



# **RMC-AVS 2023**

## **ANNUAL SYMPOSIUM & EQUIPMENT EXHIBIT**

**September 14, 2023**

**AVS: The Next Generation**

*At the*  
DoubleTree by Hilton Hotel Denver-Westminster  
8773 Yates Drive  
Westminster, Colorado

**Symposium  
Equipment Exhibit**

**AVS Short Courses  
Poster Session**



**WELCOME** to the 2023 Annual Symposium of the Rocky Mountain Chapter of the American Vacuum Society. After several years off we're all excited to be back together and hosting our annual fall symposium again this year. Thank you for joining us today!

The topic of this year's technical session is "AVS: The Next Generation". I've always been excited about next generation technologies, and thinking about how some new technology may drastically change how we do things, e.g., quantum computing or clean electricity generation at massive scales. The symposium today features talks from the next generation in a wide range of fields, as well as other issues which have been of interest to the chapter over the last year. We are thinking about the implementation of the CHIPS act and how it might impact Colorado, as well a lot of discussions about training and teaching the next generation of scientists, professors, and industrial entrepreneurs.

I am pleased to welcome over 20 vendors, showcasing the latest in vacuum products and services, to our 2023 Symposium. Please take a moment to visit some of these vendors and learn about the latest products in vacuum technology. Company representatives will be available to provide details about their equipment and answer questions about their products. The Vendor Exhibit is open from 10:00 a.m. to 6:00 p.m.

In addition to the vendor exhibit, the poster session (starting at 3:30 p.m.) will feature posters from the Colorado Front Range and beyond. The happy hour with complimentary beverages and appetizers starts at 4:00 p.m. At 5:45 p.m. cash awards will be presented to the top three student posters. Door prizes will also be given away during this time (you must be present to win!).

This year we were pleased to offer a wide program of short courses taught by leaders in their respective fields. The slate of course topics span a wide range of vacuum technologies, system design, and troubleshooting. The chapter strives to provide in demand content at this annual symposium, and suggestions for course topics are always appreciated. We also do on-site teaching at your location when the demand is large enough.

The Rocky Mountain Chapter of the AVS is an all-volunteer organization. Thank you to the many volunteers whose efforts keep the chapter running all year long and allow us to present this annual symposium today. I would also like to thank all the symposium sponsors, attendees, exhibitors, and speakers for helping to make this symposium a success.

The Rocky Mountain AVS Chapter is always looking for volunteers to get involved in the chapter and make this symposium a successful event. If you would like to get more involved with the chapter, please contact me, or any Rocky Mountain AVS Chapter board member. In addition, please feel free to provide any suggestions for improving the 2024 Symposium.

We hope you find the symposium informative, educational, and stimulating.

Steve Harvey  
RMC-AVS – *Chair*

steve.harvey@nrel.gov

## ***2023 ANNUAL SYMPOSIUM & EQUIPMENT EXHIBIT PROGRAM***

<b>8:00 a.m.</b>	Registration begins.
<b>9:00 a.m. - 11:30 a.m.</b>	Morning Oral Session
<b>9:00 a.m. - 12:00 p.m.</b>	Introduction to Vacuum Technology J.R. Gaines (K.J. Lesker, in Private Dining Room)
<b>10:00 a.m.</b>	Vendor Exhibit opens.
<b>11:30 a.m. - 1:30 p.m.</b>	Free Lunch in the Exhibit Area
<b>1:30 p.m. - 3:30 p.m.</b>	Afternoon Oral Session
<b>1:30 p.m. - 3:30 p.m.</b>	Introduction to Physical Vapor Deposition and Thin Film Growth Models J.R. Gaines (K.J. Lesker, in Private Dining Room)
<b>3:30 p.m.</b>	Poster Session opens.
<b>4:00 p.m. - 6:00 p.m.</b>	Social hour, Vendor Exhibit and Student Poster Session (Authors will be present from 3:30 p.m. to 5:15 p.m. Winners announced by 5:45 p.m.)

Vendor information is posted online at <https://www.rmccavs.org/vendor-exhibit/>.

## ***2023 RMC-AVS BOARD MEMBERS***

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## ***SYMPOSIUM PROGRAM***

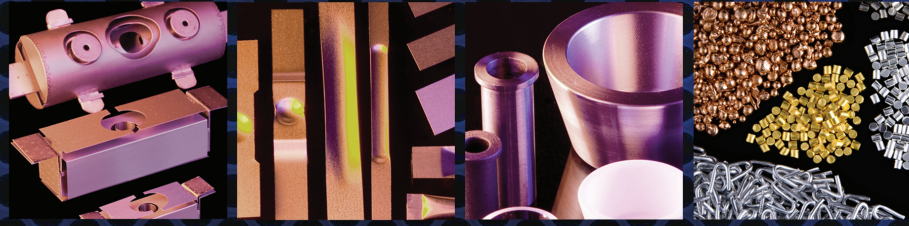
- 9:00 a.m. - 9:30 a.m.**      **Under the Ultimate Vacuum: Working and Living Off the Land Beyond Earth**  
*Angel Abbud-Madrid, Director, Center for Space Resources, Colorado School of Mines*
- 9:30 a.m. - 10:00 a.m.**      **Ammonia can be the new carbon-free petroleum**  
*Joe Beach, Starfire Energy*
- 10:00 a.m. - 10:30 a.m.**      ***Coffee Break and Vendor Exhibits***
- 10:30 a.m. - 11:00 a.m.**      **Quantum Computing**  
*Kristin Beck, Lawrence Livermore National Laboratory*
- 11:00 a.m. - 11:30 a.m.**      **Approaching carbon-free electricity by 2050: technology, policy, and some strategy**  
*Steven Christensen, Excel Energy Colorado*
- 11:30 a.m. - 1:30 p.m.**      ***Lunch and Vendor Exhibits***
- 1:30 p.m. - 2:00 p.m.**      **From automated to autonomous methods for deposition and measurements of inorganic films**  
*Andriy Zakutayev, National Renewable Energy Laboratory*
- 2:00 p.m. - 2:30 p.m.**      **Inspiring the Next Generation of Scientists and Engineers through Engaging Inquiry-based Learning**  
*Birgit Landin, Colorado Springs Utilities community educator, and DeLene Hoffner, retired Colorado science teacher*
- 2:30 p.m. - 3:00 p.m.**      **Update from Congressman Joe Neguse's office on CHIPS Act**  
*Max Coker from Congressman Neguse's office*
- 3:30 p.m. - 6:00 p.m.**      ***Poster Session, Vendor Exhibits and Social Hour***

Poster Session prizes provided by NREL <https://www.nrel.gov/>.



Abstracts are posted online at <https://www.rmcavs.org/2023-symposium/>.

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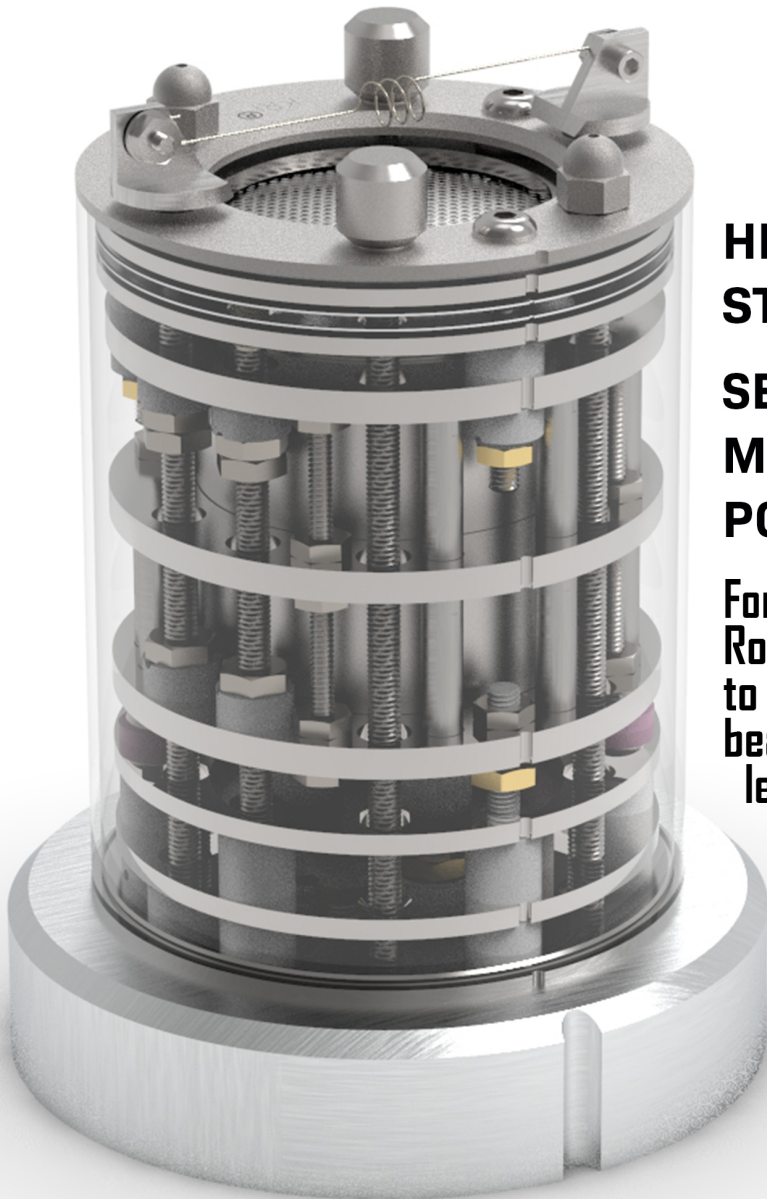
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# **Synthesis of High Entropy Perovskite Electrocatalysis Nanomaterials with Morphology Control**

Claire E. Block, Elliot Brim, Sienna Gonzalez, and Ryan M. Richards

Colorado School of Mines, Golden, Colorado 80401

**Should be considered for poster awards: Yes**

Cost efficient, earth abundant, and high-performance electrocatalysts for water splitting are of great interest. In order to move away from the Pt-group metals (PGMs) that are high-quality catalysts but are costly and rare, research has shifted to manipulating material properties of more Earth abundant elements and materials. In the quest to create catalysts that are as efficient, if not better than, PGMs and inexpensive, the primary tools in the materials scientist's toolbox are precisely controlling nanomaterial composition and morphology. Employing multiple cations with different properties into one material, creating a high entropy system, can improve catalytic performance. The work to be presented focuses on Ba, Sr, Ca, Co, Fe, and Mn cations (promising electrocatalyst candidates) in the perovskite crystal structure. In addition to composition, morphology impacts material properties. In this work, the term morphology focuses on the facets exposed and the resulting nanomaterial shape. Each facet, or plane, of a material has different surface energies and activities. Therefore, controlling the facets that are exposed in the final nanomaterial product will affect catalytic results.

Aerogel and hybrid sol-gel are two routes for high entropy perovskite materials explored in this work. Aerogel synthesis, done in an autoclave, helps promote nanomaterial production. Pseudo supercritical fluid drying allows the solvent to immediately leave the nanomaterials in the chamber and produce a powder. Previous literature using sol-gel methods have successfully created high entropy systems. However, these are not always on the nanoscale. A wet-chemical synthesis of these systems is highly desirable due to having a more facile process, a number of challenges must be overcome to realize these illusive systems. The two synthetic routes for the aforementioned high entropy perovskite systems and work towards fundamental knowledge of controlling nanomorphology (and expanding into high entropy states) will be discussed.



## **Pulsed Electron Paramagnetic Resonance Study of $\text{Na}_x\text{Si}_{136}$ type II Clathrate Films**

**Joseph Briggs**<sup>1</sup>, Yinan Liu<sup>1</sup>, Meenakshi Singh<sup>2</sup>, Reuben T. Collins<sup>2</sup>, Carolyn A. Koh<sup>1</sup>.

<sup>1</sup>Colorado School of Mines Chemical and Biological Engineering Department,  
Golden CO 80401

<sup>2</sup>Colorado School of Mines Physics Department, Golden CO 80401

**Should be considered for poster awards: Yes**

Silicon clathrates are an open cage-like allotrope of silicon that is a metastable alternative to the more common diamond silicon. Si clathrates can have interstitial guest atoms typically alkali or alkaline earth metals that are positioned inside the cages. The intrinsic optical and electrical properties of the Si clathrate lattice and the tunable guest properties have made these compounds very interesting in the field of semiconductors, solar cells, and Li batteries as potential alternative materials. The guest atoms, which are decoupled from the lattice, act as shallow donor atoms but their spin dynamics are currently poorly understood due to challenges in synthesizing these materials with low enough guest concentrations. Recent advances in synthesis of sodium doped type II Si clathrate films  $\text{Na}_x\text{Si}_{136}$  (where  $0 < x < 24$ ) have achieved low Na content well below the metal-insulator transition and these materials act like heavily-doped semiconductors and the spins dynamics can be examined.

To synthesize sodium doped type II Si clathrate films, a two-step procedure adapted from powder synthesis has been developed.[1] First, bulk sodium metal is evaporated from a Ta crucible and diffused into a silicon wafer under an inert argon atmosphere to form NaSi. The wafer is then annealed under vacuum to thermally decompose the film into clathrate. The clathrate films are then characterized through a variety of techniques including x-ray diffraction, Raman spectroscopy, and scanning electron microscopy. The low Na concentrations we have achieved with these materials now allows for the study of the spin dynamics of the remaining Na inside the crystal lattice through continuous wave and pulsed electron paramagnetic resonance (EPR).[2]

This study examines the field swept echo of low sodium  $\text{Na}_x\text{Si}_{136}$  type II Si clathrate and makes a comparison to known continuous wave EPR features. We have also examined the temperature dependence of the relaxation time and phase memory of the sodium electron spin from 6-25 K. Inversion recovery, saturation recovery, and echo decay measurements were performed on sodium doped type-II Si clathrate samples at these temperatures and fit to extract the relaxation time and phase memory and compared to phosphorous in diamond silicon. These are the first reported pulsed-EPR measurements for low sodium type-II Si clathrate films and give indication into potential advantages of these materials as an alternative to phosphorus-doped silicon for defect based applications. This work was supported by National Science Foundation award #2114569.

[1]Y. Liu et al., Appl. Phys. Rev., vol. 8, no. 4, p. 041408, 2021.

[2]W. K. Schenken et al., Phys. Rev. B, vol. 101, no. 24, p. 245204, 2020.

## Reactive Sputtering of TiN for use in Composite Hydrogen Membranes

Cameron Burst,<sup>1</sup> J. Douglas Way,<sup>2</sup> and Colin A. Wolden<sup>2</sup>

Department of Physics<sup>1</sup> and Chemical & Biological Engineering<sup>2</sup>, Colorado School of Mines,  
Golden, CO 80401

**Should be considered for poster awards: YES**

Vanadium (V) is a cost-effective material with excellent hydrogen permeability, but shows minimal permeation due to catalytic limitations. This can be overcome by applying a platinum group metal such as Pd to the surface, but unfortunately Pd rapidly alloys with V at high temperature and loses its activity. Thin metal nitrides have been identified as stable intermetallic diffusion barriers that can be inserted between V and Pd. To this end we have developed a reactive sputtering process for the deposition of titanium nitride (TiN). Films have been characterized by ellipsometry, profilometry, X-ray diffraction, and 4 point probe. A process window including target power, %N<sub>2</sub>, substrate temperature, and substrate bias was explored. Conditions were identified that produced high quality TiN films with low resistivity and the desired 002 crystal orientation, with substrate bias being identified as a key parameter. To assess the hydrogen permeability and the diffusion barrier properties of these films PdCu|TiN|Pd and V|TiN|Pd sandwich structures were fabricated, respectively. Thin layers of TiN (<10 nm) were observed to not significantly reduce hydrogen permeation. These foils were stable at temperatures of 400 °C for over 100 hours. Furthermore, high temperature annealing of V|TiN|Pd showed no evidence of V-Pd interdiffusion. These findings will be used to guide the design of composite Pd|TiN|V|TiN|Pd membranes for high temperature H<sub>2</sub> purification.

# **Molybdenum Electron-Enhanced Atomic Layer Etching (EE-ALE) Using O<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> Reactive Background Gases: Model for MoS<sub>2</sub> EE-ALE**

Michael Collings and Steven George

Department of Chemistry, University of Colorado, Boulder, CO 80309, USA

MoS<sub>2</sub> ALE is required to obtain monolayer thicknesses for future MOSFET device channels. Molybdenum (Mo) ALE was studied as a model system for MoS<sub>2</sub> ALE. In particular, Mo electron-enhanced atomic layer etching (EE-ALE) was employed with electron energies of ~100 eV and reactive background gases (RBGs). EE-ALE is a non-thermal process that can etch films at low temperatures <100°C. EE-ALE is also surface sensitive because of the low electron mean free path at ~100 eV. EE-ALE is enabled by the Hollow-Cathode Plasma Electron Source (HC-PES), which can provide electron currents greater than 100 mA over a 2" x 2" area. The HC-PES was integrated into a warm wall, viscous flow ALD reactor which allowed for *in situ* spectroscopic ellipsometry to monitor the film thickness during etching. The hollow cathode is also resistant to chemical contamination, allowing for RBGs to flow in the chamber during deposition or etching. The electrons can dissociate the RBGs and create reactive species that can readily react with the surface.

Mo can be etched by creating volatile oxychlorides on the Mo surface. In the current experiments, Mo films were oxidized with simultaneous exposures of O<sub>2</sub> and electrons. The oxidized Mo films were then etched by pulsing CH<sub>2</sub>Cl<sub>2</sub> while O<sub>2</sub> flowed continuously to maintain an oxidized surface. *In situ* spectroscopic ellipsometry was used to monitor the Mo EE-ALE. The Mo film was etched linearly at a rate of 7.4 Å per CH<sub>2</sub>Cl<sub>2</sub> exposure. *Ex-situ* AFM, XRD, XRR, and XPS were used to characterize the Mo film after EE-ALE. No change in crystallinity or surface roughness was observed after etching 10 nm of a 20 nm sputtered Mo film. XRR film thickness after etching was used to confirm the validity of the ellipsometry model. These Mo EE-ALE experiments are a prelude to Mo EE-ALE using HCl instead of CH<sub>2</sub>Cl<sub>2</sub> and later to MoS<sub>2</sub> EE-ALE after we obtain MoS<sub>2</sub> samples.

*This work was supported in part by Semiconductor Research Corporation (SRC)*

## **Synthesis of new nitride material, manganese cobalt nitride by RF sputtering.**

Sita Dugu<sup>1</sup>, Rebecca Smaha<sup>1</sup>, Shaun O'Donnell<sup>2</sup>, Karen Heinselman<sup>1</sup>, Andrew Treglia<sup>2</sup>, Stephen Lany<sup>1</sup>, Andriy Zakutayev<sup>1</sup>, Sage Bauers<sup>1</sup>

1. National Renewable Energy Laboratory, Golden, CO, 80401,
2. Colorado State University, Fort Collins, CO,

**Should be considered for poster awards:** No

Transition metal (*TM*) nitrides have potential in industrial applications due to their outstanding properties such as high hardness and strength, excellent thermal conductivity, and unique electrochemical properties. In 2019, Sun et al constructed a stability map of inorganic ternary metal nitrides using high-throughput computational methods based on a data-mined structure prediction algorithm. While this work predicted hundreds of new ternary nitrides, only one new chemical space was predicted to contain a previously unknown compound comprising nitrogen and two *TMs*: MnCoN<sub>2</sub>. In this study, a series of Mn-Co-N thin films were synthesized by RF magnetron sputtering and characterized for structural and magnetic properties.

Combinatorial Mn-Co-N thin films are deposited using reactive cosputtering at different temperatures ranging from 25 – 450°C and various process pressures. The phase of the as-grown material is checked by X-ray diffractometry. Survey density function theory total energy calculations are performed in parallel on six prototype structures based on zincblende or rocksalt lattices. Comparing the calculated structures with experimental diffraction patterns, the synthesized films better match the rocksalt-derived structures, which also exhibit lower formation energy than the zincblende candidates. However, only the primary diffraction peaks are seen, suggesting a large amount of cation antisite disorder. Manganese and cobalt concentrations are checked by X-ray fluorescence and nitrogen concentration is checked by Rutherford backscattering spectrometry, confirming nearly 1:1:2 concentrations of Mn:Co:N with some reduced N due to O impurity. Scanning electron microscopy and energy dispersive x-ray spectroscopy is also performed, which illustrated the presence of all elements at respective energy levels. Magnetic properties for MnCoN<sub>2</sub> films have been studied by SQUID magnetometer which demonstrates that the film possesses a weak antiferromagnetic moment of remnant magnetization 0.01 emu/gm and coercive field of 0.5 T. The study of moment vs temperature shows the transition temperature at ~10K. Our experimental confirmation of this new *TM<sub>1</sub>-TM<sub>2</sub>-N* ternary nitride motivates renewed effort in new materials prediction and discovery in similar ternary spaces, which we are actively pursuing.

## Autonomous Sputter Deposition of Nitride Thin Films

Davi M. Fébba, Kevin R. Talley, Kendal Johnson, Stephen Schaefer, Sage R. Bauers,  
John S. Mangum, Rebecca W. Smaha, and Andriy Zakutayev

Materials Science Center, National Renewable Energy Laboratory (NREL), Golden,  
Colorado 80401, USA

**Should be considered for poster awards:** Yes.

Autonomous experimentation has emerged as an efficient approach to accelerate the pace of materials discovery. Although instruments for autonomous synthesis have become popular in molecule and polymer science, solution processing of hybrid materials and nanoparticles, examples of autonomous tools for physical vapor deposition are scarce yet important for the semiconductor industry.

In this presentation, we will discuss the design and implementation of a closed-loop autonomous workflow for sputter deposition of thin films with controlled composition, leveraging a highly automated sputtering reactor controlled by Python, optical emission spectroscopy (OES), and Bayesian optimization [1]. By fabricating  $Zn_xTi_{1-x}N_y$  thin films with simultaneous monitoring of optical emission lines from the sputtering of elemental targets, we showed that cation composition can be expressed as a linear function of emission lines.

Informed by OES, a control algorithm with Bayesian optimization can optimize the power on each sputtering source, achieving deviations from the targeted cation composition within relative 3.5 %, which demonstrates that the methods described in this work can reliably synthesize thin films with specific composition and minimal human interference.

Moreover, we will discuss the integration of the time-series data automatically generated by this sputtering instrument with the research data infrastructure (RDI) [2]. NRELS's RDI catalogs experimental data from inorganic thin films experiments at NREL and enables the High-Throughput Experimental Materials Database (HTEM-DB) (<https://htem.nrel.gov/>) [3], which stores information about synthesis conditions, chemical composition, crystal structure and optoelectronic properties of materials.

[1] APL Mater 11, 071119, 2023

[2] Patterns, 2, 100373, 2021

[3] Scientific Data 5, 180053, 2018

## **A Novel Application of Friction Assisted Lateral Extrusion Pressed Copper to Produce Highly Antimicrobial Surface Topographies**

Clinton Hawkins, Daniela Hirsch, Terry Lowe  
Colorado School of Mines, Golden, Colorado, 80401

Naveen Kailas, Laszlo Toth, Máté Szűcs  
Laboratory of Microstructure Studies and Mechanics of Materials, Metz, France 57070

**Should be considered for poster awards: Yes**

Since their introduction nearly 30 years ago nanostructured metals have been of great interest for materials engineers across the world. With the promise of unparalleled strength, ductility, and customizability potential applications for these materials is nearly limitless ranging from aerospace parts to medical devices. Almost as varied as the applications themselves are the methods used to produce the materials, methods such as equal channel angular pressing (ECAP) and high-pressure torsion stand out as some of the most commonly employed. Despite their utility these methods, among many others, struggle with producing ultra-fine-grained copper. Traditionally forming nanometer scale copper grains required extended processing times and specialized processing techniques. Recently a group from France has developed a new nanostructuring process capable of refining coarse grained copper bars into flat bar stock with grain sizes ranging from 200 to 300 nanometers. This revolutionary process has been coined FALEP and stands for friction assisted lateral extrusion processing. In this method bulk metals or powders are subjected to enormous shear strains at room temperature resulting in grains 100s of times smaller from their initial sizes.

Another facet in the research of copper is aimed at its antimicrobial properties. Recent work from this group has shown that chemical treatments of copper can create atomically sharp surface features capable of destroying most pathogens on contact. In traditionally produced copper sheet these asperities form at grain boundaries and annealing twins leaving wide gaps where microbes can interact with the surface without being neutralized. In this work the specialized etching technique was applied to FALEP copper resulting in asperities forming in much higher densities. Electron backscatter diffraction (EBSD) was employed to characterize the FALEP copper and explain its enhanced potential as an antimicrobial surface.

This novel combination of material and method results a surface topology inhospitable to any microbes interacting with the surface and paves the way forward to a revolutionary new generation of antimicrobial filters and surfaces.

## **Nanoscale Engineering of Ceramic Supports for High Permeance Membranes**

Kagan Killough, Nolan Kelley, J. Douglas Way, and Colin A. Wolden

Department of Chemical and Biological Engineering, Colorado School of Mines, Golden, CO  
80401

### **Should be considered for poster awards: Yes**

Membrane technology is an energy efficient alternative to techniques such as pressure swing adsorption or cryogenics for gas separation. There is currently great interest in hydrogen ( $H_2$ ) as a zero-carbon fuel to mitigate climate change. However, widespread deployment of  $H_2$  is constrained by the high costs associated with its transportation and storage. An alternative is to transport  $H_2$  in the form of liquid carriers such as methanol or ammonia and reforming back to  $H_2$  at the point of use. These reforming reactions are endothermic and require separation. Our group is developing a catalytic membrane reformer (CMR) for both reaction and  $H_2$  purification in a compact, process-intensified unit operation. The CMR employs a dense, thin palladium (Pd) membrane that is deposited on ceramic supports. The productivity of these CMRs scales with permeance, but as we have reduced the Pd thickness the permeance becomes limited by the resistance of the underlying ceramic support. Current commercial asymmetric supports have a porous bulk coated with a ~25 micron thick mesoporous layer that facilitates plating of the Pd membrane. This work aims to create asymmetric supports with a similar surface structure but a significant reduction in the thickness of the mesoporous layer through atomic layer deposition (ALD). First, the reactant exposure time was shortened to limit the penetration of reactants into the porous support. This technique was applied to symmetric alumina supports and it was found that the permeance as a function of deposition thickness displayed a sigmoidal dependence. The permeance remained largely unchanged as the nominal pore size was reduced to less than 40% of its original size, before dropping exponentially as the deposition thickness approached half the nominal pore size. These ALD-engineered supports will be evaluated both for dense Pd membranes as well as surface diffusion membranes.

# Distinguishing Elements at the Sub-Nanometer Scale on the Surface of a High Entropy Alloy

Lauren Kim<sup>1†</sup>, William R. Scougale<sup>1</sup>, Prince Sharma<sup>2</sup>, Nozomi Shirato<sup>3</sup>, Sarah Wieghold<sup>4</sup>, Rose Volker<sup>4</sup>, Wei Chen<sup>5</sup>, Ganesh Balasubramanian<sup>2</sup>, and TeYu Chien<sup>1§</sup>

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<sup>2</sup>*Department of Mechanical Engineering & Mechanics, Lehigh University, Bethlehem, Pennsylvania 18015, USA*

<sup>3</sup>*Nanoscience and Technology Division, Argonne National Laboratory, Lemont, Illinois 60439, USA*

<sup>4</sup>*Advanced Photon Source, Argonne National Laboratory, Lemont, Illinois 60439, USA*

<sup>5</sup>*Department of Mechanical Engineering, Northwestern University, Evanston, Illinois 60208, USA*

**Should be considered for poster awards: Yes**

High entropy materials, including high entropy alloys (HEAs), high entropy Van der Waals materials (HEX), and high entropy perovskite oxides (HEOs), have drawn the attention of scientists and engineers for their various functionalities and physical properties. While a wide variety of physical properties are being studied in these materials, a microscopic understanding is still missing. Additionally, scanning tunneling microscopy (STM) is a powerful tool for characterizing topographic and electronic information at the atomic scale, but can typically not detect elemental differences. In this work, a synchrotron X-ray scanning tunnelling microscope (SX-STM) was used in combination with X-ray absorption spectroscopy (XAS) to study the elemental distributions on the surface of a HEA at the sub-nm scale. In this work, an element specific atomic surface configuration is simulated and presented, demonstrating that SX-STM is a viable and promising tool to study the surfaces of high entropy materials at the atomic scale.



# Composite Vanadium Metal Foil Pumps for Hydrogen Isotope Recovery in Fusion Systems

Chao Li<sup>1</sup>, J. Douglas Way<sup>1</sup>, Thomas F. Fuerst<sup>2</sup>, and Colin A. Wolden<sup>1</sup>

<sup>1</sup>Department of Chemical & Biological Engineering, Colorado School of Mines, Golden, CO 80401

<sup>2</sup>Fusion Safety Program, Idaho National Laboratory, Idaho Falls, ID 83415

## Should be considered for poster awards: Yes

The hydrogen isotopes deuterium (D) and tritium (T) are the fuel for future fusion reactors, producing helium and high-energy neutrons in dense, magnetically confined plasmas. However, only a small portion of D-T within the plasma is converted to helium. Therefore, extracting unburned D-T from helium ash and recycling it to the reactor is pivotal. One approach for direct internal recycling employs metal foil pumps (MFPs). Unlike conventional pressure-driven hydrogen separation, the MFPs operated through superpermeation, where energetic H atoms/ ions can directly enter the metal, bypassing the dissociation/absorption process. Palladium-based foils are an effective option for such applications, but high cost and limited availability are concerns. Vanadium (V) is a cost-effective and neutron-tolerant material with excellent hydrogen permeability but shows minimal superpermeation at lower temperatures (75-200 °C) due to catalytic limitations. In this study, we fabricated V-based composite membranes by depositing thin layers (~100 nm) Pd or BCC PdCu on sputter-cleaned vanadium foils (100 μm). Symmetric membranes approached superpermeation levels of pure Pd or PdCu foils. Asymmetric membranes highlighted the importance of the catalyst layer for both effective absorption of hydrogen upstream and re-combinative desorption downstream. At  $T \geq 150$  °C, composite membrane matched Pd-based foils, while flux attenuated by 2-3X at lower temperatures, attributed to vanadium hydride ( $\beta$ -V<sub>2</sub>H) formation impacting transient response. Nevertheless, no embrittlement occurred under the studied conditions. Achieving performance similar to Pd-based foils while reducing Pd usage by >99%, V composite MFPs emerge as an appealing choice for low-temperature hydrogen isotope recovery in future fusion plants.

## Thermal Atomic Layer Etching of SnO<sub>2</sub> Using HF and Al(CH<sub>3</sub>)<sub>3</sub>

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### Should be considered for poster awards: Yes

Thermal atomic layer etching (ALE) can be achieved with sequential, self-limiting surface reactions. One mechanism for thermal ALE is based on fluorination and ligand-exchange reactions. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming volatile products. Previous studies have successfully applied this thermal ALE strategy for Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, and ZrO<sub>2</sub> ALE. However, no previous investigations have explored the thermal ALE of SnO<sub>2</sub> films.

This study demonstrated the thermal ALE of SnO<sub>2</sub> thin films using sequential, self-limiting thermal reactions with hydrogen fluoride (HF) and trimethylaluminum (Al(CH<sub>3</sub>)<sub>3</sub>, TMA) as the reactants. The initial SnO<sub>2</sub> films were grown by atomic layer deposition (ALD) using tetrakis(dimethylamino) tin and H<sub>2</sub>O<sub>2</sub>. The thermal SnO<sub>2</sub> ALE process was then studied using various techniques including quartz crystal microbalance (QCM), X-ray reflectivity (XRR), quadrupole mass spectrometry (QMS) and Atomic Force Microscope (AFM).

In situ QCM experiments monitored SnO<sub>2</sub> ALE at temperatures from 225 to 300 °C. The SnO<sub>2</sub> etching was linear versus the number of HF and TMA reaction cycles. The QCM studies also showed that the sequential HF and TMA reactions were self-limiting versus reactant exposures. The SnO<sub>2</sub> etching rates increased at higher temperatures. The QCM analysis measured mass change per cycle (MCPC) values that varied from -32.58 ng/(cm<sup>2</sup> cycle) at 225 °C to -123.5 ng/(cm<sup>2</sup> cycle) at 300 °C. These MCPCs correspond to SnO<sub>2</sub> etch rates from 0.47 Å/cycle at 225 °C to 1.78 Å/cycle at 300 °C.

XRR measurements confirmed the linear removal of SnO<sub>2</sub> and the etching rates. QMS analysis revealed the volatile etching products during the sequential HF and TMA exposures on SnO<sub>2</sub> at 300 °C. These QMS investigations observed Sn(CH<sub>3</sub>)<sub>3</sub><sup>+</sup>, indicating Sn(CH<sub>3</sub>)<sub>4</sub> as the etch product during TMA exposures. Al<sub>x</sub>F<sub>y</sub>(CH<sub>3</sub>)<sub>z</sub> dimer and trimer species were identified as the ligand-exchange products. QMS studies also revealed that Al(CH<sub>3</sub>)<sub>3</sub> exposures on initial SnO<sub>2</sub> substrates released Sn(CH<sub>3</sub>)<sub>4</sub> products, as expected if Al(CH<sub>3</sub>)<sub>3</sub> converts SnO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> during SnO<sub>2</sub> ALE. The results indicate that thermal SnO<sub>2</sub> ALE using sequential HF and TMA exposures occurs by conversion/ligand-exchange and fluorination reactions.

## Arsenic Activation in Single Crystal and Polycrystalline CdTe

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**Poster awards:** Yes

Polycrystalline (pX) cadmium telluride (CdTe) is the leading thin film photovoltaic technology due to its low cost and low environmental impact<sup>1</sup>. However, a major limitation to this technology's performance is effective p-type doping. Currently, Arsenic (As) is used as the p-type dopant to address this issue, though there are difficulties with achieving a high dopant activation ratio, which is the ratio between electrically useful (active) dopants and the total concentration of dopants in the material. Poor As activation in CdTe contributes to lower carrier lifetimes because the un-activated As can act as a deep defect increasing recombination and sap voltage through electrostatic fluctuations<sup>2,3</sup>. This is a key contributor to open circuit voltage ( $V_{OC}$ ) losses with estimates as high as  $\sim 100$  mV. The best performing pX CdTe cells utilize cadmium chloride ( $CdCl_2$ ) anneals, have activation ratios of 2-3% and  $V_{OC} \sim 900$  mV, while in theory  $V_{OC}$  can be greater than 1.1V<sup>4</sup>.  $CdCl_2$  anneals are critical to produce reasonably functional pX CdTe devices, by providing passivation of defects, larger grains through recrystallizations, and removal of defects, however this process introduces high levels of Cl into the material which could be compensating by acting as a n-type dopant. While activation is low in pX CdTe, single crystal (sX) As-doped CdTe can have activation ratios of  $\sim 50\%$  without  $CdCl_2$ <sup>5</sup>, so understanding if Cl is hindering As-activation is of high interest to the CdTe community in its pursuits to increase  $V_{OC}$ .

In this study we compare different dopant activation processes on both sX and pX As-doped CdTe, with the intention to use sX to inform pX processing constraints. By using sX CdTe we can gain insight into the As-activation process in CdTe and isolate where activation losses are occurring between sX and pX material. Specifically, we assess the efficacy of  $CdCl_2$  anneals, rapid thermal anneals at different times and temperatures, and combinations of the two heat treatment types. Carrier concentrations from Hall and CV from these tests reveal an anticorrelation between sX and pX activation, and suggests that the presence of  $CdCl_2$  alone, during heat treatments, does not disrupt carrier activation.

<sup>1</sup>H. M. Wikoff, *et al.*, *Joule*, 2022

<sup>2</sup>E. Colegrove, *et al.*, *SOLMAT*, 2022

<sup>3</sup>J. Moseley, *et al.*, *JAP*, 2020

<sup>4</sup>R. Mallick *et al.*, *IEEE Journal of Photovoltaics*, 2023

<sup>5</sup>S. Farrell *et al.*, *JEM*, 2015

## **Lanthanum Nickel Perovskite-based Catalysts for Ammonia Decomposition**

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### **Should be considered for poster awards: Yes**

The global energy economy is increasingly looking to move away from carbon-based fuels due to their environmental impact. Hydrogen is a leading zero-carbon fuel, with high energy density and benign emissions. However, widespread deployment of hydrogen is constrained by the high costs associated with its transportation and storage. As such, alternative carriers have been studied. Among these, liquid ammonia has high energy density and contains a large amount of hydrogen by volume. However, catalysts are required to decompose ammonia for on-site hydrogen production. Our group is developing a catalytic membrane reformer (CMR) that both decomposes the ammonia and purifies the H<sub>2</sub> in a compact, process-intensified unit operation. Our current CMR configuration employs a commercial Ru/Al<sub>2</sub>O<sub>3</sub> catalyst, which has high activity but is an expensive transition metal. Nickel is a low cost alternative, but is only effective at very high temperature (>700°C). Metal oxide supports have been shown to increase catalytic activity of metallic nickel. Herein we describe the synthesis, characterization and activity of a promising LaNiO<sub>3</sub> perovskite based catalyst. Physical properties were studied using TGA, XRD, and TEM. The precursor is formed through a self-combustion process, and then calcined to produce the perovskite phase. Reduction under H<sub>2</sub> produces the final catalyst which is comprised of Ni nanocrystals dispersed on La<sub>2</sub>O<sub>3</sub>. TEM imaging shows that the average Ni particle size was ~10 nm. Catalyst testing is underway in a differential packed bed reactor, with preliminary results displaying significant activity for ammonia decomposition as low as 400°C. Work is underway to fully quantify this performance and baseline it relative to the Ru standard.

## Structure and Chemistry of ZnGeN<sub>2</sub> Quantum Wells for Green LEDs

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**Should be considered for poster awards:** Yes

Newly theorized hybrid II-IV-N<sub>2</sub>/III-N heterostructures, based on current commercialized (In,Ga)N light-emitting diodes (LEDs), are predicted to significantly advance the design space of highly efficient optoelectronics in the visible spectrum, specifically in the green to amber regions where LED efficiencies are orders of magnitude lower than other colors. Yet, there are few epitaxial studies of II-IV-N<sub>2</sub> materials. ZnGeN<sub>2</sub>, a ternary analogue of the wide bandgap material GaN, is explored as a potential green-to-amber emitter which can be integrated into existing GaN LED heterostructures due to structural similarity. Cation-ordered ZnGeN<sub>2</sub> has a theoretical band gap of 3.4 eV, which is expected to be reduced with cation disorder. ZnGeN<sub>2</sub> is wurtzite when disordered, and is structurally and electronically similar to GaN, possessing a lattice mismatch of ~0.8%. Past work by this group has demonstrated epitaxial growth of ZnGeN<sub>2</sub> on GaN and AlN via molecular beam epitaxy (MBE) [1,2]. Here we present the first growth of well-defined quantum wells (QW) of ZnGeN<sub>2</sub> within GaN by nitrogen plasma-assisted MBE, including successful five-layer multiple quantum well (MQW) structures.

Detailed structural and elemental analysis of the heterostructures was performed, including X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), energy dispersive X-ray spectroscopy (STEM-EDS), and atom probe tomography (APT). These methods demonstrate high-quality and abrupt interfaces in the heterostructures, even after multiple repeating heterointerfaces. Through changes in growth methodology, we also demonstrate methods to improve unintentional incorporations, including associated improvements in structural quality. We then include the first full LED stack grown by MBE with a ZnGeN<sub>2</sub>/GaN active region. Together, this data demonstrates both the promise of heteroepitaxially integrated hybrid ternary/binary nitride systems along with the challenges associated with growing such systems, including an outlook on methods to improve the materials and devices.

### References

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## **Investigating The Impact of Permanent Dipole Moment of Dopant Emitter Molecules on The Aggregation Process in Thermally Vapor-Deposited Phosphorescent OLEDs.**

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**Should be considered for poster awards: Yes.**

Phosphorescent OLEDs (Organic Light-Emitting Diodes) are a promising technology for display and lighting applications. The emissive layer of these devices is composed of a phosphorescent emitting dopant dispersed within a host matrix. However, a known issue with these devices is the aggregation of the emitting dopants [1], which leads to a phenomenon known as concentration quenching that reduces the internal quantum efficiency (IQE) of these devices [2].

In this study, we investigate the impact of the permanent dipole moment magnitude of the dopant molecules on the aggregation process in OLEDs fabricated through thermal vapor deposition. We conduct experimental morphology measurements using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging techniques. Typical phosphorescent guest molecules, such as Ir(ppy)<sub>3</sub> and Ir(ppy)<sub>2</sub>(acac), are examined in various host materials. Additionally, simulated model morphologies for thermally vapor-deposited thin films are generated using Ising-kinetic Monte-Carlo models [3]. To analyze spatial distribution and clustering of guest molecules within the host matrix, we employ spatial statistical analyses such as Ripley's K-function, G-function, and pair-correlation function [4-5].

Our findings provide direct evidence of vertical stacking of guest molecules during growth and offer insights into how the magnitude of the permanent dipole moment of the guest molecules affects surface diffusion, resulting in different degree of guest aggregation in various systems. This research contributes to a better understanding of the aggregation process in thermally vapor-deposited OLED systems.

## Thermal Atomic Layer Etching of Gold Using Sulfuryl Chloride for Chlorination and Triethylphosphine for Ligand Addition

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**Should be considered for poster awards: Yes**

Gold (Au) is one of the most revered metals with many uses including as a conductor in electronics. Nanostructured gold is also important in plasmonics and photonics. Au ALE could be used in the fabrication of gold nanostructures. In this study, Au thermal ALE was demonstrated using sequential chlorination and ligand-addition reactions. Sulfuryl chloride ( $\text{SO}_2\text{Cl}_2$ ) was used for chlorination and triethylphosphine ( $\text{P}(\text{Et})_3$ ) was used for ligand addition. Sulfuryl chloride is believed to chlorinate the gold surface and form AuCl. Triethylphosphine ligand addition then adds to AuCl and produces volatile AuClP(Et)<sub>3</sub> etch products.

This demonstration of Au ALE employed a custom quadrupole mass spectrometer (QMS) reactor to identify the etch products. High sensitivity detection is achieved when the etch products exit an aperture and form a molecular beam with line-of-sight to the ionizer. Gold nanopowders were used to maximize the surface area for the ALE reactions. Additional measurements of etch rates during Au ALE were performed using quartz crystal microbalance (QCM) studies.

The QMS experiments were performed at 150 °C at partial pressures of 2 Torr for sulfuryl chloride and triethylphosphine. During  $\text{SO}_2\text{Cl}_2$  exposures, the time-resolved QMS ion intensities for  $\text{SO}_2^+$  relative to the parent  $\text{SO}_2\text{Cl}_2^+$  were consistent with the self-limiting chlorination of the gold surface. During  $\text{P}(\text{Et})_3$  exposures, AuCl( $\text{P}(\text{Et})_3$ )<sup>+</sup> ion intensity at m/z 350 was observed as the major etch product. Corresponding experiments at 150 °C on Au-coated QCM crystals observed a mass gain for  $\text{SO}_2\text{Cl}_2$  exposures during chlorination and a mass loss for  $\text{P}(\text{Et})_3$  exposures during ligand addition. The mass changes were consistent with an etch rate for Au ALE of 0.63 Å/cycle at 150 °C.

Sequential  $\text{SO}_2\text{Cl}_2$  and  $\text{P}(\text{Et})_3$  exposures were also observed to etch Cu and Ni nanopowders. The etch product during Cu ALE was observed at m/z 432 and assigned to  $\text{Cu}_2\text{Cl}_2(\text{P}(\text{Et})_3)_2^+$ . The etch product during Ni ALE was observed at m/z 366 and assigned to  $\text{NiCl}_2(\text{P}(\text{Et})_3)_2^+$ . Additional QCM experiments on Cu-coated QCM crystals confirmed Cu ALE at 100 °C. This mechanism of chlorination and ligand addition should be useful for the ALE of many metals that form stable metal chlorides.

## **Investigation of Co Nanoparticles Supported over Ceria from Thin Films to Powder Nanocatalysts**

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**Should be considered for poster awards:** Yes

In our study, we investigated the growth of ceria-supported Co catalysts and the application in dry reforming of methane (DRM,  $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ ). DRM consumes two abundant greenhouse gases to produce the industrially important syngas, which can be further converted into value-added chemicals and fuels. Cobalt is an economical metal choice that shows a promising activity in DRM. Ceria ( $\text{CeO}_2$ ) was chosen as the catalytic support for Co due to its unique redox properties and oxygen storage that can influence the size, structure, chemical state, and thus the catalytic performance and stability of Co in DRM. We previously investigated the growth of Co over well-ordered  $\text{CeO}_2(111)$  thin films under ultrahigh vacuum conditions. Our data show that deposition of low Co coverages ( $<0.2$  ML) on  $\text{CeO}_2(111)$  at 300 K produces small particles that are one-two atomic layer high. These Co particles remain on the  $\text{CeO}_2(111)$  surface even after heating to 1000 K. The particles predominantly contain  $\text{Co}^{2+}$  species as demonstrated by XPS studies. Oxidation of Co to  $\text{Co}^{2+}$  occurs at the cost of  $\text{Ce}^{4+}$  reduction in  $\text{CeO}_2$  at 300 K, suggesting a strong metal-support interaction. Further increase in the Co coverage can primarily increase the ratio of the metallic Co/ $\text{Co}^{2+}$ . To study as practical catalysts, 5 and 10 wt.% Co dispersed over powder  $\text{CeO}_2$  supports were prepared using sol-gel and impregnation methods and  $\text{Co}_3\text{O}_4$  was identified as the major species. DRM reaction was studied over these powder catalysts using a fixed-bed flow reactor coupled with an on-line GC instrument. Our results demonstrated that the use of lower metal loading of 5 wt.% Co over  $\text{CeO}_2$  showed better DRM activity and coke resistance with more than 90%  $\text{CH}_4$  and  $\text{CO}_2$  conversions at 800 °C. When Co/ $\text{CeO}_2$  was dispersed on a commercial alumina support, the catalyst showed similar activity compared to Co/ $\text{CeO}_2$  despite having lower metal active sites with a very low extent of carbon deposition. Further study was done with doping ceria with Ti elements forming  $\text{Ce}_{1-x}\text{Ti}_x\text{O}_{2-\delta}$  ( $x=0.1-0.5$ ) as our previous study has shown that Ti-doped ceria can better anchor metal particles with a smaller particle size. Our results show that Ti dopants in  $\text{Ce}_{1-x}\text{Ti}_x\text{O}_{2-\delta}$  play an important role in the formation of  $\text{Co}_3\text{O}_4$  and  $\text{CoTiO}_3$  species as well as their activity in DRM. This research was sponsored by the National Science Foundation (Award Numbers: 2154622 and 2204074) as well as the School of Energy Resources at University of Wyoming.



## **In Situ Spectroscopic Ellipsometry Characterization of Condensed Water Layer on SiO<sub>2</sub> in a Vacuum Environment for Use in Spontaneous Etching**

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### **Should be considered for poster awards: Yes**

A novel area of interest in spontaneous etching is the use of a H<sub>2</sub>O layer upon a substrate in vacuum to act as a condensed solvent medium. The idea is that the etchant gas molecules will enter the water layer and etch the substrate as they would in a wet solution etch. Bringing the wet solution etch into vacuum would be economical and environmentally advantageous because many etchants are both expensive and toxic.

The water layer is formed by dosing various pressures of H<sub>2</sub>O vapor into a stainless-steel reactor containing a SiO<sub>2</sub> sample. The thickness of the water layer that can be formed upon the SiO<sub>2</sub> was studied with in situ ellipsometry. The ellipsometer was used to monitor the thickness as H<sub>2</sub>O was dosed into the chamber. The H<sub>2</sub>O layer thickness varied from 0.1-3.5 Å for relative humidities of 6-93% (1.5-23.5 Torr) at a SiO<sub>2</sub> substrate temperature of 26°C. The H<sub>2</sub>O thickness versus relative humidities were similar to predictions from the BET adsorption isotherm model.

Additionally, a “strongly adsorbed water layer” on SiO<sub>2</sub> that can only be desorbed via heating to 135°C was discovered by adsorbing and desorbing the water layer. This “strongly adsorbed layer” increases in thickness as the relative humidity increases and reaches ~1-1.5 Å at 90-100% relative humidity. In contrast, there was also a “weakly adsorbed water layer” that could easily be adsorbed and desorbed by adding or removing H<sub>2</sub>O pressure at 26°C. Understanding the water layer versus H<sub>2</sub>O pressure and temperature sets the stage to begin studies of etching in a liquid layer in a vacuum environment.

## **Hierarchical transparent back contacts for bifacial CdTe PV**

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**Should be considered for poster awards: Yes**

A hierarchical transparent back contact leveraging an AlGaO<sub>x</sub> passivating layer, high work function Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXenes, and a transparent cracked film lithography (CFL) templated nanogrid is demonstrated on copper-free CdTe devices. AlGaO<sub>x</sub> improves device V<sub>OC</sub> but leads to reduced fill factor when CFL is used. The inclusion of a Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> interlayer improves fill factor, removes detrimental Schottky barriers, and enables metallization with CFL by providing transverse conduction into the nanogrid. The bifacial performance of an AlGaO<sub>x</sub> / Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> / CFL Au contact is evaluated, reaching 19.5% frontside efficiency and 2.8% backside efficiency under 1-sun illumination for a Cu-free, group-V doped CdTe device.

**Comprehensive studies on proton dynamics in  $\text{BaCo}_x\text{Fe}_{0.8-x}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-d}$   
(BCFZY,  $0.1 \leq x \leq 0.7$ )**

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Katharine Page<sup>2,3</sup>, Yan-Yan Hu<sup>4</sup>, Ryan O'Hayre<sup>1</sup>

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**Should be considered for poster awards: No**

Triple-conducting oxides (TCOs) conduct three charge carriers ( $\text{H}^+/\text{O}^{2-}/\text{e}^-$ ), enhancing performance/functionality for numerous electrochemical energy conversion technologies. TCOs may also yield new types of devices (e.g., electrochemical diodes/sensors and “uphill diffusion” membranes). Yet, TCO design is still uncertain due to the complex interplay of dopants; thus, a scientific understanding of how doping affects local structures, defect concentrations, reaction kinetics, and transport behavior is essential.

To establish such understanding, we examine the effect of transition metal (TM) doping in  $\text{BaCo}_x\text{Fe}_{0.8-x}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-d}$  (BCFZY,  $0.1 \leq x \leq 0.7$ ), an archetypical TCO system. Co/Fe doping ensures sufficient electronic conductivity and promotes electrocatalytic activity; but holes are generated at the expense of protons, influencing bulk and surface kinetics. While probing these tradeoffs, tracer exchange experiments reveal that high Fe-content increases proton kinetics but decreases oxygen vacancy kinetics<sup>1</sup>.

Solid-state nuclear magnetic resonance is utilized to compare the H/D spectra and  $T_1$  relaxation times between  $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-d}$  and  $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-d}$  (an archetypical “pure” proton conductor). The methods permit the detection of differences in the extent of electron density localization and local structural environments with Co/Fe doping.

Finally, neutron diffraction and pair distribution function (PDF) studies explicate the long-range and local structure of BCFZY, providing quantification of oxygen and barium defects. Across the solid solution, a high degree of local atomic distortion related to complex oxidation states is observed. These combined experimental approaches allow us to overcome the challenge of probing proton dynamics in complex oxide environments, leading to insightful TCO studies.

**References**

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