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°. 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 AM_2P_2 (*A* = Ca, Ba, Sr and *M* = 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 $CaZn_2P_2$ and $SrZn_2P_2$. By combinatorial sputtering from metallic targets in the presence of 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_2materials, 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 ~10^4 cm^{-1} at the ~1.95 eV direct transition, near band edge optical emission, and a photoexcited carrier lifetime of up to 30 ns at a fluence of 2 10^{13} 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],* 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], 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]***, *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]***, 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_3N_5, 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_3N_5 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 $ZrTaN_3$, 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 Sobzcak,* 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.

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