxide structures using a universal machine learning interatomic potential. As such, excellent agreement between the density, structure, and H-content was obtained between theory and experiment. Moreover, measured Auger parameter shifts for Al as a function of the H-content were accurately predicted by assuming all H atoms to be present in the form of hydroxyl ligands in the randomly interconnected 4-fold, 5-fold, and 6-fold nearest-coordination spheres of Al (by O). Combined atomistic and electrostatic modeling shows in detail how measured Auger shifts depend on the complex correlations between local coordination, bond lengths, bond angles, and ligand type(s) around the core-ionized atom, which equally applies to amorphous and crystalline compounds.

This work enables the computational design of new barrier coatings for hydrogen economy, providing a comprehensive computational characterization framework able to interpret even the tiniest Auger parameter chemical shifts obtained from experimental XPS/HAXPES techniques.

2:20pm **CM4-2-MoA-3 Conditions for the Preparation of Maximum-Quality Crystalline ZnO by Molecular Dynamics Simulations of the Atom-by-Atom Film Growth**, *Jiri Houska [jhouska@kfy.zcu.cz]*, Kamila Hantova, University of West Bohemia, Czechia

Crystalline zinc oxide thin films are important due to a combination of optical transparency, electrical conductivity and piezoelectric and pyroelectric properties. These functional properties largely depend on perfection of the crystalline structure. Reproducing the growth of thin films by molecular-dynamics (MD) simulations is very useful for the disentanglement of processes and phenomena which take place in parallel in the experiment and can yield a lot of atomic-scale information which is difficult to access experimentally. After introducing MD simulations in general, classical MD based on a reactive force field is used to study the atom-by-atom growth of ZnO<sub>x</sub> films on a crystalline template. The effect of kinetic energy of fast atoms ( $E_{\text{fast}}$ ) and fraction of fast atoms ( $f_{\text{fast}}$ ) at varied elemental ratio ( $x = [\text{O}]/[\text{Zn}]$ ) is analyzed in a wide range. Following the visual inspection, the crystallinity is quantified in terms of network ring statistics.

Simulations with fixed  $f_{\text{fast}} = 100\%$  revealed that the highest crystal quality was obtained at  $x = 1.03$  (not at the intuitive ratio  $x = 1.00$ ) and  $E_{\text{fast}} = 3\text{--}12$  eV with a maximum at  $E_{\text{fast}} = 10$  eV. When only a low  $E_{\text{fast}} = 1$  eV is available, even higher  $x = 1.10$  leads to the relatively best results. Simulations with varied  $f_{\text{fast}}$  and fixed  $E_{\text{fast}} = 10$  eV revealed that the crystallinity at  $f_{\text{fast}} \geq 50\%$  is saturated. The ratio  $x = 1.03$  is optimum at all these  $f_{\text{fast}}$  values and it is

followed by  $x = 1.05$  which also leads to higher crystal quality than  $x = 1.00$ . However, the ratio  $x = 1.10$  is for the present energy distribution functions too high, not only in terms of growth rate which decreases with increasing  $x$ , but also in terms of crystal quality.

First, the results provide a quantitative insight into the role of individual deposition parameters. Second, the results explain available experimental data (for example, the dependence of the mobility of free charge carriers on the pulse-averaged target power density expresses the same character as the dependence of network ring statistics on  $E_{\text{fast}}$ ). Third, the results facilitate a further improvement of the film properties. For example, it is important that the recommended  $E_{\text{fast}}$  is comparable to achievable positions of maxima of energy distribution functions during reactive HiPIMS.

2:40pm **CM4-2-MoA-4 ML-Assisted Atomistic Modeling of Transition Metal Diborides: Mechanical Response and Phase-Dependent Phenomena**, *Shuyao Lin [shuyao.lin@tuwien.ac.at]*<sup>1</sup>, TU Wien, Institute of Materials Science and Technology, Austria; *Davide Sangiovanni, Lars Hultman*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *Paul Mayrhofer, Nikola Koutna*, TU Wien, Institute of Materials Science and Technology, Austria

Transition metal diborides (TMB<sub>2</sub>) represent materials with ultra-high hardness and melting points but limited resistance to crack propagation. Understanding the thermodynamic stability of typical TMB<sub>2</sub> polymorph structures ( $\alpha$ ,  $\omega$ , and  $\gamma$ ) at finite temperatures as well as the phase-dependence of mechanical and fracture properties has been challenging due to non-trivial synthesis and structural similarity of the phase polymorphs, complicating their detection. This work presents uniform shear and tensile strain simulations of defect-free Group IV-VII TMB<sub>2</sub> ceramics using *ab initio* molecular dynamics as well as molecular dynamics powered by machine-learning interatomic potentials (MLIP), trained in the moment tensor potential framework. Studied materials include TiB<sub>2</sub> (Group IV), TaB<sub>2</sub> (Group V), WB<sub>2</sub> (Group VI), and ReB<sub>2</sub> (Group VII), covering the  $\alpha$ ,  $\omega$ , and  $\gamma$  polymorphs. Among our main results is a robust workflow for training transferable MLIPs. These MLIPs are suitable for atomic-to-nanoscale MD simulations, allowing to understand deformation and fracture mechanisms of each TMB<sub>2</sub>, and extending the insights into phase transformation mechanisms under shear deformation. By demonstrating the outstanding mechanical performance of TMB<sub>2</sub>s in extreme environments, our predictions clearly underpin their huge application potential in protective coatings and high-temperature engineering. To deepen our understanding of fracture behavior, we additionally perform Mode-I fracture simulations allowing to quantitatively assess fracture toughness ( $K_{\text{IC}}$ ) using pre-cracked models. The results are discussed in light of relevant experimental data, including high-resolution transmission electron microscopy analysis of nanoindentation experiments on TiB<sub>2</sub> thin films.

3:00pm **CM4-2-MoA-5 Computational Modeling of Nanoelectronics and Emerging Materials**, *Chao-Cheng Kaun [kauncc@gate.sinica.edu.tw]*, Academia Sinica, Taiwan

INVITED

Using first-principles calculations, we investigate electronic transport through carbon-, oxide- and transition metal dichalcogenide (TMD)-based nanojunctions for nanoelectronic applications. Effects of biasing, defecting, contacting and quantum interfering are addressed. We study noncollinear interlayer exchange coupling in magnetic trilayers for spintronic application. Effects of spacing are uncovered. We also study the efficiencies of hybrid-protected perovskite quantum dot films for LED backlighting and hydrogen evolution reaction in oxides for sustainable-energy applications. Effects of polymer-adsorbing and material-configuring are highlighted. Moreover, we explore the plasmonic properties of complex transition metal nitrides for photonic applications.

<sup>1</sup> Graduate Student Award Finalist

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## Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

### Room Palm 1-2 - Session CM1-1-ThM

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

Moderator: Barbara Putz, Empa Thun, Switzerland

8:40am **CM1-1-ThM-3 Analysis of Deuterium by Atom Probe Tomography (Apt) - D in V Films and Fe/V Multi-Layered Films, Ryota Gemma [goettingenma@googlemail.com]**, Tokai University, Japan; **Talaat Al-Kassab, Astrid Pundt**, University of Göttingen, Germany **INVITED**

In this presentation, we will present the results of deuterium distribution and quantitative analysis by atom probe tomography (APT) in single-layered V or Fe/V multi-layered films. While V is a hydrogen-absorbing metal, Fe hardly dissolves hydrogen (H). Therefore, in Fe/V multi-layered films, almost all of the H atoms are supposed to be in the V layer, and the H distribution should show a clear contrast at the Fe/V interface. This is also the case for deuterium (D). D has a lower diffusion coefficient than H. Hence, a surface segregation of D during the APT analysis can be suppressed, enabling to visualize original D position in the host metal lattice. Furthermore, D can be distinguished from background hydrogen in the APT analysis chamber. By using a portable chamber to prevent the sample from being exposed to oxygen, we were able to measure the D concentration in V or Fe/V films over a wide concentration range. We compared the D concentration measured by APT with the compared with the results of measurements of the hydrogen concentration dependence of electromotive force (EMF) for similar samples, it was found that the average D concentration in the sample could be correctly evaluated using APT.

9:20am **CM1-1-ThM-5 Monitoring Thin Film Battery Electrodes via in-Situ/in-Operando Ellipsometry, Máté Füredi [mate.furedi@semilab.hu]**, Semilab Semiconductor Physics Laboratory Co. Ltd., Hungary; **Jialin Gu, Adam Lovett**, University College London, UK; **Bálint Fodor, András Marton**, Semilab Semiconductor Physics Laboratory Co. Ltd., Hungary; **Stefan Guldin**, Technical University of Munich, Germany; **Thomas Miller**, University College London, UK

The electrochemical energy storage behavior of nano- and microscale (thin- and thick-film) electrodes displays unique characteristics that provide crucial insights into various charge storage mechanisms, essential for the optimal design of commercial battery applications. Additionally, these films are applicable for constructing microbatteries for miniature electronic devices (such as sensors). Critically, material chemistry, crystallinity, and nanostructure significantly influence active charge transfer mechanisms in these systems, generally classified as electrochemical double layer capacitive, pseudocapacitive, or battery-type behaviors. In lithium-ion batteries specifically, the charge storage mechanism involves the (de)/intercalation of lithium ions in active electrode materials, such as silicon, graphite, or transition-metal oxides.

By optically monitoring thin-film electrodes under electrochemical charge/discharge, a range of time-resolved structural data can be obtained. This work elaborates on this by integrating operando spectroscopic ellipsometric data acquisition. Ellipsometry, highly sensitive to thin films, offers an advantage by effectively excluding any electrolyte side-reactions from measurement, thus providing accurate, real-time data on the evolving structure of lithiated electrodes across charging states. Additionally, ellipsometry tracks thickness changes, enabling precise monitoring of degradation mechanisms.

This work demonstrates (on the example of transition-metal oxide thin-film electrodes) how ellipsometry can reveal intercalation processes, diffusion limitations, and pseudocapacitive contributions. This is further correlated with the complementing electrochemical data. The considerations of this work are furthermore broadly applicable to other thin-film electrode materials.

9:40am **CM1-1-ThM-6 Exploring the Benefits of Automated, Redox Reactions in XPS Analysis, James Lallo [james.lallo@thermofisher.com]**, Thermo Fisher Scientific, UK, USA; **Robin Simpson, Paul Mack, Tim Nunney**, Thermo Fisher Scientific, UK

This presentation investigates the benefits of automated, in-situ redox reactions for the purpose of producing well controlled oxide growth on the surface of various sample types. The driving force behind using such a procedure is in the potential for generating a sequence of spectra from a progressively chemically-modified surface to remove ambiguities that can lead to misinterpretation, thus aiding in faster understanding of the

unmodified surface. Our study presents XPS results from coupled stepwise oxidation/reduction of surfaces, to aid in resolving such ambiguities across a wide array of materials. We use gas-phase oxidation agents to control the redox states of a specimen, leveraging the logarithmic growth of oxide thickness. This oxidation is implemented using vacuum ultraviolet light (VUV) and the generation of ozone and gas-phase hydroxide free radicals close to the surface of the specimens within the entry-lock of the Thermo Scientific Nexsa surface analysis instrument. This work focusses on the benefits of automating this process to ascertain the potential merits of including it into a standard operating procedure for XPS analysis.

## Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

### Room Town & Country C - Session CM2-1-ThM

#### Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes I

Moderators: **Matteo Ghidelli**, CNRS, France, **David Holec**, Montanuniversität Leoben, Austria

8:00am **CM2-1-ThM-1 Nano-Mechanical Characterization and Modeling of Plasticity in Metallic Materials, Takahito Ohmura [ohmura.takahito@nims.go.jp]**, Kyushu University/NIMS, Japan **INVITED**

Plastic deformation behavior is characterized through nano-mechanical testing in a small scale associated with microstructures including inter-phase and grain boundary in metallic materials. Deformation behavior was evaluated for Fe-Si bicrystal with different grain boundary plane with S9{221} and S9{114}1. The resistance to a slip transfer at the grain boundary depends on a combination of crystallographic orientation and dislocation character. Plasticity initiation behavior was characterized for ferrite-cementite interface with different coherency in a pearlitic steel2). The critical stress for the plasticity initiation is lower for a semi-coherent interface than that for an incoherent one, suggesting a potential reason for the continuous yielding phenomenon in macroscopic stress-strain curve of the steel with semi-coherent interface. Transmission Electron Microscope (TEM) in-situ straining was applied to reveal dislocation-grain boundary interactions. In the case of ultra-fine grain steel, dislocations in grain interior can sink at the grain boundary with no remarkable pile-up3). This behavior indicates a dislocation density dominance for the extra-hardening in the UFG steel. Dislocation-Dislocation interaction was also captured through TEM in-situ straining4). The dislocation reaction forms a stable grain boundary, which could be an elementally step of grain refining during severe plastic deformation. The critical stress for a slip transfer was estimated for  $\Sigma 3$  boundary of pure Al5). The mechanism of the slip transfer can be modeled in a simple dislocation reaction generating a grain boundary dislocation. Deformation mechanisms of plasticity initiation and subsequent behavior were modeled through stochastic analysis based on a pop-in phenomenon on a loading segment obtained from nanoindentation measurement6). The critical stress for the plasticity initiation shows Gaussian like distribution function, indicating a thermally-activated process including a nucleation of shear loop dislocation at defect-free region. In the subsequent stage, the loading curve shows intermittent plasticity, and the probability function for the event magnitude shows power-law type, suggesting a catastrophic phenomenon with a fractal dimension such as dislocation avalanche.

#### References

1. M. Wakeda, Y.-L. Chang, S. Li, T. Ohmura, Int. J. Plasticity, 145, (2021) 103047.
2. Y. Wang, Y. Tomota, T. Ohmura, W. Gong, S. Harjo, M. Tanaka, Acta Mater., 196, (2020) 565-575.
3. H. Li, S. Gao, Y. Tomota, S. Li, N. Tsuji, T. Ohmura, Acta Mater., 206, (2021) 116621.
4. H. Li, S. Li, N. Tsuji, T. Ohmura, Scripta Mater., 207, (2022) 114275.
5. S. Li, T. Enami, T. Ohmura, S. Tsurekawa, Scripta Mater., 221, (2022) 114953.

8:40am **CM2-1-ThM-3 Accelerating Workflows for High-Throughput Nanoindentation, Eric Hintsala [eric.hintsala@bruker.com]**, Kevin Schmalbach, Douglas Stauffer, Bruker Nano Surfaces, USA

Heterogenous microstructures are commonly employed across a wide range of applications as a tool for materials scientist to engineer the bulk properties, which can be seen in composite materials, multi-phase alloys or even surface treatments and coatings. Sometimes, property distributions

can also arise due to processing history, with laser-based techniques with micro-scale heat affected zones being of particular interest recently. In most cases these structures are nano- to microscale in size, so to isolate mechanical properties from individual regions high-throughput nanoindentation-based techniques have become increasingly popular.

Two recent advances in nanoindentation mapping are highlighted here. First, the indentation depth controls the finest spacing that can be utilized without affecting the subsequent nearby indentations and thereby defines the resolution of a nanoindentation map. Displacement control is particularly important when mapping samples with highly variable hardness. To address this, recent enhancements for the Hysitron TI 990 TriboIndenter (Bruker, USA) allows for trigger points to be used to switch segments and feedback control all within one test. This enables a high-throughput workflow where translation between positions is followed by approach, surface detection, and a displacement-controlled indent. This mode works with both high load and low load transducers for addressing a large range of depths and spacings.

Secondly, relating the measured mechanical properties to local structure and composition is also essential for materials development. This can be done by switching instruments from the nanoindenter to the SEM, but this is time consuming and generally necessitates use of fiducial markers. To facilitate this process, the Hysitron PI 89 Auto (Bruker, USA) in situ SEM indenter utilizes a rotation-tilt stage to move the sample between 3 distinct positions: Indentation position, top-down SEM and EDS position, and 70° tilted EBSD position. The accompanying software enables the same sample region to be co-located in all 3 positions easily, such that regions of interest from an EBSD or EDS map can be directly targeted for indentation testing.

**9:00am CM2-1-ThM-4 Understanding the Fracture Behavior, Interface Characteristics of Micro and Nanocrystalline Diamond Laminates Through Flexural Studies, Krishna Sarath Kumar Busi [sarath.busi@tu-darmstadt.de],** Technical University Darmstadt, Germany; **Tim Fuggerer,** University of Erlangen-Nuremberg, Germany; **Sebastian Bruns,** Technical University Darmstadt, Germany; **Timo Fromm,** Stefan M Rosiwal, University of Erlangen-Nuremberg, Germany; **Karsten Durst,** Technical University Darmstadt, Germany

Diamond metallic laminates (DML) have been demonstrated to exhibit an improved toughening mechanism by modifying the crack driving force with alternate hard and ductile layers [1]. These laminates were produced from free-standing diamond foils using HFCVD, exhibiting distinct crystalline morphologies microcrystalline (conventional) and nanocrystalline integrated with metallic layers deposited through PVD. A systematic investigation was set up to understand the mechanical behavior, interface characteristics of these multilayer system through macro 3PB and micro cantilever flexural studies. Nanocrystalline diamond foils exhibited better toughness, and their fracture sensitivity was analyzed by recording continuous stiffness change with respect to crack propagation for notched cantilevers using nanoindentation. Significant delamination was observed in nanocrystalline laminate (nDML) exhibiting weak interfacial strength between diamond and metal layers. Suitable analytical laminate models were effectively applied to investigate shear stress distribution, critical cracking events and the extent of delamination. Additionally, A 2D model of FEM with cohesive interactions was designed in same experimental scenarios (3-point bending, micro cantilever bending) to understand the diamond-metal interfacial properties, showed strong alignment with the analytical models and offered valuable insights to optimize the overall design of the laminate.

**Keywords:** Laminates, nanoindentation, toughness, fracture, bending, FEM.

## References:

- [1] Yang Xuan et. al (2021), A simple way to make tough diamond/metal laminate, Journal of European Ceramic Society 41 (2021) 5138–5146.
- [2] Timo Fromm et. al (2022), Bioinspired damage tolerant diamond-metal laminates by alternating CVD and PVD processes, Materials & Design, Volume 213, 2022, 110315, ISSN 0264-1275.

**10:20am CM2-1-ThM-8 Mechanical Properties of Thin Films Studied using 4D-STEM, Christoph Gammer [christoph.gammer@oeaw.ac.at],** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; **Alice Lassnig,** Montanuniversität Leoben, Leoben, Austria; **Lukas Schretter, Simon Fellner,** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; **Jürgen Eckert,** Montanuniversität Leoben, Leoben, Austria

## INVITED

The mechanical behavior of thin films is highly dependent on their microstructure. Micromechanical testing can be used to study small-scale mechanical properties. Modern thin film systems are becoming increasingly complex and their overall mechanical properties are influenced by strong variations in the local elastic and plastic response. Therefore, to understand their deformation behavior the local nanoscale stress distribution during loading has to be considered. The overall load-displacement curve is not sufficient. Recently, we have demonstrated that 4D-STEM allows to perform strain mapping at the nanometer scale during continuous *in situ* deformation in the TEM. In the present talk we will present recent advances demonstrating how 4D-STEM can be used to understand the deformation mechanisms in single-crystalline, nanocrystalline and amorphous thin films.

**11:00am CM2-1-ThM-10 Investigating the Interplay between Biaxial Multicracking of Nanometric Thin Films and Their Magnetic Properties: A Nuanced Separation of Magnetoelastic and Magnetostatic Effects, Hatem Ben Mahmoud, Damien Faurie [faurie@univ-paris13.fr],** Laboratoire des Sciences des Procédés et des Matériaux (LSPM) – CNRS, France; **Pierre-Olivier Renault, Pierre Godard,** Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; **Dominique Thiaudière, Philippe Joly, Christian Mocuta,** Soleil Synchrotron, France; **Eloi Haltz, Noël Girodon-Boulandet, Fatih Zighem,** Laboratoire des Sciences des Procédés et des Matériaux (LSPM) – CNRS, France

The magnetoelectronic systems of the future will be designed to adapt to complex geometries. Flexible electronics have seen rapid growth, offering promising applications in areas such as confined environments and flexible displays [1]. These systems rely on polymers, which are lighter and more cost-effective than silicon. Understanding the interplay between mechanical strain and magnetic properties is essential [2]: at low strains, magnetic anisotropy is key, while at higher strains, microscopic damage (e.g., fragmentation and decohesion) becomes critical [3].

However, the relationship between thin film fragmentation and magnetic properties [4], especially under biaxial tension, remains poorly studied. This thesis aims to fill this gap through novel experimental techniques and studies on model systems. We investigated flexible magnetic systems using *in situ* methods, applying significant mechanical strain (up to 10%) while simultaneously probing their magnetic properties. A magneto-optical Kerr effect (MOKE) magnetometer was developed at the DiffAbs beamline of the Soleil synchrotron. Our research focuses on the distribution of stress (before and during cracking) and its impact on the magnetic response, along with the underlying mechanisms.

Two main mechanisms are identified: first, stresses generated during mechanical loading can induce a strong magnetoelastic field that alters the magnetic response; second, magnetostatic fields between fragments separated by cracks can contribute to coercivity during magnetization cycles. However, these effects have yet to be fully quantified. To address this, we studied magnetization cycles under large deformations in Ni80Fe20 films (with negligible magnetoelastic contribution), of varying thickness, with or without W layers of different thicknesses to modify fragment size. We demonstrate that the magnetostatic contribution is closely linked to the aspect ratio (diameter/thickness) of the fragments. This study, compared with research on Co layers, clearly distinguishes between geometric (magnetostatic) effects and stress-induced (magnetoelastic) effects.

- [1] D. Makarov, M. Melzer, D. Karnaushenko, O. G. Schmidt, Applied Physics Review 3, 011101 (2016)
- [2] F. Zighem & D. Faurie, Journal of Physics: Condensed Matter 33, 233002 (2021)
- [3] B. Putz, T.E.J Edwards, E. Huszar, L. Pethő, P. Kreiml, M. J. Cordill, D. Thiaudière, S. Chiroli, F. Zighem, D. Faurie, P.-O. Renault, J. Michler, Materials & Design 232, 112081 (2023)
- [4] H. Ben Mahmoud, D. Faurie, P.O. Renault, F. Zighem, Applied Physics Letters 122, 252401 (2023)

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11:20am **CM2-1-ThM-11 Cross-Sectional Nanoindentation Mapping of Sputtered Inconel 725 Films**, *Ikponmwosa Iyinbor [iyinbor@usc.edu]*, Mork Family Department of Chemical Engineering and Materials Science, University of Southern California., USA; *Jin Wang*, Institute of Energy Materials and Devices, Microstructure and Properties of Materials (IMD-1), Forschungszentrum Jülich GmbH., Germany; *Ruth Schwaiger*, Institute of Energy Materials and Devices, Microstructure and Properties of Materials (IMD-1), Forschungszentrum Jülich GmbH., Germany; *Andrea Hodge*, Mork Family Department of Chemical Engineering and Materials Science, University of Southern California., USA

Heterogeneous nanostructured materials (HNMs) offer significant potential for overcoming the strength-ductility trade-off observed in conventional homogeneous nanostructured materials. Recently, we have demonstrated the influence of heterogeneous stress distribution on the development of unique nanostructured features in sputtered nanotwinned Inconel 725 thick films after undergoing heat treatment. A gradient microstructure with three distinct nanodomains featuring a nanocrystalline equiaxed region, a nanotwinned region with carbides, and a region featuring abnormal recrystallization wherein abnormally large grains, delta-phase precipitates, and rafted structures were observed. This unique combination of nanodomains is expected to contribute distinct responses to mechanical deformation behavior.

In this work, two different HNMs of 8  $\mu\text{m}$  and 20  $\mu\text{m}$  film thicknesses were synthesized and heat treated. A nanoindentation mapping technique using a Femto-Tool NMT04 in-situ SEM nanoindenter was performed in order to generate high-spatial resolution hardness and elastic modulus property maps. The nanoindentation maps show a good correlation to the observed heterogeneous microstructure, revealing trends that provide an understanding of the local deformation behavior of these HNMs. Understanding the contribution of each nanodomain to the overall deformation behavior of the films enables the optimization of design and fabrication strategies to provide a superior combination of properties.

11:40am **CM2-1-ThM-12 Fracture Behaviour of Crystalline Metal/Amorphous Oxide Nanolaminates**, *Thomas Edwards [thomas.edwards@nims.go.jp]*, NIMS (National Institute for Materials Science), Japan; *Hendrik Jansen*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; *Seiichi II*, NIMS (National Institute for Materials Science), Japan; *Barbara Putz*, *Johann Michler*, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

The extent of the embrittlement in ductile-brittle multilayers often depends on the modulation period ( $t_{\text{brittle}} + t_{\text{ductile}}$ ) as well as on the modulation ratio ( $t_{\text{brittle}}/t_{\text{ductile}}$ ) [1]. Ductile-brittle thin film multilayers of crystalline Al and amorphous  $\text{AlO}_x$  are studied by our group, produced by atomic layer ( $\text{AlO}_x$ ) and physical vapour deposition (Al) uniquely combined within a single deposition system. Such multilayer films are thermally stable up to 0.85  $T/T_m$ . Using this ALD/PVD combination, neighbouring layer thicknesses can easily differ by one order of magnitude or more, and both the amorphous oxide layer thickness and that of the metal have been optimised previously for strength (over 1 GPa) and ductility. Here, the effect of this divergence between layers in chemistry, crystallinity and length scale on the fracture behaviour of these thin films was studied by notched microcantilever fracture testing, including at high temperature, and *in situ* TEM tensile loading of notched testpieces to evaluate the role of the amorphous-crystalline interfaces on crack propagation at the nanoscale. The outcomes are compared to those of alternative materials and using other measurement methods.

References:

[1] K. Wu, J.Y. Zhang, J. Li, Y.Q. Wang, G. Liu, J. Sun, *Acta Mater.* 100 (2015) 344–358.

**Advanced Characterization, Modelling and Data Science for Coatings and Thin Films**

**Room Town & Country D - Session CM3-1-ThM**

**Accelerated Thin Film Development: High-throughput Synthesis, Automated Characterization and Data Analysis I**

**Moderators:** *Davi Marcelo Febba*, NREL, USA, *Sebastian Siol*, Empa, Switzerland

8:00am **CM3-1-ThM-1 Combinatorial Screening of Quaternary Piezoelectric Nitrides, Enabled by HiPIMS**, *Nathan Rodkey [nathan.rodkey@empa.ch]*, *Jyotish Patidar*, *Federica Messi*, *Sebastian Siol*, EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

Increasing demand for data and the surge of AI technologies is escalating the needs of telecommunication devices. RF filters are a limiting factor in this regard, where improvements in bandwidth and selectivity are needed. Advanced RF filters rely on piezo thin films like AlN, valued for its linear response and strong electromechanical coupling, with Sc doping enhancing its  $d_{33}$  and overall performance. While AlScN is considered state-of-the-art, many proposed dopants (e.g. B, Y, La) could further improve its properties. High-throughput experiments are instrumental in exploring quaternary or multinary materials, but few studies examine combinatorial screening of piezoelectric materials. This is because piezoelectric materials are difficult to screen effectively, as their device properties strongly depend on the c-axis texture of the film. During combinatorial gradient deposition the shallow deposition angles and static substrate can cause significant grain tilt towards the dominant source, convoluting composition and texture gradients. In high-power impulse magnetron sputtering (HiPIMS), additional energy can be introduced to arriving species by synchronizing a substrate bias to arriving metal ions. This improves the adatom mobility of species, removing grain tilt, and resulting in highly textured films without substrate rotation. In this work, we use AlScYN as an example material to demonstrate how HiPIMS enables effective device screening of piezoelectric properties.

Before the use of HiPIMS, DCMS screening is used to assess solubility limits in the quaternary phase space. This is typically done using X-ray diffraction mapping while applying the disappearing phase method. However, in combinatorial screening of materials this method loses effectiveness, as precipitates can be tilted out of the diffraction plane. Consequently, we use the peak shift of the (0001) plane to track discontinuities from Vegard's law and identify precipitation. Despite the larger ionic radius of Y, the combined solubility of Y and Sc increases, reaching a maximum of ~50%. For context, the solubility limit of AlScN is ~40%. Materials libraries were then made using metal-ion synchronized HiPIMS. The libraries are highly textured, with rocking curve FWHMs of  $<2^\circ$ . Following this, the coupling ( $k$ ) and clamped  $d_{33}$  coefficients of these libraries were mapped, showing their dependence on the combined Sc and Y contents. Importantly,  $d_{33}$  coefficients were mapped using a double beam laser interferometer (DBLI) for improved accuracy.

8:20am **CM3-1-ThM-2 High-Throughput Experiments Informed by High-Throughput Theory Reveal Zintl Phosphides as a New Family of High-Performance Semiconductors**, *Sage Bauers [sage.bauers@nrel.gov]*, 15013 Denver West parkway, USA

INVITED

The discovery of a new structural class of semiconductor is a rare occurrence. For example, in the case of solar absorption, nearly all relevant semiconductors can broadly be described as materials derived from the tetrahedrally-coordinated diamond structure (e.g., Si, III-Vs, II-VIs, chalcopyrites, kesterites). This is part of the reason that new high-performing materials, such as perovskites, which are made up of octahedral bonding motifs, garner so much interest and help generate new materials design concepts. Using high-throughput computational workflows, we recently discovered that several  $\text{AM}_2\text{P}_2$  ( $A = \text{Ca, Ba, Sr}$  and  $M = \text{Cd, Zn}$ ) compounds possess the requisite intrinsic materials properties for high optoelectronic performance, including solar-spectrum matched band gaps, strong optical absorption, and benign intrinsic defects, leading to long photoexcited carrier lifetimes. This family of compounds, which exhibits a mixed octahedral + tetrahedral bonding motif, has been known for several decades but the optoelectronic properties had been almost entirely unexplored.

Using a combinatorial synthesis approach based on a hybrid PVD/CVD method, we recently prepared the first thin films of Zintl phosphides  $\text{CaZn}_2\text{P}_2$  and  $\text{SrZn}_2\text{P}_2$ . By combinatorial sputtering from metallic targets in the presence of  $\text{PH}_3$  at low temperature, we prepare films across the

ternary composition space. Growths at higher temperatures result in much narrower compositional spreads pinned around the  $AM_2P_2$  composition, indicating an adsorption-controlled growth regime can be realized. Mapping measurements including x-ray fluorescence, x-ray diffraction, UV-vis spectroscopy, photoluminescence, and Raman spectroscopy are used to probe the properties of the zintl phosphide films. To establish the photoactivity and semiconducting nature of the  $AM_2P_2$  materials, minority carrier lifetimes and electronic properties were measured via time resolved microwave conductivity, transient absorption, and van der Pauw/Hall effect. To summarize the characterization of  $CaZn_2P_2$  as an example, we observe high optical absorption of  $\sim 10^4 \text{ cm}^{-1}$  at the  $\sim 1.95 \text{ eV}$  direct transition, near band edge optical emission, and a photoexcited carrier lifetime of up to 30 ns at a fluence of  $2 \cdot 10^{13} \text{ cm}^{-2}$ . Films are intrinsic, but p-dopable with +1 elements such as Na (A site dopant) or Cu (M site dopant). Such performance metrics are usually not observed in inorganic solar absorber materials until well into their development, highlighting the value of coupling high-throughput theory, high-throughput experiments, and targeted experiments toward new functional materials.

9:00am **CM3-1-ThM-4 High-Throughput Nanoindentation Methodology for Combinatorial Thin Film Material Libraries**, **Andre Bohn** [[bohndama@usc.edu](mailto:bohndama@usc.edu)], University Of Southern California, USA; **Adie Alwen**, **Andrea Maria Hodge**, University of Southern California, USA

Combinatorial and high-throughput (CHT) methods offer an accelerated pathway for the discovery and development of novel materials with wide ranging biological, electronic, and structural applications. One common approach to accelerate synthesis is the deposition of large compositionally graded thin film arrays with hundreds of distinct samples, often referred to as thin film material libraries. High-throughput characterization techniques are then employed to quickly assess processing-structure-property relationships, which generates large datasets for machine learning models and screens for promising next-generation materials. For assessing mechanical behavior in these libraries, nanoindentation is particularly suitable due to the ease of automation, minimal sample preparation requirements, and compatibility with thin films. However, despite the widespread use of this technique in CHT research, many inconsistencies between reported methodologies in literature can be identified. This work presents a CuNi alloy library to identify how to improve data reliability while minimizing experimental times and costs. Emphasis is given to optimizing the number of indents per sample and the distribution of samples tested. By improving method standardization, both efficiency and reproducibility of combinatorial studies can be enhanced, thus expanding the value of material libraries to the scientific community.

9:40am **CM3-1-ThM-6 Streamlining Inorganic Thin-Film Data Management with the High-Throughput Experimental Materials Database (HTEM)**, **Davi Febba** [[dfebba@nrel.gov](mailto:dfebba@nrel.gov)], **Nicholas Wunder**, **Hilary Egan**, **Max Gallant**, **Andriy Zakutayev**, National Renewable Energy Laboratory, USA

Artificial intelligence (AI) is ushering in a new era of progress in materials science, where self-driving laboratories and autonomous instruments are performing experimental research that was once the exclusive domain of humans. Central to this paradigm shift is effective data management, as AI-driven laboratories make decisions based on the data they collect. Ensuring that materials science data is Findable, Accessible, Interoperable, and Reusable (FAIR) is crucial for accelerating materials discovery, as it facilitates seamless integration of diverse datasets and enhances collaboration across research teams.

In this presentation, we will discuss NREL's Research Data Infrastructure (RDI) [1], which catalogs experimental data from inorganic thin-film experiments at NREL and underpins the High-Throughput Experimental Materials Database (HTEM-DB) (<https://htem.nrel.gov/>) [2]. The HTEM-DB stores comprehensive information about synthesis conditions, chemical composition, crystal structure, and optoelectronic properties of materials, making the data readily accessible and reusable for the research community.

Will also present recent advancements in the HTEM's extract-transform-load (ETL) pipeline. These advancements not only allow for large-scale AI analysis of X-ray diffraction (XRD) patterns [3] but also enable the containerization of applications and instruments, making the database more modular and maintainable. Enabled by the recently developed Hybrid Environment Resources and Operations (HERO), these improvements help to lower the barriers to accessing NREL's computational resources, data analysis, and visualization capabilities. By facilitating both AI integration and modular design, HERO empowers scientists to share their research and collaborate with external partners through interactive applications.

[1] Patterns, 2, 100373, 2021

[2] Scientific Data 5, 180053, 2018

[3] PEARC '24, 39, 1-5, 2024

10:20am **CM3-1-ThM-8 A Python-Based Approach to Sputter Deposition Simulations in Combinatorial Materials Science**, **Felix Thelen** [[felix.thelen@ruhr-uni-bochum.de](mailto:felix.thelen@ruhr-uni-bochum.de)], **Rico Zehl**, **Jan Lukas Bürgel**, Ruhr University Bochum, Germany; **Diederik Depla**, Ghent University, Belgium; **Alfred Ludwig**, Ruhr University Bochum, Germany

In combinatorial materials science, magnetron sputtering plays a key role for the exploration of future high-performance materials due to its capability to produce well-defined, continuous compositional gradients in form of thin-film libraries. Its scalability from laboratory settings to industrial applications, relatively high deposition rates, and compatibility with a wide range of materials make it an effective choice for combinatorial synthesis [1]. However, achieving precise control over the deposition profile and compositional distribution often requires multiple preliminary experiments to optimize process parameters - an approach that can be time- and resource-intensive.

Aiming to predict those properties, several analytical and numerical simulations were reported in literature over the past decade [2-4]. However, only the magnetron sputter deposition model SIMTRA [4] was made publicly available. Based on the Monte Carlo approach, it allows to simulate the deposition profile of a single magnetron source, while taking into account the dimensions of the components through a graphical user interface.

In order to make this tool more suitable for the application in combinatorial materials science, the command line version of the SIMTRA application was wrapped in a Python environment, enabling the definition of sputter chambers through code and executing the time-consuming Monte Carlo calculations through user defined scripts. This approach also enables parallel simulation of multiple magnetrons by using multi-threading, decreasing simulation times significantly, especially when simulating co-sputtering systems with 5-8 cathodes. The accuracy of SIMTRA and the capabilities of the Python wrapper are demonstrated by comparing the compositions predicted by simulation and measured by energy-dispersive X-ray spectroscopy of seven materials libraries in the system Ni-Pd-Pt-Ru.

References:

[1] Gregoire, J. M., Zhou, L., and Haber, J. A. (2023). 'Combinatorial synthesis for AI-driven materials discovery'. *Nature Synthesis*, vol. 2, no. 6.

[2] Ekpe, S. D., Bezuidenhout, L. W. and Dew, S. K. (2004) 'Deposition rate model for magnetron sputtered particles', *Thin Solid Films*, vol. 474, no. 1.

[3] Bunn, J. K., Metting, C. J. and Hattrick-Simpers, J. (2014) 'A semi-empirical model for titled-gun planar magnetron sputtering accounting for chimney shadowing', *The Journal of The Minerals, Metals & Materials Society*, vol. 67, no. 1.

[4] Mahieu, S., Buyle, G., Depla, D., Heirweigh, S., Ghekiere, P. and De Gryse, R. (2006) 'Monte Carlo simulation of the transport of atoms in DC magnetron sputtering', *Nuclear Instruments and Methods in Physics Research*, vol. 243, no. 2.

10:40am **CM3-1-ThM-9 Discovery and Development of Transition Metal Nitride Semiconductors for Photoelectrochemical Energy Conversion**, **Ian Sharp** [[sharp@wsi.tum.de](mailto:sharp@wsi.tum.de)], **Walter Schottky Institut**, Technische Universität München, Germany

**INVITED**

Transition metal nitride semiconductors are rapidly emerging as a promising class of materials for advanced optoelectronic and energy conversion applications. Compared to oxides, nitrides offer narrower bandgaps, stronger bond covalency, and improved carrier transport properties that make them well suited for harvesting sunlight in photovoltaic and photoelectrochemical systems. Despite this considerable promise, far fewer nitrides than oxides have been experimentally investigated due to their synthetic complexity and a broad range of new compounds remain to be explored. Furthermore, synthesis challenges have led to poorly controlled defect and impurity properties within this class of materials. In this work, we overcome these limitations using reactive co-sputtering to synthesize thin film nitride semiconductors with controlled compositions, exploring both dopants and new compounds in the Ti-Ta-N, Zr-Ta-N, and Hf-Ta-N composition spaces. Starting with orthorhombic  $Ta_3Ns$ , which stands as the best performing photoanode material within this class, we investigate the critical roles of native and impurity defects on carrier transport and recombination, showing that substitutional Ti and Zr doping with rationally optimized concentrations can be used to improve

photoconversion efficiencies. While high Ti contents in Ta<sub>3</sub>N<sub>5</sub> lead to the precipitation of a secondary TiN phase, different behavior is observed for the case of Hf and Zr. In particular, solid solutions with broadly tunable compositions across the Hf-Ta-N(O) and Zr-Ta-N(O) composition spaces are investigated, leading to bandgap-tunable compounds that exhibit remarkably large refractive indices suitable for photonics applications. Moreover, deposition of a stoichiometric 1:1 Zr:Ta ratio leads to formation of a new ternary nitride compound, bixbyite-type ZrTa<sub>3</sub>N<sub>3</sub>, that it is a strong visible light absorber, functioning as an active photoanode material. Complementary DFT calculations indicate a direct bandgap that is tunable based on cation site occupancy. Thus, this material offers exciting prospects not only for solar energy conversion but also for optoelectronics applications. Overall, these results highlight the promise of both established and new transition metal nitride semiconductors for solar energy harvesting, as well as the importance of precise composition engineering to tune optoelectronic and charge transport characteristics. Considering the compositional complexities of these compounds, exploration and optimization can be dramatically accelerated through use of gradient sputtering and rapid characterization approaches.

11:20am **CM3-1-ThM-11 XRD and STEM Analysis of Structural Variation in Nanocrystalline Cu-Ag Thin Films**, *Kyle Dorman [krdorma@sandia.gov], Sadhvikas Addamane, Sandia National Labs, USA; Mark Rodriguez, Sandia National Labs, USA; Paul Kotula, Alejandro Hinojos, Luis Jauregui, Suzanne Vitale, Catherine Sobczak, Sandia National Labs, USA; Finley Haines, Sandia National Lab, USA; David Adams, Sandia National Labs, USA*

Nanocrystalline thin films are a topic of interest in applications such as sliding metal contacts for their potential to enhance mechanical performance beyond that of their bulk polycrystalline counterparts. During analysis of the results of wide-ranging combinatorial Cu-Ag survey, STEM imaging and XRD diffractogram analysis reveal intragranular compositional modulation at intermediate compositions and grain boundary segregation of solute species at extremal compositions. These microstructural variations are influenced by processing parameters during film growth and provide further avenues for improvement in Cu-Ag performance. Furthermore, while EDS composition maps provide stark, visually clear evidence, it is shown that the high-throughput and automation-viable XRD measurements capably reveal the structure across the full dataset without the practical limitations of STEM in such a large-scale survey. XRD is particularly able to noninvasively identify preferential collection of solute at grain boundaries from below 15 at.% Cu and above 75 at.% Cu. A complimentary annealing study employing STEM demonstrates that the grain boundary segregation in nanocrystalline Cu/Ag is thermally stable up to at least 100°C, before undergoing secondary phase formation by 300°C.

**SAND2025-01110A**

# Thursday Afternoon, May 15, 2025

## Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

### Room Palm 1-2 - Session CM1-2-ThA

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

**Moderators:** Damien Faurie, Université Sorbonne Paris Nord, France, Barbara Putz, Empa Thun, Switzerland

1:20pm **CM1-2-ThA-1 Crystalline-Amorphous Interface Fracture Explored Across Different Length Scales, Alice Lassnig** [[alice.lassnig@unileoben.ac.at](mailto:alice.lassnig@unileoben.ac.at)], Montanuniversität Leoben, Austria; Michael Meindlhuber, Montanuniversität Leoben, Austria; Stanislav Zak, Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; Megan Cordill, Christoph Gammer, Austrian Academy of Sciences, Austria; Andrew Minor, Lawrence Berkeley Lab, USA **INVITED**

Interfaces separating bi- and multilayered thin film structures, are susceptible to premature failure due to the challenge of bridging distinct physical properties of adjacent materials. Thus, the reliability of these interfaces significantly influences the overall lifespan of such structures. Consequently, a thorough investigation of their reliability and a comprehensive understanding of the underlying failure mechanisms are essential for enhancing novel material composites and combinations.

In this study, we investigate the fracture behavior of model crystalline-amorphous interfaces, specifically focusing on Cu thin films delaminating from bulk glass substrates and nanocrystalline Cu – amorphous CuZr multilayers. Utilizing advanced characterization techniques, we aim to study the delamination behavior, interface adhesion, and fracture under static and cyclic loading of such structures using advanced experimental techniques spanning both the meso-scale and nanoscale, incorporating in situ transmission electron microscopy for a detailed exploration of these phenomena.

2:00pm **CM1-2-ThA-3 Tailoring Structure and Mechanical Properties of TiZrHfTa Refractory Alloy Thin Films, Gregory Abadias** [[gregory.abadias@univ-poitiers.fr](mailto:gregory.abadias@univ-poitiers.fr)], Hocine Slimani, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; Pietro Vecchietti, Politecnico Milano, Italy; Meriadeg Chalopin, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; Ferenc Tasnádi, Linköping University, IFM, Sweden; Matteo Ghidelli, Philippe Djemia, Laboratoire des Sciences des Procédés et des Matériaux (LSPM) – CNRS, France

Complex concentrated alloys (CCAs), including medium- and high-entropy alloys, offer attractive thermomechanical properties which make them promising candidates for various technologies such as corrosion resistant or radiation tolerant structural materials. Among the various CCAs, alloys with multi-principal refractory elements (RCCA) have drawn significant attention for hydrogen (H) storage applications [1-3] due to their ability to reversibly absorb H in the form of metal hydrides. However, up to now, studies on RCCA for H storage have only focused on bulk materials, with limited attention to thin film counterparts, which could be considered as model materials enabling an easy tailor of composition, phase and microstructural features (grain size, porosity or texture), providing valuable insights on the mechanisms of hydride formation and dissolution in RCCAs.

In this work, (TiZrHf)<sub>100-x</sub>Ta<sub>x</sub> thin films, with thickness up to 700 nm and Ta content ranging from 0 to 60 at.%, were synthesized by co-sputtering deposition. The phase composition, crystal structure, morphology and elemental composition was determined using a combination of analytical techniques (XRD, SEM/TEM, EDS), while the intrinsic stress was measured *in situ* during deposition by wafer curvature method. The mechanical properties of the films were assessed by nanoindentation and opto-acoustics (Brillouin light scattering and picosecond laser ultrasonics) methods. By tuning the Ta content, different phases were stabilized in these quaternary alloys, from hcp to bcc and amorphous. These structural changes are accompanied by variation in growth morphology (evolving from nanocolumns to vein-like patterns), stress reduction and a progressive softening of hardness, shear and elastic modulus with increasing Ta content. The experimental findings are discussed and compared with results obtained from atomistic models of random alloys and amorphous phases, using *ab initio* molecular dynamics simulations combined with machine-learned interatomic potentials, as well as relevant data from the existing literature [4].

#### References:

1. Marques, F., Balcerzak, M., et al., *Review and outlook on high-entropy*

*alloys for hydrogen storage*. Energy Environ. Sci. 14, 5191 (2021)

2. Kong, L., Cheng, B., Wan, D., Xue, Y., *A review on BCC-structured high-entropy alloys for hydrogen storage*, Front. Mater. 10, 1135864 (2023)

3. Shahi, R. R., Gupta, A. K., Kumari, P., *Perspectives of high entropy alloys as hydrogen storage materials*, Int. J. Hydrogen Energy 48, 21412 (2023)

4. Huang, S., Li, W., Holmström, E., Vitos, L., *Phase-transition assisted mechanical behavior of TiZrHfTa high-entropy alloys*, Sci. Rep. 8, 12576 (2018)

2:20pm **CM1-2-ThA-4 Exploring Mechanical Properties of Thin Films Through Synchrotron X-Ray Diffraction, Digital Image Correlation and Electrical Resistivity Measurements, Pierre-Olivier Renault** [[pierre.olivier.renault@univ-poitiers.fr](mailto:pierre.olivier.renault@univ-poitiers.fr)], University of Poitiers, France **INVITED**

Mechanical behavior of thin films deposited on polymeric substrates was investigated under in-situ controlled tensile biaxial loading conditions. The study employed synchrotron X-ray diffraction (XRD), digital image correlation (DIC) techniques, and electrical resistivity measurements. The combination of X-ray diffraction and digital image correlation provides classical stress-strain curves.

The three complementary measurement techniques allow for a comprehensive analysis of the deformation characteristics of each component of the thin film. This approach helps to identify and distinguish the various deformation regimes that arise during mechanical loading. Beyond the yield stress, distinct mechanical behaviors are observed in the stress-strain curves, which can be attributed to plasticity and fracture phenomena. These behaviors are identified as characteristic signatures of material failure modes.

Additionally, the experimental setup offers the capability to assess whether deformations are fully transmitted through the interfaces between the thin film and the substrate, providing also insight into the interaction between different layers in a multilayer coating.

After describing the experimental setup, examples of the mechanical behaviors observed in metallic bilayer or trilayer systems and, oxide-metal films deposited on polyimide substrates will be presented. These examples illustrate the range of deformation responses that can arise in such multilayer systems. Differences in the mechanical behavior of films are shown to be influenced by factors such as type of interface or the presence of residual stresses in the as-deposited films, as well as variations in film thickness and grain size. These factors play a key role in determining the overall mechanical performance of the thin film systems.

3:00pm **CM1-2-ThA-6 A Combined X-ray Microdiffraction and Micromechanical Testing Approach for Direct Measurement of Thin Film Elastic Constants, Rainer Hahn** [[rainer.hahn@tuwien.ac.at](mailto:rainer.hahn@tuwien.ac.at)], CDL-SEC, TU Wien, Austria; Rebecca Janknecht, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland; Nikola Koutná, Institute of Materials Science and Technology, TU Wien, Austria; Anna Hirle, CDL-SEC, TU Wien, Austria; Anton Davydok, Helmholtz-Zentrum Hereon, Germany; Klaus Boebel, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; Szilárd Kolozsvári, Peter Polcik, Plansee Composite Materials GmbH, Germany; Christina Krywka, Helmholtz-Zentrum Hereon, Germany; Paul H. Mayrhofer, Institute of Materials Science and Technology, TU Wien, Austria; Helmut Riedl, CDL-SEC, TU Wien, Austria

The direct measurement of elastic constants for thin films is not yet a routine procedure and presents a number of significant technical and analytical challenges when compared to the analysis of bulk materials. *Ab initio* density functional theory calculations can provide a theoretical basis for understanding the properties of materials. However, discrepancies between model systems and real-world properties persist, primarily due to a lack of available experimental data for newly emerging material systems. Furthermore, computationally affordable models are typically constrained to defect-free single crystals, thereby excluding microstructural effects that exert a pronounced influence on the material's behavior.

This study addresses this gap by proposing a novel experimental approach to measure direction-dependent elastic constants, combining synchrotron microdiffraction and micropillar compression. The approach was tested on a polycrystalline face-centered cubic TiN thin film, where linear elastic failure prevails. An advanced in-situ testing environment has been established to enable the continuous recording of the load-displacement of the indenter, while simultaneously collecting the material's deformation response to uniform uniaxial compression. This dynamic approach permits the evaluation of the orientation-dependent elastic strain components and the macroscopic uniaxial compressive stresses, each over time, thereby



enabling a differential analysis to assess the elastic and X-ray elastic constants.

The excellent agreement between experimental and ab initio data serves to corroborate the here-proposed robust method for direct elastic constant measurements, which is of crucial importance for advancements in thin film material testing.

**3:20pm CM1-2-ThA-7 Real-Time Particle Detection for Enhanced Coating Deposition Processes, Constant Boris Rieille [constant.rieille@bfh.ch], Sylvain Le Coultre, Berner Fachhochschule BFH, Switzerland**

Industries in photonics, optics, and semiconductors are increasingly challenged by particles emitted during PVD/ALD deposition processes. As device miniaturization advances, stricter requirements on defect size and particles inclusions make effective control essential to ensure product conformity.

Currently, these industries rely on preventive maintenance schedules that do not account for unexpected particle emissions or variations in machine usage. When particles appear, repeated maintenance is required due to the lack of a system to detect or locate their source. Integrating a real-time particles sensor into machines would transform this approach by enabling predictive monitoring, reducing downtime, and improving operational efficiency.

This session will deliver key insights into particle emissions during PVD deposition, explore market trends, and present business cases for the PVD/ALD market.

**4:00pm CM1-2-ThA-9 Real-Time Monitoring of Sputter Deposition Process: Application in the Context of Ag-Based Low-Emissive Coatings, Rémi Lazzari [remi.lazzari@insp.jussieu.fr], CNRS/Sorbonne Université, France**

**INVITED**

The challenge of green-house gas reduction pushes towards a better thermal insulation of housing. In this context, glass industry strives to decrease the infra-red radiative transfer across windows while keeping transparency. In the so-called low-E or solar control glazings, the functionality is provided by a complex stack of layers deposited by magnetron sputtering in which the active component is a ~10 nm thick Ag film encapsulated in between ZnO dielectric layers. Because of its noble character, Ag follows intrinsically a Volmer-Weber growth mode and is prone to dewetting upon thermal treatments such as windows tempering. Thus, there is tremendous need of understanding and control of its out-of-equilibrium growth process.

In this context, this presentation will illustrate the interest of combining real-time measurements (UV-vis spectroscopy<sup>1,2</sup>; stress measurement via wafer curvature and digital image correlation<sup>3</sup>; film resistivity) with *in situ* photoemission spectroscopy to have a full overview on the Ag growth mechanism. Among others, the impact of sputtering deposition parameters and of gas additives on stress build-up and relaxation, on film percolation and on Ag chemistry will be discussed<sup>4-6</sup>. The second part of the talk will show the contribution of model experiments in understanding the epitaxy at Ag/ZnO interface<sup>7</sup>, the reactivity<sup>8</sup> and band alignment<sup>9</sup> at metal/ZnO interfaces as seen by *in situ* hard x-ray photoemission and the various contributions to Ag film resistivity<sup>7</sup>.

[1] I. Gozhyk, L. Dai, Q. Héroult, R. Lazzari, and S. Grachev. *J. Phys. D: Appl. Phys.*, 52:095202, 2018.

[2] R. Lazzari, J. Jupille, R. Cavallotti, E. Chernysheva, S. Castilla, M. Messaykeh, Q. Héroult, and E. Meriggio. *ACS Appl. Nano Mater.*, 3:12157–12168, 2020.

[3] S. Grachev, Q. Héroult, J. Wang, M. Balestrieri, H. Montigaud, R. Lazzari, and I. Gozhyk. *Nanotechnology*, 33:185701, 2022.

[4] Q. Héroult, I. Gozhyk, M. Balestrieri, H. Montigaud, S. Grachev, and R. Lazzari. *Acta Mater.*, 221:117385, 2021.

[5] R. Zapata, M. Balestrieri, I. Gozhyk, H. Montigaud, and R. Lazzari. *ACS Appl. Mater. Interfaces*, 15:36951–36965, 2023.

[6] R. Zapata, M. Balestrieri, I. Gozhyk, H. Montigaud, and R. Lazzari. *Appl. Surf. Sci.*, 654:159546, 2024.

[7] F. Corbella, V. Haspot, Y. Zheng, D. Guimard, H. Montigaud, and R. Lazzari. *submitted*, 2024.

[8] E. Chernysheva, Rensmo H. Philippe, B., O. Karis, M. Gorgoi, E. Burov, S. Grachev, M. Montigaud, and R. Lazzari. *Appl. Surf. Sci.*, 680:161409, 2023.

[9] E. Chernysheva, W. Srour, B. Philippe, B. Baris, S. Chenot, R. F. Duarte, M. Gorgoi, H. Cruguel, H. Rensmo, H. Montigaud, J. Jupille, G. Cabailh, S. Grachev, and R. Lazzari. *Phys. Rev. B*, 97:235430, 2018.

Thursday Afternoon, May 15, 2025

**4:40pm CM1-2-ThA-11 A Combination of Real-Time Diagnostics Probing the Impact of N<sub>2</sub> on Ag Thin Film Growth, Michal Kaminski [michal.kaminski@kit.edu], KIT, Germany; Gregory Abadias, David Babonneau, Institut Pprime, France; Alessandro Coati, Yves Garreau, Synchrotron SOLEIL, France; Anny Michel, Institut Pprime, France; Anton Plech, KIT, Germany; Andrea Resta, Synchrotron SOLEIL, France; Karan Solanki, Institut Pprime, France; Alina Vlad, Synchrotron SOLEIL, France; Baerbel Krause, KIT, Germany**

Silver thin films are used in a number of applications (e.g., transparent and conductive electrodes and plasmonic devices) which require a continuous layer with thickness below a few nanometers. However, Ag films grown by magnetron sputtering have the tendency to form 3D-structures on weakly interacting substrates, what prevents their application as transparent and conductive layers. It is reported that the use of gas additives (particularly N<sub>2</sub> [1]) allows for obtaining a continuous layer at earlier deposition stage.

A thorough understanding of the nanoscale mechanisms of thin film formation requires real-time techniques [2]. In particular the widely used *ex situ* diagnostics can provide misleading information, as the structure of the thin film can evolve even under high vacuum conditions. We employ a simultaneous combination of real-time grazing incidence small-angle x-ray scattering (GISAXS), grazing incidence diffraction (GID), and substrate curvature measurements to get information about polycrystalline thin film evolution during growth. In particular, GISAXS reveals changes in nanoscale morphology, GID gives insight into the crystallinity of thin films, and substrate curvature measurements provide information about the average intrinsic stress. With our methodology we can study the interdependence between stress state, thin film structure and morphology, using the quantitative information obtained from the scattering techniques. Since the influence of the substrate curvature can be crucial for grazing incidence condition x-ray techniques, we show that in the curvature regime encountered in our experiment the effect on GISAXS is negligible.

Using the information from all three techniques, we will discuss the impact of nitrogen additive on all growth stages (from initial stages of island nucleation, growth, and coalescence, up to formation of percolated and continuous films), including the relaxation of the film during growth interruptions.

**Acknowledgements:** The work is performed within the frame of the ANR-DFG project IRMA (491224986).

**Literature:**

[1] A. Jamnig et al., *ACS Appl. Nano Mater.* 3, 4728-4738 (2020)

[2] B. Krause et al., *ACS Appl. Mater. Interfaces* 15, 11268-11280 (2023)

## Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

### Room Town & Country C - Session CM2-2-ThA

## Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes II

**Moderators:** Thomas Edwards, NIMS, Japan, Matteo Ghidelli, CNRS, France

**1:20pm CM2-2-ThA-1 Influence of Applied Deformation on Magnetic Properties of Ferromagnetic Ni<sub>60</sub>Fe<sub>40</sub> Thin Films Deposited on Polymeric Substrate, Alejandro Toledano Povedano [alejandro.toledano.povedano@univ-poitiers.fr], Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; Dominique Thiaudière, Synchrotron SOLEIL, France; Pierre Godard, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; Eloi Haltz, Laboratoire des Sciences des Procédés et des Matériaux (LSPM) - CNRS, France; Damien Faurie, Fatih Zighem, Laboratoire des Sciences des Procédés et des Matériaux (LSPM) - CNRS, France; Anny Michel, Pierre-Olivier Renault, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France**

Metallic ferromagnetic thin films are key components in devices including sensors, data storage, and signal processing systems. With the rise of flexible electronics, understanding the relationship between magnetic properties and mechanical deformations in the low and high strain regimes is critical. These deformations induce homogeneous elastic strains as well as strain heterogeneities due to crystalline defects and cracks, impacting the magnetic properties of films through magnetostriction and dipolar interactions. This study focuses on how mechanical strain and controlled crack propagation affect the magnetic properties of thin films on polymer substrates. The research aims to reveal the relationship between controlled microstructural changes (residual stress, film thickness) and magnetic

properties, from initial strain to crack onset and subsequent propagation. These insights are critical for developing flexible magnetic devices that maintain performance under mechanical stress. To investigate these effects, a multi-scale approach has been carried out thanks to a unique setup developed at Synchrotron SOLEIL (DiffAbs beamline). It combines four techniques to study, in situ, the crystalline and magnetic properties of the sample subjected to equibiaxial or sequenced uniaxial tensile testing: X-ray diffraction to monitor the local lattice strain, digital image correlation to measure macroscopic distortions, electrical resistivity to reveal the crack onset and Magneto-Optical Kerr Effect to track the evolution of magnetic reversal. Ni60Fe40 thin films with varying thicknesses (20 and 200nm) have been deposited by ion beam sputtering on flexible polymer substrates and characterised under strain with this setup. Deformation tests of Kapton/Mo/Ni60Fe40 systems highlight the important role of the magnetoelastic field, induced by the difference of the in-plane stress components, for multi-cracking dynamics. The study also examined different film thicknesses to determine whether these variations were linked to fragmentation effects or magnetoplasticity. These findings show how crack density (which varies with thickness) influences the material's magneto-mechanical properties. The hysteresis loops initially show a square shape. As applied deformation increases, the loops change and exhibit features typical of a direction that resists magnetization, attributed to the negative magnetostrictive coefficient of Ni60Fe40. Beyond the maximum of the lattice strain, the loops appear to return to a square shape.

**1:40pm CM2-2-ThA-2 The Local Electrical Fingerprint of Deformation and Growth -Induced Defects in Alloys, Hanna Bishara [hbishara@tauex.tau.ac.il], Tel Aviv University, Israel INVITED**

A microstructural defect, whether spontaneously or intentionally induced, impacts the electrical properties of its surroundings. Defects dominate the electrical behavior of materials only when they become sufficiently dense. Therefore, capturing the defect's electrical characteristics is usually performed on a macroscopic scale, leading to averaging over multiple defect's types. This prevents studying the structure-properties relations in defects. This talk provides advanced electrical characterization methods of individual defects on surface and within the volume of bulk and thin film alloys.

The presentation initially introduces an experimental procedure to measure the local electrical resistivity of defect segments - with high sensitivity and spatial resolution *in-situ* scanning electron microscopy (SEM). The studied defects, i.e. pure and segregated grain boundaries (GBs), dislocations, stacking faults, and phase boundaries are either growth-controlled or deformation-induced. The segments are chemically and structurally characterized by electron backscatter diffraction (EBSD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and atom probe tomography (APT), in addition to molecular dynamics (MD) simulations.

In the context of grain boundaries (GBs), we report that the GB resistivity spans over a spectrum of values, depending on the boundary's excess volume. The resistivity values might increase by an order of magnitude due to segregation effects in metallic systems. However, segregation-influenced complexions are found to boost the electrical conductivity of semi-metallic materials. Additionally, the talk relates to the formation and electrical characterization of near-surface dislocations in brittle Heusler alloys.

Revealing the contribution of different GB types to electrical resistivity would pave the path for predicting the electrical degradation of materials upon controlled mechanical deformation. In addition, it allows a novel defect engineering to optimize the performance of conductors and functional alloys.

**2:20pm CM2-2-ThA-4 On the Effect of Thin Film Residual Stress on the Crack Propagation Resistance of ALD Coated Nano-Ceramics, Edoardo Rossi, Università degli studi Roma tre, Dipartimento di ingegneria Civile, Informatica e delle Tecnologie Aeronautiche., Italy; Marco Sebastiani [seba@uniroma3.it], Università degli studi Roma Tre, Dipartimento di Ingegneria Civile, Informatica e delle Tecnologie Aeronautiche, Italy**

The present work aims at investigating the effects of Atomic Layer Deposition (ALD) coatings on 3D printed ceramic micro-pillars, which were produced by Two-photon polymerization-direct Laser Writing (TPP-DLW). With a uniform 50 nm layer of Al<sub>2</sub>O<sub>3</sub> under varying processing conditions (Plasma Enhanced-ALD at 200 °C, Thermal ALD at 200 °C, and 350 °C), the study first evaluated how these coatings influenced the retainment of fracture toughness through the splitting of glassy carbon (GC) pillars across a spectrum of Relative Humidity levels (below 5% and above 60%). Then, incorporating spatially resolved stress measurements through Focused Ion

Beam (FIB) ring-core analysis, the specific interface effects of the coatings on the crack propagation process were investigated. A corresponding investigation of lithographically produced fused quartz micro-pillars treated with the same ALD parameters provided a comparative foundation to gauge the coatings' effectiveness in enhancing the composite fracture toughness.

Additionally, the research detailed how the found residual stresses within the ALD coatings, significantly varying depending on the deposition temperature, are critical for the understanding of crack initiation and propagation mechanisms, suggesting that the observed reduction in fracture toughness, when compared to undefective, uncoated pillars under similar humid conditions, might be attributed to premature crack tip opening.

The research clarified these interplayed dynamics with the coating's stresses through the silica system's response to ALD coatings, significantly improving the baseline crack resistance. Indeed, uncoated silica experience an approximate 134% increase in fracture toughness for a 50 nm deposition at 200 °C, while a 100 nm coating at 300 °C resulted in around a 165% enhancement. This illustrates how interface engineering (deposition temperature and induced stresses from ALD coatings) can fine-tune fracture toughness in 3D TPP micro-ceramics, depending highly on the substrate material and surface defects (likely missing in lithography silica structures).

**2:40pm CM2-2-ThA-5 Micromechanical Testing of Ceramic Coatings for Nuclear Applications up to 1000°C, Dong (Lilly) Liu [dong.liu@eng.ox.ac.uk], University of Oxford, UK INVITED**

Multi-layered ceramic coatings, such as SiC and PyC, have been used to encapsulate spherical nuclear fuel kernels for use in the next generation of nuclear fission reactors. These coatings are typically between 30 µm to 100 µm thick and will subject to harsh environments such as elevated operation temperatures and neutron radiation during service. It is important to acquire local mechanical properties of these individual coating layers as well as the interfacial strength between the coatings for better understanding of their structural integrity and to support performance modelling. In this work, nanoindentation tests were carried out on SiC and PyC coatings over a range of temperatures from ambient to 1000°C with and without in-situ SEM imaging. The change of modulus and hardness as a function of temperature will be presented and the challenges associated with the high-temperature tests will be discussed. In addition, micro-cantilever bending method was utilized to evaluate the interfacial strength between the SiC and PyC coatings. During the coating deposition process (chemical vapour deposition), residual stresses were generated in the coatings and affected the local properties. Therefore, the residual stresses in each coating layer were characterised by focussed-ion-beam digital image correlation (FIB-DIC) method on unirradiated and neutron irradiated coatings where the magnitude of residual stresses are further modified due to radiation induced dimensional changes. The local mechanical properties and residual stresses measured are correlated with the coating deposition process, radiation damage and 3D microstructure generated using FIB tomography based on conventional Ga+ FIB and Plasmas FIB.

## Advanced Characterization, Modelling and Data Science for Coatings and Thin Films

**Room Town & Country D - Session CM3-2-ThA**

### Accelerated Thin Film Development: High-throughput Synthesis, Automated Characterization and Data Analysis II

**Moderators: Davi Marcelo Febba, NREL, USA, Sebastian Siol, Empa, Switzerland**

**1:20pm CM3-2-ThA-1 Feature Selection and High-Throughput Synthesis: Can They Be Used to Predict Adsorption Energies on Multinary Materials?, Hannah-Noa Barad [hannah-noa.barad@biu.ac.il], Bar-Ilan University, Israel INVITED**

Electro-reduction of CO<sub>2</sub> to sustainable fuels and value-added chemicals is one of the most promising paths for closing the anthropogenic CO<sub>2</sub> cycle. The catalyst, the main component of the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), is used to reduce CO<sub>2</sub> dissociation activation energy. Metal and metal oxide catalysts have been studied as catalysts for CO<sub>2</sub>RR, yet selectivity towards desired products remains elusive. To overcome this issue, discovery of new materials with more components (e.g., ternary, or quaternary materials), is paramount. These multinary materials, have the potential to improve the selectivity and activity toward a desired product, due to synergistic effects between the elements. However, the exploration

space is enormous and needs to be decreased. An important descriptor for realizing the reaction mechanism leading to a specific product by a given catalyst is the adsorption energy of the reaction intermediates, like  $^*CO$ . Yet, adsorption energies on these new and complex materials have not been studied systematically.

Here, we present the development of a machine learning model for the prediction of adsorption energies of materials. Our model is based on a simple description of the adsorption environment by choosing very basic features, and more intricate structural features, like orbital field matrix.<sup>[1]</sup> We also apply the moments theorem for the density of states (DOS)<sup>[2]</sup> to depict our materials in terms of closed paths in their lattices, from which we obtain features relating to the adsorption site. We also use high-throughput synthesis and characterization methods to try and obtain more experimental data points on new multinary materials to enhance our dataset. These methods will support prediction of adsorption energies of multinary materials to discover new highly active and selective  $CO_2RR$  catalysts.

[1] T. Lam Pham, H. Kino, K. Terakura, T. Miyake, K. Tsuda, I. Takigawa, H. Chi Dam, *Sci. Technol. Adv. Mater.* **2017**, *18*, 756.

[2] J. P. Gaspard, F. Cyrot-Lackmann, *J. Phys. C Solid State Phys.* **1973**, *6*, 3077.

2:00pm **CM3-2-ThA-3 Autonomous Experiments for Thin Films and Solid Materials**, **Taro Hitosugi** [[hitosugi@g.ecc.u-tokyo.ac.jp](mailto:hitosugi@g.ecc.u-tokyo.ac.jp)], The University of Tokyo, Japan

**INVITED**

Integrating machine learning, robotics, and big data analysis into established research methodologies can significantly accelerate materials science research. Many studies have already demonstrated the potential of autonomous (self-driving) experiments in materials science [1, 2]. The rapid advancement of digital technologies is changing the way we conduct research.

Here, we discuss the status and prospects of data- and robot-driven materials research using autonomous experiments. We have developed an autonomous experimental system for thin-film materials. We constructed a system that automates sample handling, thin-film deposition, optimization of growth conditions, and data management. By using Bayesian optimization in conjunction with robots, our approach facilitates high-throughput experiments and generates comprehensive datasets that cover many aspects of materials (X-ray diffraction, Raman spectroscopy, scanning electron microscopy, optical transmittance measurement, electronic conductivity measurement). We tuned the hyperparameter for Bayesian optimization using the domain knowledge of chemistry; the number of trials to reach the global optimum is reduced.

The system demonstrated the synthesis and optimization of the electrical resistance in Nb-doped  $TiO_2$  thin films [5]. Moreover, this autonomous approach has enabled the discovery of new ionic conductors [6]. We discuss the potential impact of this technology in accelerating materials science research, particularly in solid materials.

[1] Autonomous experimental systems in materials science, N. Ishizuki, R. Shimizu, and T. Hitosugi, *STAM Methods* **3**, 2197519 (2023).

[2] The rise of self-driving labs in chemical and materials sciences, M. Abolhasani and E. Kumacheva, *Nature Synthesis* **2**, 483–492 (2023).

[3] Tuning of Bayesian optimization for materials synthesis: simulation of the one-dimensional case, R. Nakayama, T. Hitosugi *et al.*, *STAM Methods* **2**, 119-128 (2022).

[4] Tuning Bayesian optimization for materials synthesis: simulating two- and three-dimensional cases, H. Xu, R. Nakayama, T. Hitosugi *et al.*, *STAM Methods* **3**, 2210251 (2023).

[5] Autonomous materials synthesis by machine learning and robotics. R. Shimizu, T. Hitosugi *et al.*, *APL Mater.* **8**111110 (2020).

[6] Autonomous exploration of an unexpected electrode material for lithium batteries. S. Kobayashi, R. Shimizu, Y. Ando, T. Hitosugi, *ACS Materials Lett.* **5**, 2711–2717 (2023).

## 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<sub>2</sub> 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  $\sigma_f$  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<sub>2</sub>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 ( $\alpha$  and  $\omega$ ). 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  $\alpha$ -phase TMB<sub>2</sub>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  $\alpha$ - and  $\omega$ -WB<sub>2</sub> 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<sub>2</sub>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 Nunnay, 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 LiNi<sub>1-x</sub>CoyMn<sub>1-x-y</sub>O<sub>2</sub> (NCM)/LiCoO<sub>2</sub> [NMC] composite cathode and Sodium Ion Fe/Mg cathode materials as examples. We employ 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 underscores 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 Wiczorek, 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.<sup>[1]</sup> 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.<sup>[2]</sup> However, durability concerns remain a major obstacle for large-scale deployment.<sup>[3]</sup> 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.<sup>[4]</sup> Using vapor deposition techniques, large parameter spaces can be covered on single substrates, whereas automated characterization and data analysis facilitate rapid properties screening.<sup>[5]</sup>

In this work, we present a comprehensive workflow for the aging of thin-film MHPs which includes structural, optical and chemical characterization.<sup>[6]</sup> 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<sup>-2</sup> 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] Wiczorek 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 *StrataPHI* analysis software has been developed to reconstruct quantitative, non-destructive depth profiles from angle-dependent and single-angle photoelectron spectra. The latest version of *StrataPHI* 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 *StrataPHI*, 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<sub>wp</sub> 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 Diff.* 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](mailto: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>

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