

**U.S. Department of ENERGY (DOE), Office of Science, Basic Energy Science,
Synthesis & Processing Science (SPS) Program
In Materials Sciences and Engineering (MSE) Division**

2025 Synthesis and Processing Science Principal Investigators' Meeting

Organizers: Craig Henderson, craig.henderson@science.doe.gov
and Tim Kidd, timothy.kidd@science.doe.gov

Special Thanks to: James Dorman, former DOE Program Manager for Synthesis &
Processing Science (SPS) Program

Location: Hilton Washington DC/Rockville Hotel & Executive Meeting Center
Date: July 22-24

Agenda and Preliminary Abstract Book

Tuesday, July 22, 2025

8:00 – 8:55 am	Registration & ***Breakfast***
8:55 – 9:00 am	Welcome to Day 1: Craig Henderson
9:00 – 9:30 am	Division & Program Updates Andrew Schwartz, Director, DOE MSE Division Craig Henderson, Lead, Materials Discovery, Design, and Synthesis

Session 1	Honoring Alexandra Navrotsky Chair: Craig Henderson
PLENARY 9:30 – 10:30 am	Alex Navrotsky (Arizona State Univ.) “Order - Disorder and Thermodynamic Control of Synthesis in Complex Solids”
10:30 – 11:15 am	Maik Lang (Univ. Tennessee) “Understanding High Energy Mechanical Action through Synthesis of metastable Material Phases”
11:15 – 12:00 pm	Jeff Rimer (Univ. Houston) “Elucidating Pathways of Zeolite Crystallization Through Combined Experiments and Simulations”
12:00 – 1:30 pm	*** Break for Lunch ***

Session 2	Chair: To Be Confirmed
1:30 – 2:15 pm	Julia Chan (Baylor Univ.), “In Situ Probing and Investigation of the Crystal Growth of Highly Correlated Intermetallics”
2:15 – 3:00 pm	Mark Hersam (Northwestern Univ.) “Tailoring Quantum Phenomena in Atomically Thin Boron Materials via Confined Growth” (virtual)
3:00 – 3:30 pm	*** Break ***
3:30 – 4:15 pm	Jim Edgar (Kansas State Univ.) “Synthesis and Crystal Growth of Boron-Carbon-Nitrogen Metastable Materials”
4:15 – 5:00 pm	Zhiqiang Mao (Penn State Univ.) “Precise control of crystal stoichiometry of chalcopyrite compounds using a double-crucible Bridgman crystal growth technique”

5:00 – 6:30	Poster Session A Craig Henderson
End of Day 1	*** Dinner on your own ***

Wednesday, July 23, 2025

8:00 – 9:00 am	*** Breakfast ***
Session 3	Chair: Peter Sushko (PNNL)
9:00 – 9:40 am	Matthew Steiner (Univ. Cincinnati) “Bulk Synthesis of Rare-Earth-Free Tetrataenite Permanent Magnets”
9:40 – 10:20 am	Adam Printz (Univ. Arizona) “ECRP: Understanding Nucleation and Film Growth Processes of Solution-Processable Renewable Energy Materials Printed from Confined Volumes”
10:20 – 10:35	*** Break ***
10:35 – 11:15 pm	Daniel Schwalbe-Koda (UCLA) “ Atomistic Information Theory of Materials Synthesis and Free Energy Landscapes”
11:15 – 11:55	Sridhar Seetharaman (Arizona State Univ.) “Fundamental studies of hydrogen arc plasmas for high-efficiency and carbon-free steelmaking”
11:55 – 1:15 pm	*** Break for Lunch ***

Session 4	Chair: Jacek Jasinski (Louisville Univ.)
1:15 – 1:55 pm	Xiaodan Gu , (S. Mississippi Univ.) “DREAM: Data-driven Reinvigorated Advanced Membrane Discovery Platform”
1:55 – 2:35 pm	Anubhav Jain , (LBNL) “Data-Driven Synthesis Science (D2S2)” (virtual)
2:35 – 3:05 pm	Kai Xiao , (ORNL) “Autonomous synthesis with pulsed laser deposition: integrating in situ diagnostics and machine learning”
3:05 – 3:20 pm	*** Break ***
Session 5	Chair: Yingge Du (PNNL)
PLENARY 3:20 – 4:00 pm	Paul Chu (University of Houston) “The never-ending Frontier of Advancing the Tc to New Heights”
4:00 – 4:30 pm	Rongying Jin (Univ. S. Carolina) “Directed Assembly of Metastable States for Harnessing Quantum Effects”
4:30 – 4:45 pm	Sanchari Chowdhury (New Mexico Tech) “Light Mediated Synthesis of Single Atom and Single Atom Alloy Catalysts”
4:45 – 5:00 pm	Yunxiang Gao (Prairie View A&M) “Solution-based Synthesis of Structurally Well-defined Carbon Nanobuds and Their Energy Applications”

5:00 – 6:30	Poster Session B Craig Henderson
End of Day 2	*** Dinner on your own ***

Thursday, July 24, 2025

8:00 – 8:50 am	*** Breakfast ***
Session 6	Chair: To Be Confirmed
PLENARY 8:50 – 9:30 am	Chad Mirkin (Northwestern University) “Exploring the Matterverse Through Nanomaterial MegaLibraries and AI”
9:30 – 9:50 am	Atieh Moridi (Cornell University) “Unraveling Grain Refinement Mechanisms in Multi-Principal Element Alloys”
9:50 – 10:20 am	Michelle Personick (Univ. Virginia) “An Integrated Electrochemical Approach to the Precision Synthesis of Sustainable Catalyst Materials”
10:20 – 10:50 am	Jason Kawasaki (Univ. Wisconsin) “Direct synthesis of curved and twisted Heusler heterostructures on graphene”
10:50 – 11:00 am	Break
11:00 – 11:30 am	Guangwen Zhou (SUNY Binghamton) “In Situ Visualization and Theoretical Modeling of Early Stages of Oxidation of Metals and Alloys”
11:30 – 11:45 am	Yijia Gu (Missouri S&T) “Harnessing Recycled Aluminum for Enhanced Alloy Performance: Primary Intermetallic Phase Control through Rapid Solidification”
11:45 – 12:00 noon	Robert Makin (Univ. W. Michigan) “Investigation and Prediction of Structural Ordering in Monocrystalline Nitrides Through Classical and Generative Machine Learning and Tunable Energetics”
12:00 pm	*** Closing Remarks *** Craig Henderson

Tues July 22, 2025 5:00 – 6:30 PM	Poster Session A Craig Henderson
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Poster A1	Mirkin, Chad	Northwestern University	Data-driven discovery of multicomponent metal halide perovskites using megalibraries
Poster A2	Wang, Haiyan	Purdue University	Achieving Long Range Ordering in Oxide-Metal Hybrid Materials - A Combined Experimental and Modeling Approach
Poster A3	De Yoreo, Jim	Pacific Northwest National Laboratory	Anisotropic Surface Potentials Induced by Ion Adsorption Enable Synthesis of Complex Nanostructures
Poster A4	Yakobson, Boris	Rice University	Unraveling the synthesis-algorithms for novel 2D materials
Poster A5	Eom, Chang-Beom	University of Wisconsin-Madison	Novel Synthesis of Quantum Epitaxial Heterostructures by Design
Poster A6	Martinson, Alex	Argonne National Laboratory	Selective Interface Synthesis: Directing Atomic Structure at Defective Interfaces
Poster A7	Engstrom, James	Cornell University	Extending the Reach and Breadth of Nanofabrication to Atomic-Scale Precision in Three Dimensions using Self-Limiting Deposition Processes
Poster A8	Fedorov, Andrei	Georgia Tech	Focused Electron Beam Induced Deposition (FEBID) in Far-from Equilibrium Dispersed Liquid Precursors
Poster A9	Song, Xueyan	West Virginia University	Atomic Layer Deposition and Post-synthetic Self-Assembly Of Thermally Stable Non-Epitaxial Thin Film Oxide Surface Nanoionics
Poster A10	Liu, Bin	Kansas State University	Data-driven Approach for Controlled Icosahedral Boron-Rich Compound Growth
Poster A11	Clarke, Amy	Colorado School of Mines	In-situ Visualization and Modeling of Microstructure Evolution in Metallic Alloys under Additive Manufacturing Conditions
Poster A12	Liu, Chong	University of Chicago	Electric field driven precision material synthesis
Poster A13	Jasinski, Jacek	University of Louisville	Electrochemical Sculpting of Highly Anisotropic Layered Materials to Produce Nanoribbons for Energy Applications

Poster A14	Sushko, Peter	Pacific Northwest National Laboratory	CM: Design of structural inhomogeneities to control functional properties
Poster A15	Estroff, Lara	Cornell University	SPIRAL: Synthesis and Processing Informed by Rational Algorithmic Learning
Poster A16	Olevsky, Eugene	San Diego State University	Electro-Nano-Pulsing (ENP) Processing of Advanced Materials
Poster A17	Sun, Wenhao	University of Michigan	Temperature-Time-Transformation (TTT) Diagrams for Predictive Solid-State Ceramic Synthesis
Poster A18	Johnson, David	University of Oregon	A Mechanistic Approach to Solid State Synthesis by Controlling Interfacial Reactions in Designed Precursors
Poster A19	Moridi, Atieh	Cornell University	Unraveling Grain Refinement Mechanisms in Multi-Principal Element Alloys
Poster A20	Schadler, Linda	University of Vermont	Acoustic-Field Driven Nanoparticle Organization in Semi-Crystalline Polymer Matrix
Poster A21	Kumar, Sanat	Columbia University	Directional Crystallization (Zone Annealing) of Polymer Blends
Poster A22	Robinson, Richard	Cornell University	Chiral Control of Nanocluster-Fiber Architectures via Confined Evaporative Assembly
Abstract Only	Wang, Qiang	Colorado State University	Automated Workflow for Coarse-Grained MD Simulations of Block Copolymer Self-Assembly
Abstract Only	Taylor, André	New York University	Metallic Glass Nanoparticles Synthesized via Flash Joule Heating
Abstract Only	Ramsurn, Hema	University of Tulsa	Understanding the Mechanisms of Robust Coatings for Extreme Temperature Composites

Wed July 23, 2025 5:20 – 6:30 PM	Poster Session B Craig Henderson
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Poster B1	Naskar, Amit	Oak Ridge National Laboratory	CEM: Targeted, Scalable Synthesis of Multidimensional Macromolecules to Transform Additive Manufacturing
Poster B2	Bertoni, Mariana	Arizona State University	Acoustic Modification of Crystallization and Dislocation Dynamics in Energy Materials to Reduce Carbon-Intensity
Poster B3	Sushko, Maria	Pacific Northwest National Laboratory	Molecularly Organized Nanostructural Materials
Poster B4	Bent, Stacey	Leland Stanford Junior University	Understanding and Controlling Nucleation in Atomic Layer Deposition for Materials Synthesis
Poster B5	Fichthorn, Kristen	Pennsylvania State University	Science of Shape-Selective Nanocrystal Synthesis
Poster B6	Luo, Jian	University of California-San Diego	A Mechanistic Study of Ultrafast Sintering: Capillary versus Enthalpy and Entropy Driven Processes from Simple to Compositionally Complex Silicides
Poster B7	Du, Yingge	Pacific Northwest National Laboratory	Electronic, Magnetic and Optical Properties of Doped Metal Oxide Epitaxial Films and Interfaces
Poster B8	Jin, Wencan	Auburn University	In Situ Studies of Charge Transfer Phenomena in Complex Oxide Heterostructures
Poster B9	Palmstrom, Chris	University of California-Santa Barbara	Synthesis of Thin Films using Cryogenic MBE Processes
Poster B10	Cheng, Zhe	Colorado State University	Fundamental Mechanism for Flash Sintering of Highly Conductive High Temperature Ceramics
Poster B11	Hartman, Ryan	New York University	Catalyzed CO ₂ Hydrate Crystallization and Dissociation in Nanoconfinement
Poster B12	Cao, Gang	University of Colorado	Field-Tailoring Science and Technology for Novel Materials Synthesis
Poster B13	Jain, Himanshu	Lehigh University	Early Stages of Single Crystal Formation in Glass under External Constraints
Poster B14	Tringides, Michael	Ames National Laboratory	Surface Structures Far-From-Equilibrium

Poster B15	Auerbach, Scott	University of Massachusetts Amherst	Integrated Synthesis and Simulation Study on Engineering Defects and Crystallization Kinetics: A 3rd Route to Zeolite Formation
Poster B16	Arnold, Michael	University of Wisconsin-Madison	Directing C On-Surface
Poster B17	Goldman, Rachel	University of Michigan	A Unified Model for Epitaxy of Metastable Crystal Polytypes at the Nanoscale
Poster B18	Shoemaker, Daniel	University of Illinois - Champaign	Active Control of Crystal Growth from Fluxes and Vapors
Poster B19	Legg, Ben	Pacific Northwest National Laboratory	From Ion Ordering to Microphase Separation: How Charge Frustration Organizes Ions at Surfaces
Poster B20	Marschilok, Amy	Brookhaven National Laboratory	Design of Cementitious Chemistries for Enhanced Geothermal Systems
Poster B21	Lu, Yiping	University of Central Florida	Polymorph-Dependent Synthesizability Prediction of High-Entropy Materials
Poster B22	Koh, Carolyn	Colorado School of Mines	Catalyzed CO ₂ Hydrate Crystallization and Dissociation in Nanoconfinement
Abstract Only	Sooby, Elizabeth	University of Texas – San Antonio	Integration of in situ Monitoring and Artificial Intelligence in the Synthesis of Uranium Alloys and Compounds to inform Performance Following Melt Fabrication Processes

PRELIMINARY ABSTRACT BOOK

Thermochemical Insights into Ternary Transition Metal Bismuth Oxides

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Keywords: thermochemical, ternary, metal, bismuth, oxides

Research Scope

Ternary transition metal oxides exhibit a range of fascinating properties, making them significant for diverse technological applications, including energy storage, photocatalysis, and optoelectronics. They have high thermal stability and moderate band gaps, contributing to their functional versatility. Despite extensive studies on their synthesis and functional properties, limited thermodynamic data exist to understand their stability and formation energetics. We synthesized and characterized a number of these phases, including halide and oxide perovskites via solid state reactions and evaluated their thermodynamic stability through high-temperature oxide melt solution calorimetry. Their enthalpies of formation from binary oxides were interpreted in terms of differences in acid-base properties of the oxide components, larger differences leading to greater stability.

Recent Progress

Rutile-structured oxides are potentially useful ultrawide bandgap semiconductors but often suffer from inhibited p-type conductivity. Doping with appropriate group-III compounds may resolve this limitation. In particular, stishovite, a high pressure polymorph of SiO₂ with the rutile structure has been proposed as an ideal case, having the lowest acceptor ionization energies when doped with Ga, In, or Al, and a bandgap near 8.5 eV. Stishovite is routinely produced in the multianvil press. (1)

We are working in collaboration with John McCloy's group at WSU to synthesize and test doped stishovite at high pressure and temperature in the multianvil press, and to produce single crystals large enough for quality resistivity measurements. Once single crystals of doped stishovite have been produced, the experiment will be scaled in the larger presses in FORCE to allow synthesis of much larger single crystals (~3-5 mm). 0.05 % Ga was added to crystalline SiO₂ (quartz). Preliminary XRD confirms the stishovite structure in the resulting powder and a portion of the sample is currently with WSU for resistivity measurements. Next steps include Ga concentration measurements on the remaining portion and further doping and single crystal synthesis.

We completed the thermodynamic characterization of MnTi DRX cathode phases, published paper in JACS. We completed thermodynamic characterization of MnZr DRX cathode phases, paper submission imminent. We developed a thermodynamic mixing model for NMC cathodes to predict enthalpies for entire ternary of compositions. We completed synthesis and thermodynamic characterization of sodium stabilized Li-ion cathodes ($\text{Li}_{1-x}\text{Na}_x\text{CoO}_2$). Structural characterization is ongoing. Additionally, we synthesized and characterized sodium-stabilized Li-ion cathodes ($\text{Li}_{1-x}\text{Na}_x\text{CoO}_2$), with structural analysis ongoing. Papers are in preparation on this work. During the next year these projects should be completed and published.

We are exploring and expanding the use of Ga and other potential alloy -based solvents by the use and optimization of a custom-made experimental design built into a commercial MHTC-96 (Setaram) calorimeter. Through this design the experimental enthalpy of formation and mixing in different metallic systems can now be determined. The new method designed into the MHTC-96 calorimeter shows consistency in values for the NiSb system with comparable energetics to those measured in the AlexSYS (Setaram) system with more conventional methods. The energetics for NiSb and its constituents are determined through their dissolution in Ga instead of by oxidative drop solution calorimetry in molten sodium molybdate. This methodology adds flexibility and improves accuracy. A key advantage of this novel technique is the dramatic reduction in dissolution times for alloys like NiSb. This methodology not only decreases the required time to obtain quality thermodynamic data but also lowers the absolute uncertainty by mitigating the effects of baseline fluctuations via shorter experiments. Additionally, a reducing gas atmosphere simplifies the thermochemical cycles used by eliminating oxidation, further improving accuracy.

We investigated thermodynamic stabilization by high-temperature drop solution calorimetry in hydrous M-BTC MOFs by varying the rare earth metal atoms. The choice of the metal atom and the presence of guest water molecules can enthalpically stabilize the structure by as much as 4000 kJ mol⁻¹. The framework employing La shows the greatest stability. Among isostructural MOFs (Eu-BTC and Y-BTC), the high thermodynamic stability of Eu-BTC implies more favorable interactions between water and the Eu-BTC framework.

We synthesized a series of flexible MIL-88B MOFs, i.e., Fe-BDC, Cr-BDC, and V-BDC, to study the systematic effect of metal node change on thermodynamic stabilization. Calorimetry is being completed and analyzed.

Future Plans

Michael Bustamante will complete his PhD to include work on metallic and nonmetallic systems by late July 2025. Ongoing work on perovskites and rare earth compounds will be completed and prepared for publication. New techniques for the thermochemistry of complex oxide solid solutions are being developed.

References

1. T. Li, T. Geraci, K.P. Koirala, A. Zohar, E. Bassey, P. Chater, C. Wang, A. Navrotsky, R. Clement, *Structural Evolution in Disordered Rock Salt Cathodes*, J. Am. Chem. Soc., **146**, 24296-24309, 2024.
2. N. Novendra, G.P. Nagabhushana, A. Navrotsky, *Thermodynamics of Hybrid Manganese Formate Perovskites*, RSC Advances, **14**, 29301-29307, 2024.
3. M. Bustamante, K. Lilova, A. Navrotsky, J.-P. Harvey, K. Oishi, *Enthalpies of Mixing for Alloys Liquid Below Room Temperature Determined by Oxidative Solution Calorimetry*, J. Thermal Analysis Calorimetry, **149**, 4817-4826, 2024.
4. M. Scharrer, L. Bonatti, T. Geraci, S. V. Ushakov, J. Majzlan, M. Bustamante, H. Kojitani, X. Guo, H. Xu, L. Zhang, K. Lilova, S. Hayun, T. Subramani, A. Navrotsky, *The Joys and Jitters of High Temperature Calorimetry*, J. Am. Ceram. Soc., DOI: 10.1111/jace.20381, 2025.

Publications

1. Author, C. D. Author, and E. F. Co-Author, *Title of the Publication*, Journal **Volume**, page (year).

1. M. Bustamante, K. Lilova, A. Navrotsky, J.-P. Harvey, K. Oishi, *Enthalpies of Mixing for Alloys Liquid Below Room Temperature Determined by Oxidative Solution Calorimetry*, J. Thermal Analysis Calorimetry, **149**, 4817-4826, 2024.
2. W. Gong, D. Zhang, L. Xiao, J. Zhao, T. Wang, K. Li, Z. Zhao, M. Scharrer, A. Navrotsky, *Formation Kinetics and Thermodynamic Stability of the Aurivillius Compounds in Bi₄Ti₃O₁₂-BiFeO₃ System*, J. Amer. Ceramic Soc., 1-9, 2024.
3. Y. Han, Y. Ou, H. Sun, J. Kopaczek, G. Leonel, X. Guo, B. Brugman, K.D. Leinenweber, H. Xu, M. Wang, S. Tongay, A. Navrotsky, *Thermodynamic Properties and Enhancement of Diamagnetism in Nitrogen Doped Lutetium Hydride Synthesized at High Pressure*, PNAS, **121**, e2321540121, 2024.
4. T. Li, T. Geraci, K.P. Koirala, A. Zohar, E. Bassey, P. Chater, C. Wang, A. Navrotsky, R. Clement, *Structural Evolution in Disordered Rock Salt Cathodes*, J. Am. Chem. Soc., **146**, 24296-24309, 2024.
5. N. Novendra, G.P. Nagabhushana, A. Navrotsky, *Thermodynamics of Hybrid Manganese Formate Perovskites*, RSC Advances, **14**, 29301-29307, 2024.
6. M. Scharrer, L. Bonatti, T. Geraci, S. V. Ushakov, J. Majzlan, M. Bustamante, H. Kojitani, X. Guo, H. Xu, L. Zhang, K. Lilova, S. Hayun, T. Subramani, A. Navrotsky, *The Joys and Jitters of High Temperature Calorimetry*, J. Am. Ceram. Soc., DOI: 10.1111/jace.20381, 2025.

Structural Manipulation of Ceramic Materials *via* Extreme Conditions

Maik Lang

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Phase transformations in ceramics play a critical role in developing new materials such as metastable phases or structures that exhibit desirable properties for technological applications. This talk presents recent experimental investigations on phase transformations in ceramic materials that are triggered by swift heavy ion irradiation and/or high energy ball milling. Simple oxide (AO, A_2O_3 , AO_2) materials were exposed to 5-10 MeV/nucleon heavy ions and/or processed by high energy ball milling. Detailed characterization was performed by synchrotron X-ray diffraction and neutron total scattering techniques to gain insight into the multi-scale structural modifications that evolve with ion fluence and milling time. Varying parameters such as ion species, energy, milling tool materials, and operating speed, a variety of phase transformations were observed, including transitions to metastable high-temperature and high-pressure polymorphs that are otherwise non-recoverable. These results contribute toward an improved understanding on the highly transient extremes associated with ion irradiation and ball milling. This work also demonstrates that neutron total scattering with pair distribution function (PDF) analysis combined with high-temperature calorimetry is a suitable strategy for the characterization of metastable material phases.

Elucidating Pathways of Zeolite Crystallization Through Combined Experiments and Simulations

Jeffrey D. Rimer (PI) and Jeremy C. Palmer (Co-PI), University of Houston

Nonclassical crystallization is an emerging area of research defined by materials growth via the addition of species more complex than monomers, ranging from oligomers to amorphous particles. Zeolites are a class of materials that grow via a combination of nonclassical pathways governed by the addition of (alumino)silicate precursors and by classical routes involving monomer-by-monomer addition. Given the widespread commercial use of zeolites as sorbents and catalysts in U.S. energy markets, developing a fundamental understanding of zeolite growth mechanisms is essential for initiatives seeking to transition zeolite synthesis from an art to a science. Indeed, current trial and error approaches to optimize zeolites is both time and cost intensive, and often fails to achieve the desired goal(s) for creating new/improved materials. Critical challenges in zeolite synthesis stem from an inability to *a priori* tune crystal properties and limited, often phenomenological, understandings of fundamental pathways of crystallization. The goal of this project is to develop a fundamental understanding of zeolite synthesis, and to use this knowledge as a versatile platform for tailoring their physicochemical properties. These studies are motivated by opportunities and practical needs to implement rational design in zeolite synthesis, while also addressing aspects of nonclassical crystallization that may prove to be applicable to a broader class of crystalline materials. The project involves the following specific aims:

- *Elucidating the Mechanisms of Zeolite Crystallization:* We are using in situ techniques, such as high temperature liquid atomic force microscopy (AFM), to elucidate the classical and nonclassical pathways of zeolite growth and the cooperative impact of inorganic and organic structure-directing agents (SDAs) and modifiers that either accelerate or inhibit the kinetics of zeolite crystallization. Findings from these studies will be used to guide the synthesis of high-performance materials with optimal physicochemical properties.
- *Cooperative Structure Direction:* Preliminary studies have revealed that combinations of organic and/or inorganic SDAs control key properties of zeolites and dramatically decrease energy constraints. The concept of cooperative SDAs is a relatively new advancement in the field that is being explored through a combination of zeolite synthesis, state-of-the-art characterization, and molecular modeling to identify the mechanisms underlying SDA cooperativity. One of the central hypotheses that will be tested is the role of ion hydration in zeolite structure direction, and its impact on zeolite properties.
- *Controlling Aluminum Chemistry:* The ability to alter Al incorporation in zeolite structures has a pronounced impact on their performance in commercial applications. A major challenge in zeolite synthesis is the ability to control the spatial distribution of aluminum in the crystal framework. In this project, we are exploring methods of controlling Al siting and chemistry through the use of cooperative SDAs, including divalent ions to promote paired Al sites, via experiments and modeling.

This project is part of a broader initiative aimed at developing strategies to rationally design microporous materials through facile and efficient synthesis schemes. The overarching trajectory of this project is to implement multifaceted approaches to characterize, model, and tailor crystallization, recognizing that predictive control of growth has universal appeal for many applications. The design principles established in this project will serve as a foundation for addressing a range of zeolites using a synergistic combination of experiments, characterization, and advanced computational techniques.

Growing Insights: The Role of In Situ Diffraction in the Formation of Single-Crystalline Quantum Materials

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Keywords: Targeted Synthesis, Rare Earth Intermetallics, In-situ Synthesis and Diffraction, Highly Correlated Systems

Research Scope

To discover new quantum materials, it is essential to determine how to grow high-quality samples. Scientists worldwide are studying emergent materials, topological magnets, and superconductors. Selecting the most suitable candidate is a crucial first step for single crystalline growth. We present our tolerance maps combined with thermal methods and in situ diffraction to elucidate the flux growth process of single crystals. Building on our preliminary work with flux growth methods, recently validation of concentration of flux has proven to be an effective strategy to grow germanides and stannides. Our new approach will enable us to determine consider growth parameters of rare earth intermetallics.

With our efforts to grow single crystals of a new homologous series $A_{n+1}B_nX_{3n+1}$ (A = Lanthanides, B = Co, Fe; X = tetrels),¹ we seek to address the fundamental questions of 1) how do crystals that are built from subunits form during crystallization and 2) what determines how these subunits arrange. By understanding the assembly of subunits, strategies to affect process could emerge, which will ultimately lead to controlled “heterostructural” stacking of various subunits in the growth of bulk materials. Our aim to answer the hypotheses of the growth processes of novel quantum materials will impact on the synthesis and crystal growth intermetallics. We will perform (1) thermal analysis (DSC-TGA) to determine thermodynamic properties for each batch (2) in-situ synchrotron and neutron synthesis and structural characterization.

Recent Progress

Improving upon our previous in-situ furnace for flux growth synthesis,² we have developed a new model using silicon carbide heating elements and alumina insulation, while retaining the motorized vertical sample orientation favorable for liquid samples (Figure 1). Additionally, the use of alumina capillaries allows for a low cost, inert sample environment that can be epoxy sealed under inert atmosphere. This choice allows for (1) an internal standard consistent across experiments and (2) creates an inert environment analogous to bulk flux growth synthesis that is not compromised during the experiment. Initial testing of the high temperature furnace was successful with the furnace easily achieving temperatures of 1300 °C, as illustrated in Figure 1, and with temperatures as high as 1450 °C. This furnace marks a significant milestone in the synthesis community, providing an easy-to-use format with samples that can be prepared in the home lab for optimum experimental control.³ Work is ongoing to characterize experiments performed at the 11- ID-C

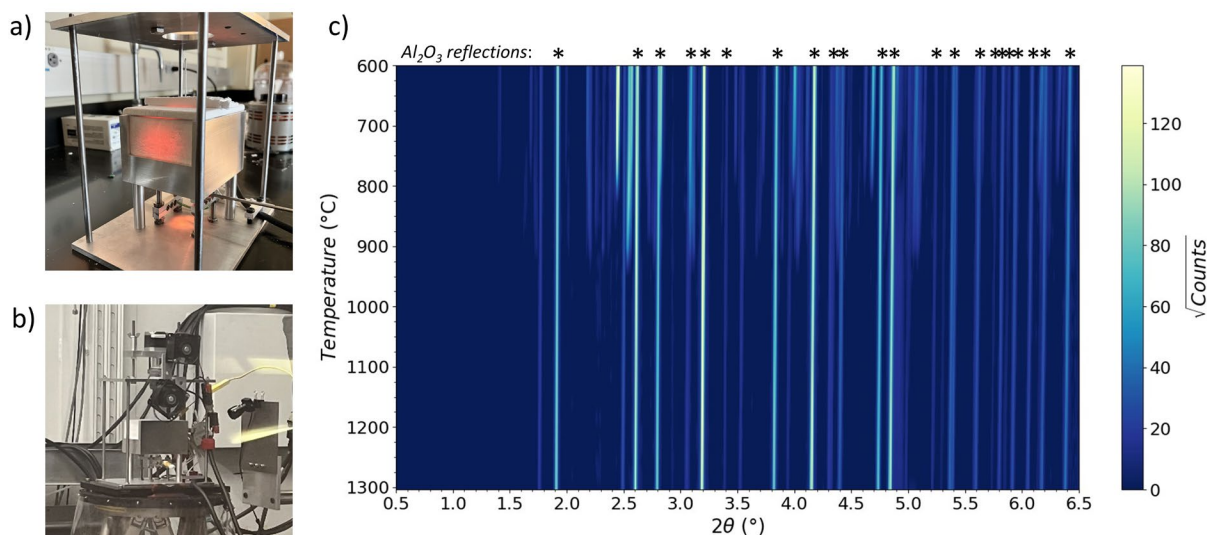


Fig. 1 a) New high temperature in-situ furnace at temperatures more than 1200 °C. b) An in-situ flux growth experiment of Pr-Co-Ge-Sn performed at 11-ID-C with results (c) confirming temperatures of approximately 1300 °C using alumina as an internal standard. Data shown was collected at $l = 0.1147$ Å. (Kyrk and Chan et al., *Chem. Mater.*, **2025**, 37, 2603–2610)

beamline at the Advanced Photon Source of Argonne National Laboratory using a highly absorbing Sn flux as a medium to grow air-sensitive materials.

As part of our efforts to grow $\text{Pr}_{n+1}\text{Co}_n\text{Ge}_{3n+2}$, we discovered two polymorphs of $\text{Pr}_2\text{Co}_3\text{Ge}_5$,^{4,5} and subsequently the identification of a high temperature phase transformation associated with a shift in Pr valence from Pr^{3+} in the high temperature orthorhombic polymorph of $\text{Pr}_2\text{Co}_3\text{Ge}_5$ to a dominantly Pr^{4+} state in the room temperature monoclinic polymorph (Fig. 2). A highlight of this work is that a valence state this near to Pr^{4+} has not previously been observed in an intermetallic compound, making $m\text{-Pr}_2\text{Co}_3\text{Ge}_5$ a particularly unique example for

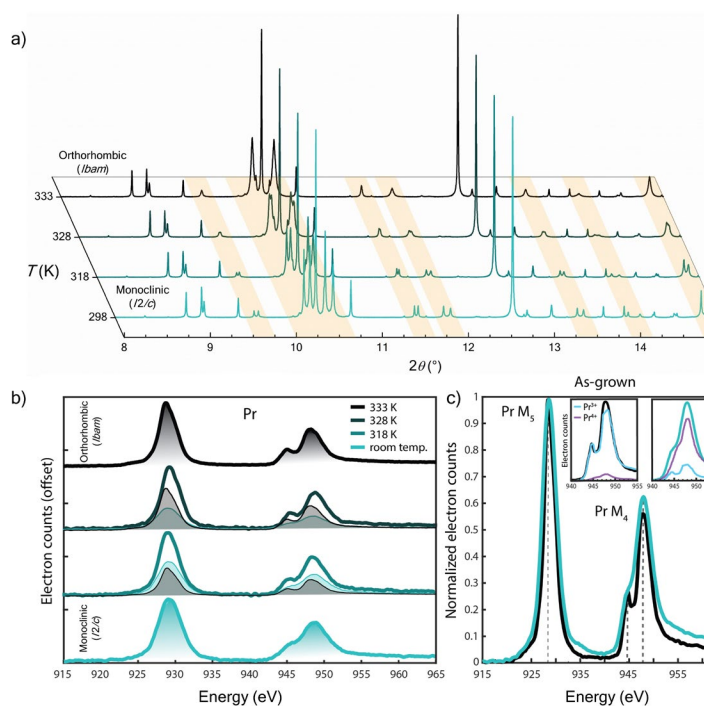


Fig. 2. Temperature dependent powder X-ray diffraction (a) of $m\text{-Pr}_2\text{Co}_3\text{Ge}_5$ performed at 11-BM illustrating a structural phase transformation in tandem with (b) a valence changes in Pr determined by electron energy-loss spectroscopy at the Molecular Foundry. The shift in Pr valence corresponds well with that observed from room temperature measurements (c) on $m\text{-Pr}_2\text{Co}_3\text{Ge}_5$ and $o\text{-Pr}_2\text{Co}_3\text{Ge}_5$. (Kyrk and Chan et al, *Sci Adv.*, **2024**, 10, ead2818)

studies concerning the itinerancy of 4f electrons.

Future Plans

Understanding how materials form is key to growing single crystals for measurements to study their physical properties, and applying our new maps to target valence instable intermetallics is a strategy for next steps. The focus of the project is on controlling the synthesis of valence instable Remeika phases (Figure 3), particularly those with Ce, Sm, and Yb. This project aims to develop a method for growing intermetallics adopting the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$, $\text{Er}_5\text{Rh}_6\text{Sn}_{18}$, or BaNiSn_3 structure types. Our aim and proposed plan are to incorporate (A) valence instable lanthanides that are predicted by tolerance metric to selectively adopt either the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$, the $\text{Er}_5\text{Rh}_6\text{Sn}_{18}$, or the BaNiSn_3 structure types.

Selected candidate materials will then be studied using a (B) combined thermal and (C) *in situ* diffraction analysis to determine the reaction temperature profile. Our

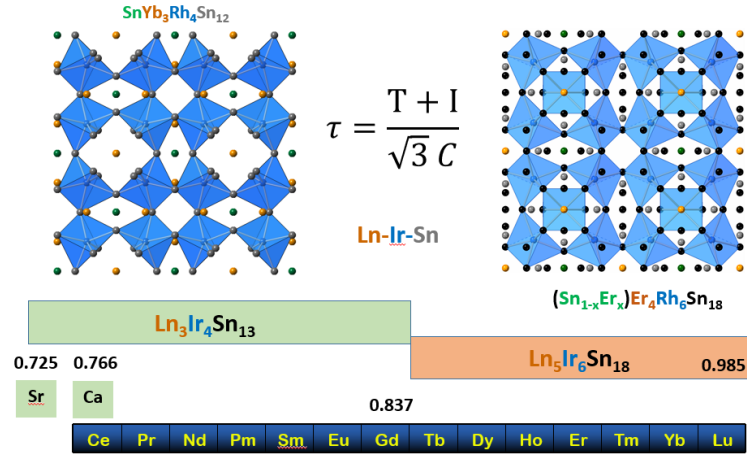


Fig. 3. Structural comparison between the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ (left) and $(\text{Sn}_{1-x}\text{Er}_x)\text{Er}_4\text{Rh}_6\text{Sn}_{18}$ (right) structure type. The $\text{Er}_5\text{Rh}_6\text{Sn}_{18}$ unit cell is partially shown to directly compare with the cubic $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ structure type.

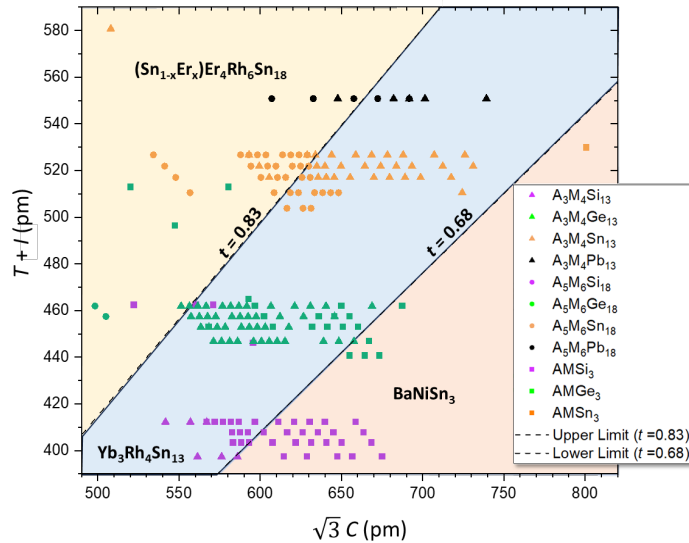


Fig. 4. Graph of the calculated $T + I$ (height of the trigonal prism as T , distance between opposite equilateral triangular faces in the icosahedra as I , and that of the cuboctahedron as C) as a function of the calculated C for the reported BaNiSn_3 (squares), $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ (triangles) and $(\text{Sn}_{1-x}\text{Er}_x)\text{Er}_4\text{Rh}_6\text{Sn}_{18}$ (circles) structures and their respective hettotypes. The dotted lines correspond to $t = T + I/C\sqrt{3}$ values of 0.83 and 0.68, which we empirically established as the $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$ structure type stability range, creating three domains. Moving from the top left to the bottom right, each domain corresponds to $(\text{Sn}_{1-x}\text{Er}_x)\text{Er}_4\text{Rh}_6\text{Sn}_{18}$, $\text{Yb}_3\text{Rh}_4\text{Sn}_{13}$, and BaNiSn_3 , respectively. The color of the symbols corresponds to distinct X elements: purple for Si, green for Ge, orange for Sn, and black for Pb. The salmon area on the bottom right denotes phases that should adopt the BaNiSn_3 structure type.

new modified differential scanning calorimetry (DSC) method allows the study of thermodynamic events in an inert atmosphere to inform the evolution of phase formation. This DSC study will in turn lead to more efficient *in situ* experiments that will be performed at Argonne APS 11-BM synchrotron beamline using a furnace developed by our group and help establish and strengthen our collaboration with at POWGEN beamline at SNS. Improving control over reaction products through in-situ synthesis will shed light towards the mechanism of crystal growth and tuning of microstructural changes. The infrastructure developed here will generate a feedback loop between prediction and in-situ synthesis, creating a model that can be extended to other families of quantum materials driving the discovery of technologically relevant intermetallic compounds towards a “materials by design” approach.

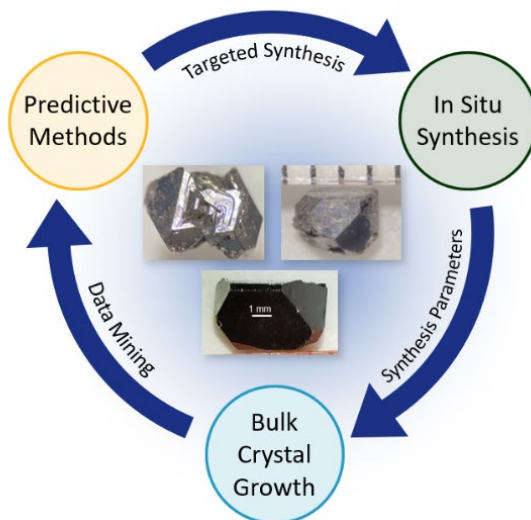


Fig. 5. Feedback loop to accelerate synthesis and growth of intermetallics

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Tailoring Quantum Phenomena in Atomically Thin Boron Materials via Confined Growth

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The recent experimental realization of atomically thin boron (i.e., ‘borophene’) has spurred broad interest in its unique material attributes such as in-plane anisotropy, seamless phase intermixing, massless Dirac fermions, and phonon-mediated superconductivity. The polymorphic nature of borophene, which is rooted in the rich bonding configurations of boron, further distinguishes it from other two-dimensional (2D) materials and offers an additional means for tailoring its properties [1]. This presentation outlines a multi-faceted basic research program aimed at realizing the diverse quantum phenomena that have been predicted for borophene as a function of its atomic structure, interfacial interactions, and lateral confinement. For example, vertically confined growth at buried interfaces is predicted to yield unprecedented borophene polymorphs and twisted moiré heterostructures [2]. In addition, templated growth on high-index substrates and nanomesh superstructures provides opportunities for realizing quantum-confined borophene nanoribbons and borophene quantum dots, respectively [3]. Moreover, the propensity for boron to diffuse into the sub-surface region of many metals creates additional possibilities for 2D boride compounds [4]. These 2D borides (i.e., ‘boridenes’) have been theoretically predicted for several metals with diverse magnetic, electronic, optical, and chemical properties. Ultimately, this research program seeks to tailor quantum phenomena in atomically thin boron materials via confined growth, thereby establishing a novel material platform with implications for frontier DOE-relevant quantum technologies. To achieve this overall goal, three research objectives are being pursued:

(1) *Vertically Confined Growth of Borophenes*: By synthesizing borophene via ultra-high vacuum molecular beam epitaxy at buried interfaces between disparate materials, vertically confined growth allows the exploration of unprecedented borophene polymorphs and vertical moiré heterostructures with overlying van der Waals materials such as hexagonal boron nitride.

(2) *Laterally Confined Growth of Borophenes*: By employing substrate templating on highly stepped vicinal surfaces and nanomesh moiré superstructures, laterally confined growth enables the synthesis of one-dimensional borophene nanoribbons and zero-dimensional borophene quantum dots that have been theoretically predicted to show quantum confined electronic states.

(3) *Sub-Surface Confined Growth of Boridenes*: While negligible boron solubility in silver results in surface-localized borophene growth on Ag substrates, the ability of boron to diffuse into the sub-surface region of substrates with finite boron solubility presents a pathway for the synthesis of 2D borides (i.e., boridenes), which is a relatively unexplored family of 2D materials with broad potential for tailoring magnetic, electronic, optical, and chemical properties.

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Synthesis and Crystal Growth of Boron-Carbon-Nitrogen Metastable Materials

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Keywords: Metastable materials; crystal growth; machine learning, quantum calculations, high resolution microscopy

Research Scope

Metastable single crystals based on boron, carbon, and nitrogen will be grown by taking advantage of the exceptional catalytic and tunable structure-stabilizing properties of molten metal solutions. Our goal is to develop methods for synthesizing diamond and cubic boron nitride (cBN) under atmospheric pressure, where they are metastable, avoiding the limitations of synthesis by high-temperature – high pressure or chemical vapor deposition techniques which are difficult to scale. Toward the vision of controlling complex crystallization to create custom metastable high-performance materials, this research will focus on addressing two fundamental questions:

- How can specific elements in the solvent direct the formation of sp^3 C-C and B-N bonds in the metastable polymorphs (diamond and cBN) rather than the sp^2 bonds of the stable polymorphs at atmospheric pressure (graphite and hBN) during the nucleation stage?
- How do the interactions and migrations of crystal grains influence the 2D and 3D morphology of the B-N-C metastable crystals?

This will be accomplished by integrating modeling and simulations (to guide experiments), synthesis and crystal growth, and detailed structural and compositional analysis (Figure 1).

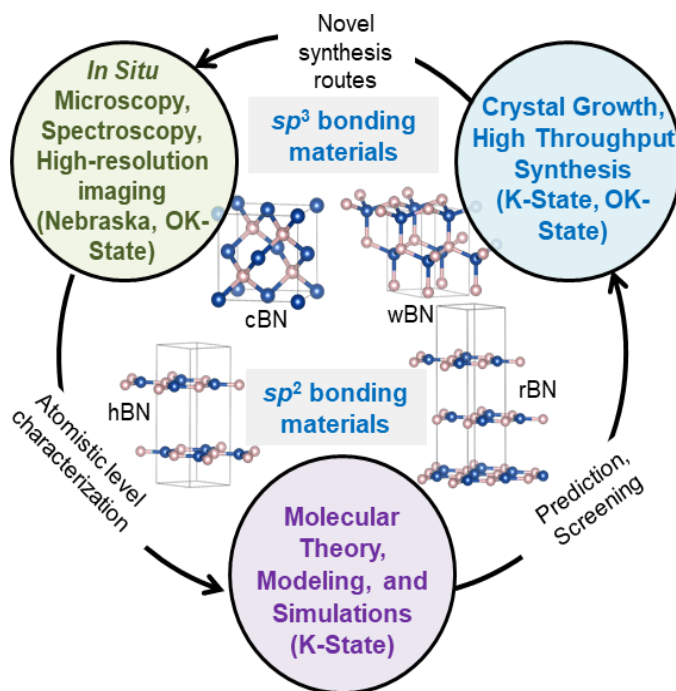


Figure 1. Synthesis of metastable B-C-N materials from molten metal solutions by building multi-disciplinary, multi-institution research infrastructure. Structures of BN polymorphs with sp^3 and sp^2 bonds are shown. Analogous carbon polymorphs will also be studied.

Background

Carbon allotropes (diamond, graphite, and graphene) and compounds composed of boron and nitrogen (cubic boron nitride and hexagonal boron nitride) have extraordinary, physical, thermal, optical, and electronic properties unmatched by any other materials. Metastable versions of these elements and compounds such as hexagonal diamond, rhombohedral boron nitride, and Bernal boron nitride have the potential to realize an even wider spectrum of properties of interest for future technologies.

In this project, we explore the use of metal fluxes to synthesize metastable materials. These are liquid metals or alloys employed as solvents to dissolve, react, and crystallize solutes (upon cooling) during crystal growth. Metal fluxes will be employed for new material discovery, and with the goal of stabilizing phases that would otherwise not form under equilibrium condition. As demonstrated by the low-pressure solution growth of metastable diamond by Gong *et al.* [1], multi-component fluxes offer great flexibility in tuning growth parameters and directing nucleation and growth toward unconventional crystalline phases. We hypothesize that solvent elements or additives in the flux possess chemical and/or catalytic properties that can alter nucleus surface energies to favor the formation and growth of metastable nuclei while disfavoring stable nuclei.

Future Plans

The project is a collaboration between efforts in crystal growth, molecular-scale theory, modeling and simulation, and advanced microscopy aimed at discovering the microscopic mechanisms underlying the selection of metastable B-C-N phases in liquid metal environments. Major tasks include:

Task 1. Simulation-driven metastable polymorph synthesis and selectivity (Comer and Liu)

A computationally efficient approach will be adopted to screen hundreds of different flux compositions, temperatures, nucleation locations (bulk flux solution, flux surface, flux interface with solids such as graphite), and nucleus structures. Rapid machine learning potentials (MLPs) and ReaxFF will be used for the coarsest stage. Quantum methods, as well as larger scale MD simulations of crystal growth, will be used to verify the results for the most promising cases.

We will start with free-energy perturbation (FEP) calculations as diagrammed in Figure 2. Short (0.5–2 ns) simulation of a slab of the selected flux (300–500 atoms) in contact with the appropriate gas mixture (such as CH₄/H₂, C₂H₂/H₂, C₂H₂) and/or a solid material will be performed to determine reasonable concentrations of species in the solution. Next, large-scale simulations (1200–5000 atoms) will employ conditions identified as promising in the initial stage. Temperature replica exchange will be used to accelerate sampling, identify spontaneous formation of crystal nuclei and, in separate simulations, study growth or decrystallization of nanocrystals.

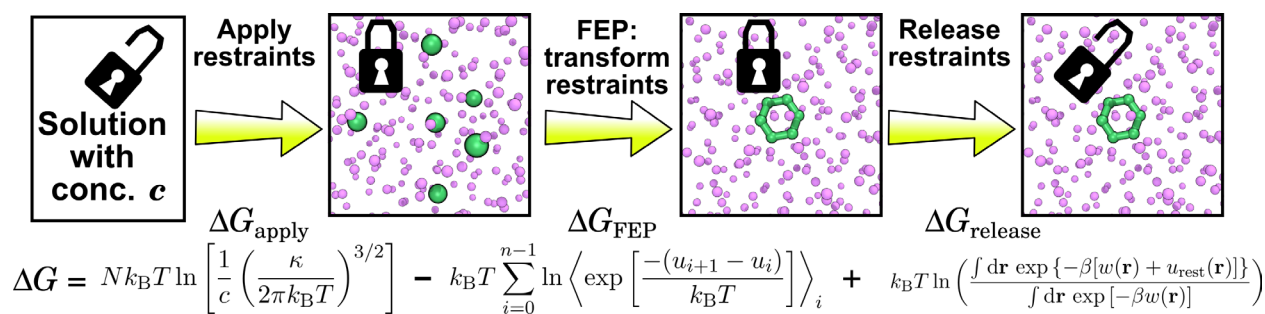


Figure 2. Free energy perturbation (FEP) protocol to efficiently estimate free energies for forming crystal clusters in bulk fluxes and at interfaces.

Task 2. Microscopic pathways toward metastable compounds (Liu)

Quantum mechanical methods (i.e., density functional theory, *ab initio* MD) will be employed to determine key intermediate states, validate microscopic reaction pathways, and supplement classic molecular dynamics simulations (by Comer's group) with training and validation data. In this task, quantum mechanical calculations will also be driven by the hypothesis that elemental species (e.g., Si) added to the flux favor specific types of C-C and B-N bonding (i.e., sp^3 versus sp^2), as well as specific nucleus geometries (i.e., 3D versus 2D).

Task 3. Solution-based crystal growth (Edgar)

Crystals will be grown in Edgar's lab (KSU) from solid elemental sources of boron, carbon and gaseous nitrogen, using solvents (e.g., Ga, Fe, Ni, Cr, or Co) and doping impurities (Si, Be), identified by simulation as the most promising to produce the metastable crystal structures. The crystal growth process will be monitored in situ via optical microscopy, and the structural properties of the crystals will be assessed by optical microscopy, Raman spectroscopy, and x-ray diffraction.

Task 4. Non-equilibrium BN growth (Sachan)

Thin films (a few monolayers to ~20 nm thickness) of cBN will be grown using a laser-induced melt-state phase separation, which consists of (i) pulsed laser deposition (PLD) of metal/BN mixed films, and (ii) liquid phase separation and transition to cBN from the metal/BN mix by pulsed laser irradiation (PLI). In this process, BN separates from the metal/BN mixed film in the melt state and forms cBN layers on the surface under liquid-phase regrowth by laser-induced ultrafast (<100 ns) melting and quenching. With a nanosecond pulsed laser, precise control over metastable cBN growth may be achieved by regulating the melt lifetime and temperature of the metal/boron mixed films. This control is achieved through the interplay of candidate mixed metal, laser pulse irradiation, energy density, and thin film thickness. Combinatorial thin film synthesis and laser irradiation will be employed for high-throughput experimentation.

Task 5. In situ microscopy and spectroscopy of nucleation and growth of metastable and equilibrium crystals from metallic melts (Eli and Peter Sutter)

Powerful *in situ* microscopy and spectroscopy experiments, jointly directed by co-PIs E. Sutter and P. Sutter (UNL), will be used to investigate key aspects of the growth of metastable carbon allotropes and boron nitride polymorphs, including: (i) The initial nucleation and growth, and especially the role of short-range structural motifs in the melt as well as nucleation modifiers in steering the nuclei toward the metastable phase; (ii) the competition between the metastable and equilibrium phases (i.e., the fraction of each among the nucleation products) depending on factors such as the composition of the host melt and the concentration of additives. Carried out via both real-time surface microscopy and transmission electron microscopy, and complemented by in-situ spectroscopy up to near-ambient pressures, these experiments will be designed to obtain mechanistic insight into the role of the melt, added nucleation modifiers, the supersaturation of solutes, etc., while providing a direct experimental validation of computational results obtained by co-PIs Comer and Liu (Task 1-2).

Task 6: High-resolution characterization of structure and properties (E. & P. Sutter and Sachan)

Atomic-scale studies will be performed to quantitatively understand the atomic arrangement, composition, and correlated electronic structure of the synthesized materials. Atomic level imaging, diffraction, and associated chemical analysis of grown diamonds and cBN will provide critical insights on crystal structure, crystal orientation, grain size and distribution, as well as composition. The emerging properties of the metastable C-B-N crystal phases targeted in the project will be analyzed at the atomic scale (e.g., in the defect-free bulk, as compared to sites near defects or impurities) using advanced electron microscopy techniques. These include (i) atomic-resolution core-loss EELS to investigate the electronic states at defect sites and correlate them with the atomic structure as a function of solution synthesis methods and conditions; (ii) monochromated STEM-EELS to probe the emergence of shallow-level/midgap states at defects; and (iii) cathodoluminescence in STEM to identify and characterize emerging optoelectronic properties, e.g., single-photon quantum emitters. In addition, advanced machine-learning-based imaging/spectroscopic data analysis/interpretation techniques will be incorporated to develop an across-the-scale understanding of structure, chemistry, and properties of the metastable crystal phases.

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Precise control of crystal stoichiometry of chalcopyrite compounds using a double-crucible Bridgman crystal growth technique

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Keywords: Double crucible, Bridgman crystal growth, crystal stoichiometry and defects

Research Scope

This research project aims to overcome the limitations of conventional melt-growth techniques, such as the Czochralski and Bridgman methods, which often yield inhomogeneous crystals with non-stoichiometric compositions that compromise their functional properties. The project introduces a novel crystal growth protocol for producing high-quality chalcopyrite compounds—intermetallic chalcogenides and pnictides with desirable properties for technological applications. The team employs the high-pressure double-crucible vertical Bridgman (DCVB) method, which uniquely integrates high pressure with continuous feeding of source materials to achieve precise compositional control. This technique stands apart from traditional methods by enabling the growth of homogeneous, stoichiometric crystals. Notably, Penn State houses the first academic DCVB furnace. The Mao group not only develops DCVB growth protocols for chalcogenide materials but also conducts comprehensive analyses of the resulting crystals, examining their composition, structure, and properties using a range of advanced characterization techniques. Complementing these experimental efforts, the project integrates computational studies to uncover the mechanisms underlying compositional control. These include first-principles calculations and statistical mechanical modeling to assess defect densities, formation energies, and migration barriers—insights that guide post-growth processing strategies. This integrated approach advances the frontiers of materials synthesis while providing interdisciplinary training in crystal growth and computational physics, with broad implications for next-generation materials in energy and technology applications.

Recent Progress

DCVB growth of Bi_2Se_3 : Unlike conventional Bridgman growth, where crystals are grown from the melt in a single crucible moving from the hot to cold zone, the DCVB furnace employs a two-crucible geometry, as shown in Fig. 1a. This design allows for the continuous feeding of source material from an upper crucible to the growth crucible, facilitating traveling solvent growth within the Bridgman furnace. Combined with liquid encapsulation and high pressure, both of which effectively suppress the vaporization of volatile elements, this approach allows for better control of melt composition throughout the growth process. As a result, it can enable crystal growth for incongruent melting compositions and yield crystals with improved homogeneity and stoichiometry. Recently, we demonstrated the capability of the DCVB through successful test growths of Bi_2Se_3 , a prototype topological insulator [1,2]. We show that Bi_2Se_3 crystals grown

with this technique exhibit significantly lower carrier density compared to those grown by the conventional Bridgman method.

We synthesized Bi_2Se_3 single crystals in the DCVB furnace both with and without the feeding function. The batch grown without source material feeding is designated as DCVB1 below, while the batch grown with continuous source material feeding is labeled DCVB2. Comparing these two batches allows us to evaluate the crucial role of continuous source material feeding in achieving low-carrier-density crystal growth. The source material initially loaded into the growth crucible had a Bi:Se molar ratio of 34:66 ($\sim 2:3.88$), corresponding to a Se-rich composition, with excess Se (29.3%) serving as a flux.

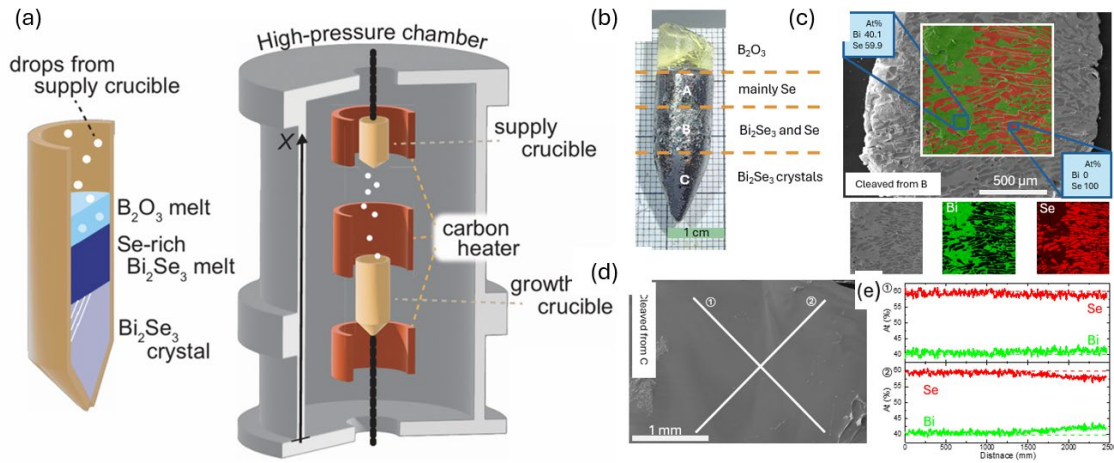


Figure 1. (a) Schematic description of the DCVB technique; the left panel shows cross-sectional illustration of the growth-crucible configuration used for the DCVB growth of Bi_2Se_3 . (b) Image of the Bi_2Se_3 crystal ingot grown using the DCVB furnace without feeding. The crystal can be divided into four regions: B_2O_3 , a predominantly Se region (A), a Bi_2Se_3 -Se mixture region (B), and a pure Bi_2Se_3 single-crystal region (C). (c) EDXS mapping of a single crystal cleaved from region B. (d) SEM image and (e) line EDXS scan of a single crystal cleaved from region C, where ① and ② in (d) and (e) indicate the scanned lines.

Figure 1(b) shows the final product of DCVB1 extracted from the alumina crucible. The yellow top layer is B_2O_3 , used as a liquid encapsulant during growth. Since B_2O_3 reacts with quartz but not alumina, an alumina crucible was chosen for Bi_2Se_3 growth. The B_2O_3 layer, combined with high pressure, effectively suppressed Se vaporization. To assess structural phases and composition, we performed XRD and EDXS analysis on different regions of the ingot, dividing it into three parts (A, B, and C; Fig. 1b). Part A, beneath the B_2O_3 , is mainly Se with minor Bi_2Se_3 . Part B is a Bi_2Se_3 -Se mixture, as seen in the EDXS mapping (Fig. 2c). Only Part C, the bottom region, yielded pure Bi_2Se_3 , though in significantly smaller quantity, indicating low crystal yield. EDXS line scans on millimeter-scale cleaved pieces from Part C revealed mixed compositional uniformity. Some line scans (Fig. 2d-e) showed minimal variation, while other line scans exhibited Se ranging from 60% to 57.5% and Bi from 40% to 42.5%. These results confirm that combining Bridgman and excess Se-flux growth does not produce large, homogeneous Bi_2Se_3 crystals. Over half of the material crystallized as a Bi_2Se_3 -Se mixture. This is consistent with the proposed growth mechanism: as Bi_2Se_3 forms from a Se-rich melt (initially 29.3% excess Se), the melt composition shifts toward the Bi_2Se_3 -Se eutectic, resulting in dominant formation of the mixed-phase region (Part B) over pure Bi_2Se_3 (Part C).

The issues of low crystal yield and inhomogeneous composition encountered in the DCVB growth without source material feeding (DCVB1) were effectively resolved in the DCVB growth with continuous source material feeding (DCVB2). Figure 2a shows the crystal ingot obtained from the DCVB2 batch. The top gray layer consists of Bi_2O_3 , which appears gray rather than yellow (Fig. 3a) due to the incorporation of a small amount of Bi_2Se_3 within B_2O_3 as it solidified during cooling. This occurred because the Bi_2Se_3 source material was fed into the growth crucible through the liquid B_2O_3 encapsulation layer.

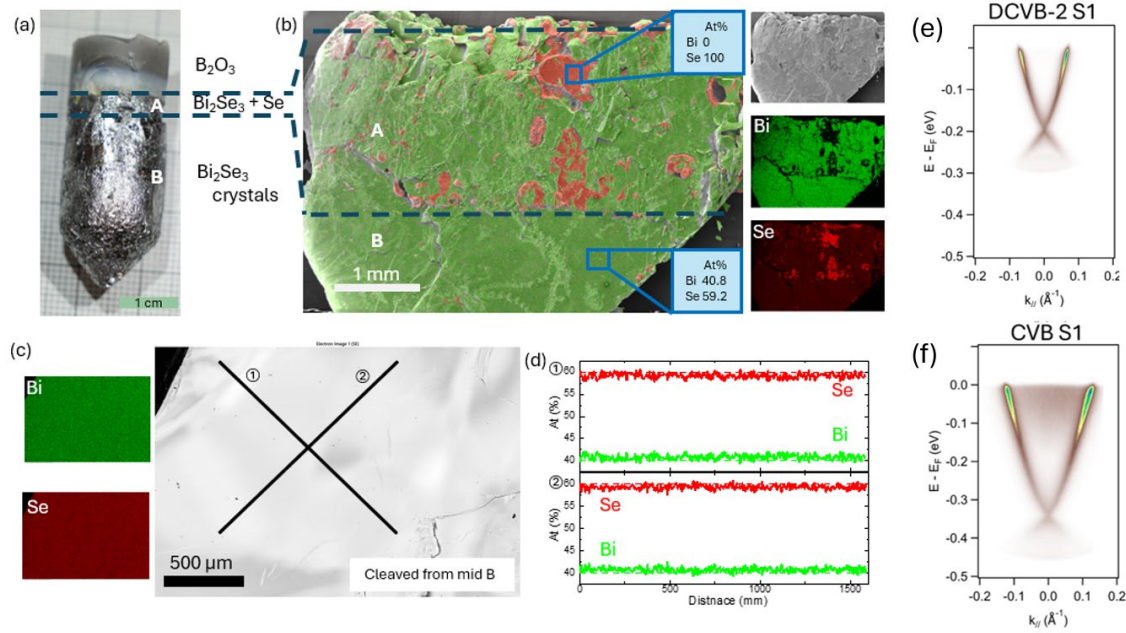


Figure 2. (a) Image of the Bi_2Se_3 crystal grown using the DCVB furnace with continuous feeding (DCVB2). The crystal is divided into three regions: B_2O_3 , a Bi_2Se_3 -Se mixture region (A), and a pure Bi_2Se_3 single-crystal region (B). (b) SEM-EDXS mapping of a single crystal cleaved from the top part of the ingot, containing material from both regions A and B. (c) SEM-EDXS mapping of a single crystal cleaved from the middle of region B. (d) SEM-EDS line scans for the single crystal cleaved from the middle of region B, where ① and ② in (d) indicate the scanned lines in (c). (e-f) Band dispersion through the Brillouin zone center probed by ARPES at 40 K with the photon energy of 6 eV for a representative DCVB2 crystal (e) and a representative CVB-grown Bi_2Se_3 crystal (f).

To investigate the crystal structure and composition of the DCVB2 ingot, we performed XRD and EDXS measurements on cleaved crystals from various regions. The composition distribution in DCVB2 differs significantly from that in DCVB1. Notably, no Se-rich region analogous to Part A in DCVB1 was observed. Although a Bi_2Se_3 -Se mixed-phase region (Part A, Fig. 2a) is still present in DCVB2, it is much smaller, and Bi_2Se_3 is the dominant phase. Most importantly, the pure Bi_2Se_3 region (Part B, Fig. 2a) is substantially larger than that in DCVB1, due to the continuous source material feeding during growth. This demonstrates that traveling-solvent growth (TSG) combined with continuous feeding significantly improves crystal yield and enables the growth of large Bi_2Se_3 crystals. Previously, TSG had only been realized in floating zone [1] and traveling heater [2] method for oxide growth. Our work represents the first demonstration of TSG in a Bridgman furnace for intermetallic crystal growth.

Despite the presence of multiple domains, EDXS analyses show that crystals from Part B in DCVB2 are generally compositionally homogeneous. One representative cleaved crystal (Figs.

2c–d) reveal flat surfaces and uniform Bi:Se atomic ratios (~40%:60%) over ~1.5 mm distances, confirmed by composition mapping and line scans. These results underscore the improved compositional control achieved in DCVB2. Transport measurements further highlight the quality of DCVB-grown crystals. DCVB1 and DCVB2 crystals exhibit carrier densities in the range of 1.9×10^{17} to $1.5 \times 10^{18} \text{ cm}^{-3}$, which are one to two orders of magnitude lower than those of conventional Bridgman (CVB)-grown Bi_2Se_3 . This reduction suggests fewer Se vacancies. ARPES measurements on DCVB2 crystals reveal well-defined Dirac surface states. For samples with the Dirac point ~0.2 eV below the Fermi level, no bulk conduction band crosses the Fermi level (see Fig. 2e), sharply contrasted with the CVB-grown crystals which show remarkable bulk bands crossing the Fermi level (Fig. 2f), indicating near-stoichiometric composition. While some other DCVB2 pieces still show bulk conduction, further tuning of growth parameters may yield consistently stoichiometric crystals. These results demonstrate that stoichiometric Bi_2Se_3 can coexist with a Se-rich melt phase and be grown from incongruently melting, Se-excess compositions using the DCVB method. This study has been submitted and posted on arXiv [3].

Computational Study: Supporting Bi_2Se_3 Experiments and Exploring $\alpha\text{-In}_2\text{Se}_3$

To complement experimental advances in DCVB crystal growth, we performed DFT calculations to investigate native point defect formation in Bi_2Se_3 under Se-rich conditions. The Se-on-Bi antisite has the lowest formation energy (0.834 eV), followed by Se vacancies (1.475 eV), indicating these are the most prevalent defects. Notably, defect formation enthalpies increase with pressure, consistent with the high-pressure DCVB process's ability to suppress defect generations, supporting the observed low carrier densities. To extend the defect analysis framework, we performed a parallel study on $\alpha\text{-In}_2\text{Se}_3$, a ferroelectric material which we plan to grow using DCVB. We investigated ten intrinsic defects and identified Se-on-In antisites ($\text{Se}_{\text{In}2}$) and middle-layer Se vacancies ($\text{V}_{\text{Se}2}$) as the most energetically favorable under Se-rich conditions. Their stability is attributed to local bonding environments—specifically, longer bond lengths and weaker coordination compared to other layers. These results offer predictive insight into defect behavior in $\alpha\text{-In}_2\text{Se}_3$ and highlight the broader applicability of our approach in guiding crystal growth for chalcogenide materials.

Future Plans: First, we aim to address remaining challenges in DCVB growth of Bi_2Se_3 : (a) Although EDXS shows homogeneous composition in DCVB2 crystals, ARPES reveals residual inhomogeneity, with some regions showing the bulk conduction band crossing the Fermi level; (b) this variation also leads to fluctuations in carrier density. According to the Bi–Se phase diagram, increasing the excess Se flux—e.g., using a non-congruent composition near the eutectic point (Bi:Se = 30:70)—may improve stoichiometry and uniformity. Second, having demonstrated that DCVB enables effective TSG and composition control, we plan to extend it to other systems such as the ferroelectric In_2Se_3 and the nonlinear optical material $\text{AgGa}(\text{S}/\text{Se})_2$, with the goal of reducing their defect densities. On the theoretical side, we will continue work on three projects: defect studies in In_2Se_3 , color centers in diamond, and monovacancies in semiconductors and metals. Joint efforts between Sun's and Mao's groups are expected to result in three manuscripts. In particular, our computational studies of In_2Se_3 defects will help elucidate its growth mechanism and guide experimental characterization within Mao's group.

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Data-driven discovery of multicomponent metal halide perovskites using megalibraries

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Keywords: Multicomponent; Metal Halide Perovskites; Nanolithography; Machine Learning

Research Scope

Metal halide perovskites (MHPs) are appealing materials for a range of applications due to their composition- and structure-dependent optoelectronic, semiconducting, and ferroelectric properties. They are of interest to the DOE as components in energy conversion technologies spanning photovoltaics, light-emitting diodes, photocatalysts, self-powered devices, and wearable electronics. However, the best-performing MHPs often rely on Pb-based compositions, which present toxicity concerns and stability issues. But, the immense compositional flexibility of MHPs allows for the preparation of a near-infinite number of materials, creating a vast design space that remains underexplored.

To address this challenge, a data-driven, high-throughput platform is being developed to systematically discover and understand reduced Pb and Pb-free multicomponent MHP (MMHP) nanomaterials. This platform leverages nanoparticle (NP) “megalibraries,” millions of compositionally and structurally distinct nanomaterials that are positionally encoded on centimeter-scale chips and analyzed in single experiments. Characterization methods that complement megalibrary-enabled rapid and highly parallelized nanomaterials synthesis are being developed and used to study dynamic NP crystallization processes and the associated evolution of NP structure-dependent physical and optoelectronic properties. Unprecedentedly large datasets from these libraries are being used to develop machine learning (ML) models to predict the MHP compositions that have particular targeted features. This integrated approach will elucidate the mechanisms of MHP formation and establish design rules governing crystalline phase, elemental distribution, and morphology. The fundamental synthetic understanding uncovered through this work will provide a new basis for designing and realizing functional energy-conversion materials to address the long-term needs of the DOE.

This research integrates three core objectives: (1) Combinatorial synthesis of NP megalibraries to define the design rules for Pb-free MMHP synthesis; (2) *in situ* and high-throughput characterization techniques for investigating dynamic crystallization processes and exploring structure-function relationships; and (3) high-throughput computation-assisted synthesis of MMHP NPs with deliberate on-demand material design.

Recent Progress

Perovskite nanocrystal megalibraries were synthesized and high-throughput methods were developed to investigate their optical and structural properties. Specifically, trimethylchloromethylammonium (TMCM)-based MHP compositions, known to demonstrate piezoelectric responses,¹ were explored.

Evaporation crystallization polymer pen lithography (EC-PPL) was used to synthesize TMCM-based MHP megalibraries that contain >1 million NPs. During EC-PPL, polymer pen arrays are used to deposit nanoreactors containing precursor solutions onto substrates, which crystallize to form highly ordered and uniform TMCMCdCl₃ particles (Figure 1a). By precisely controlling reaction conditions at the attoliter scale, EC-PPL enables the reproducible synthesis of compositionally distinct MHPs on diverse substrates of interest.² The resulting nanoparticles were well-faceted TMCMCdCl₃ crystals (Figure 1b). Using EC-PPL, TMCM_x-tetramethylammonium (TMA)_(1-x)-CdCl₃ megalibraries were created with gradients of nanocrystal compositions by spraying two different inks (TMCMCdCl₃ and TMA CdCl₃) on opposite corners of the polymer pen array (Figure 1c). To map the composition at each point in the library, time-of-flight secondary ion mass spectrometry (ToF-SIMS) (Figure 1d) was used, confirming the successful preparation of the megalibraries. These results fulfill a key task of Objective 1.

Additional measurements were performed to structurally characterize the patterned nanoparticles. Energy-dispersive X-ray spectroscopy (EDS) confirmed that the expected elements (C, Cd, N, and Cl) were uniformly distributed within the patterned nanoparticles, indicating their well-defined

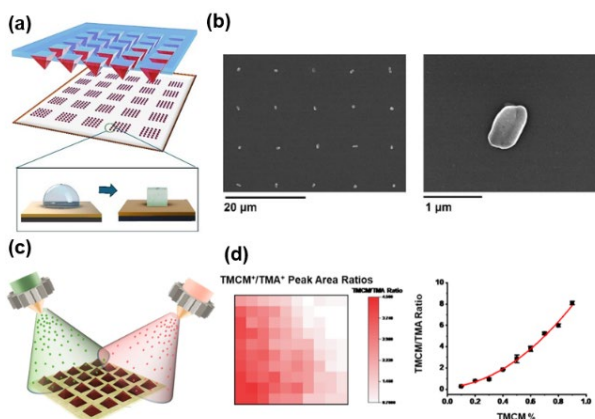


Figure 1. (a) Schematic of EC-PPL. (b) SEM of patterned particles, showing the formation of nanocrystal arrays. (c) Schematic of the spray-ink process for megalibrary synthesis. (d) ToF-SIMS signal gradient of a TMCM_xTMA_(1-x)CdCl₃ megalibrary and the calibration curve for conversion to composition.

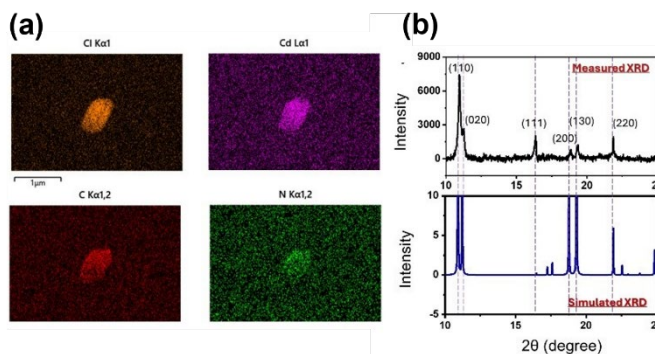


Figure 2. (a) EDS analysis of a TMCMCdCl₃ particle. (b) Thin-film XRD of the nanoarray (top) displaying the same peaks as the expected TMCMCdCl₃ crystal structure (bottom).

Additional measurements were performed to structurally characterize the patterned nanoparticles. Energy-dispersive X-ray spectroscopy (EDS) confirmed that the expected elements (C, Cd, N, and Cl) were uniformly distributed within the patterned nanoparticles, indicating their well-defined

structures (Figure 2a). To evaluate the crystallinity of the patterned nanoparticles, the nanoarrays were analyzed using thin-film X-ray diffraction (XRD). The observed diffraction peaks matched well with those reported for TMCdCl_3 crystal structures, confirming the successful patterning of 1D perovskite nanoparticles (Figure 2b).

Under Objective 2, a new high-throughput screening method—scanning confocal second harmonic generation (SHG) microscopy—was developed (Figure 3a). Because non-centrosymmetric materials exhibit SHG and centrosymmetric ones do not, it was hypothesized that confocal microscopy could be used to rapidly detect SHG signals in MHP megalibraries and enable the identification of centrosymmetric versus non-centrosymmetric structures.³ To detect SHG response, the particles were excited with an IR laser, and the resulting emissions were analyzed to confirm they displayed clear SHG signatures (i.e., the emission of photons at

precisely half the wavelength of the incoming light) (Figure 3b). Composition-dependent phase boundaries were identified by measuring the SHG signal intensity over the $\text{TMCd}_x\text{TMA}_{(1-x)}\text{CdCl}_3$ arrays. These measurements indicated the presence of both centrosymmetric and non-centrosymmetric phases, and a composition located at the phase boundary was identified (Figure 3c); these phase boundary regions are anticipated to display enhanced piezoelectric performance.⁴ This integrated EC-PPL synthesis and SHG characterization approach is being used to investigate high-entropy molecular crystals. Computational methods are also being used to analyze their structures and properties, as described in Objective 3.

In parallel, additional high-throughput optical and structural characterization methods are being developed to accelerate the discovery of optoelectronic materials via the megalibrary platform. To enable more sensitive techniques that require larger material amounts than PPL-based methods provide, we are employing thin-film based megalibraries. This approach enables the use of characterization techniques such as position-dependent absorbance and XRD mapping, which cannot be used to interrogate the nanoparticles in megalibraries prepared using EC-PPL. Together with the developed SHG screening approach, these ongoing efforts represent key materials characterization advancements under Objective 2.

Future Plans

To rapidly and accurately identify bulk compositions in nanocrystal megalibraries, ion etching will be incorporated into the current ToF-SIMS approach, and other non-destructive, high-

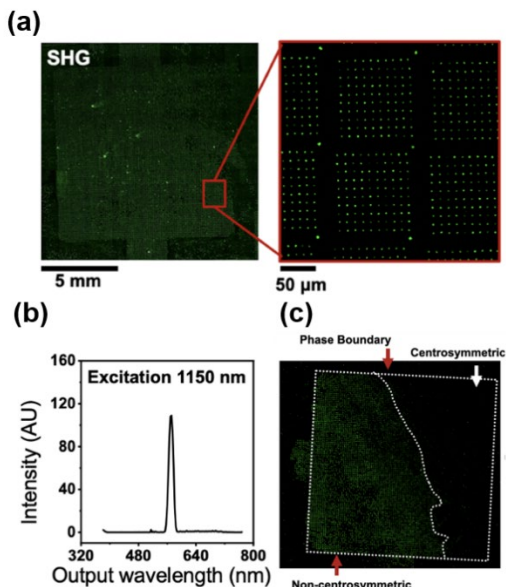


Figure 3. (a) SHG microscopy of a TMCdCl_3 array. (b) SHG response of a TMCdCl_3 particle. (c) SHG microscopy of a $\text{TMCd}_x\text{TMA}_{(1-x)}\text{CdCl}_3$ megalibrary.

throughput methods, such as X-ray fluorescence (XRF) and automated scanning electron microscopy (SEM)-based EDS, will be developed in the context of the megalibrary platform. The throughput of the current measurement methods will also be improved by tuning experimental setups and parameters, such as by refining the plate design, performing spot calibrations, and optimizing beam settings. Furthermore, temperature variations will be incorporated into SHG, XRD, and absorbance measurements to uncover temperature-dependent structure–property relationships. Single-particle micro-focus wide-angle X-ray scattering will also be performed in collaboration with Argonne’s Advanced Photon Source (APS) to gain crystallographic insights into select NP compositions.

To generate complete MMHP phase diagrams across temperatures and compositions, a cluster expansion + special quasirandom structure (SQS) workflow will be developed and validated. This approach will complement the high-throughput characterization methods by providing information about favorable structures and compositions that can be used to guide future experiments. In addition, ML-powered automated image and spectral analysis will be developed to classify two-photon SHG and luminescence signals on a particle-by-particle basis, reduce user intervention, and enable the rapid mapping of synthetic parameters to structural and functional behaviors across entire combinatorial libraries.

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Achieving Long Range Ordering in Oxide-Metal Hybrid Materials —A Combined Experimental and Modeling Approach (DOE-BES DE-SC0020077)

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Keywords: oxide-metal nanocomposite, self-assembly, multifunctional thin films, kinetic Monte Carlo

Research Scope

Ordered, high-density metallic nanopillars in oxide matrices offer nanoscale composites with applications in nanodevices such as nanophotonic and plasmonic devices, high-density magnetic storage devices and reader heads and in thermoelectrics. Nanostructures of this type are often fabricated through multiple steps involving laser patterning, e-beam lithography, or focused ion beam (FIB). These methods are limited to small patterning areas, low resolutions (typically in 50-100 nm), and slow speed. In this project, we use thin film epitaxy of two-phase nanocomposites, guided by computational modeling, to circumvent these limitations and achieve highly ordered nanoscale metallic pillars in oxide matrixes. Specifically, we aim to achieve single-step, direct growth of self-assembled oxide-metal epitaxial nanocomposite systems with potential long-range in-plane ordering of metal nanopillars in an oxide matrix.

The impact of this research is multi-faceted. First, the fundamental understanding of the two-phase self-assembly process leads to the further development of the concept of thin film epitaxy, which allows the growth of large mismatch systems or the deposition of materials that are hard to grow epitaxially; Second, it will lead to development of guidelines for the design and processing of ordered oxide-metal hybrid materials a wide range of applications in optical, plasmonic, piezoelectric devices and catalysis. Finally, the computational models developed in conjunction with our experimental effort will have broader impacts towards understanding the morphology evolution in multiphase thin films and control of the growth parameters.

Recent Progress

1. Abnormal epitaxy relationship between the Au pillars and the CeO₂ matrix (published in *Materials Horizon* 2023) [1] Through the growth of various oxide-metal vertically aligned

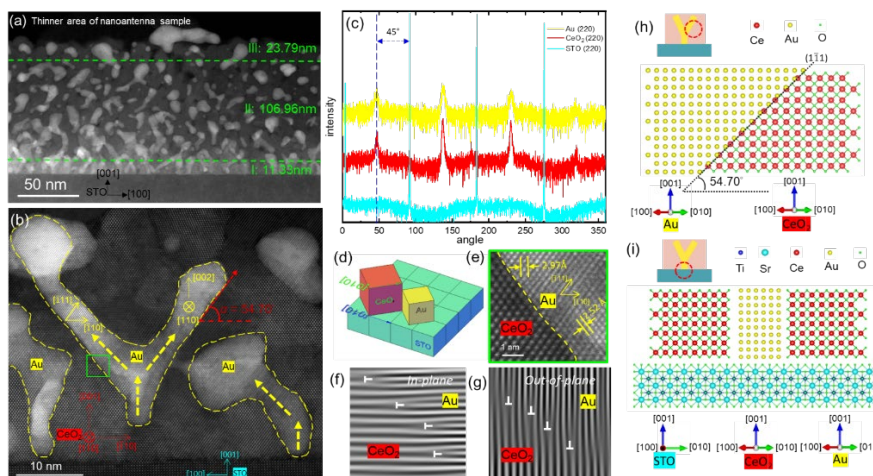


Fig.1. An abnormal in-plane epitaxy between the Au nanopillars and CeO₂ matrix contributes to the strain compensation model. (a-b) STEM images showing the cross-sectional morphology of Au going through three growth phases. (c-g) Au nanopillars follow the in-plane epitaxy of CeO₂ (45° rotation relative to STO) in despite of high lattice mismatch with the STO substrate. (h-i) atomic models demonstrating lattice matching relationships¹

nanocomposite (VAN) systems, we observed a very interesting and unexpected observation is the abnormal epitaxy relationship between the CeO₂ matrix and the Au nanopillars in the CeO₂-Au VAN system on STO substrates. By adjusting the background pressure, Au demonstrates three

distinctive morphologies: nanoparticle, nanoantenna and nanopillar, due to the complex play of kinetic and thermodynamic factors during the nucleation and growth process. The investigations into the in-plane lattice matching show that, Au selected the in-plane orientation as that of CeO₂

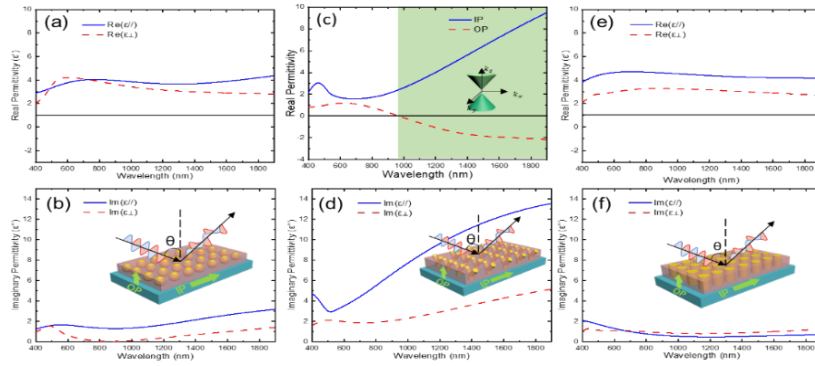


Fig.2. Effective tuning in anisotropic optical responses of three different CeO₂-Au nanocomposite systems with Au nanoparticles, nanoantennas, and nanopillars. Type I metamaterial responses were observed in the nanoantenna sample, with a wide range of hyperbolic dispersions from 970 nm to 1900 nm¹

lattices, which is 45° rotated relative to the STO substrate (Fig. 1), regardless of the high strain between Au and STO lattices. This is evidence of lateral strain dominating over the substrate clamping effect, which is considered unique and advantageous in VAN systems. Type I hyperbolic metamaterial responses are also observed at a wavelength range of 970-1900 nm in the nanoantenna sample (Fig. 2). The results from COMSOL simulation analysis attributes that to the complex morphology and the tilting of Au nanopillars.

2. Novel nanoscale electric field concentrators by VAN designs in memristors enabling selective conductive filament formation for high performance electronic synapses (Published in *ACS-Applied Materials Interfaces*, 2024) [2]

Beyond investigating the growth mechanisms and exploring optimized deposition methods, we have also explored potential applications in advanced microelectronic devices using these novel oxide-metal VAN systems. Memristors, known as resistive random-access memory (ReRAM), have attracted tremendous research interests due to their potential as next generation memory and as a bridge for implementing computing in memory and neuromorphic computing microchips. Critical needs in memristor research lie in enhancing its power efficiency and device reliability, and minimizing device-to-device variation. To address these needs, we designed a novel bilayer (BL) memristor by integrating a CeO₂-based memristor with Co-CeO₂ VAN thin film (Fig. 3). The Co-CeO₂ VAN layer significantly strengthens the electric field beneath the metal nanopillars, enabling selective formation of conductive filaments instead of random formation. This innovation has resulted in substantial performance improvements: over 60%

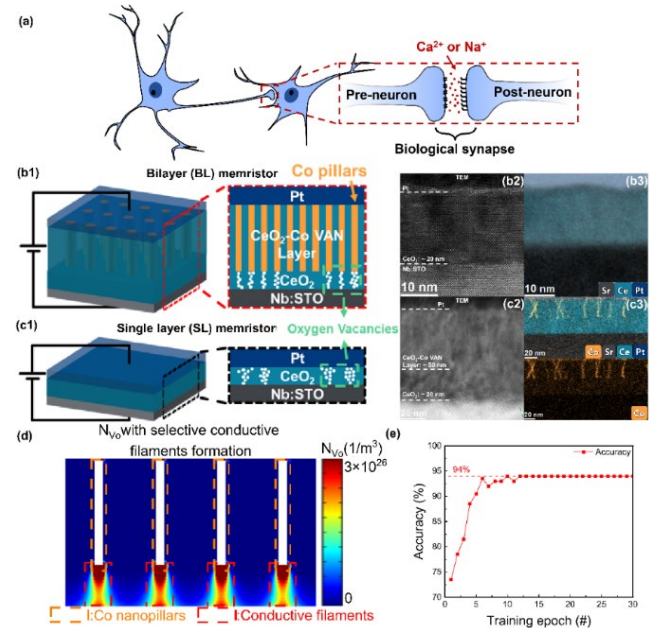


Fig.3. Schematic diagram for (a) biological synapse, (b1) bilayer (BL) memristor, and (c1) single layer (SL) memristor. TEM images for (b2) BL memristor and (c2) SL memristor. EDS mapping for (b3) BL memristor and (c3) SL memristor. (d) COMSOL simulation results of oxygen vacancies in BL memristor under bias. (e) Recognition rate of the spiking neural network (SNN).²

reduction in set/reset voltage, enhanced reliability (endurance $> 10^6$ cycles, retention $> 10^3$ seconds), and better device-to-device uniformity. Furthermore, investigations into device plasticity—such as long-term potentiation/depression (LTP/LTD), paired-pulse facilitation (PPF), and spike-timing-dependent plasticity (STDP)—highlight its promise for neuromorphic computing. Several challenges remain including (1) achieving better long-range ordering in oxide-metal VAN thin films to further reduce device-to-device variation, and (2) optimizing device structure, e.g., a tri-layer metal-oxide VAN memristor, to improve power efficiency, on/off ratio, and reliability, all calling for ordered VAN growth.

3. Modeling for Kinetics of Nucleation, Phase Separation and Growth: [4] An asynchronous parallel kinetic Monte Carlo (kMC) method has been developed to describe nucleation, growth and phase separation in VAN systems³. In our work, the kMC method is coupled with elastic strain field in the multi-phase film, which requires that the energy parametrization, done in our case by density functional theory (DFT), to depend on the strain⁴. The elastic strain is obtained using a Fast Fourier Transform mechanics solver⁵. The overall framework has been applied to the Au-CeO₂-STO (pillar, matrix, substrate) system. It was found that the elastic interactions make surface diffusion anisotropic due to symmetry breaking caused by strains⁶. This parametrization involves the atomic binding and hopping barriers of Au adatoms CeO₂ ad-molecules on Au, CeO₂ and STO strained and relaxed surfaces. Designed to take into consideration the binding energy differences between initial and final sites in addition to the hopping energy barrier (following the Bortz–Kalos–Lebowitz algorithm), the coupled DFT-FFT-kMC framework thus accounts for both the thermodynamics and kinetics of diffusion, clustering and nucleation and phase separation and growth. While both Au and CeO₂ are co-deposited on the surface, the model neatly revealed that the separation of the metal and oxide phases readily occurs at higher temperature, lower pulse-rate and lower deposition flux due to the rapid diffusion kinetics and/or longer diffusion time, as well as the difference in binding energies (thermodynamics) (**Fig. 4**). Fig. 5 shows kMC results for which the elastic strain effect is shown, at different temperature with fixed frequency. As shown in Figs. 4 and 5, the elastic strain does is shown to alter the size and density of the pillars, as well as the shape of the pillar, basically making the pillars straighter. In addition, we observe self-organization close to square quasi-configuration when adding the elastic strains in the growth simulations. The simulations show that including elastic strains in the kMC framework reveal.

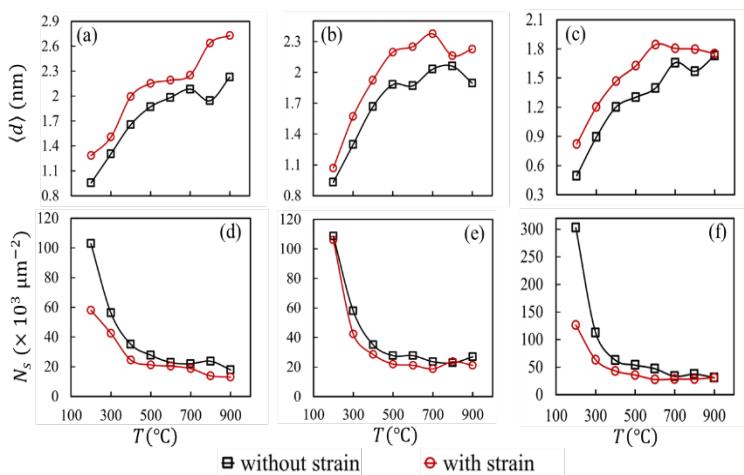


Fig. 4: kMC simulated Au pillar average diameter (a,b,c) obtained at 2Hz, 5 Hz and 10 Hz, respectively. And similarly pillar density (d,e,f) as function of temperature revealing the role of including elasticity.

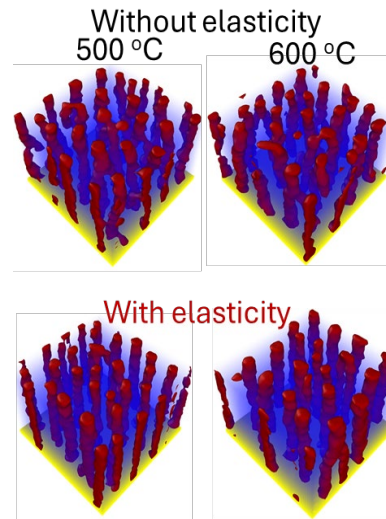


Fig. 5: kMC simulation output of $35 \times 35 \times 20 \text{ nm}^3$ revealing the role of including elasticity in the simulations obtained at 5 Hz with average flux of 0.2 ML/sec.

Future Plans In the next fiscal year, we plan to undertake the following tasks. We are working to explore substrate types and orientation effects on two phase epitaxy and nucleation, explore very slow growth rate impacts on ordering, demonstrate free layer transfer of two-phase nanocomposite systems onto other substrates that could not achieve epitaxy, and complete the modeling framework for simulating the complex two-phase growth. In parallel, we are also growing oxide-metal nanocomposites using sputtering methods where more growth controls can be achieved by controlling the sputtering deposition power, gas pressure, substrate bias, and plasma conditions.

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Nucleation and Self-Assembly of Hierarchical Materials: Predicting Pathways, Dynamics, and Outcomes

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Keywords: Nucleation, Oriented attachment, Surface potential, Ion adsorption

Research Scope

The long-term vision of this project is to develop a predictive understanding of the physical principles connecting atomic-scale interactions to ensemble responses that control solution synthesis of crystalline materials via complex pathways not envisioned in classical theories (Fig. 1).¹ We are advancing that vision through four scientific objectives that target key knowledge gaps: (1) When crystalline phases emerge along nucleation pathways that start from a dense liquid phase and are accompanied by an evolution in chemical composition, how does stoichiometry evolve, how is solvent eliminated, and what is the impact of specific ion solvation energies?² (2) How does the surface potential, either inherent or applied, affect interfacial structure, surface speciation, and the formation of nuclei, and how does the outcome depend on the specific solute species?³ (3) How do physicochemical details of a nanocrystal system, including (a) interfacial solution structure and the resulting interfacial properties and (b) anisotropies in nanocrystal shape and properties control the short-range forces and torques that drive oriented attachment (OA), as well as the kinetics of coalignment and attachment?⁴ (4) How do surface-bound organic ligands and solution electrolytes affect interfacial solution structure and resultant dielectric and transport properties and interparticle forces to enhance or hinder OA?⁴ Our proposed approach delineates nonclassical synthetic pathways of nanostructured materials by exploiting *in situ* methods including TEM, NMR, 3D AFM, and laser tweezers, and produces a mechanistic understanding by utilizing novel methods of theory and simulation to predict speciation, cluster evolution, interfacial structure, and interparticle forces and dynamics. The outcome will be a predictive description of nonclassical crystallization that crosses scales to connect atomistic details with macroscopic, ensemble outcomes via development of models of reduced detail, thus advancing translation of transformative materials science to disruptive materials technologies.

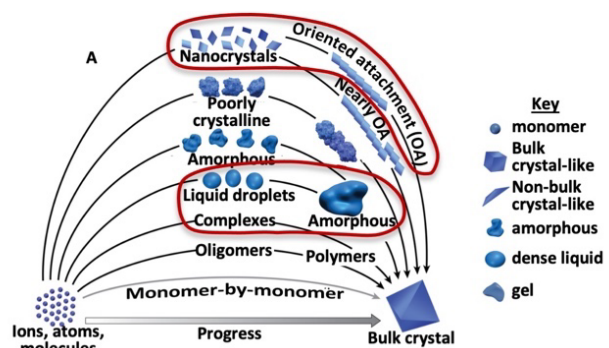


Fig. 1. Stable bulk crystals often form from species of higher order than monomers .

Recent Progress

Nucleation: Our previous research on nucleation at charged surfaces showed that $\text{Al}(\text{OH})_3$ films form on negatively charged mica surfaces through a barrier-free process that involves initial adsorption of isolated AlOH_2^+ ions followed, as temperature is increased, by formation of clusters whose size distribution cannot be described by classical nucleation theory.³ Moreover, these clusters evolve into monolayer-thick islands separated by gaps that never fill. We showed that the electrostatic charge of the surface and the ions drives this outcome. In essence, this mesostructured film results from a need to balance charge while minimizing edges, leading to a characteristic island size and spacing, with the islands and gaps together comprising a single 2D phase.³

We have now found that, if instead of increasing temperature, pH is raised, the coverage of ions increases until a 4-fold symmetric ordered ion network (OIN) forms with a $15\text{\AA}$ ion-to-ion spacing (Fig. 2a,b). Concomitantly, the surface potential climbs from an initial negative value to $\sim 200\text{mV}$ (Fig. 2c,). With further pH increase, the OIN collapses into clusters, and the corresponding surface potential ζ precipitously drops. As pH continues to rise, the clusters aggregate to form the mesostructured film previously described. This is followed by classical multilayer growth and, finally, by film dissolution.

A novel lattice Monte Carlo model that includes charge frustration due to the electrostatic interactions between the adsorbed

ions and between the ions and the surface predicts all observed structural classes, which sequentially emerge as the adsorbate charge is decreased, mimicking the hydroxylation of the Al-ions with increasing pH. Moreover, the same behavior is observed for all electrolytes of trivalent cations tested, including, Fe^{3+} and Cr^{3+} , this evolution with pH is observed. In contrast, for electrolytes of divalent cations (Mg^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+}), which have little charge when hydrolyzed, only classical nucleation and growth is observed, corresponding to the low-q region of the phase diagram in Fig. 2c. Thus, we find there is universal behavior in which the adsorbate charge, surface charge density, solution dielectric, and adsorbate-adsorbate interaction energy, can predict the outcome of ion adsorption and film formation.

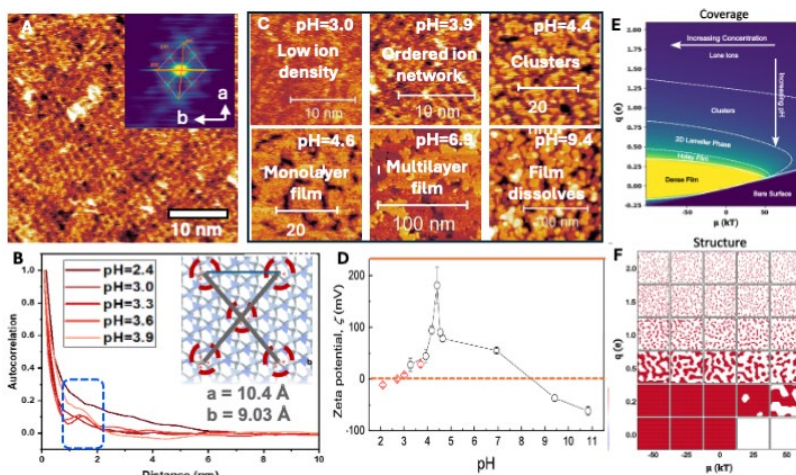


Fig. 2. (A) Development of an OIN of adsorbed $\text{Al}(\text{OH})_2^+$ on mica. Inset shows 2D autocorrelation. (B) 1D autocorrelation and positions of adsorbed ions on mica lattice. (C) Evolution of adsorbate and film structure with pH. (D) Corresponding evolution in zeta potential. (E, F) Phase diagram (E) and morphology (F) predicted by a charge frustrated lattice Monte Carlo simulation for fixed ion-ion interaction energy.

Oriented attachment: Following on our previous research investigating the role of steric forces associated with ligands on the elimination of defects in superlattices of Pd nanocubes, we investigated the effect of evolving surface potentials due to adsorption of electrolytes and organic ligands on growth by OA starting from Pt nanoparticles (NPs). Using in situ liquid phase (LP), high resolution (HR), and cryogenic (cryo) TEM, we found that OA of Pt NPs leads to formation of branched particles with a cubic core defined by approximate (100) faces and branches aligned along the (111) directions (Fig. 3a). The development of these structures occurs as follows. First, the Pt NPs nucleate through a reduction reaction. Then they begin to aggregate into clusters of unattached NPs. Once the clusters are sufficiently large, the NPs begin to attach on (100) faces, starting from the central region of the cluster, as the number of free NPs decreases — and thus the total surface area of Pt decreases — the particles switch from attaching on (100) to (111), thus forming the branches.

To understand why this switch in facet selection, and therefore this complex particle morphology, comes about, we investigated the evolution of surface potential and its impact on forces and torques. Zeta potential measurements show that the

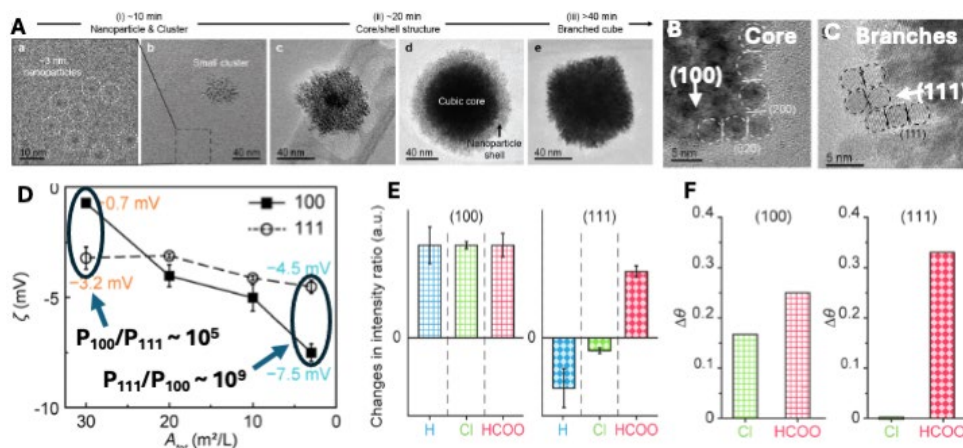


Fig. 3. (A) Development of branched Pt nanoparticles. (B, C) Attachment directions in core (B) and branches (C). (D) Switch in zeta potential with drop in total Pt surface area and facet-dependent contact probabilities. (E, F) Measured and predicted changes in ion coverage from initial stage to late stage.

continual decrease in surface to volume ratio that comes about due to OA of the NPs leads to a switch in the surface potentials of the two facet directions, with (111) possessing the greater charge at early times and (100) becoming more charged at later times. Calculations of the orientational probability distribution function described by the Smoluchowski equation, which embodies the balance between Brownian and electrostatic torques of the resulting electrostatic forces and torques, show that the relative probability of achieving contact on (100) vs (111) — i.e., $P_{100}:P_{111}$ evolves from $10^3:1$ to $1:10^9$. Thus, the observed behavior is controlled by the evolution in the electrostatic torque arising due to the changing surface potentials.

Time of flight - secondary ion mass spectrometry (TOF-SIMS) shows that the source of this evolving surface potential lies in the facet-specific adsorption of H^+ , Cl^- and HCOO^- . As the total surface area of Pt decreases, the coverage of all three ions increases on the (100), with the increased adsorption of the anions dominating and leading to a significant shift from near-neutral

to negative zeta potential, while a decrease in H^+ and Cl^- coverage on the (111) is balanced out by an increase in HCOO^- coverage, leaving the surface potential nearly constant. To establish a basis for this behavior in the energetics of competitive ion adsorption, we employed density functional theory (DFT) calculations with ab initio thermodynamics, which delineates the (100) and (111) surface configurations with the lowest energy as a function of the chemical potential of solution-phase Cl^- and HCOO^- relative to the gas phase. The resulting minimum surface energy diagram predicts an evolution in coverage of the solution phase ions that aligns well with the experimental findings. Thus, the results demonstrate that the interplay of ion adsorption and resultant surface potential can be used to manipulate the progress of OA, enabling creation of complex nanoparticle morphologies. Moreover, this study is the first to reveal the importance of electrostatic torque in driving facet selection during OA, pointing towards a general approach to utilizing this effect simply through the use of pH as a means to tune the relative surface potentials of distinct facets.

Future Plans

In order to decouple the surface potential from the solution composition and substrate chemistry, we have developed an electrochemical cell that allows us to utilize a charged MoS_2 substrate in place of mica to investigate the physics of field-driven ion adsorption, organization and nucleation. We will utilize this system to determine how applied fields can be used to drive the system through the phases predicted by our charge-frustrated lattice Monte Carlo models. In addition, following on our investigation of nucleation via a dense liquid phase (DLP) in the CaCO_3 system, we have begun to probe the impact of solvation energies on the formation, transformation, and lifetime of the DLP, by substituting Mg^{2+} for Ca^{2+} . We will utilize cryo- and LP-TEM, combined with NMR and molecular simulations to fill this knowledge gap.

Following on the investigation of OA by Pt NP, we have begun probing the mechanism by which the NPs transition from an initial stage in which they form solvent-separated clusters, presumably due to hydration barriers, to attaching on (100) faces. We hypothesize that the transition is driven by osmotic pressure when the NP clusters reach a critical size. We have also begun a systematic investigation of the impact of ligand length, rigidity, hydrophobicity, headgroup charge, and inter-ligand interactions on interfacial structure and forces that drive OA.

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Unraveling the synthesis-algorithms for novel 2D materials

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Keywords: 2D materials, lateral epitaxy, nucleation, gas phase reactions, flash-sintering

Research Scope

Exploration of two-dimensional (2D) materials remains of great interest, revealing new remarkable functionalities, in physics, optics, catalysis, etc. For many desired 2D forms (e.g., III-V compounds, borophene, 2D-ferroics, 2D diamonds aka diamanes, or perovskites), the choice of substrate and feedstock remain crucial and often challenging. Achieving any of these targets by design, controllably (composition, number of layers, defects type and concentration, and reaching the coveted “wafer size”) and at sufficient growth rates, is of great value in itself, justifying the quest for theoretical insight and quantitative, predictive models for each special case. We aim, however, to try more, and to also advance methodology: based on previous models of 2D nucleation and growth (notably *nanoreactor* [i]). At the same time, progress in specific materials behaviors, especially in association with the underlying synthetic routes, has already been achieved, to be presented. A very recent work on borophene vs metal-boride “bifurcation” in the two-dimensional epitaxy [2]; synthetic mechanism of a transition metal chalcogenides/TMC, as coveted 2D-magnetics [ii] will be presented, along with added exploratory “into 3D” branch-study of solid bulk syntheses, to understand the flash-sintering [iii-iv, 6], its principles and versatility, towards important class as ceramics, e.g. high-temperature and ablation-resistant types.

Recent Progress

At this time point, roughly a year into our current funding period, we choose to discuss three advances of interest (I-III), one being just reported in public domain [2] and on two others the manuscripts being prepared [ii, v].

(I) Our theoretical predictions of borophene synthesis (2013, Ref. [v]— an early work from different project, supported then by DOE), its proposed realization on Ag(111) or Au(111) was achieved in the labs in just a couple of years. 2D boron has excited community by its polymorphism and as a host for solid-state quantum phenomena. Notably, our same Ref. [v] had a word of caution about Cu substrates: the DFT data suggested too strong B-Cu binding. Now in collaborative work [2], atomic-resolution scanning tunneling microscopy (STM) and field-emission resonance (FER) spectroscopy were used to elucidate the structure and properties of atomically thin boron phases grown on Cu(111). FER reveals charge transfer and electronic states that strongly differ from the decoupled borophene phases observed on Ag, suggesting that the deposition of boron on Cu results indeed in strong covalent bonding characteristic of a 2D copper boride, Fig. 1. The finding is reinforced by STM of line defects, consistent with DFT calculations for atomically thin Cu_8B_{14} . This evidence for 2D copper boride should motivate future synthetic efforts aimed to expand the relatively unexplored family of atomically thin metal boride materials. Formally a transition metal boride, it points to a class of high-resistant ceramic coatings.

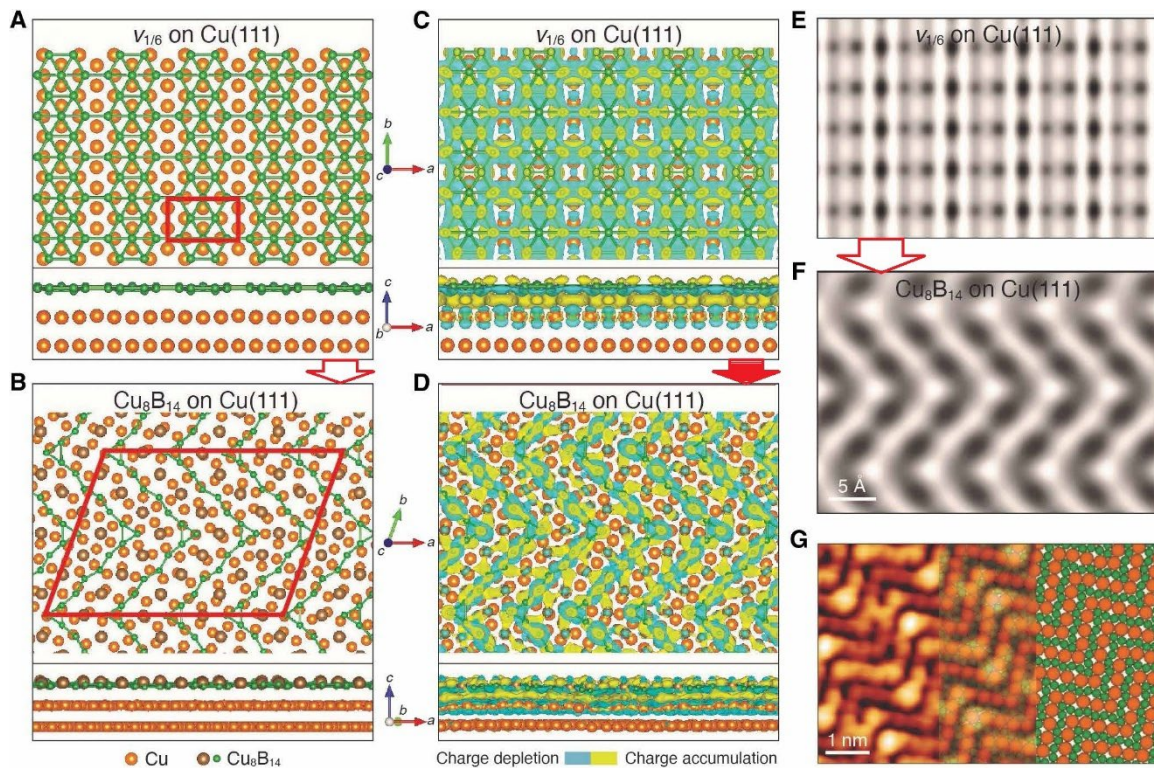


Fig. 1 DFT models of borophene and copper-boride on Cu(111). (A) Top and side view of $v_{1/6}$ borophene on Cu(111). The red rectangle is the unit cell of $v_{1/6}$ borophene. (B) Top and side view of Cu_8B_{14} on Cu(111). The red rhomboid is a supercell where the corner B atoms sit atop the second-layer Cu atoms. (C and D) Computed charge redistribution of the structures in (A and B). (E and F) Simulated STM images of $v_{1/6}$ borophene and Cu_8B_{14} . (G) STM-experiment topography overlapped with the Cu_8B_{14} structure model. [2]

(II) 2D magnetic materials attract interest for their physical properties. The synthesis of atomic-layer 2D transition-metal chalcogenides (TMC) has been achieved via chemical vapor deposition, CVD. However, the chain of reactions, long way from precursors to materials, at elevated temperature remain poorly understood. Molecular insights into growth mechanisms are needed for any conceivable optimization of synthesis process and the product quality. We focused on the complete growth process of tetragonal FeTe (*t*-FeTe) nanosheets – one experimentally synthesized – to elucidate it by first-principles theory, with the most used precursors metal-chloride (FeCl_2) and tellurium powders. Among the multiple gas-phase species observed in AIMD (ab initio molecular dynamics), a partially tellurized cluster FeTe_4Cl emerges as the lowest-lying (in energy scale) with high concentration in the considered reactions network. The following crystal growth occurs through reaction of FeTe_4Cl on the telluride-passivated armchair FeTe island edge, accompanied by the critical byproducts, Te_2Cl or ClTeH (Fig. 2). The reaction kinetics analysis revealed that hydrogen carrier gas has a dual functionality pivotal to crystal growth: (1) it prevents iron-chloride cluster aggregation and accelerates FeTe_4Cl emergence rather than participating in gaseous reactions directly; (2) it also eliminates the byproducts and partakes in the edge recovery during growth. Our findings provide a mechanistic explanation for two essential requirements in

CVD synthesis: controlled tellurium supply and essential H_2 flow. This work not only advances the fundamental understanding of t -FeTe growth dynamics but also offers valuable guidelines for optimizing synthesis parameters of other similar TMC more broadly. Computed reaction-barriers and accordingly the rates of accretion-growth to different crystallographic edges, leads to predict, via so called kinetic Wulff construction, the shapes of growing 2D-crystals.

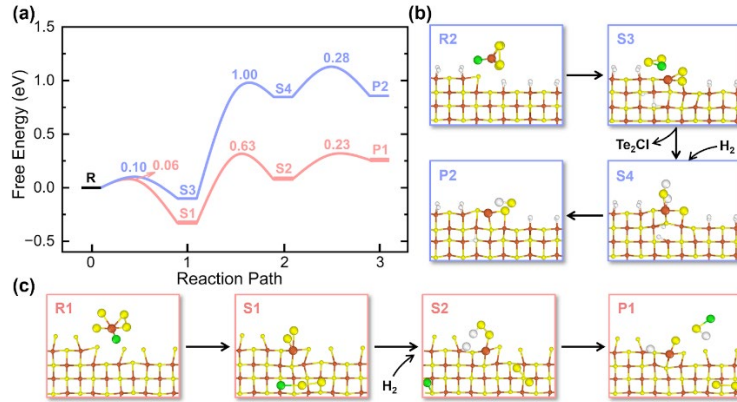


Fig. 2. Incorporation of building unit ($FeTe_4Cl$) into t -FeTe crystal lattice kink site of Te-/2H-passivated AC and ZZ-Te edges.

(a) The free energy profiles of $FeTe_4Cl$ incorporation. Two routes are considered: the light-blue and pink represent the $FeTe_4Cl$ incorporation into the 2H-AC and Te-AC edges. Only the values of bottleneck barriers are shown. **(b-c)** The snapshots of reactants,

intermediates and products of these three routes. The orange, yellow, green and white balls represent the Fe, Te, Cl and H atoms. For comparison, the atoms in the original t -FeTe crystal lattice are shown in smaller balls, while those atoms in $FeTe_4Cl$ and H_2 additive are highlighted as larger. Unpublished work [ii].

(III) Our time-investments, within other collaborative projects on flash-synthesis and flash sintering or 2D materials [iii,iv] paid off by advancing our understanding of the rich physics underlying the flash Joule heating acceleration of ceramics sintering. The atomistic mechanisms of flash sintering remained speculative, despite its efficiency and versatility in materials processing. We focused on one ‘iconic’ (judging by the relative large number of published studies) 3D material, yttria-stabilized zirconia (YSZ). Employing first-principles calculations we demonstrate how charge compensation of a range of defects in the Y-stabilized cubic ZrO_2 leads to Fermi level shifts during flash sintering, thereby accelerating cation migration for fast mass transport, Fig. 3. The charge (q) transition of Zr vacancy, V_{Zr}^q , reduces its bulk diffusion barrier by 2 eV, in V_{Zr}^{-4} state during flash, relative to V_{Zr}^0 before flash current surges. The charge transition $0 \rightarrow -4$ is triggered by the charge equilibration of nonstoichiometric defects to a specific Fermi level. The presence of aliovalent substituent Y_{Zr} as electron acceptor favors V_{Zr}^0 before flash whereas excessive oxygen vacancies V_O , thermally generated by “exhaling” some crystal-body oxygen at flash sintering onset, upshift the Fermi level, and thus bring about V_{Zr}^{-4} as a thermodynamic ground state. The proposed mechanism of Fermi-level mediated cation diffusion for YSZ is generalized to other flash-sintered ceramics and has considerable bearing on the general theory of flash sintering techniques in oxide ceramics.

Future Plans

Our plans are subject to change, to reflect the dynamic nature of the field. Even in the near term, we have already added exploration of mechanisms of flash-sintering in the class of ceramics of high contemporary interest (suffice to mention the USTC). Building on already revealed feedback loop (involving chemical reactions modulating the Fermi level which in turn controls the charge state and thus diffusive mobility of the key ions), we plan to immediately continue and try to detail and customize this mechanism for other ceramic materials, not only insulating like YSZ but possibly gapless metallic, which appears challenging.

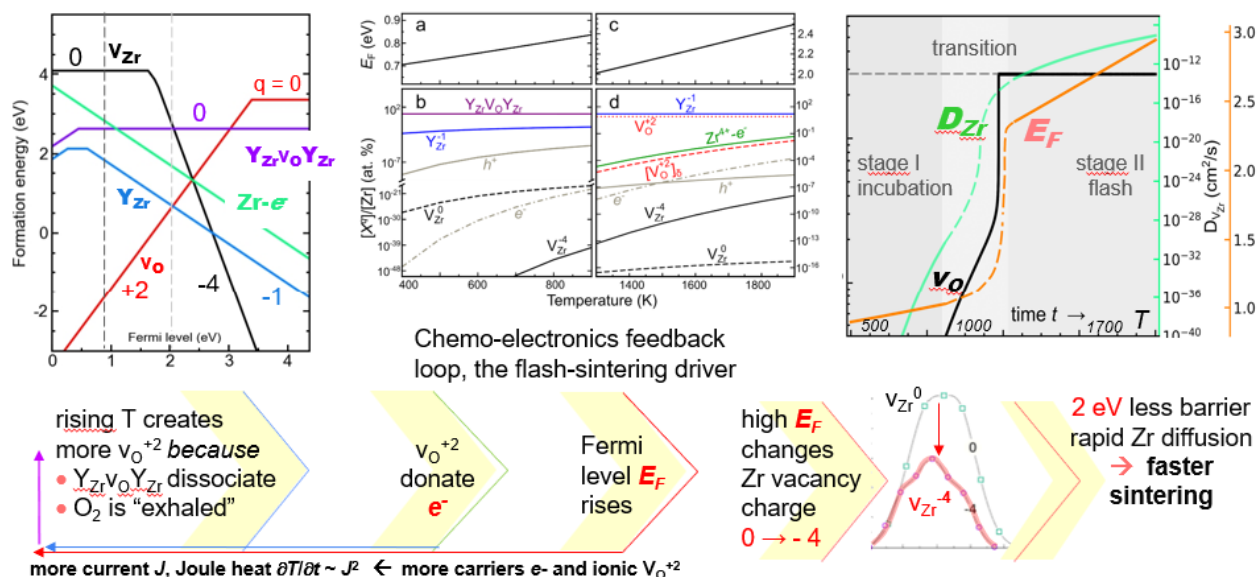


Figure 3. Feedback loop of chemistry-electronics, driving the flash-sintering in semiconductor ceramics YSZ: $Y_xZr_{1-x}O_{2-x/2}$. Panels shown are: Top left, formation energy $E_f[X^q]$ versus E_F for point defects X^q (only segments with the lowest formation energy for different charge-states). Top middle, computed (a, c) Fermi level, E_F , and (b, d) defect concentrations $[X^q]$ from charge neutrality condition, in stage I (a, b) and stage II (c, d) of flash sintering. Only defect concentrations of interest are shown. Top-right, the V_{Zr} diffusion coefficient D_{VZr} , the Fermi level E_F , and the concentration of mobile oxygen vacancies V_O contributing to the conductivity throughout the flash sintering. The background shading makes the key stages as labeled. The dashed lines are guides to the eye. Unpublished work [iv].

We remain committed to the theme of more automated, algorithmic search for the reaction paths, mostly in the gas phase (solid $\rightarrow$ gas $\rightarrow$ solid) in the typical CVD processes of 2D materials synthesis. Although some progress is made already, we have not reached the “show case” stage to report yet, but this line of work is actively ongoing. Specific materials case-studies will complete the 2D-magnetic FeTe. Further attempt will be detailing the mechanisms of 2D perovskites synthesis, following initial success in experiments, but structurally challenging for a atomistic kinetic scheme. Recent spike of interest in nano-diamond, as a host for SPE defects like NV centers for quantum computing. Topochemistry of diamane formation (from bi- or few-layer graphene, [vi]) is to be explored: reaction front formation and propagation, local nucleating

pressure requirements, possibly combinations into C-BN hybrids may open more exciting opportunities and guide experiments.

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Twisted oxide membrane interface by local atomic registry design

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Keywords: Thin Film Synthesis, Quantum Heterostructures, Heterointerfaces, Superconductivity

Program Scope

Quantum materials such as unconventional superconductors, interfacial 2D electron gases (2DEGs), and multiferroics have been fertile ground for new discoveries. We develop novel synthesis routes to create a new generation of epitaxial quantum thin film and membrane heterostructures for study of fundamental science. These films can be of comparable or higher quality than available bulk single crystals, but more importantly film deposition conditions can be maintained far from equilibrium, so that metastable phases (nonexistent in nature) can be obtained through epitaxial stabilization. But these novel systems are sensitive to constraints of thin film heterostructures, including interaction with the substrate, the difficulty in controlling stoichiometry and point defects, and the challenge of forming atomically perfect interfaces.

Our goal is to design substrate interactions, control point defects and stoichiometry, and to fabricate atomically perfect interfaces and single crystal free standing membranes to reveal new phenomena and discover fundamental intrinsic properties of quantum materials by leveraging dimensionality, anisotropy, and electronic correlations. We have developed a unique free-standing oxide stacked membrane fabrication technique to address these challenges, which can also apply large dynamic strain through a piezoelectric layer. We control stoichiometry and point defects through a Hybrid Pulsed Laser Deposition (HPLD), and have begun to understand a route to new discoveries through control of highly perfect and defect free films and heterostructures.

The **thrusters** of the proposed new work expand into new materials systems:

Fabrication of Novel Quantum Material Platforms

Novel Hybrid PLD Synthesis Route – We continue to develop hybrid PLD, in particular for Nb doping of $KTaO_3$ (KTO). We have demonstrated that the ferroelectric quantum critical point can be controlled by Nb doping and strain, possible only with thin films. Hybrid PLD is seemingly the only approach to synthesize high-quality KTO thin film membranes.

Complex oxide membranes We are developing a registry design synthesis approach for twisted heterostructures expanding the landscape of quantum heteromaterials. This new approach assembles complex oxide and nitride membranes into twisted heterostructures.

Fundamental Science of Novel Quantum Materials Platform

LaAlO₃/KTaO₃ interface superconductivity – We propose to control the KTO carrier concentration with Nb doping and electrostatic gating to move the system toward the quantum critical point, enhancing superconductivity. We will also use dynamic strain of KTO membranes to understand the role of the quantum critical point in KTO superconductivity.

Strain controlled twisted oxide membranes heterostructures - building on our discovery of 2D charge configurations at SrTiO₃ (STO) moiré interfaces, we investigate structural, electronic, and magnetic phenomena in different types of complex oxide moiré heterostructures including 2D charge localization, structured 2D polarization-vortex crystals, and topological spin textures at twisted oxide interfaces in heterostructures assembled from freestanding membranes with a relative twist around their crystalline axes.

Ba(Pb_xBi_{1-x})O₃ superconducting films and membranes with strong spin-orbit coupling –We have shown that BPBO shows strong spintronic effects as well as high-temperature superconductivity.

Recent Progress The interplay of lattice-orbital-charge in strongly correlated oxides has hosted a plethora of exotic quantum phases and physical properties. Even though stacked heterostructures of freestanding oxide twisted membranes can provide an extended pathway regarding moiré engineering with local lattice control, research on lattice-driven electronic structural modulations of twisted oxide bilayers remains unexplored. We have developed synthesis routes for epitaxial thin-film oxide freestanding membranes and their controlled-twist assembly into layered heterostructures and made atomic scale measurements of the atomically clean, high-quality interfaces necessary to establish exotic moiré phenomena¹.

SrTiO₃ twisted membrane heterostructures We constructed a twisted bilayer system using freestanding SrTiO₃ and adapt STEM and EELS as a proper toolset to investigate lattice-electron correlation

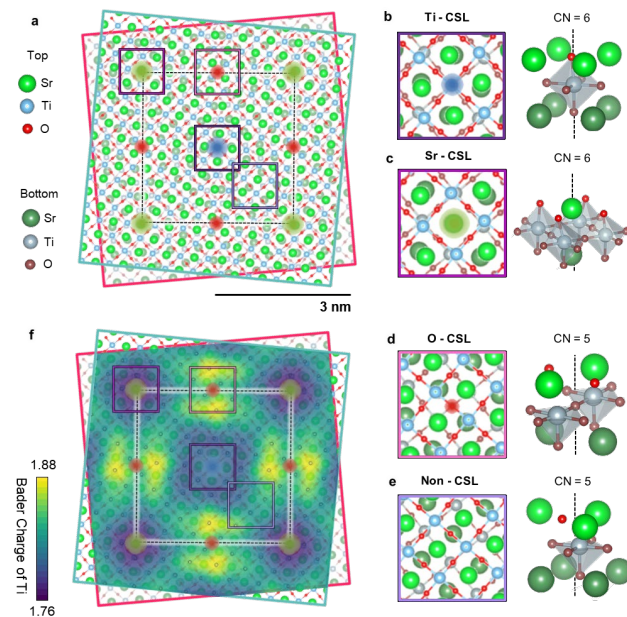


Figure 1 | Self-mediated moiré electronic lattice. **a**, Schematic representation of commensurate moiré lattice of 10.4° twisted STO bilayers under Σ 61 CSL boundary. The white dashed box represents a moiré supercell and CSL components are highlighted as violet (Sr), dark violet (Ti), red (O), pink (Non) color squares in

at the moiré interface. We found theoretical and experimental evidence of locally and periodically reconstructed electronic structure under the coincidence site lattice (CSL) condition, as well as of directly coupled interfacial atomic geometries. The moiré charge localizations accompany the emergence of localized states, and bandwidths controlled by atomic reconstructions, determined by the twist angle relative to coincident lattice values. Our work gives a novel insight into interfacial phenomena at the twisted interface and opens pathways to discovering new moiré-electronic properties and functionalities.

For example, we designed a SrTiO₃ (STO) membrane bilayer with a twist angle of 10.4° (Σ 61) and a 3.04 nm periodic moiré supercell (Fig. 1a). The oxide bilayer has the stoichiometric interfacial geometry terminated by an SrO plane at top membrane and TiO₂ plane at the bottom membrane, respectively. The three non-equivalent atoms in STO form three unique CSLs, where Sr, Ti, and O align in columns at different commensurate points within the moiré cell, in addition to an incommensurate point (non-CSL), as shown in Fig. 1a.

At Ti-CSL points, four Sr atoms surround the Ti ion in the upper and lower layers, replicating the Ti-O octahedral structure characteristic of bulk STO at the interface (Fig. 1b). Similarly, the Ti-O polyhedral structure around Sr-CSL sites form octahedral structures where the Ti ion coordinates with six oxygen atoms (Fig. 1c). Since both types of cation-centered CSLs exhibit minimal structural differences at the interface, there is little change in Ti oxidation states. However atomic rearrangements at some local CSL structures can exceed the limits for octahedral coordination, leading to different properties. In our case, this leads to a lower coordination number (CN), changing the charge state of Ti. For instance, at the O-CSL point centered around a corner-sharing oxygen atom the oxygen atom at the interfacial Ti-O polyhedron remains 5-fold coordinated due to the absence of a structural connection with the SrO layer in the top STO (Fig. 1d). As a result, this O-CSL point exhibits a relatively low coordination number CN = 5, and the Ti-O polyhedron in non-CSL structure with atomically staggered distributions also coordinates with only five oxygen atoms (Fig. 1e).

We have the ability to create twisted (in-plane rotation) and tilted (different crystalline orientation) membrane heterostructures. The delicate balance in the couplings among structural symmetry, electronic properties, and spin configurations in modern complex materials positions twist and tilt interactions across interfaces as a natural knob to dynamically control and design functional thin-film properties.

In addition, new properties can be strain-activated by utilizing an electrically controlled piezoelectric layer. However, the traditional growth techniques of such epitaxial thin-film heterostructures are challenged by the limited range of functional materials compatible with growth on piezoelectric layers, the in-plane strain-restricting clamping by growth substrates, and the limited accessible strain configurations in piezoelectric materials.

Our recent advances allow us to synthesize epitaxial thin film functional membranes free from substrate clamping and assemble them into piezoelectric activated membrane heterostructures, overcoming these limitations. This ability to synthesize heterostructures with incompatible structure and lattice constant, and generate new properties with designed dynamic strains provides pathways to new functionalities.

We employ a sacrificial layer method, to create membranes by releasing epitaxial films from their growth substrate (Fig. 2a). Fig. 2b shows a schematic of the instrument we have created to controllably assemble functional membranes into twisted heterostructures. One membrane is twisted with a controllable rotation, while the other is assembled into place with a micromanipulator creating a twisted heterostructure, as shown in Fig. 2c. We have demonstrated a precise twist angle control and successfully assembled twisted membranes of SrTiO_3 , ferroelectric BaTiO_3 , and ferromagnetic SrRuO_3 and LaSrMnO_3 .

Our preliminary experimental results on twisted membrane assembled heterostructures are intriguing, showing their excellent structural quality and unexpected electronic properties.

Fig. 3 shows results of characterization for a fabricated 10.4° -twisted SrTiO_3 bilayer with a 5 nm thick SrTiO_3 membrane. Our depth sectioning-based TEM method, allowing selective

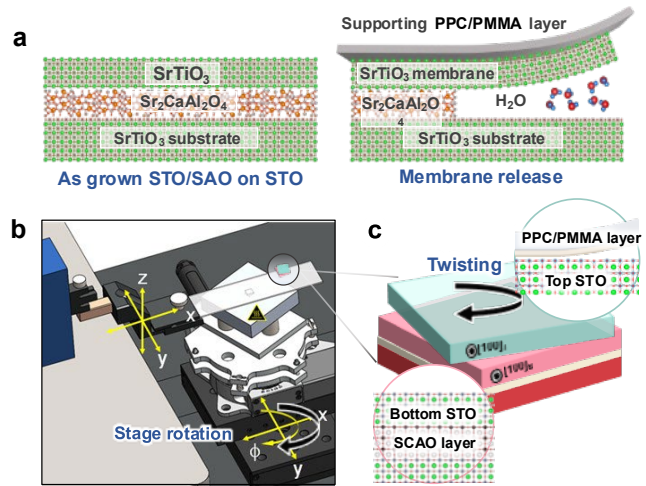


Fig. 2 (a) Fabrication of twisted moiré heterostructure of SrTiO_3 membranes using a water soluble $\text{Sr}_2\text{CaAl}_2\text{O}_6$. (b) Schematic of a manipulator for fabrication of twisted bilayers. (c) Schematic of a twisted SrTiO_3 bilayer.

imaging of depth-dependent SrTiO_3 atomic planes across the bilayer (Fig. 3a), clearly resolves the moiré periodic structure at the twisted interface (Fig. 3b).

The observed atomic structure is in excellent agreement with our model (Fig. 3c). Moreover, using depth-resolved electron energy loss spectroscopy (EELS), we observe a modulated e_g-t_{2g} energy peak difference in a Ti-L₃ edge spectrum indicating electronic reconstruction within the moiré cell.

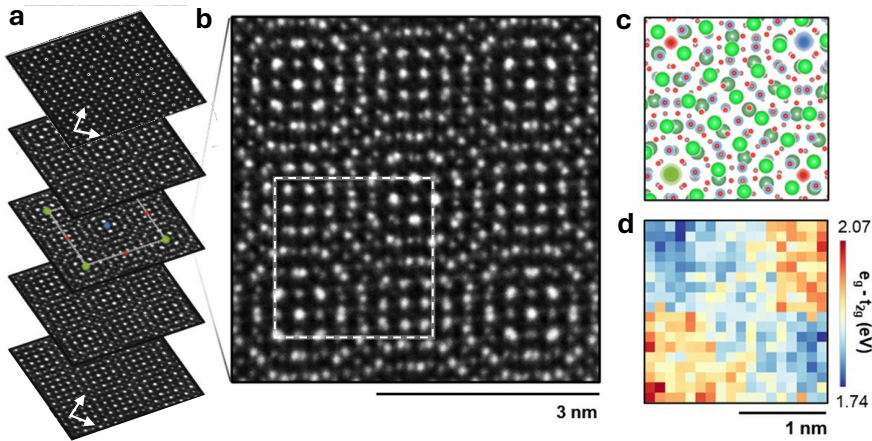


Fig. 3 (a) A focal series of HAADF-STEM images STO planes from top to bottom in a 10.4°-twisted STO bilayer. The white arrows indicate the in-plane orientations of the top and bottom STO layers. The components of moiré supercell are highlighted as green (Sr-), blue (Ti-), and red (O-) overlapped circles. (b) Atomic-scale HAADF image of moiré supercell for 10.4°-twisted STO bilayer. (c,d) Atomic structure (c) and mapping of the e_g-t_{2g} energy peak difference in a Ti-L₃ edge EEL spectrum for a region in (b) outlined by a dashed

Our theoretical modeling signifies clear correlation of the EELS mapping with our calculated Bader charge, demonstrating that the electronic behavior at the twisted interface is controlled by the local atomic registry.

This observation

demonstrates how the strong interlayer bonding in oxide moiré heterostructures can lead to pronounced modulation of electronic properties

through variations in atomic registry, potentially enabling new functionalities through enhanced coupling between structural and electronic degrees of freedom.

Future Plans

(1) Strain controlled twisted oxide membranes heterostructures,

The delicate balance in the couplings among structural symmetry, electronic properties, and spin configurations in modern complex materials positions twist and tilt interactions across interfaces as a natural knob to dynamically control and design functional thin-film properties. We plan to investigate structural, electronic, and magnetic phenomena in different types of complex oxide moiré heterostructures including 2D charge localization, structured 2D polarization-vortex crystals, topological spin textures at twisted oxide interfaces.

(2) KTaO_3 interface superconductivity

We plan to use Hybrid PLD for growth of electronic grade KTaO_3 thin films, $\text{LaAlO}_3/\text{KTaO}_3$ heterostructures of different crystallographic orientations, and KTaO_3 membrane films and heterostructures for fundamental explanations of the mechanism of recently observed

superconductivity. We will use electrostatic gating layer to vary the carrier concentration and Nb doping to approach the ferroelectric quantum critical point of KTO. This task will be achieved by employing $\text{Ba}_{1-x}\text{Sr}_x\text{RuO}_3$ sacrificial layer, during the growth of KTaO_3 (001) and (111) heterostructures.

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Selective Interface Synthesis: Directing Atomic Structure at Defective Interfaces

Alex B. F. Martinson and Cong Liu (Argonne National Laboratory); Adam S. Hock (Illinois Institute of Technology)

Keywords: atomic layer deposition, interfaces, defect repair, targeted synthesis, calorimetry

Research Scope

We pursue a new approach to interface synthesis to make possible non-epitaxial, polycrystalline, and amorphous material interfaces that exhibit uniform and predictable electronic properties. We develop and leverage the science of selective interface reactions (SIRs, **Figure 1**), an atomic layer deposition (ALD)-based approach in which vapor-phase surface reactions are chemically tailored to react only at undesirable defect sites. A precision approach to interface synthesis, based on control of well-defined atom *connectivity*, not crystallinity, targets undesirable atomic arrangements to enable selective repair of electronically defective surface sites. Simultaneously we develop and leverage ALD calorimetry as a uniquely sensitive, time-resolved measurement of surface reaction heat to test computationally-predicted synthesis mechanisms. The outcomes are design rules and advanced characterization methods that enable the synthesis of heterogeneous interfaces that forgo epitaxial perfection yet can still exhibit homogenous electronic properties.

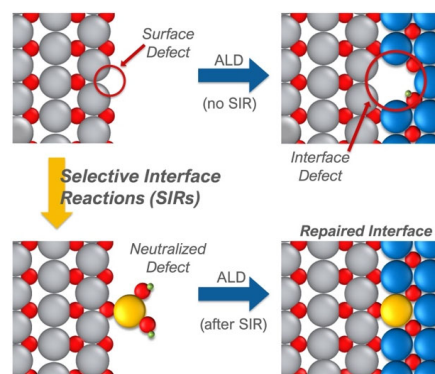


Figure 1. Idealized schematic of an SIR tailored to a defective surface site to repair an undesirable electronic state.

Recent Progress

We have investigated the surface chemistry of SnO_2 facets to evaluate their potential for site-selective ALD using the selective hydration strategy. Despite the structural similarity of rutile SnO_2 and TiO_2 , we computationally predict a difference in the hydration temperature of $>200^\circ\text{C}$.^{1,2} We further probed the surface reconstruction and site-dependent hydration of r-cut Fe_2O_3 with scanning tunneling microscopy (STM) to reveal hydration kinetics under ultra-high vacuum. We also probed the thermodynamics of MgO surface reactions with ALD calorimetry and compare to a detailed computational model that predicts both enthalpy and entropy drive ALD.³ The temperature-dependent and facet-specific stretching frequency and stability of surface hydroxyls on faceted In_2O_3 and TiO_2 nanoparticles was investigated via in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). We additionally investigated the ALD coating of and precision ellipsometric measurement on ultrathin oxide films for quantum-relevant surface passivation⁴ and eliminate dark electron spin noise below the detection limit.

Site-Specific Surface Reactivity of SnO_2 and Effects of Surface Reaction Byproducts. Site-selective ALD using the selective surface hydration strategy requires detailed understanding of

site-specific hydration. The thermodynamics of hydration for each SnO₂ facet is examined in analogy to previous studies of TiO₂ and In₂O₃.^{1,2} Despite the structural similarity of rutile SnO₂ and TiO₂, we computationally predicted a striking difference in the hydration temperature of SnO₂, **Figure 2**. Furthermore, stoichiometric and defect free (001), (101), and (110) SnO₂ facets were predicted to react with TMA and DMAI monomers, even in the dehydrated state. This excludes both precursors from site-selective ALD processing on these SnO₂ facets at temperatures above which the monomers exist in the gas phase. The same SnO₂ facets are also predicted to be heavily hydrated at most ALD-relevant temperatures, further excluding site-selective growth with a selective hydration strategy. However, a narrow window for oxygen vacancy selectivity with DMAI is predicted between 264 and 347 °C on SnO₂ (100), opening the possibility of site-selective growth at higher ALD growth temperatures. *In situ* ellipsometric studies of ALD Al₂O₃ nucleation confirm that rapid (unselective) nucleation occurs on polycrystalline SnO₂ at 150 °C as expected. Rapid nucleation of the DMAI/H₂O ALD process on hydrated SnO₂ at 150 °C stands in strong contrast to inhibited growth on isostructural rutile TiO₂ (110), the stoichiometric surface of which is already dehydrated at 150 °C. The demonstrated agreement between computation and experiment in isostructural metal oxides confirms the utility of first-principle DFT calculations to predict site-selectivity of ALD processes with molecular level precision.

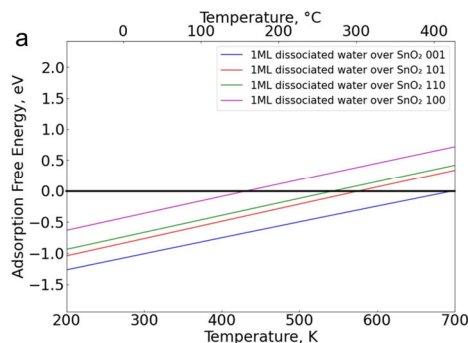


Figure 2. Adsorption free energy of 1 ML of dissociated water on rutile SnO₂ facets as a function of temperature.

Site-selective ALD processes provide an opportunity for the detailed investigation of uniform surface sites with atomistic accuracy. However, the effects of the ALD reaction byproducts on nucleation and growth mechanisms are rarely considered. Reaction byproducts produced during ALD result in unintentional and variable exposure to small molecules, which may alter the site-specific mechanistic pathways for ALD nucleation. Wide variability in the nucleation density of ALD Al₂O₃ on oxidized TiO₂ (110) single crystals is significantly reduced by intentional pretreatment with one of the reaction byproducts – isopropanol.⁵ The first cycle of ALD growth is observed to be an early and strong indicator of the ALD nucleation density, substantiating previously reported nucleation models that rely upon this largely untested assumption. Rapid and nondestructive small molecule pretreatments, including isopropanol and water, are also observed to be a probe of surface defects, including oxygen vacancies, that are correlated with site-selective ALD nucleation. The nonidealities associated with reaction byproduct production during ALD inspire novel surface pretreatment methods that improve reproducibility and may serve to more efficiently probe defects/minority sites surfaces.

Testing Computationally-Predicted Surface Synthesis Mechanisms. The realities of atomic layer deposition (ALD) surface reactions often deviate from the simple ligand exchange frequently used to illustrate the technique. A detailed understanding of these reactions is necessary to develop

greater surface synthetic control including chemical selectivity for patterning or to target defects. We bridge the gap between idealized surface reaction models and realistic surfaces by measuring the heat released during each MgO atomic layer deposition (ALD) reaction and comparing to computational models.³ A direct experimental measurement of ALD reaction heat under standard ALD operating conditions, combined with first-principles models that account for the addition and

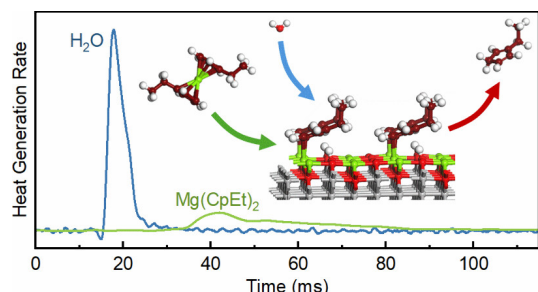


Figure 3. Real-time experimental heat measured from ALD reaction of water and $\text{Mg}(\text{CpEt})_2$. Inset: Hypothetical reaction mechanism and optimized structure of reactants, surface reaction intermediates, and byproducts.

coordination of multiple precursor molecules, helps to build our understanding of the complexity and nonuniformity of saturating ALD reactions on realistic surfaces. The thermodynamics of surface reactions relevant to MgO ALD were investigated using pyroelectric calorimetry to measure the time-resolved heat generation for alternating $\text{Mg}(\text{CpEt})_2$ and H_2O reactions, respectively, **Figure 3**. The total reaction heat closely matches the standard reaction enthalpy for bulk MgO, supplemented with first-principles molecular calculations. First-principles models further reveal

that while simple ligand exchange is favorable during surface reactions, the required increase in Mg-coordination number from two in the precursor to six in bulk MgO requires additional coverage-dependent surface reactions, which depend on the availability and stability of proximal surface hydroxyls. Analysis of possible reaction steps was investigated with molecular precursor reactions on periodic slab models. We note that while there is a thermodynamic driving force for the removal of both CpEt ligands during the $\text{Mg}(\text{CpEt})_2$ surface reaction on a hydroxylated surface, in the case when one ligand remains, the reaction of this second ligand becomes less favorable when precursors react in close vicinity to each other due to the availability and stability of different surface hydroxyls. By modeling the addition of multiple precursor molecules, we reveal the critical role of entropy in driving surface reactions and how the average reaction thermodynamics change as an ALD surface reaction approaches saturation.

Synthesis and Processing Science of Quantum Information Material Surfaces. Surface termination and interfacial interactions are critical for advanced solid-state quantum applications. We demonstrate that atomic layer deposition (ALD) can both provide valuable insight on the chemical environment of the surface, having sufficient sensitivity to distinguish between the common diamond (001) surface termination types and passivate these interfaces as desired. We uniquely combine deterministic synthesis of near surface NV centers in diamond, analytical ALD, and in-situ ellipsometry to demonstrate the applicability of ALD to both study and control the surface of (001) diamond. Specifically, we investigated the sensitivity of ALD nucleation as a function of quantum-relevant diamond surface termination schemes.⁴ In addition, we investigate how ALD can be used to passivate diamond surfaces, paving the way for long-term stability and spin coherence studies in the future. We selected diamond substrates exhibiting both smooth and anomalously rough surfaces to probe the effect of morphology on ALD nucleation. High resolution

in situ spectroscopic ellipsometry, **Figure 4**, reveals the surface reaction with sub-angstrom resolution, to evaluate the nucleation of an ALD Al_2O_3 process as a function of different ex and in situ treatments to the smooth diamond surface. We demonstrate clear distinguishability between the commonly reported diamond surface termination schemes via their nucleation susceptibility during Al_2O_3 ALD. For example, in situ water dosing and high vacuum annealing provided the most favorable environment for nucleation of dimethylaluminum isopropoxide and water ALD. Hydrogen termination passivated both smooth and rough surfaces while triacid cleaning passivated the smooth surface only, with striking effectiveness. This work paves the way for a facile termination characterization methodology and quantum-relevant surface passivation.

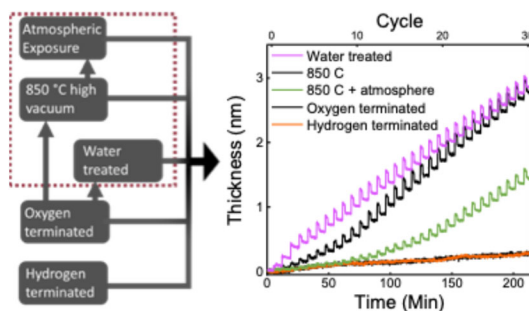


Figure 4. (Left) Workflow of ex situ and in situ (in red box) surface treatments. (Right) In situ ellipsometric measurements of the thickness of Al_2O_3 on the smooth diamond surface.

Future Plans

Quantitative Microkinetic Modeling of ALD. We will complete the assembly and benchmarking of an ALD reactor designed for isothermal operation and plug flow precursor delivery. An array of calorimeters will be installed and compared to reactor scale simulations to realize quantitative microkinetic modeling of ALD processes.

Site-Specific Synthesis at Interfaces for Quantum Science. Precision oxide coatings at diamond-air interfaces will be evaluated for spin noise and coherence times of proximal NV centers. Computational models will elucidate the surface chemistry that governs nucleation.

Defect Repair at R-cut Hematite Surfaces. We will probe the effect of Fe_2O_3 surface defects on excited state lifetimes and electrochemically active traps density. Multiple SIRs targeted at surface defects will be evaluated for their effectiveness to ameliorate distinct defect sites.

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Extending the reach and breadth of nanofabrication to atomic-scale precision in three dimensions using area-selective and self-limited deposition processes

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Keywords: Atomic layer deposition, Area-selective deposition, Competitive interactions, Nanofabrication, Density functional theory

Research Scope

Area-selective deposition (ASD) has the potential to enable next-generation manufacturing and patterning at the single nm nodes and beyond, with direct applications in the nanofabrication of functional layers such as gate dielectrics, metal contacts, and capping/barrier layers. ASD will also play an important role in the increasingly three-dimensional nature of device features. We use a tightly integrated combination of theory and experiment to elucidate the fundamental mechanisms producing selectivity as well as the mechanisms underlying the loss of selectivity. Essential to our strategy is the deliberate and simultaneous introduction of multiple chemical species, such that competition can occur between the species. Interactions between multiple species introduces challenges, but also provides opportunities that are not present with other approaches.

In this Extended Abstract we describe our results aimed at developing the fundamental framework behind the use of small molecules to achieve ASD, examining the deposition of Al_2O_3 on a variety of substrates including SiO_2 , Cu and Co. The overall approach is to examine explicitly the effects of the choice of the precursor, the co-reactant, and the selectivity directing species, including how the latter species are introduced, and how many. We have examined 2 precursors, 9 co-reactants, 2 blocking molecules and 1 co-adsorbate. We have also examined the effects of temperature, and dosing strategy, i.e., pre-exposure, co-exposure, and repetitive exposure of the selectivity directing species. We find that proper selection of the precursor, co-reactant, co-adsorbate and blocking molecule leads to superior results concerning selectivity.

Recent Progress

Effect of the co-reactant on an ALD process and the underlying growth surface. In this work, we examined the ALD of Al_2O_3 using trimethylaluminum, $\text{Al}(\text{CH}_3)_3$ (TMA), as the precursor and *t*-BuOH and H_2O as the co-reactants, focusing on the effects of the latter on both the ALD process and the possible modification of the underlying substrate [P-1]. We employed a quartz-crystal microbalance (QCM) to monitor ALD *in situ* and in real-time, and the deposited thin films were characterized using X-ray photoelectron spectroscopy, spectroscopic ellipsometry, X-ray reflectivity, and atomic force microscopy. We found that thin films deposited using *t*-BuOH exhibit comparable properties to those deposited using H_2O , including stoichiometry (O/Al ratio, from XPS), density (from XRR), and the level of impurities (C, from XPS). We also found that growth with *t*-BuOH has a reduced temperature window—we observed growth at $T = 285^\circ\text{C}$, but

not at 120 °C. Finally, independent of the co-reactant, we found that ALD of Al_2O_3 on Cu did not result in oxidation of the underlying substrate. On Co, in contrast, only the process using *t*-BuOH (at $T = 285$ °C) as the co-reactant results in a clean, non-oxidized Co| Al_2O_3 interface.

ALD of Al_2O_3 with alternative co-reactants. As described in the previous section, we have observed that Al_2O_3 can be deposited using TMA as the precursor and *t*-BuOH as the co-reactant. There are reports concerning the growth of oxides using alcohols such as ethanol, $\text{CH}_3\text{CH}_2\text{OH}$, as co-reactants [1-4]. Thus, we asked the question: can these and other alcohols be used effectively as co-reactants to deposit Al_2O_3 with TMA as the co-reactant? Contrary to some published reports [1,3], we have found that *only the tertiary alcohols lead to steady growth with TMA*, and that growth only occurs at 285 °C, not at 120 °C. In Fig. 1 we present results from QCM for ALD with TMA and *n*-propanol, 2-butanol, and 2-methyl-2-butanol, i.e., a primary, secondary and tertiary alcohol. As may be seen, only the tertiary alcohol gives steady growth. Similar results were observed with the five other alcohols we have examined.

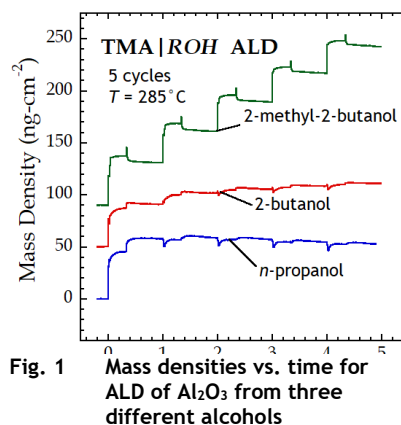


Fig. 1

We performed a series of advanced DFT calculations employing state-of-the-art dispersion-inclusive hybrid functionals [P-2] to shed light on these observations. These calculations show that the critical intermediate involves an alcohol interacting with a bound alkoxy formed by the same alcohol. This intermediate then decomposes to form a bound -OH(a)—which allows ALD to proceed—and releases both an alcohol and alkene into the gas phase. In Fig. 2, we plot the computed rate coefficients for the rate-limiting step that forms a bound -OH(a) for a series of alcohols. These results support the observation that the reaction rates are only sufficiently large for the tertiary alcohols at $T = 285$ °C (and H_2O at both 120 °C and 285 °C).

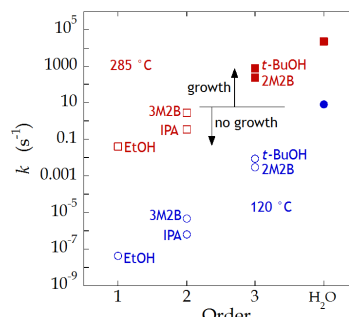


Fig. 2

Effect of the precursor on an ALD process. In this work, we examined the ALD of Al_2O_3 using two thin film precursors: TMA and a heteroleptic Al-amine precursor, $\text{Al}(\text{N}(\text{CH}_3)_2)_2(\text{-N}(\text{C}_2\text{H}_5)\text{-C}_2\text{H}_4\text{-N}(\text{C}_2\text{H}_5)_2)$, where the latter ligand is a bidentate diamine with one N covalently bound to Al and the other N interacting via a dative bond with the Al center. We have dubbed this molecule BDMADA-Al [P-3]. Thin films can be deposited using H_2O as the co-reactant at both $T = 120$ and 285 °C, similar to when TMA is the precursor, and these thin films exhibit comparable properties to those using TMA, including stoichiometry (O/Al ratio, from XPS), density (from XRR), and level of impurities (C, from XPS). Using BDMADA-Al as the precursor and *t*-BuOH as the co-reactant, we observed steady growth at $T = 285$ °C, while growth quickly plateaus at $T = 120$ °C, again similar to what is observed with TMA. Examining results from QCM for each half cycle of ALD we found that our results are consistent with the retention of the dimethylamido (DMA)

ligands, $-\text{N}(\text{CH}_3)_2$. Interestingly, our quantum chemistry calculations show that the (bidentate) diamine ligand is the most strongly bound, and the dimethylamido ligands the weakest [P-4].

Effect of co-adsorbates on the ALD of Al_2O_3 on the non-growth surface. We also examined the effect of two species, (dimethylamino)trimethylsilane (DMATMS), $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$, and octadecyltrichlorosilane (ODTS), $\text{Cl}_3\text{Si}(\text{CH}_2)_{17}\text{CH}_3$, on the ALD of Al_2O_3 on SiO_2 [P-5]. Here, SiO_2 is the non-growth surface (NGS), and metals such as Cu and Co are the growth surface (GS). An important difference between these two blocking molecules is that DMATMS can be delivered in the gas phase [5], while ODTS is best delivered in the solution phase. This has consequences on their use in high volume manufacturing, where vapor phase delivery is strongly favored. In this work, in addition to these two blocking molecules, we have examined two precursors (TMA and BDMADA-Al), two co-reactants (H_2O and $t\text{-BuOH}$), and one co-adsorbate (ROH). We have also examined the effects of temperature, and dosing strategy, i.e., pre-exposure, co-exposure, and repetitive exposure of the selectivity directing species. All told, these represent 20 unique combinations that could block and/or attenuate growth of Al_2O_3 on SiO_2 . Our results are too extensive to completely cover here, so we shall stick to the major conclusions.

Molecular size matters. First, we begin with the effect of the size of the co-adsorbate/blocking molecule. Adsorption of these molecules will be limited to a monolayer, hence their ability to form a tightly packed layer is as important, if not more so, than their size. ODTS, when formed in the solution phase can form dense, highly packed layers. For a fixed set of conditions (ALD chemistry, temperature) we find that ODTS blocks growth more effectively than DMATMS, a result consistent with expectations. Secondly, we consider the size of the precursor, or more importantly, the size of the ligands on TMA ($-\text{CH}_3$ groups) and BDMADA-Al [$-\text{N}(\text{CH}_3)_2$ and the diamine]. We find that BDMADA-Al is more effectively blocked vs. TMA with either blocking molecule at either temperature. Finally, although use of $t\text{-BuOH}$ as a co-reactant is essential to minimize oxidation of the underlying metallic substrate, it does not have great impact concerning the ability to block growth vs. H_2O .

Temperature matters. We have examined the effect of temperature concerning the effectiveness of the blocking layers for all combinations of precursor, co-reactant and blocking molecule. In Fig. 3 we display results from QCM for ALD of Al_2O_3 using TMA and H_2O with ODTS pre-adsorbed on the SiO_2 surface at $T = 120$ and 285°C . We see that temperature has a significant effect on the effectiveness of ODTS—the amount of Al_2O_3 deposited decreased by a factor of ~ 4 by increasing the temperature from 120 to 285°C . We have observed a similar trend with

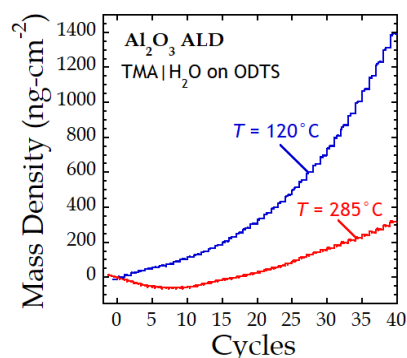


Fig. 3 Mass densities vs. time for ALD of Al_2O_3 using TMA/ H_2O at $T = 120$ and 285°C , where ODTS is pre-adsorbed on SiO_2 .

temperature concerning all of the other combinations of precursor, co-reactant, and blocking molecule.

Dosing strategy matters. Finally, we have considered the effects of different dosing strategies. First we considered repetitive exposures of the blocking molecule (an “ABC” process) vs. a single pre-exposure. In Fig. 4 we display results from QCM for Al_2O_3 ALD using TMA and *t*-BuOH at $T = 285^\circ\text{C}$. Comparing results from a single pre-exposure of the SiO_2 surface to DMATMS and an experiment where DMATMS is both pre-exposed and dosed during each ALD cycle, we find that for all three processes involving BDMADA-Al (H_2O at $T = 120$ and 285°C , *t*-BuOH at $T = 285^\circ\text{C}$) that repetitive exposure produces superior results in all cases. A final important process we have examined involved co-exposure of a co-adsorbate and the precursor in an “ABC” process, involving DMATMS as the blocking molecule. Using BDMADA-Al and H_2O at $T = 120^\circ\text{C}$ we find that growth of Al_2O_3 on SiO_2 can be blocked more effectively than any other combination using DMATMS, and is indistinguishable from the result with BDMADA-Al with ODTs as the blocking layer at $T = 285^\circ\text{C}$. This is an important result as this process is all vapor phase.

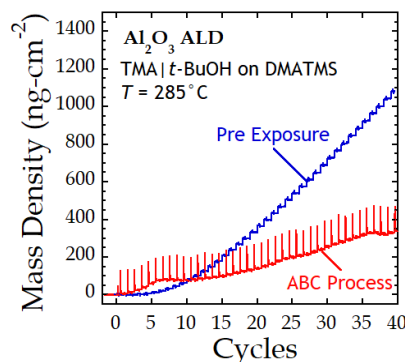


Fig. 4 Mass densities vs. time for ALD of Al_2O_3 using TMA | *t*-BuOH at $T = 285^\circ\text{C}$, where DMATMS is only pre-adsorbed vs. sequentially dosed on SiO_2 .

Future Plans

Year 1. Metal-on-metal (MoM) area-selective deposition. We will focus on the deposition of thin films of Mo, but we will also consider metals such as Ru and Nb.

Year 2. Dielectric-on-dielectric (DoD) area-selective deposition. We will focus on deposition of thin films of SiO_2 , but we will also consider dielectrics such as ZrO_2 and HfO_2 .

Year 3. Having established a better understanding of MoM and DoD processes we will combine these to develop a novel, potentially generic process, anisotropic ALD.

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- [P-3] J. V. Swarup, H.-R. Chuang, J. T. Jensen, J. Gao, A. L. You, and **J. R. Engstrom**, *Non-Pyrophoric Alternative to Trimethylaluminum for the ALD of Al_2O_3* , J. Vac. Sci. Technol. A **43**, 022404 (2025). **Supported by DOE-BES SPS award DE-SC0022059**. 546 article views as of 7/8/2025.
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Focused Electron Beam Induced Processing in Ammonia-Based Liquid Films

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Keywords: Focused Electron Beam Induced Processing (FEBIP); Nanofabrication

Research Scope

Synthesis of structures at the nano- to the micro-scale has become an area of great importance in nanoengineering. To enable direct-write 3D fabrication of topologically complex nanostructures, Focused Electron Beam Induced Processing (FEBIP) method has been developed. FEBIP is a class of techniques leveraging directed delivery of energetic electrons to facilitate localized chemical reactions. FEBIP encompasses two complementary processes: Focused Electron Beam Induced Deposition (FEBID), and Focused Electron Beam Induced Etching (FEBIE). In addition, electron beam mediated processes have been used for doping materials such as boron nitride and graphene. Electron beam irradiation has also shown assist in strain lithography and defect engineering. Although all these FEBIP processes differ in their outcomes, they all utilize the ability of a tightly focused electron beam to locally activate reactions at an interface. The utility of FEBIP has been shown in material science applications including magnetics, plasmonics, nanoelectronics, and optics [1,2]. The FEBIP process generally takes place in the vacuum chamber of a Scanning Electron Microscope (SEM). An electron beam acts as a source of focused, high-energy electrons directed to the substrate where they interact with the substrate material and precursor molecules on the substrate surface. Consequently, the selection of precursor phase is an important consideration for FEBIP, as it largely dictates the rate of reaction, final material purity, and achievable spatial resolution [1].

Use of liquid phase precursors for FEBIP (LP-FEBIP) offers higher growth rates and higher purity as compared to gas phase precursors, as well as a broader selection of material chemistries [3]. However, the use of liquid-phase precursors in FEBIP is challenging due to the inherent difficulty of handling liquids within a high-vacuum environment. Liquids are prone to evaporation, freezing, and instability under vacuum, complicating the interactions with the electron beam. With support from the U.S. DOE BES,

we have developed a novel technique, **NanoElectrospray-Assisted Focused Electron Beam Induced Processing (NESA-FEBIP)**, to overcome the limitations associated with liquid-phase precursors in FEBIP [4,5]. In this approach,

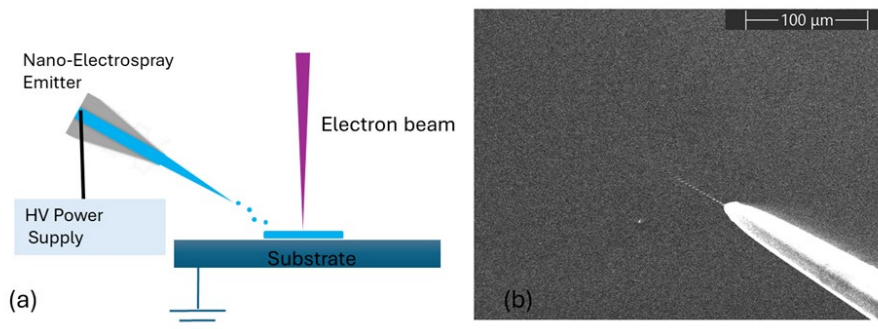


Fig. 1: Nanoelectrospray-assisted liquid delivery (a) An electric field applied to the liquid-filled capillary charges the liquid precursor and electrokinetically generates a nanoelectrospray jet from the emitter toward the grounded substrate (b) High-vacuum SEM micrograph of the nanoelectrospray jet emerging from the emitter

liquid precursors are electrohydrodynamically delivered via a nanoelectrospray emitter, forming an ultrathin free-surface film on the substrate. The thinness of the film allows the focused electron beam to penetrate and initiate deposition or etching reactions directly at the substrate-solution interface, rather than at the liquid-vacuum boundary. This significantly enhances spatial resolution and deposit-substrate adhesion. Fig. 1 (a) illustrates the nanoelectrospray process, in which the liquid jet emerges from a tapered capillary emitter and spreads across the substrate surface. The SEM micrograph of the electrospray jet under operational conditions is shown in Fig. 1 (b), confirming stable jet formation and controlled liquid delivery during electron beam exposure.

Recent Progress

Electrochemical Lensing for Rapid High-Resolution Nanomanufacturing: Electron beam irradiation of aqueous media generates a cascade of radiolytic species: reducing agents such as solvated electrons (e_{sol}^-) and oxidizing agents including hydroxyl radicals ($OH^\bullet$), oxygen (O_2), and hydrogen peroxide (H_2O_2). The local balance between these species controls whether irradiation drives net reduction (deposition) or oxidation (etching). To break the conventional trade-off between growth rate and spatial resolution in liquid phase FEBID, we introduced **electrochemical lensing** by adding ammonia to the aqueous silver nitrate precursor. Ammonia imposes a nonlinearity on the system via two mechanisms: (1) NH_3 binds Ag^+ to form $Ag(NH_3)_2^+$, creating a new reduction pathway whereby H_2O_2 —exclusively an oxidizer in pure water—also reduces $Ag(NH_3)_2$, (2) Both free NH_3 and its radiolytic fragment $NH_2^\bullet$ consume $OH^\bullet$ and O_2 , suppressing oxidation and making the environment more deposition friendly.

To investigate the key pathways driving electrochemical lensing, we carried out a series of reaction-transport simulations

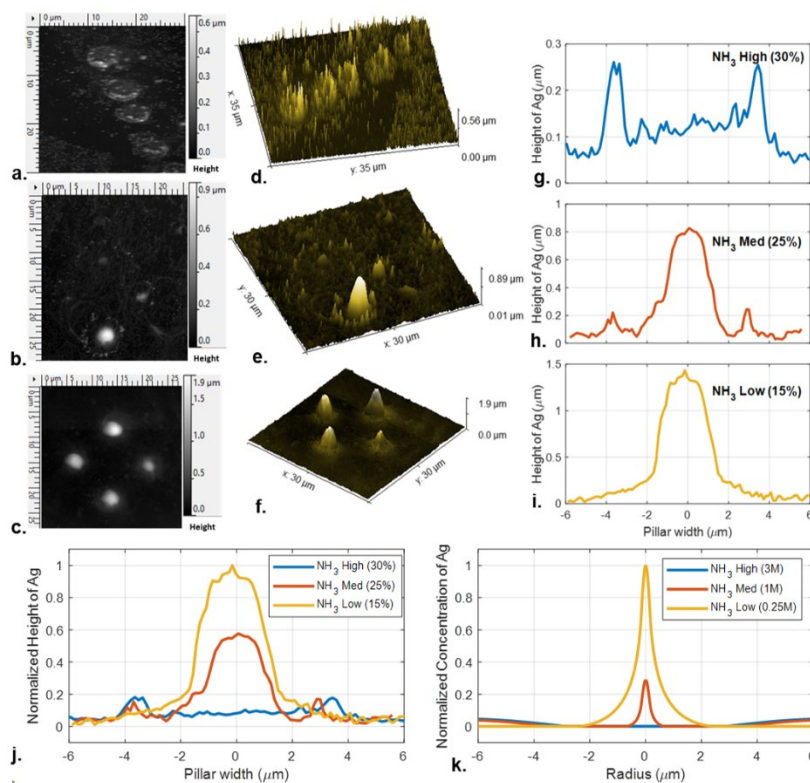


Fig. 2: AFM images of nanostructures from NESA-FEBID using water-ammonia solutions with 250 μM $AgNO_3$ at 30%, 25%, and 15% NH_3 concentrations in top-view 2D (a-c) and 3D (d-f) radial profiles (g-i). Nanostructures are created with 1s 30 kV electron beam in 'spot' mode. Ag growth varies with NH_3 concentration, showing focused near-field growth at 15% NH_3 and increased far-field growth at 25% and 30% NH_3 . Normalized experimentally determined pillar profiles (j) are compared to simulated Ag concentration profiles at varying NH_3 levels (k), showing qualitative agreement and presence of an optimal NH_3 concentrations for focused near-field Ag growth, the signature of the electrochemical lensing.

alongside corroborating NESA-FEBID experiments. In these experiments, a 250 μM AgNO_3 solution was electrosprayed onto the substrate and exposed in ‘spot’ mode to a 30 kV electron beam for 1 s, using water–ammonia solvents at 30 %, 25 %, and 15 % NH_3 stock concentrations. In pure water, no silver pillars form, confirming a highly oxidizing environment. At 15 % NH_3 , narrowly confined deposits appear at the beam impact site, as shown in the top-view AFM image (Fig. 2 (c)) and corresponding 3D profile (Fig. 2 (f)). Increasing NH_3 to 25 % and 30 % slows near-field pillar growth and produces progressively broader far-field deposition, evident in the top-view images Fig. 2 (b, a) and 3D reconstructions, Fig. 2 (e, d). Comparison the normalized experimentally determined pillar heights, Fig. 2 (j), and simulated Ag concentration profiles, Fig. 2 (k) reveals the optimum ammonia concentration for electrochemical lensing, where rapid near-field deposition occurs with negligible far-field growth, enabling high-rate, high-resolution nanopillar fabrication.

Redox-Mediated Copper Etching and Deposition: We further extended the ammonia-based solvent approach to precursor-free electron-beam patterning of copper, revealing that adjusting

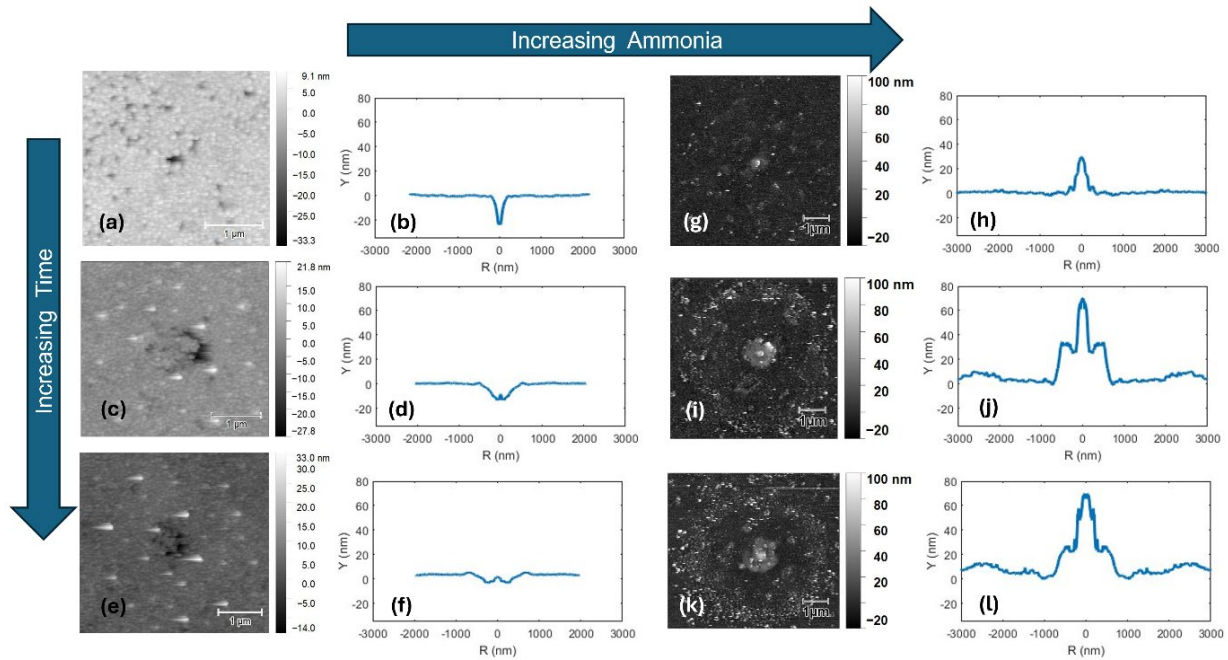


Fig. 3: AFM images and their corresponding angularly averaged height profiles show the evolution of copper nanostructures under different ammonia concentrations and electron-beam irradiation times. (a,b) At low ammonia (5%) and short irradiation (0.5 s), a predominantly oxidizing environment leads to net copper etching. (c,d) Increasing the irradiation time to 1.5 s under the same low ammonia conditions causes widening of the etch via oxidation. The copper ions/ion-complexes formed due to prior oxidation diffuse towards and redeposit in the center at the e-beam impingement spot, forming the characteristic “peak-in-valley” structure. (e,f) A 2.5 s e-beam exposure at same (5%) ammonia concentration further widens the etched region and grows the redeposited peak. (g,h) At higher ammonia concentration (25%), copper is rapidly deposited even at short (0.5 s) irradiation time from the precursor cations released to the solution from the substrate on contact with ammonia, forming a nanopillar (i,j) At 1.5 s e-beam irradiation exposure, stronger reducing conditions and more copper-amine ion complexation drive rapid copper deposition at the center, but with an additional off-center ring formation. (j,k) Extending the irradiation to 2.5 s under high ammonia results in a plateau of the deposit height due to local depletion of copper ions/ion-complexes, slowing further pillar growth.

ammonia concentration can lead to net oxidation (etching) or reduction (deposition). At low ammonia (5%) and short exposure (0.5 s), the oxidizing environment etches the copper surface, removing a shallow pit, Fig. 3 (a,b). After a longer e-beam irradiation, a release and accumulation of deposition precursor cations into the film occurs via oxidation of the surface, increasing the precursor local concentration. Extending irradiation to 1.5 s widens the etch zone via surface oxidation by the diffusing radiolysis species, while also initiating redeposition at the center from reduction of Cu/Cu-complex cation-rich environment, Fig. 3 (c,d). This is consistent with the simulation prediction that higher released cation concentration leads to locally reducing conditions, Fig. 3 (c). Further exposure (2.5 s) amplifies this effect, widening the etched “valley” and growing the central “peak”, Fig. 3 (e,f). Conversely, high ammonia (25%) and short exposure (0.5 s) yield immediate copper deposition due to a large generation of cations in ammonia-rich environment, Fig. 3 (g,h). At 1.5 s, the central pillar grows and there is a creation of a ring-like structure Fig. 3 (i,j), attributable to radial diffusion of solvated electrons and precursor ions in opposite directions. Prolonged e-beam irradiation (2.5 s) plateaus pillar growth due to local precursor depletion by solvated electron reduction, Fig. 3 (k,l).

Future Work

The underlying chemistry, anchored by the pivotal role of ammonia, can prove equally relevant for other precursor species. (1) Identifying various precursor material chemistries with redox behavior modulated by ammonia (and other) solvents that follow similar competitive transport-kinetics pathways towards preferential reduction/deposition or oxidation/etching is an area for further inquiry, (2) exploiting redox kinetics and transport pathways to enable beam-directed deposition of nanoscale heterostructures, and (3) development of droplet-to-deposit (D2D) FEBIP technique for electron-beam-activated NESA-in-flight-droplet nanostructure synthesis.

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Atomic Layer Deposition and Post-synthetic Self-Assembly of Thermally Stable Non-Epitaxial Thin-Film Oxide Surface Nanoionics

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Keywords: Atomic layer deposition, interfaces, surface nanoionics, Non-epitaxial thin films, Elevated temperatures

Research Scope

Nanoionics represent one of the most promising approaches for overcoming the composition-optimized limit of ionic conductors and increasing the ionic conductivity by orders of magnitude.[1] While the elevated temperature, which is generally required for either their synthesis or the application for oxide, has been a "show-stopper" that limits the incorporation of nanoionics into energy technology, [2] the self-assembly of nanostructured materials through post-synthesis modification at elevated temperature is believed to be the only viable approach to realizing nanoionics. This project focuses on designing, synthesizing, and creating a new category of materials, oxide thin film surface nanoionics, [3-5] with orders of magnitude higher conductivity than bulk ceramics at elevated temperatures of $\sim 800^{\circ}\text{C}$. Those thin-film surface nanoionics were previously perceived as impossible to achieve at temperatures exceeding 400°C . Atomic layer deposition (ALD) is utilized to create the designed, conformal, and uniform thin film. The as-deposited ALD film, either in an amorphous or nanocrystalline state, is subsequently subjected to further nucleation, self-limiting nonequilibrium grain growth, and self-assembly through **post-synthetic modification** at elevated temperatures.

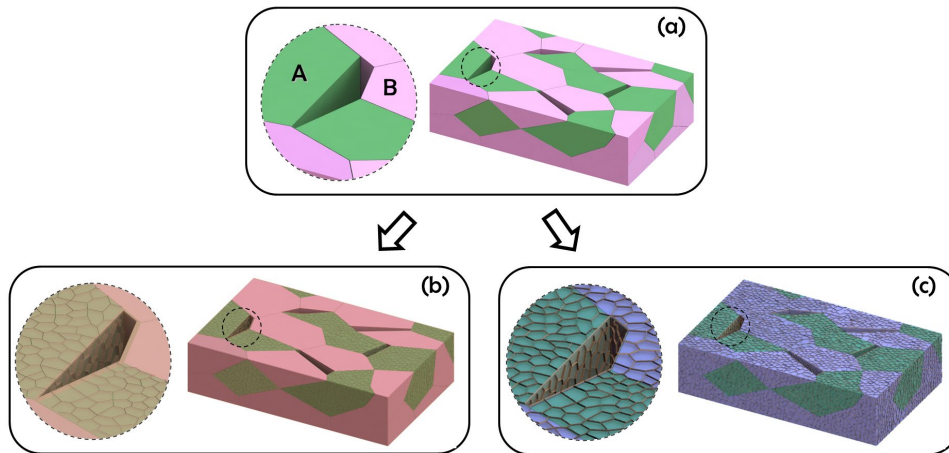


Figure 1. (a). Schematic of the polycrystal composite with Phase A and Phase B, external and internal surfaces; (b). Conformal coating with bimodal structure of surface nanoionics on Phase A and single crystal film on Phase B; (c). Modifying the interface energy between the film and substrate and creating the conformal coating of surface nanoionics on both Phase A and Phase B.

The main goal of the proposed post-synthetic modification is to avoid the undesirable thermodynamically stable agglomeration of the nanograins and the discrete islands. Instead,

through controlling the dominance of interface strain of the heterogeneous interface between the film and the substrate, the post-synthetic modification will render the conformal ALD film to self-assemble into either epitaxial thin-film single crystal or non-epitaxial thin-film surface nanoionics with single-layer of randomly oriented nanograins, as shown in Fig. 1. The ultimate goal of the proposed work is to enable the designing of such thermally stable surface nanoionics and to realize the synthesis of surface nanoionics using various oxides, including electronic conductors, ionic conductors, and electrocatalysts, and realize "Synthesis by design". The formation of these non-epitaxial conformal surface nanoionics is completely controlled by the substrate and is independent of the substrate topography and crystal orientation. Furthermore, the ALD coating enables the delivery of conformal and uniform surface nanoionics where they are needed, either on the external or internal surface of materials and devices on various substrates, thereby realizing "Synthesis on demand."

Recent Progress

One of the goals is to understand interface-controlled pathways and facilitate the formation of surface nanoionics on surfaces that do not initially favor this process. The test bed system is composed of composite ceramics, consisting of a ZrO_2 ionic conductor and an ALD coating layer of CeO_x , as well as other rare-earth oxides. We have been continuously working on the ALD coating and TEM samples using porous ceramic samples. The ALD layer has been deposited on the internal surface of the pores of the porous ceramics that are underneath the FIB surface protection layer, allowing for TEM imaging without interference from the FIB coating layer. To evaluate the impact of the interface energy on the formation of surface nanoionics, we designed the experiments for simultaneously facilitating the formation of the bimodal and unimodal distribution of the ALD layer on the surface of the oxide composite consisting of two kinds of oxides with different chemistry, thus possessing different interfaces with the identical ALD coating layer that was simultaneously applied to the two different oxide phases. Through this project, we demonstrate a straightforward approach to experimentally incorporating nanoionics onto a ceramic substrate consisting of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ (LSM), which is a pure electronic conductor lacking ionic conductivity, and is mixed with the ionic conductor scandium-stabilized Zirconium (SSZ) oxide. We performed ALD to coat conformal thin films, which is aimed at subsequently forming surface nanoionics on the internal surface of the porous composite substrate. We applied ALD coating to a minute amount of rare earth oxide of ReO_x , which possesses electronic conductivity four orders of magnitude lower than that of LSM and ionic conductivity three orders of magnitude lower than that of SSZ at the bulk scale.

The as-deposited state of the uniform ALD layer of ReO_x is amorphous, and an indifferent coating is present on the LSM and SSZ, as shown in the transmission electron microscopy (TEM) image of Fig. 2A. The composite oxide matrix with ALD coating was subjected to thermal treatment and conductivity electrochemical testing at an extended thermal treatment of >1030 hours at 850°C . After the testing, the dissected image of the porous oxide composite, as shown in Fig. 1A, displayed that ~ 15 thick layer ReO_x appears to diffuse into LSM and has formed the solid solution of $(\text{La}_{0.6}\text{Sr}_{0.17}\text{Re}_{0.22})\text{MnO}_x$. By contrast, the ReO_x on SSZ forms nanoionics with nanograins elongated ~ 30 nm along the SSZ surface and ~ 15 nm in thickness. As such, the ReO_x

ALD coating has led to the bimodal nanostructure distribution on the internal surface of LSM/SSZ substrate after 1030 hours of electrochemical testing at 850°C, as schematized in Fig. 2C.

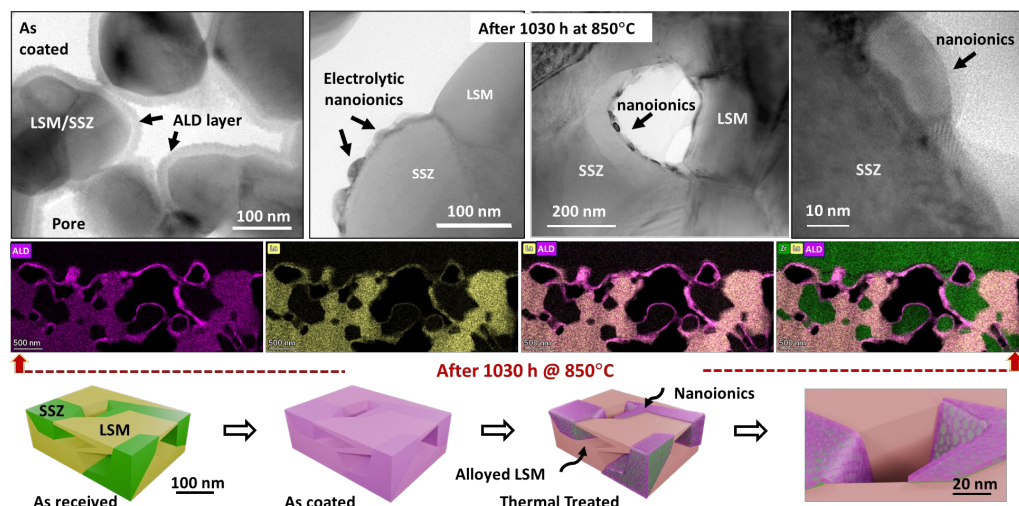


Fig. 2. Bimodal structured electrode backbone surface. (A). TEM images of uniform as-deposited ALD coating of ReO_x and the bimodal structure after electrochemical testing at 850 °C for 1030 hours; (B). Scanning TEM (STEM) image of chemistry maps of different elements after 1030 hours at 850°C. (c). The schematic of the bimodal structure. On the surface and the internal surface of the oxide composite consisting of oxide phases, the nanoionics are present

To evaluate the influence of the interface on the formation of the nanoionics and explore the possibility of forming unimodal nanoionics on both the SSZ and the LSM, the CeO_x was chosen as the subjacent layer for the superjacent ReO_x.

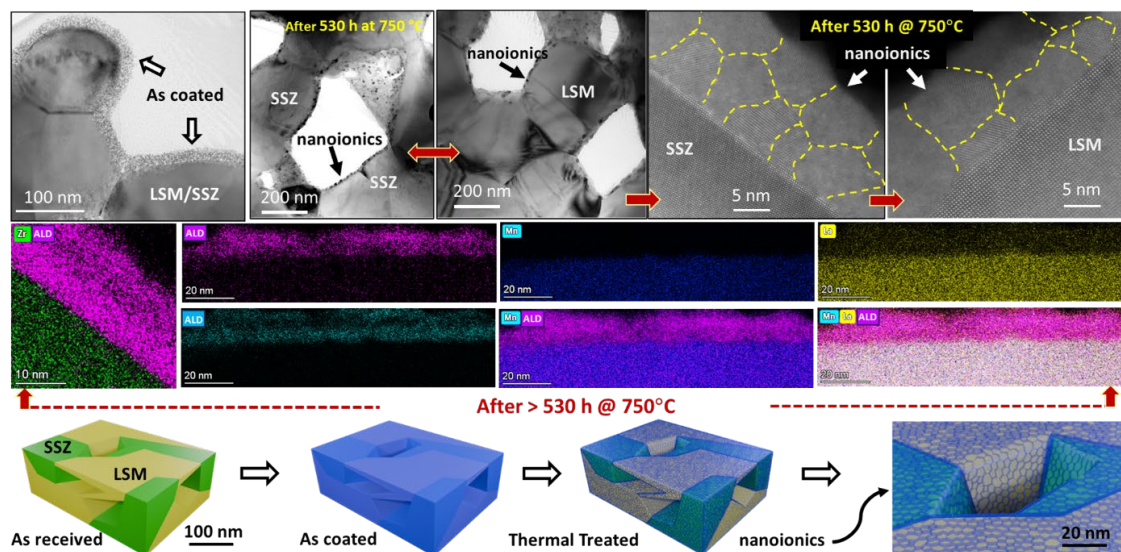


Fig. 3. Unimodal nanoionics on the backbone surface. (A). TEM and STEM image of uniform as-deposited ALD coating of CeO_x and the unimodal structure after at 750°C for 530 hours; (B). Chemistry map of different elements after 530 hours at 750°C. (c). The schematic of the bimodal structure and nanoionics on SSZ.

The ALD coating with a thickness of ~10 nm was achieved through ALD coating of 3 nm subjacent CeO_x first, as shown in Fig. 2 A, followed by superjacent alternating ReO_x and CeO_x . The composite substrate was subjected to 750°C for an extended period of over 530 hours. TEM image of the air electrode is shown in Fig. 3A, B. ALD coating layer establishes conformal unimodal and dual-layered nanoionics on both LSM and YSZ, independent of the substrate surface roughness and substrate grain orientation. The nanograins are non-epitaxial with the substrate and with random crystal orientation. Accordingly, we successfully transitioned the surface coating layer of ReO_x from forming a solid solution to establishing stable surface nanoionics on LSM. We rendered the formation of stable, unimodal surface nanoionics on both the SSZ and LSM. The unimodal distribution of the nanoionics on the LSM/SSZ substrate after 530 hours at 750 °C is schematized in Fig. 3. C. With the above comprehensive set of experiments, we have successfully tuned the physical properties of the interface between the oxide coating layer and the substrate, rendering the formation of surface nanoionics on the surface that did not initially favor such formation.

Future Plans

We will perform in-situ TEM imaging on the nanopionics under heating and biasing. In addition, (1). We will continue working on the tasks for Objective A, focusing on understanding the magnitude of strain energy in the formation of nanoionics. The ALD layer thickness will be tuned to reveal the crystal thickness needed for retaining the nanoionics. (2) We will continue working on Objective B: Tuning heterogeneous interface energy to facilitate the formation of nanoionics. (3). We will continue working on Objective C: Oxide surface nanoionics self-assembly of complex oxides with large anisotropy by investigating the self-assembly of nanoionics with large anisotropy.

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Accelerated Material Simulations Aided by Machine Learning Interatomic Potentials

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Keywords: Icosahedral boron synthesis, first-principles modeling, machine learning interatomic potentials, molecular dynamics simulation

Program Scope

Machine learning interatomic potentials (MLIPs) have evolved into powerful surrogate models of first-principles methods to explore complex potential energy surfaces. In material research, they are increasingly used to investigate the phase stability, phase transition, and prediction of a range of mechanical and thermodynamic material properties. Hence, MLIPs have demonstrated feasibility for material synthesis and processing.

Depending on training set data generation, computational resources, material characters, and applications, a range of MLIPs are available. For example, the artificial neural network (ANN) is one of the best-known and most mature MLIPs. High-dimensional ANN (HD-ANN) MLIPs have a relatively simple architecture and can be trained using most readily available data types. The training process is also more straightforward than other MLIPs. Yet, to obtain stable, accurate HD-ANN MLIPs, a large, comprehensive dataset is desirable. Recently, MLIPs obtained from active learning schemes have gained popularity. Streamlined processes are developed, allowing training set data generation and model training to be carried out sequentially. In this project, MLIPs developed using the data from the so-called on-the-fly molecular dynamics scheme were obtained and applied to predict material properties relevant to material processing.

A sparse Gaussian process (SPG)-type MLIP was developed to study the thermodynamic stability of boron crystals. As illustrated in Figure 1, boron allotropes, α -B (rhombohedral, B12), β -B (rhombohedral, B105), and γ -B (orthorhombic, B28) all consist of B12 icosahedra as the fundamental building block. Although density functional theory (DFT) has been widely used to obtain the free energies of pure boron phases [1, 2], previous studies showed that standard ground state energies are inadequate to account for the temperature effect on lattice kinetic energies and cell volume expansion (or contraction). The high computational costs of *ab initio* molecular dynamics (AIMD) limit the length scale and efficiency of obtaining thermodynamic properties, particularly phonon dispersions.

Research Progress

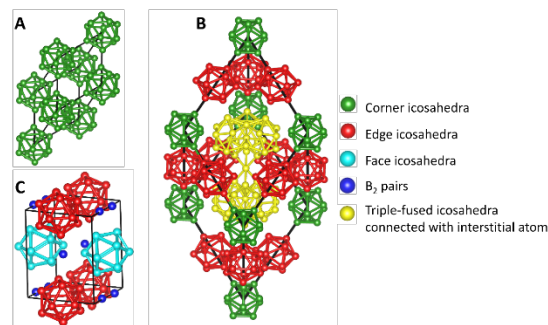


Figure 1. Primitive cells of (A) 12-atom α -B in a rhombohedral cell, (B) 105-atom β -B in a rhombohedral cell, and (C) 28-atom γ -B in an orthorhombic cell. The basic building blocks are displayed in different colors: corner icosahedra (green), edge icosahedra (red), face icosahedra (cyan), interstitial B₂ pair (blue), and triple-fused icosahedra (yellow).

To overcome such a deficiency, Liu's group focused on (i) developing suitable MLIPs and (ii) implementing these MLIPs to perform classical MD simulations of mechanical and thermodynamic properties.

We reported the training procedure and MD results based on the SGP potential for icosahedral boron crystals. We adopted a training process consisting of two stages: (i) on-the-fly (OTF) MD and (ii) offline training. The working principles of the OTF-MD scheme were initially introduced by the Kozinsky group [3]. All OTF MD simulations were run for 1,000 steps with an NVE ensemble. Material configurations are generated at each MD step, and the more expensive DFT run is called only when the prediction uncertainty exceeds the pre-determined threshold. Once OTF MD simulations were completed, all structures with high uncertainty were combined with DFT-calculated energies and forces and used as the training set. Offline training was performed based on the training set generated by OTF MD to obtain the final SGP potential. Offline training estimates uncertainties of training set structures in sequence. When a high-uncertainty structure (exceeding the threshold of 0.01 eV/Å) is encountered, the SGP will start a new iteration of training and add representative environments to the sparse set. The training and testing results are shown in Figure 2 [4].

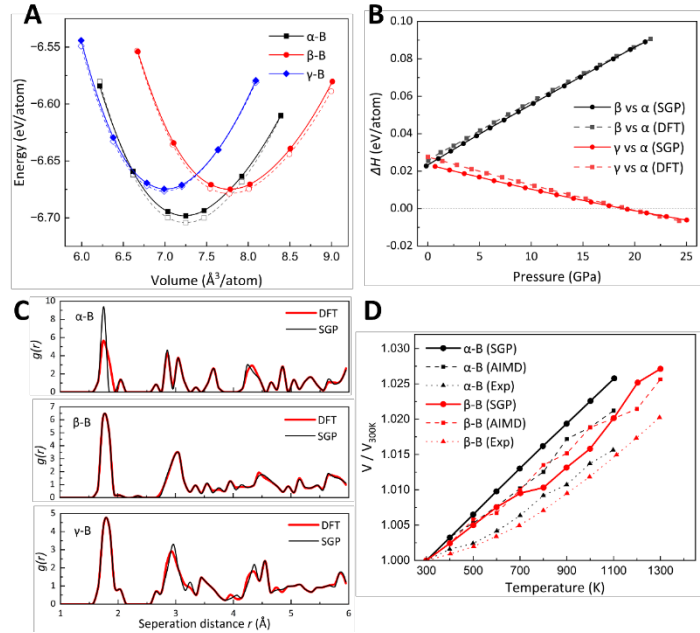


Figure 2. (A) Equations of state for α -B, β -B, and γ -B. (B) Enthalpy differences (ΔH) for β -B (black) and γ -B (red) versus α -B. (SGP: solid lines; DFT: dashed lines) (C) Radial distribution functions of solid-state α -B, β -B, and γ -B. (D) Volume expansions of α -B (black) and β -B (red). SGP: solid lines with circles; AIMD: dashed lines with squares; experimental volume expansion of α -B and β -B: dotted lines with triangles.

The lattice vibrations in boron crystals were simulated to demonstrate that the new MLIP can replace expensive quantum mechanical calculations to obtain solid-state vibrational entropies and zero-point energies. Herein, phonon dispersions and phonon density of states (PDOS) were calculated using Phonopy. As shown in Figure 3 [4], we observed qualitative resemblance with DFT-calculated phonon dispersions for all boron allotropes. The phonon density of states (PDOS), aligned with the corresponding phonon dispersion, was utilized to reveal differences in the fine structures of phonon frequency distributions. The characteristic peaks produced by the SGP potential and quantum mechanical methods agree well for phonon frequencies below 20 THz. Larger discrepancies are noted at higher frequencies for all boron allotropes.

With the new potential, we also generated the phase diagram for boron crystals. Moreover, we showed that the defect-free β -B₁₀₅ becomes thermodynamically more favored over

β -B₁₀₄ at $T > 1100\text{K}$. The stabilization due to the B₁₃ vacancy will likely occur at relatively low temperatures and pressures.

Future Plans

Liu's group aims to combine quantum mechanical methods with the emerging MLIP model development technique to investigate material behaviors that are generally too expensive or inefficient for standard DFT calculations. We anticipate this work will also impact research on crystal phase transition, nucleation, and crystal formation.

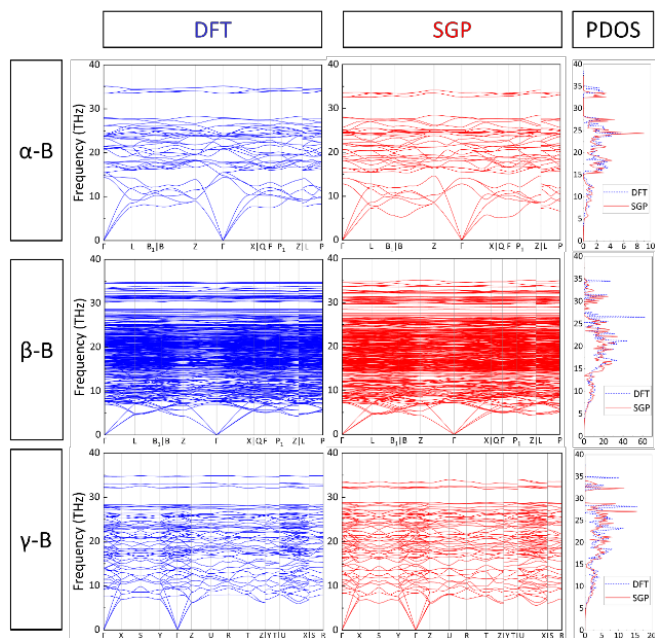


Figure 3. Phonon dispersion and phonon density of states (PDOS) of α -B, β -B, and γ -B calculated from DFT (blue) and MD simulations (red).

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In-situ Visualization and Modeling of Microstructure Evolution in Metallic Alloys under Additive Manufacturing Conditions

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Keywords: Solidification, Phase Field, Additive Manufacturing, Dynamic Transmission Electron Microscopy, Microstructure

Research Scope

Many potential benefits exist to using additive manufacturing (AM) - also known as three-dimensional (3D) printing - for making metal parts, rather than conventional manufacturing processes. AM is highly customizable, can produce complex structures, and can be used for the economical fabrication of small numbers of metal components. To achieve the strict specifications needed for some applications, the microscopic structure of printed metal objects must be controlled. Also, 3D printing is still in its infancy. There is a need for new approaches that combine AM with other processing methods to provide flexible architectural control over a wide range of length scales, from the nanoscale up to the macroscale, of AM builds. Here we seek to enhance our understanding of structure-processing relationships under AM conditions by novel experiments performed in the laboratory and at U.S. DOE national user facilities and by modeling to visualize microstructural development and explore new processing routes by three aims. The first aim is to gain novel insights into fundamental mechanisms of microstructure formation and grain texture evolution under far-from-equilibrium AM conditions by experimental and computational approaches that can reliably predict the microstructures of 3D printed metals. The second aim is to unambiguously determine the genesis of grain refinement, by constitutional supercooling during solidification and/or eutectoid formation in the solid state during thermal cycling, in Ti-Cu alloys designed for AM. The third aim is to explore a new, promising avenue that combines AM and dealloying for scalable manufacturing of nanocomposites. This builds upon preliminary computational modeling results that reveal rapid melting and re-solidification of a single-phase intermetallic provides a powerful new dealloying method to make nanoscale, interpenetrating phase bi-continuous structures for typical AM melting conditions.

Recent Progress

Here we highlight recent progress related to our first aim. A peer-reviewed journal article was recently published to answer our second aim. Work related to our third aim is ongoing.

Inferring anisotropic crystal growth properties from statistical analysis of grain texture evolution. Texture evolution under rapid solidification conditions was studied in Al-Si thin films (≈ 100 nm thick) with Si contents of $\approx 1, 3$ and 6 wt. %, exhibiting initial homogeneous grain sizes and random textures. In-situ imaging was performed during laser spot melting by Dynamic

Transmission Electron Microscopy (DTEM), where the melt pool boundary at different solidification times was tracked. Mean radius (r) and solidification velocities (V_s) with time (t) were determined. Ex-situ TEM-based orientation mapping was performed to evaluate the crystallographic textures produced by DTEM. We then analyzed crystallographic mapping data as a function of t for the different Al-Si alloys (based upon DTEM solid-liquid interface position) (Fig. 1a). For every filtered grain that exceeds a 5 degree inner-grain misorientation threshold, a grain coordinate system is established. We define three key directions to quantitatively characterize the grain texture (Figs. 1b-1d) and calculate statistical Z-scores to characterize the deviation of a given data set from the mean of a random distribution relative to the standard deviation. The Z-scores are then compared to those for perfect alignment. The results confirm that as solidification progresses, [011] and [100] directions tend to align with the X and Y axis, respectively. We refer to this approach as the Statistical Analysis of Texture Evolution (SATE), which is being used to understand grain competition in these thin-film, rapid solidification experiments.

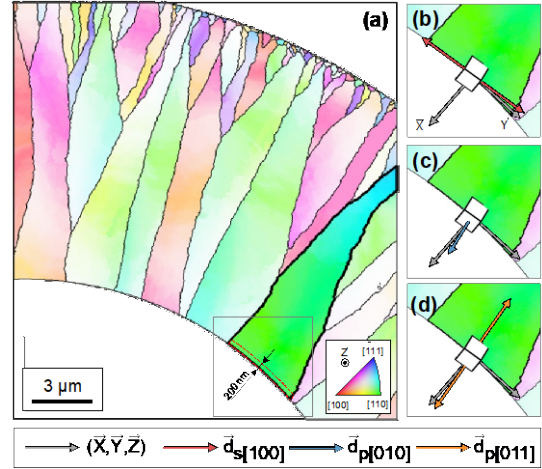


Fig. 1. Schematic diagram showing SATE variables on an example IPF map. (a) IPF (out-of-plane direction $\vec{Z}$) map for Al₃Si at 15 μs. Black lines delimit grains calculated assuming a 5° inner-grain misorientation threshold. The green grain on the right is selected to highlight the coordinate system and variables. The red dashed line delimits the pixels near the solid-liquid interface selected for analysis. The gray box shows the area magnified in the panels on the right-hand side. The methodology explained in the main text is used to define, for every grain time-step (b) the secondary [100] direction or $\vec{d}_{s[100]}$ (red), (c) the primary [010] direction or $\vec{d}_{p[010]}$ (blue), and (d) the primary [011] direction or $\vec{d}_{p[011]}$ (orange). The grain coordinate system $(\vec{X}, \vec{Y}, \vec{Z})$ is shown in panels b-d.

Phase field (PF) modelling of AlSi thin films: To replicate experimentally observed grain textures using the PF method, we employ a two-parameter form of anisotropy for interfacial free energy with parameters $(\varepsilon_1, \varepsilon_2) = (0.06, 0)$ that reduces to the well-established one-parameter anisotropy. To quantitatively assess the deviation of grain directions from a random distribution, we define Z-scores for key directions. The high Z-score of the primary [010] direction and pole figure results indicated a strong $\langle 100 \rangle$ growth direction. But this diverges from the experimentally observed texture. To address this, we adopt anisotropic parameters closer to those derived for pure Al by molecular dynamics simulations, yielding values of $(\varepsilon_1, \varepsilon_2) = (0.06, -0.006)$. This adjustment positioned near the $\langle 100 \rangle$ to hyperbranched dendrite boundary reveals a preferential $\langle 110 \rangle$ growth direction (Fig. 2), quantitatively verified by the large Z-scores in the secondary [100] direction. These results suggest that during rapid solidification in thin-film alloys, grain texture is strongly governed by interfacial free energy anisotropy.

Single-crystal PF simulations with varied orientations demonstrate rotation around the Y-axis (perpendicular to the solidification X-axis) achieves minimal undercooling with $(\varepsilon_1, \varepsilon_2) =$

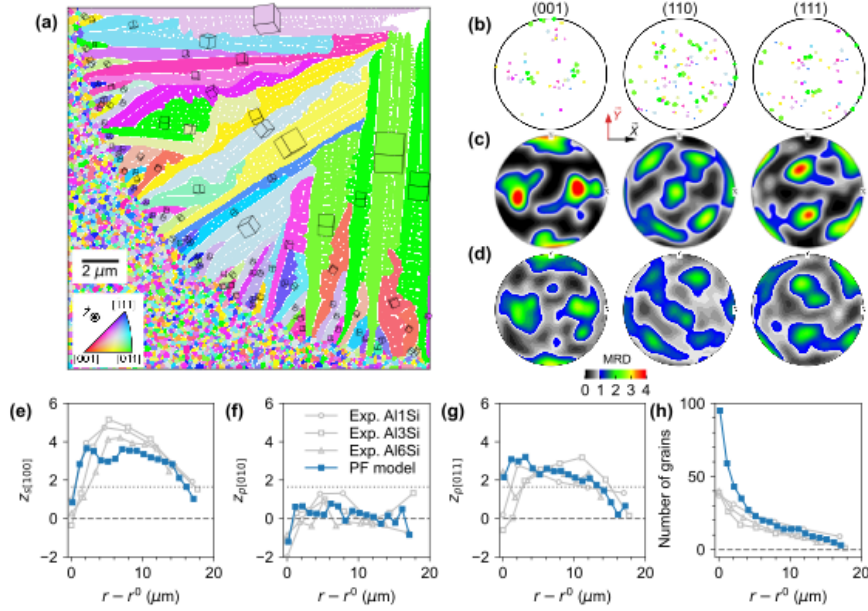


Fig. 2. PF simulations of grain texture selection in a rapidly solidified, Al1Si alloy thin film. The anisotropic interfacial free-energy parameters are $(\varepsilon_1, \varepsilon_2) = (0.06, -0.006)$. (a) Representative grain texture with 60 grain orientations shown by rotated cubes. (b) Pole figures of panel (a) with the solid-liquid interface determined at the same position as the simulation at 15 μs . (c) Density pole figure of panel (a). (d) Density pole figure of 4 simulations. (e) $Z_{s[100]}$ or Z-score of the projection sum of the secondary [100] direction on the Y axis as a function of solidification distance. Blue squares correspond to the simulation shown in panel (a). Grey open circles, squares, and triangles correspond to experimental results for Al1Si, Al3Si, and Al6Si, respectively. (f) $Z_{p[010]}$ or Z-score of the projection sum of the primary [010] direction on the X axis. (g) $Z_{p[011]}$ or Z-score of the projection sum of the primary [011] direction on the X axis. (h) Number of grains within the melt pool shown in panel a.

(0.06, -0.006), whereas rotation around the X-axis produces the minimum undercooling with $(\varepsilon_1, \varepsilon_2) = (0.06, 0)$. The orientations with minimum undercooling correspond to the preferred ones in polycrystalline simulations, indicating that grain competition during rapid solidification of thin-film alloys follows a minimum undercooling criterion.

Microstructure selection in Al-Ag and Al-Cu alloys: AM involves high V_s and the potential for novel solidification patterns like banding. To explore

this, DTEM experiments simulating rapid solidification under AM conditions have been performed with Al-Ag and Al-Cu alloys. To achieve electron transparency, these melt pools were ~ 100 nm thick (by ~ 100 microns in diameter), which suppresses convective flow and enables more direct comparison to 2D modelling.

Example banding produced during DTEM experiments is shown in Fig. 3 for Al-Cu. The solidification sequence begins as a planar front at the edge of the melt pool, progresses into a dendritic seaweed structure, and finishes with banding. The transition to banding allows for the first grain to begin banding to rapidly grow laterally, quickly outcompeting many other grains and establishing a singular crystallographic orientation for a large region. Once in the banding regime, the microstructure consists

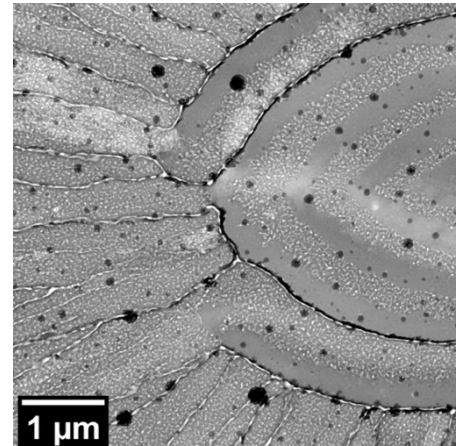


Fig. 3. STEM-HAADF image of the transition to banded structure in Al-Cu, showing the alternating layers of precipitated and unprecipitated regions and rapid lateral sweep of banding grains outcompeting non-banding grains.

of alternating layers of heavily precipitated and minimally precipitated regions. Grain competition in the banding regime is dominated by grains nearer to the major axis of the elliptical melt pools formed by DTEM; orientation effects are a potential secondary criterion.

PF modeling of Al-Ag. Our previous quantitative PF model, originally developed for dilute binary alloys, has been extended to model non-dilute binary alloys, specifically Al-Ag hypo-eutectic alloys. We utilize the Gibbs free energy following the classical CALPHAD method. Using a 1D PF model, we calculated the Al-Ag phase diagram, which demonstrates that with increasing pulling velocity, the solidus and liquidus lines converge. Experimentally, banding structures are absent across various Ag compositions, prompting a reduction in the kinetic coefficient to mitigate the barrier responsible for banding cycles. PF simulation results for microstructure selection mapping reflect this adjustment with a reduced kinetic coefficient of 0.1 m/s/K, demonstrating a clear morphological transition from cellular/dendritic to planar structures as Ag composition increases. These results qualitatively align with experimental observations, where the cellular structure spacing ranges from 300 to 500 nm, providing quantitative agreement with experiments.

Future Plans

During the next reporting period, we will complete a peer-reviewed journal article on grain texture and competition in rapidly solidified, thin-film Al-Si DTEM samples and SATE. Additional articles on pattern selection and solid-state microstructure development in Al-Ag DTEM samples under AM conditions, dendrite orientation transition (DOT) in Al-Ag laser melt tracks and DTEM samples, and banding in Al-Cu produced during DTEM experiments are in preparation. Microstructural characterization of DTEM samples is ongoing.

For PF modeling of concentrated Al-Ag DTEM thin films, we aim to incorporate solid-state diffusion to reduce composition peaks at cellular boundaries, aligning the simulated composition profile more closely with experimental measurements. We will also explore parameter adjustments to achieve planar interfaces at lower velocities and reduced compositions. Importantly, we plan to systematically identify growth regimes—cellular/dendritic, banding, and plane front growth—across an extended composition and velocity space. For composition-dependent interfacial free energy modeling with machine learning-based interatomic potentials, we will generate large datasets for pure Al and Al-based alloys using Quantum Espresso, leveraging density functional theory (DFT). With these new datasets, we will train ACE and UF3 potentials to capture composition-dependent interfacial free energy. Following model training, our approach will leverage LAMMPS for extensive MD simulations and employ our established C++ codes to calculate the anisotropy of crystal-melt interfacial free energy and kinetic coefficient through the capillary fluctuation method. This structured approach will enable a rigorous and computationally efficient analysis, yielding critical insights into DOTs under additive manufacturing conditions.

We will also pursue the viability of Ti-Ag dealloying under AM conditions and the formation of nanoscale hierarchical structures.

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Electric Field Driven Precision Material Synthesis

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Keywords: Electric Field, Ultrathin Membrane, Angstrom Resolution Nanopore, Molecular Beam Epitaxy, Scanning Transmission Electron Microscopy

Research Scope

Precision ultrathin films with atomically controlled and spatially resolved compositions, defects, and phases are essential for energy systems and quantum technologies. Methods that can fabricate uniformly distributed zero-dimensional defects or nanopores with precise angstrom-scale features, controllable location registry, and density on any given substrate are still lacking.

The goal of the project is to enable electric field as a new tool for cross-scale material synthesis and processing with both single-site and spatial location control (from atomic to micron scales), and to extend the generality of the tool to broad classes of thin-film materials. The team, with unique synthesis, processing, and characterization capabilities, aims to pinpoint the fundamental mechanisms of materials transformation under an electric field and finally achieve inverse design via the control of materials characteristics (such as composition, crystal structure, electronic structure, thickness, grain size, exposed facets, and defect level), electric field (strength, duration, and wavefunctions), and electrolyte (composition and conductivity). We aim to understand the effect of each tuning knob and reveal the reaction pathway via (1) the creation of defined starting material states; (2) characterization of reactions and materials evolutions; (3) atomic resolution characterization of the final material states.

Recent Progress

Our team has made important progress on three fronts: 1) We have demonstrated successful in situ pore generation driven by an electric field, which is the key method proposed in the project.¹ Moreover, we demonstrated that crystal orientation control can effectively guide nanopore formation. 2) Our team has developed a wafer-scale molecular beam epitaxy (MBE) film liberation technique that expands the library of materials with defined electronic structures as precision starting thin films.² Furthermore, the MBE development enabled the growth of millimeter-scale high-quality $(\text{Bi}_2\text{Te}_3)_n$ and $\text{MnBi}_2\text{Te}_4/(\text{Bi}_2\text{Te}_3)_n$ thin films. 3) Our team has successfully developed electron microscopy (EM) characterization methods for measuring thin-film thickness and achieving atomic resolution imaging for pore identification, which are critical for understanding the pore creation mechanism. Below, we highlighted two key efforts in detail.

Grain orientation effect on in situ nanopore formation under electric field

In situ nanopore creation was investigated in an electrochemical system where an ultrathin film material of interest is suspended in the electrochemical cell with both surfaces exposed to the electrolytes in two isolated chambers. An electric field is applied to this ultrathin barrier material

using two remote electrodes. With the electric field, cations and anions are accumulated across the barrier to induce electric double-layer gating (**Fig. 1a**). In our first work, we demonstrated that the grain boundaries of horizontal polycrystalline MoS₂ thin-film serve as the weak points to nucleate nanopores under electric field in situ.¹ Our molecular dynamics (MD) simulation revealed that increasing the layer number (from monolayer to 6-10 layers) can significantly enhance ion selectivity. However, for the horizontal polycrystalline MoS₂, we revealed that basal plane etching occurs simultaneously with perpendicular out-of-plane etching through grain boundaries, leading to heterogeneity in thin-film thickness around the nanopore and its dimensions (**Fig. 1b, d**).

To address this challenge, the Liu group designed a vertically aligned MoS₂ layer on top of the horizontal polycrystalline layer (**Fig. 1c**). In this configuration, the basal plane etching direction of the vertically aligned layer is aligned with the pore drilling direction (out-of-plane) of the underlying horizontal layer. Therefore, the triangular grain boundaries of the vertically aligned layers can serve as masks to confine the etching areas of the nanopores. The triangular grain boundary exposure areas can be controlled via post-synthesis annealing to be ~ 1 nm (**Fig. 1e, f**). With in situ electric field induced pore generation, we can consistently achieve enhanced monovalent ion selectivity compared with the horizontal polycrystalline MoS₂ without the vertical layer (**Fig. 1g**). The achieved K⁺ to Li⁺ selectivity is better compared with porous thin-film membranes synthesized using other two-dimensional materials including graphene, MoS₂, and

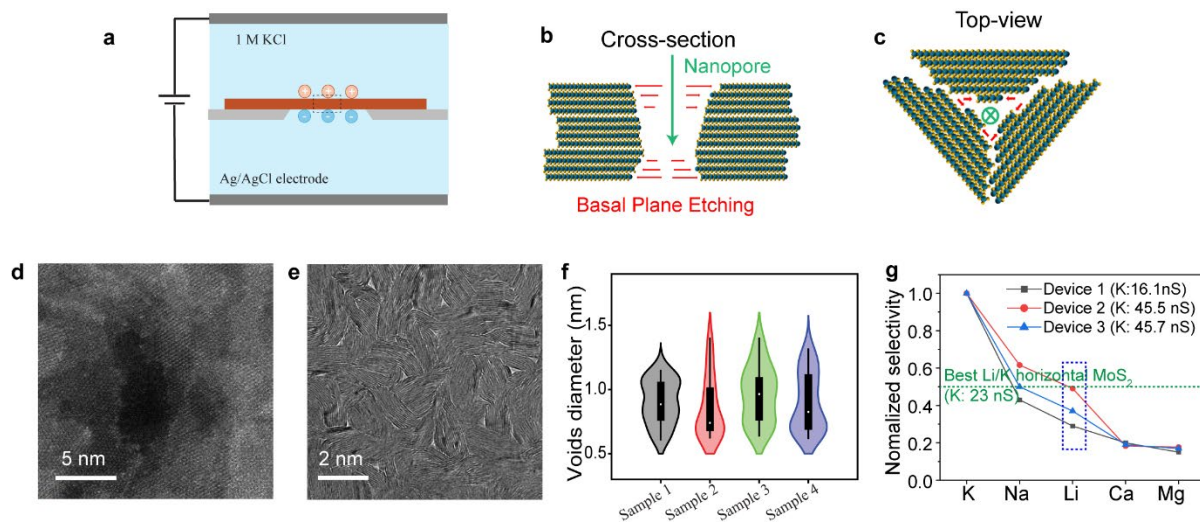


Figure 1. Grain boundary confined nanopore creation. (a) Schematic showing the platform for electric field driven synthesis. An ultrathin film is transferred onto a SiN window with tunable window size. (b, c) Schematic showing the MoS₂ film configurations. During in situ electric field driven pore generation, grain boundary evolves in a way that both perpendicular out-of-plane etching (green) and basal plan etching (red) occur at the same time for horizontal polycrystalline MoS₂ without (b) and with (c) vertical layer. (d) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image showing evidence of basal plane etching under electric field. (e) STEM bright field image showing initial opening of grain boundaries. (f) Statistics of grain boundary opening size of vertical MoS₂ layer from four samples. (g) Normalized ion selectivity and K⁺ ion conductance for membrane devices with grain boundary confinement from the vertical MoS₂ layer.

BN. This work is currently in preparation for publication.

Millimeter-scale 2D topological insulators

Low-dimensional topological phenomena, such as the quantum spin Hall effect³ and quantum anomalous Hall effect,⁴ provide the material foundation for new paradigms of quantum electronics and spintronics. However, so far, these fascinating quantum phenomena are mostly realized at exceedingly low temperatures and microscopic scales. Through meticulous control of molecular beam epitaxy (MBE), the Yang group has developed a synthesis protocol to fabricate high-quality $(\text{Bi}_2\text{Te}_3)_n$ and $\text{MnBi}_2\text{Te}_4/(\text{Bi}_2\text{Te}_3)_n$ thin films, which exhibit a digitally varied electronic structure with thickness uniformity across millimeter scales (**Fig. 2a-e**). Most importantly, among these films, the 2 quintuple-layer (2 QL) Bi_2Te_3 and heterobilayer $\text{MnBi}_2\text{Te}_4/\text{Bi}_2\text{Te}_3$ exhibit inverted bandgaps of 100 and 150 meV, respectively. This means that these materials are potential candidates for a room temperature quantum spin Hall effect.

The high material quality is demonstrated using STEM images taken by the Liu group (**Fig. 2f**). The thickness of 2 QL Bi_2Te_3 grown on SrTiO_3 (111) substrates is uniform across both nano- and micro-meter scales. Laser-based angle-resolved photoemission spectroscopy (ARPES) with a 10 μm resolution verifies that the uniformity extends over at least a $1 \times 1 \text{ mm}^2$ region. Rich physics is revealed by the layer-by-layer ARPES measurements. Three spectral features attest to the high quality of these films. First, in the valence band region, one can clearly identify a digitally

incremented number of valence sub-bands. This observation suggests that the films effectively form 1D confinement along the thickness direction for valence electrons to be quantized. Second, for 3 QL and 4 QL Bi_2Te_3 , secondary Dirac cones lie below the primary ones. These correspond to the topological surface states

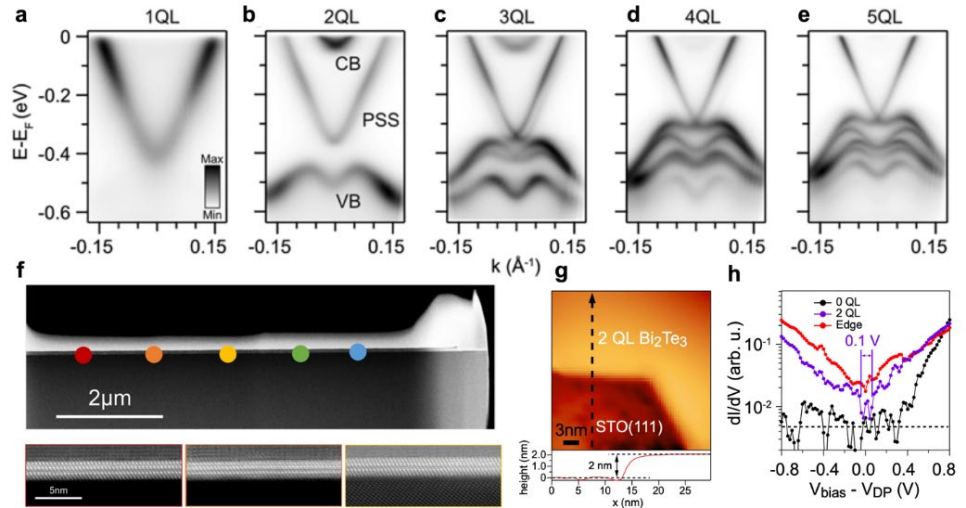


Figure 2. Comprehensive study of millimeter-scale 2D topological insulators. (a-e) Angle-resolved photoemission spectroscopy (ARPES) measurements on ultrathin Bi_2Te_3 films. (f) Cross-sectional scanning transmission electron microscopy (STEM) taken at color-coded points with approximately $1.5 \mu\text{m}$ intervals in a 2 quintuple-layer (2 QL) Bi_2Te_3 film lamella. (g) Topography image of 2 QL Bi_2Te_3 and bare SrTiO_3 substrate. The dashed black arrow defines the trajectory for taking differential conductance measurements. (h) Differential conductance spectra for 0 QL, 2 QL, and the edge.

(TSSs) from the bottom surface. In 3 QL Bi_2Te_3 the primary and secondary TSSs hybridize with anti-crossing gaps. Third, in 2 QL Bi_2Te_3 a 100 meV inverted bandgap is resolved. Photon-energy

dependent and time-resolved ARPES (not shown here) demonstrate the inverted orbital characters of this bandgap. Since 100 meV is four times the room temperature energy scale (26 meV), 2 QL Bi₂Te₃ is a strong candidate for realizing the room-temperature quantum spin Hall effect.

To verify the topological property, we collaborated with Prof. Mark Hersam's group at Northwestern University and performed scanning tunneling microscopy/spectroscopy (STM/STS). We successfully located an edge between the topologically nontrivial 2 QL Bi₂Te₃ and the bare SrTiO₃ surface (**Fig. 2g**). We observe the expected inverted 0.1 eV bandgap on 2 QL Bi₂Te₃ and a much larger bandgap > 1.2 eV on SrTiO₃ (**Fig. 2h**). Most importantly, the differential conductance has an obvious enhancement at the edge, reflecting the emergence of the topologically protected edge state (**Fig. 2h**). It is notable that such films can be exfoliated from the substrate,² enabling future engineering of flexible topological electronics. This work is currently in revision with Nature.⁵

Future Plans

For the mechanism study, we will investigate the pore generation mechanism by controlling the electric field strength and electrolyte composition. For synthesis, our team will investigate the fabrication of carpet-mode transition metal dichalcogenide heterostructures. For atomic registry control, we will introduce point defects or atomic composition heterogeneities into single-crystalline MoS₂. Moreover, we will use layer assembly to enable atomic registry recognition using Moire lattices. In parallel, for STEM characterization, four-dimensional (4D) STEM and direct phase contrast imaging will be developed for defect and light element imaging. We aim to demonstrate optimized and decoupled control of defect size and density in thin film materials of interest.

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Electrochemical Sculpting of Nanoribbons: Composition-Dependent Nanostructuring and Phonon Confinement in BP and b-As_xP_{1-x} Alloys

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Keywords: nanoribbons, electrochemical intercalation, phosphorene, b-As_xP_{1-x} alloys, ARPRS

Research Scope

Recently, we have demonstrated that electrochemical insertion of Na⁺ into black phosphorus (BP) - a highly anisotropic layered van der Waals (vdW) material - can be used to produce uniform, sub-10 nm-wide phosphorene nanoribbons (PNRs) [1, 2]. In this process, which we term *electrochemical sculpting*, bulk BP is nanostructured into densely packed bundles of zigzag-oriented PNRs separated by parallel amorphous channels (Fig. 1). Our research aims to explore and understand the electrochemical sculpting process and nanoribbon (NR) formation in BP and related materials, including black arsenic phosphorus (b-As_xP_{1-x}) alloys and group IV–VI monochalcogenides (AB compounds, where A = Ge, Sn and B = S, Se). The work integrates synthesis and electrochemical processing with advanced experimental techniques and first-principles calculations to (i) identify key factors governing sculpting, (ii) establish relationships between processing variables and NR properties, and (iii) elucidate microscopic mechanisms of NR formation. Here, we report two recent studies: one investigating the effect of As concentration in b-As_xP_{1-x} on NR morphology and sculpting dynamics, and another [3] employing angle-resolved polarized Raman spectroscopy (ARPRS) to show how electrochemical nano-structuring of BP alters vibrational properties through nanoscale phonon confinement.

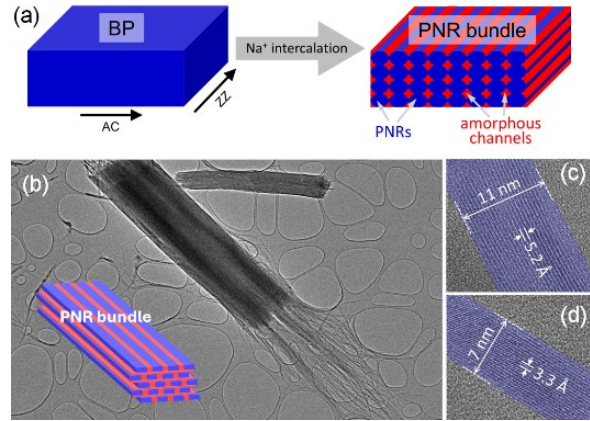


Fig. 1. (a) Schematic of BP transforming into bundles of PNRs upon Na⁺ intercalation. (b) TEM image of a PNR bundle. (c,d) HR TEM images of individual PNRs.

Recent Progress

To understand how alloy composition affects electrochemical sculpting and NR morphology, we synthesized $b\text{-As}_x\text{P}_{1-x}$ alloys with varying As content ($0 \leq x \leq 0.62$) and intercalated them with Na^+ ions. EDS was used to determine As content, while STEM-HAADF imaging provided three key morphological parameters of the resulting NRs: width, aspect ratio (length/width), and angular deviation from the zigzag (ZZ) direction (Fig. 2). The results reveal a clear increase in NR width with increasing As content, rising quickly at low x and saturating beyond $\sim 40\%$ As (Fig. 2a). This trend suggests that As incorporation promotes thicker NR formation, likely due to enhanced chemical stability and higher defect formation energies. In contrast, the NR aspect ratio decreases by over an order of magnitude with increasing x , dropping from >1000 for pure BP ($x = 0$) to <100 for $x > 0.4$ (Fig. 2b). This is accompanied by increased deviation from the ZZ direction, rising from $<1^\circ$ at $x = 0$ to $\sim 15^\circ$ at $x \sim 0.6$ (Fig. 2c). Monte Carlo (MC) simulations help explain these observations. Due to the strong anisotropy of BP, the energy barrier for Na^+ hopping between nearest-neighbor sites differs significantly by direction. Our DFT-based nudged elastic band (NEB) calculations show that for BP, the hopping barrier is ~ 0.1 eV along the armchair (AC) direction and ~ 1 eV along ZZ, yielding an anisotropy ratio ($\chi = \Delta E_{ac}/\Delta E_{zz}$) of ~ 10 . At such high χ , MC simulations predict strictly unidirectional ion migration along ZZ (Fig. 2g), leading to localized high ion concentrations and associated lattice strain, stacking disorder, and amorphization - all aligned with the ZZ direction. This scenario results in straight-edged, well ZZ-aligned NRs, consistent with observations in pure BP. As χ decreases, ions follow increasingly irregular paths (Fig. 2h-i), leading to more disordered, misaligned NRs as seen in high- x $b\text{-As}_x\text{P}_{1-x}$ samples (Fig. 2e-f). Lower χ also increases NR edge deviation from the ZZ direction.

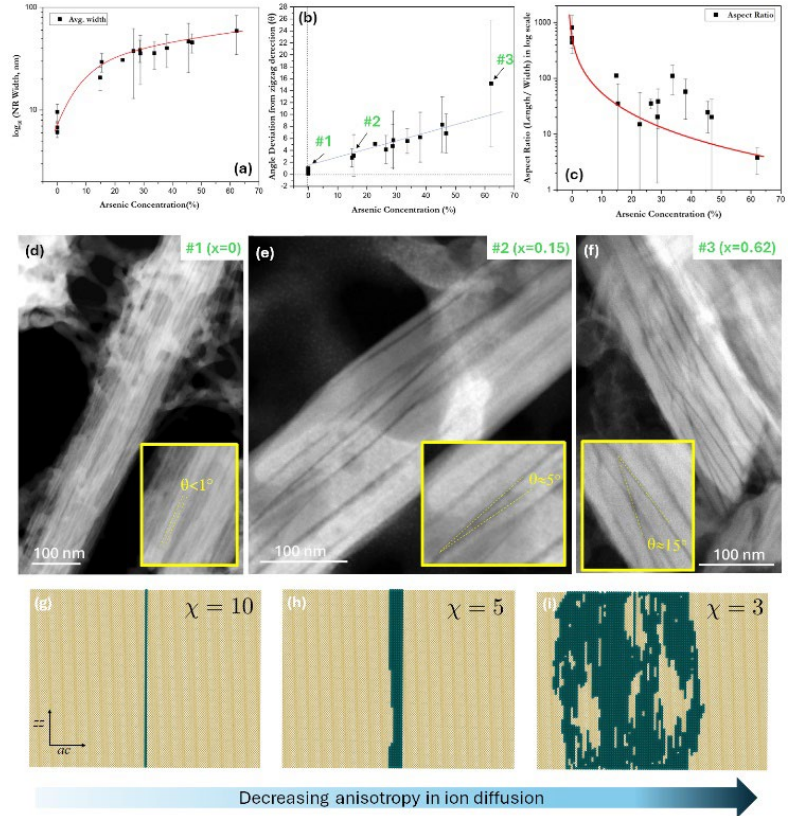


Fig. 2. (a–c) NR width, deviation angle (θ), and aspect ratio vs. As content x in $b\text{-As}_x\text{P}_{1-x}$. (d–f) STEM images of Na^+ -intercalated $b\text{-As}_x\text{P}_{1-x}$ for $x = 0, 0.15$, and 0.62 . (g–i) MC simulations of ion migration in bilayer phosphorene-like structure at anisotropy ratios $\chi = 10, 5$, and 3 over 10^6 steps under ambient conditions.

Electrochemical sculpting transforms BP into PNR bundles, which, as revealed by *in situ* Raman spectroscopy, exhibit six new peaks (P1-P6) alongside the intrinsic BP modes (A_g^1 , B_{2g} , A_g^2) (Fig. 3). We conducted a detailed ARPRS study of all the modes to probe vibrational and structural anisotropy (Fig. 4a). For comparison, we also examined Li^+ -intercalated BP (Fig. 4b), which forms fragmented, weakly connected NR-like strips [4]. Interestingly, both Na^+ - and Li^+ -intercalated BP show the P1-P6 peaks. These exhibit angle-independent intensity in parallel polarization and near-zero intensity in crossed polarization, indicating isotropic vibrations associated with amorphous regions. However, clear differences emerge in ARPRS-derived polar plots of the intrinsic modes of BP. In Na^+ -intercalated BP, the B_{2g} mode transitions from the four-lobed "cloverleaf" polar plot of pristine BP to a butterfly-like one under parallel polarization. This change is attributed to phonon confinement and in-plane vibrational mode mixing, as confirmed by theoretical modeling. The A_g^1 and A_g^2 modes also deviate from their expected four-fold symmetry under crossed polarization, displaying reduced symmetry and increased anisotropy. Li^+ -intercalated BP shows even more pronounced deviations. Under parallel polarization, the A_g^1 and A_g^2 modes display less defined, two-lobed shapes, while the B_{2g} mode loses its distinct four-lobed character. In the crossed configuration, all three modes show significantly reduced anisotropy compared to pristine or Na^+ -intercalated BP. These differences likely stem from structural variations: Na^+ intercalation produces densely packed, high-aspect-ratio NRs, while Li^+ intercalation yields fragmented, irregular segments with lower structural coherence.

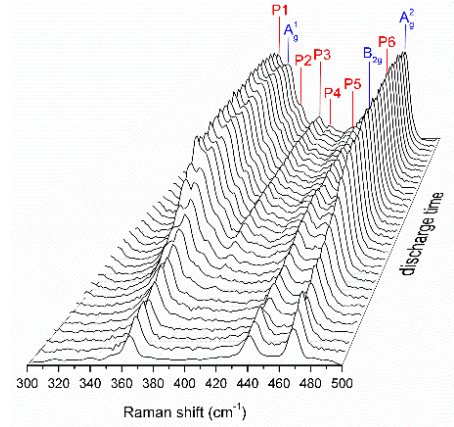


Fig. 3. In situ Raman of BP during Na^+ intercalation, showing the emergence of new peaks (P1–P6).

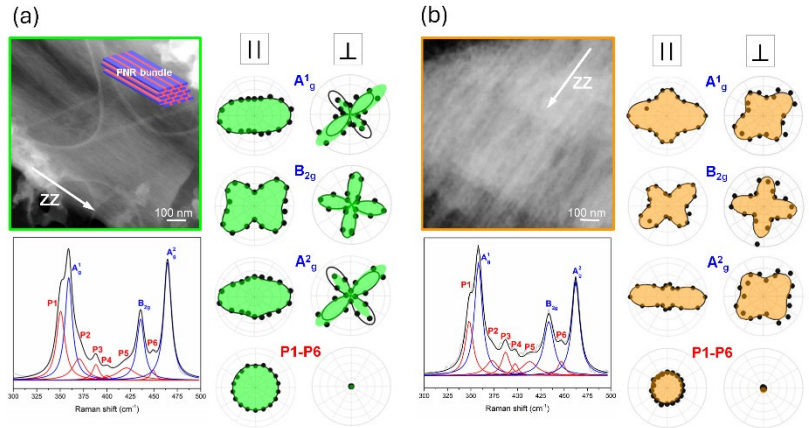


Fig. 4. STEM images, Raman spectra, and ARPRS polar plots of vibrational modes for (a) Na^+ - and (b) Li^+ -intercalated BP.

To interpret these observations, we conducted vibrational frequency density of states (FDOS) calculations for ZZ and AC monolayer PNRs. The simulations reveal significant band folding in the 410-425 cm^{-1} range (A_g^2 - B_{2g} region), leading to mode mixing. This explains the butterfly-shaped B_{2g} polar plot in Na^+ -intercalated BP. A linear combination of A_g^2 and B_{2g} in-plane modes reproduces the experimental angular dependence, whereas modeling the B_{2g} mode alone fails, highlighting the role of confinement-induced phonon coupling.

Future Plans

Our future work will combine theoretical and experimental efforts to further elucidate electrochemical sculpting and control NR formation in anisotropic layered systems. On the theory side, we will perform DFT calculations on special quasi-random structures to investigate how As chemical ordering in $b\text{-As}_x\text{P}_{1-x}$ alloys affects (a) intercalation energetics of Li^+/Na^+ ions and (b) ion-hopping barriers. Classical molecular dynamics (CMD) simulations with enhanced sampling and newly developed reactive force fields will be used to identify physical factors governing NR formation. Specifically, we will study how composition, chemical disorder, intercalant size, and electrolyte properties modulate the competition between exfoliation and sculpting.

Experimentally, we will continue electrochemical intercalation studies on group IV–VI monochalcogenides, beginning with GeSe, for which bulk layered crystals have already been synthesized. ARPES and *in situ* Raman spectroscopy will be applied to these systems and to various $b\text{-As}_x\text{P}_{1-x}$ alloys to probe nanoribbon formation and properties. These efforts will be complemented by advanced electron microscopy (AC-STEM and 4D-STEM), in part conducted at NCEM (LBNL) under a recently awarded user proposal. These studies aim to map strain and amorphization at the nanoscale during electrochemical sculpting. In addition, we plan X-ray scattering and diffraction studies on Na^+ -intercalated BP using the NSLS-II synchrotron at BNL (user proposal submitted). The goal is to determine whether amorphization arises from point defect accumulation, strain-induced instability, or electrolyte effects. Wide-angle X-ray scattering (WAXS) will probe crystallinity, anisotropy, and domain size, while small-angle X-ray scattering (SAXS) will detect nanoscale ordering and amorphous channel formation. WAXS will track structural evolution via peak broadening, halo formation, texturing, and anisotropic strain - enabled by large BP flakes (5–10 μm) yielding sharp diffraction peaks. SAXS will complement WAXS by resolving nanostructural features such as amorphous channels in PNR bundles. Pair Distribution Function (PDF) measurements will also be performed to resolve short- and medium-range order and identify atomic pair correlations in amorphous and nanocrystalline domains. These results will be integrated with Raman, TEM, and WAXS data to construct a multiscale picture of structural transformation during electrochemical sculpting.

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Design of structural inhomogeneities to control functional properties

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Keywords: nanomaterials, strain, interfaces, grain boundaries, transformations

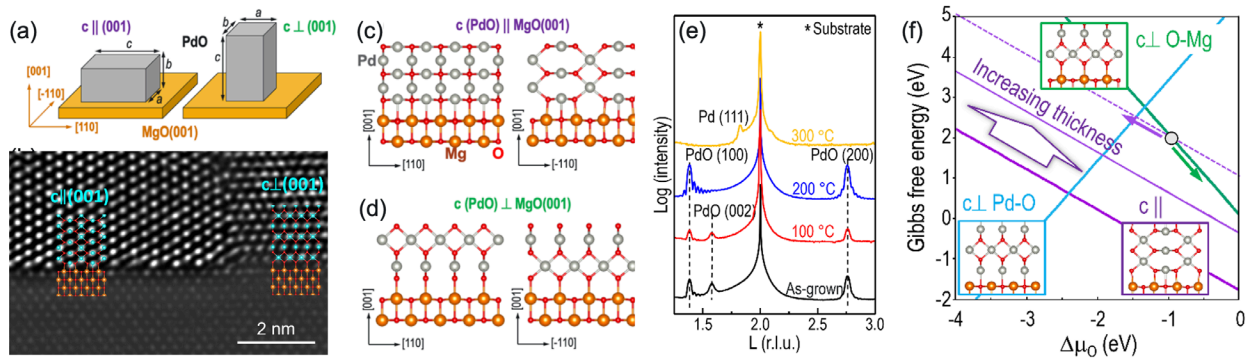
Research Scope

This project aims to achieve a mechanistic understanding of how the structural and electronic properties of inhomogeneously strained materials based on platinum group elements (PGEs) underpin their catalytic performance under reaction conditions, discover approaches for controlling the coupling between deformations and catalytic activity, and develop materials design rules to enable replacing PGE with abundant transition metal (TM) elements. We advance toward this vision by (1) establishing relationships between the structure and composition of the materials' building blocks and the character of inhomogeneous deformations, (2) revealing the atomic-scale origin of these relationships, and (3) applying this knowledge to discover materials that manifest strong deformation-induced effects. We target knowledge gaps that limit our ability to predictively utilize the complexity afforded by heterostructures to perform catalytic functions: (1) Which synthetic routes allow us to control the structural and compositional characteristics of extended defects and the corresponding deformation fields? (2) What are the relationships between the structures and composition of these defects, the character of their transformations depending on the chemical environments, and the effect of these transformations on the materials' properties? Our approach is to reveal the effects of complex deformations by examining dissimilarities in the behaviors of heterointerfaces in epitaxial films and assemblies of nanoparticles. Interfacial structures, properties, and phenomena are characterized using ex-situ and in-situ techniques, interpreted using ab initio simulations of the interactions, transport, and electronic structure; the results of these simulations are also used to predict the effect of specific defects and compositions, thus guiding follow-up experimental studies.

Recent Progress

Transformations of strained nanostructures. Control of crystal orientations in thin films of functional materials allows for predictive tuning of their strain states, electronic properties, and surface chemical reactivity. We demonstrated that tetragonal PdO films, grown on the MgO(001) substrate using oxygen plasma assisted molecular beam epitaxy, exhibit two co-existing orientations with the PdO c-axis parallel ($c\parallel$) and perpendicular ($c\perp$) to the substrate, where domains of $c\parallel$ and $c\perp$ orientations are subjected to the tensile and compressive strain, respectively (Figure 1). We examined the roles of epitaxial strain, interfacial interactions, and environmental conditions in stabilizing these competing orientations. Our ab initio modeling reveals that

accounting for the effect of epitaxial strain alone makes $c\perp$ orientation more thermodynamically preferred, while experiments show that $c\parallel$ orientation dominates. This inconsistency in the relative abundance of the $c\perp$ and $c\parallel$ orientations is resolved by considering the effects of interfacial interactions: the PdO/MgO attachment energy is significantly larger in $c\parallel$ than in $c\perp$ orientations, which determines the dominant orientation at the initial deposition stages. In addition, their stability can be regulated by the oxygen chemical potential, with $c\perp$ and $c\parallel$ being more stable in the O-rich and O-poor limits, respectively. Experimentally, we demonstrated that post-synthesis thermal annealing of these films in a vacuum, i.e., in oxygen-poor conditions, initiated structural reorganization, leading to $c\parallel$ becoming the dominant orientation. These findings provide insight into the interplay between the structural parameters, interactions, and synthesis conditions to create competing film orientations, tune their stability, and facilitate orientation transformations [1].



Controlled formation of (reversible) metal hydride phases is a potent way to tune material

Figure 1. (a) Epitaxial relationships between the tetragonal PdO film and the MgO(001) substrate. (b) Cross-sectional STEM of the as-grown PdO film shows the coexistence of $c\parallel$ and $c\perp$ domains. (c,d) The most stable interface structures for the $c\parallel$ and $c\perp$ orientations. (e) Evolution of the surface XRD patterns for as-grown and vacuum annealed (100-300°C) PdO films. As the annealing temperature increases, the (002) reflection diminishes while the (100) peaks become more dominant; a metallic Pd(111) peak appears at 300°C. (f) Gibbs free energies of the lowest-energy PdO/MgO interface configurations vs. oxygen chemical potential (μ_O).

properties. Grain boundaries (GBs) are believed to be key defect structures facilitating metal hydride formation, yet their specific role remains poorly understood due to the structural complexity of GB-rich materials. We observed a dramatic difference in the kinetics of hydrogenation (Figure 2) of stand-alone Pd nanoparticles (NPs) and nano-structured Pd formed by assembling these NPs into interconnected quasi-one-dimensional chains (Pd gels). The key distinguishing characteristic of Pd gels is the co-existence of a large surface area and a high density of NP-NP interfaces in the form of well-defined $\Sigma 3(111)$ GBs and strain exerted by the particles on each other through coupled interfaces. These structures are uniquely suited for investigating the effects of coupling between chemical environments and materials transformation, as they allow for direct, high-resolution characterization of GB dynamics during hydrogenation. We reveal the novel behavior of nanostructured Pd using a combination of synchrotron-based in-situ X-ray diffraction, in-situ transmission electron microscopy (TEM), and ab initio simulations. We observe

rapid phase transitions from Pd to PdH_x and back, with strain mapping showing localized strain accumulation at GB sites. In-situ TEM imaging indicates that hydrogen preferentially inserts at $\Sigma 3(111)$ GBs; our simulations show that hydrogen accumulates near concave regions adjacent to the GB and that tensile strain in these regions lowers the hydrogen insertion barrier. These linkages between the kinetics of the hydride formation, sample morphology, and strain distribution provide a new atomic-level insight into how GBs influence the rates of H transfer and suggest strategies for the design of H-trapping and H-transfer materials [2].

Coupled effects of strain and subsurface species.

The ability of Pd to absorb hydrogen and form a bulk hydride is vital for chemical transformations that involve hydrogenation reactions. Nano-structured Pd catalysts allow tuning these reaction rates by exploiting variations of binding energies of reactants depending on the surface structure and morphological constraints that result in inhomogeneous strain. However, the interplay between the

surface topography, morphology, strain, and subsurface Pd hydride needs to be better understood. We consider the effects of these factors on the conversion of benzaldehyde (BZ) to benzyl alcohol in two qualitatively different samples: Pd NPs and Pd gels. Our electrochemical measurements and modeling suggest that surface concave sites and tensile strain, inherent to Pd gels, facilitate hydrogen transfer to the Pd subsurface region, thus weakening BZ binding to the surface. These findings demonstrate how structurally complex materials, such as gels, provide degrees of freedom for controlling the behavior of metal catalysts that are not present in NPs, paving the way for new approaches in the design of catalytic materials [3].

Charge transfer and strain distributions in pseudomorphic layers. Pt is a critical constituent of catalytic systems; it is also scarce and expensive, which elevates the need to use it efficiently. We examined the possibility of enhancing the catalytic performance of Pt (face-centered cubic lattice) in the limit of a sub-monolayer amount adsorbed on the W(110) surface (body-centered cubic lattice). Our results suggest that Pt forms a weakly strained pseudomorphic layer and induces electron charge transfer from the W substrate. The combined effect of the deformations and charge transfer modifies the H and OH binding energies to the Pt layer and W substrate, resulting in

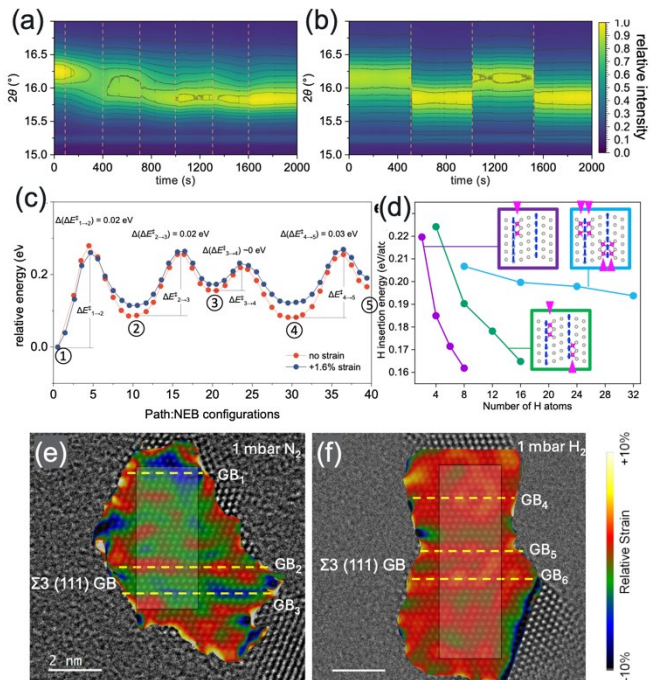


Figure 2. (a, b) Pd(111) diffraction peak for Pd NP and Pd gel. The dashed lines indicate the switching points between air and H₂/Ar gas flows. (c) Potential energy profiles along the H insertion path into a model Pd gel, with and without 1.6% tensile strain along [111]. (d) H insertion energy depending on the H content and diffusion path. (e, f) HRTEM images and strain maps of Pd gel under (e) 1 mbar N₂ and (f) 1 mbar H₂.

enhanced rates of the hydrogen evolution reaction [4]. Based on these simulations, we developed criteria for the design of catalytically active structural motifs (Figure 3).

Future Plans

Interfacial effects. The fast hydrogen insertion in the GB-rich Pd gel samples illustrates the significance of the linkages between the particle-particle interfaces, strain, stability of the hydride phases, and H diffusion barriers. We will continue to work on building predictive relationships between these factors and extend our work to bimetallic gels and thin films, aiming to control orientations of the terminating surfaces and GB distribution.

Subsurface species. Our observation that the charge distribution and strain associated with subsurface H in Pd gels allow for tuning adsorption energies of prototypical reactants raises questions about how this effect extends to other metals and subsurface species and which factors define its magnitude and spatial distribution. Therefore, our future work will focus on the near-surface charge and strain distribution driven by subsurface anionic species.

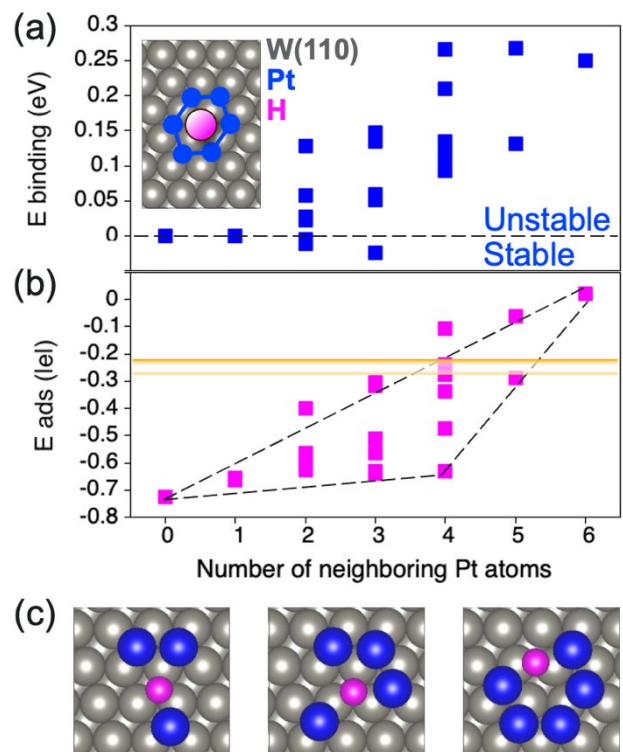


Figure 3. The calculated stability of small Pt clusters supported on the W(110) surface (a) and the corresponding binding energy of H atoms (b) provide criteria for the arrangements of the surface Pt atoms (c) to tune adsorption energies of chemical species. We are developing synthesis strategies to create the desired arrangements of the Pt adatoms.

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SPIRAL: Synthesis and Processing Informed by Rational Algorithmic Learning

PI: Lara A. Estroff¹; co-PIs: Paulette Clancy², Rigoberto Hernandez², John Marohn¹, Rebecca Lindsey³, David Moore⁴, Jinhui Tao⁵

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Keywords: Crystallization, Ab initio Molecular Dynamics, Solution Speciation, Electric Force Microscopy, Machine Learning Models

Research Scope. Grand challenges remain to understand the most complex nucleation and crystal growth scenarios relevant to the synthesis and processing of energy materials, especially regarding: (1) how to characterize and predict (experimentally and computationally) solution speciation as a function of solution composition and to identify the most critical species in solution leading to nucleation; (2) how to assemble these species to capture nucleation and growth phenomena and guide materials properties, employing information transfer across 10 to 15 orders of magnitude in space and time; (3) how to control material stability by understanding defect formation and migration under operational conditions, with the ultimate impact on high-quality processing. We address these questions as three interlinked “spirals” that we iteratively improve to understand materials synthesis and processing. We have interwoven in-house machine learning (ML) tool development and cutting-edge experimental approaches for this purpose. Our current focus improves the synthesis and processing of energy-related materials, especially, lead halide perovskites, to produce targeted stability and durability. The tools developed here are materials-agnostic, broadening their ability to accelerate the transformation of energy systems through the development of stable and reproducible devices from low-cost, low-energy, solution-processing protocols, earth-abundant components, and ones that are agile in the event of element shortages.

Recent Progress.

Data Science Methods Development (Clancy, Hernandez, Lindsey). Innovative machine learning algorithm development is a hallmark of this team. We have created three new algorithms specifically for materials discovery: Hernandez’s Nested AutoEncoders,¹ Lindsey’s Hierarchical Transfer Learning Method,² and Clancy’s PAL 2.0.³

PAL 2.0: A physics-driven Bayesian optimization framework for material discovery (Fig. 1). The lack of efficient materials discovery tools that are chemistry-informed remains a major bottleneck to enabling advances in the next-generation energy, health, and sustainability technologies. One main factor lies in taming the large combinatorial space of materials (with respect to compositions and/or processing conditions) that make the problem essentially intractable to explore experimentally or computationally. Searching this large

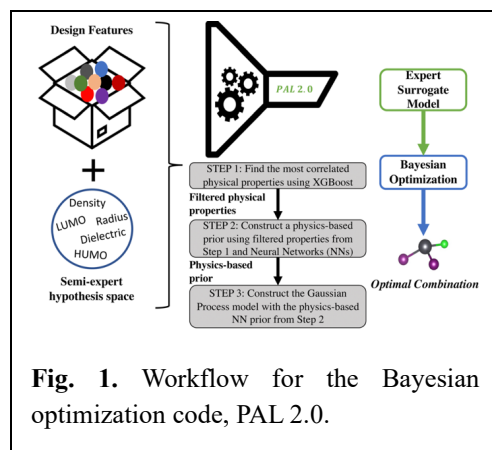


Fig. 1. Workflow for the Bayesian optimization code, PAL 2.0.

parameter space is often influenced by expert knowledge and clustered close to material configurations that are known to perform well, ignoring potentially high-performing candidates in unanticipated regions of composition- or processing-space. We developed PAL 2.0 to combine a physics-based surrogate model within a Bayesian optimization framework. A key factor of its success is the ability to create a physics-based hypothesis using XGBoost and a Neural Network pre-train. This hypothesis provides a physics-based "prior" (or initial beliefs) to a Gaussian process model, which then performs a search of the material design space. Our results indicated that PAL 2.0's approach outperforms other state-of-the-art methods in its efficiency to search the material design space for the optimal candidate, *e.g.*, finding the best MOF amongst 70,000 candidates capable of storing the most methane. To the best of our knowledge, there is no competing algorithm capable of this useful combination for materials discovery, especially those for which data are scarce.

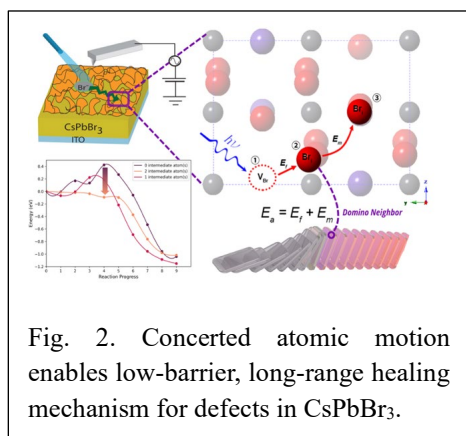
PAL 2.0 has proven to be an efficient discovery tool for materials discovery of better compositions and processing optimization. We have successfully used PAL 2.0 to study a broad set of materials: (1) discovery of metal halide perovskites with desired photovoltaic properties; (2) design of metal halide perovskite-solvent pairs that produce the best solution-processed films; (3) design of organic thermoelectric semiconductors; (4) MGI-like "closed loop" discovery of multiple principal element alloys for spacecraft actuators (objective: maximize strength), finding exceptionally strong alloys, including some with elements "out of distribution" (*i.e.*, not in the original database on which it was trained), a severe test for machine learning tools;³ (5) designing the best solvation protocol for thermoelectric polymer design (validated by experiments for two classes of material (DPP-based and IDT-based polymers));⁴ (6) dealing with two competing objectives: maximizing strength and minimizing corrosion. In this case, we looked for new magnesium-rich alloys for orthopedic implant materials, specifically the impact of high-temperature thermal processing on the mechanical and degradation attributes of a lean Mg-Zn-Ca-Mn alloy, ZX10. The PAL 2.0 code base is available on *github*.

Other key SPIRAL algorithm development "snapshots:" *1. Nested AutoEncoders (Hernandez).* We developed a "deep learning" approach using a hierarchically structured machine (a NestedAE) consisting of supervised or unsupervised autoencoders fed by features of a given scale. We combined previously published databases for band gaps and perovskite devices to explore two length- scales simultaneously using NestedAE. A critical piece is the use of some/all of the latent space variables of a given scale as an autoencoded feature in the autoencoder *at the next scale*. We have demonstrated that NestedAE can optimally recapitulate data from a multiscale synthetic database even when its size is relatively small—*viz*, 100s of examples rather than millions.¹

2. Machine-learned interatomic models (ML-IAMs) using ChIMES (Lindsey). While *ab initio* simulations provide critical insights into speciation, they are limited in accessible spatiotemporal scale due to their expense. To enable accelerated studies of speciation and nucleation from the liquid phase, Lindsey is developing scalable and efficient machine-learned interatomic models (ML-IAMs) using her ChIMES framework. This approach offers quantum-accurate predictions at

a fraction of the computational expense, making large-scale and long-timescale simulations feasible. But applying ML-IAMs to solution-phase perovskite synthesis is a significant challenge due to the presence of many chemically distinct elements. To overcome this, Lindsey developed Hierarchical Transfer Learning to decompose high-complexity ML-IAM fitting problems into smaller, tractable sub-problems.² This method accelerates model development, enables rigorous validation, and enhances transferability across physicochemical conditions. Critically, it introduces explicit chemical extensibility, allowing expansion of existing models to include new elements without retraining any existing portion of the model, as is required by all previously available strategies. These models will enable investigations into melt-phase nucleation processes, including speciation in the melt and halide partitioning behaviors in mixed-halide lattices, phenomena that are challenging to study experimentally or with conventional simulation methods.

Low-energy pathways lead to self-healing defects in CsPbBr₃ (Clancy, Marohn, Moore).



This research tackled a critical question in the field of metal halide perovskites: how do intrinsic atomic defects migrate (and not just form) under operational conditions, and are these materials able to successfully recover from defect formation? Focusing on CsPbBr₃, the team conducted a comprehensive computational study using density functional theory (DFT) and Nudged Elastic Band (NEB) methods to investigate how interstitials and vacancies migrate and recombine within the crystal lattice. We discovered a cooperative “domino effect” mechanism, wherein bromine interstitials move through the lattice, not

in isolation, but in a cascade of coordinated atomic motions that allows a distant vacancy to be healed (Fig. 2).⁵ This concerted behavior leads to surprisingly low activation energies for defect migration (~0.5 eV) closely matching experimental measurements by **Marohn** of slow, thermally activated conductivity recovery. This work goes beyond literature calculations of formation energies by providing a database of defect migration pathways, corrections for charged defect calculations, and consideration of metastability. These findings offer a clear picture of defect healing in CsPbBr₃, supporting the emerging hypothesis that perovskites are not just defect-tolerant but defect-responsive. This insight is essential to design robust solar cells, LEDs, and radiation-hardened optoelectronic devices.

Elucidating Solution Speciation and Solvation Dynamics via DFT and Nuclear Magnetic Resonance Spectroscopy (Estroff, Clancy, Marohn).

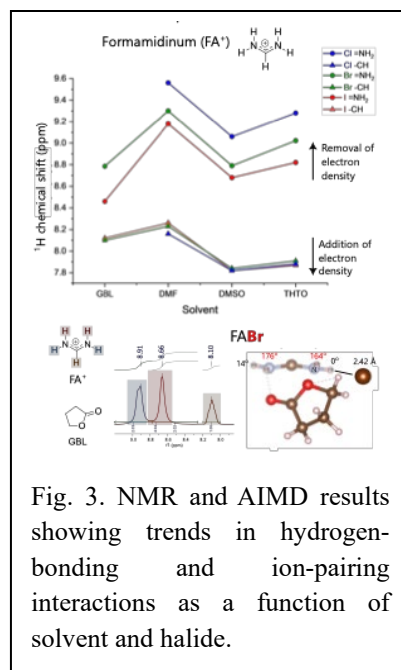
Solution crystallization pathways in lead halide perovskites, in particular, the roles of solution speciation of the precursor salts, remain poorly understood. We are combining molecular simulations and solution-phase nuclear magnetic resonance (NMR) spectroscopy to elucidate effect of solvent and halide on the growth pathways of formamidinium lead halides (FAPbX₃; X=I, Br, Cl) and methylammonium lead halide (MAPbX₃). NMR spectroscopy revealed that the local coordination environments surrounding ammonium protons (=NH₂⁺ in FA⁺ and -NH₃⁺ in MA⁺) and alkyl protons (-CH in FA⁺ and -CH₃

in MA^+) varied with solvent and halide (Fig. 3): As the electronegativity of the halide counterion increases, the nitrogen-bound protons are deshielded. *Ab initio* molecular dynamics (AIMD) simulations suggest that deshielding arises from stronger hydrogen-bonding between the solvent molecules and the organic cation. 2-D Nuclear Overhauser Effect spectroscopy (NOESY) showed that the halide identity (I vs. Br) influenced bond rotation dynamics: FABr has two peaks for the *cis* and *trans* protons, indicating restricted rotation about the C=N partial double bond, while FAI has a single averaged peak for *cis* and *trans* protons, indicating proton exchange due to bond rotation. From the AIMD simulations, we proposed that the bromide facilitates complexation between the FA^+ and solvent molecules, breaking the dihedral angle symmetry and preventing bond rotation (Fig. 3).

Addition of the lead source to the FAPbI_3 -forming precursor solution leads to changes in the NMR spectra consistent with a change in the number and strength of hydrogens between the organic cations and solvent molecules. DFT models provide additional insights showing a solvent-dependent change in the ratio of different iodoplumbate complexes. Combining DFT/AIMD and NMR spectroscopy is providing new insights into the structural features and intermolecular interactions between species in solution that will help elucidate their role in the perovskite crystallization pathways. We are currently determining the link between solution speciation, as characterized by NMR, and single crystal growth quality. Understanding the roles of each component, and the identities of predominant species in solution required to form perovskite single crystals, is a key step towards realizing the reproducible production of device-quality materials.

Future Plans. Our team will continue to uncover mechanistic pathways for crystal nucleation and growth. The computational team will continue to develop new ML algorithms to tackle the multiscale processes involved in crystallization. The experimental team will provide experimental data across orders of magnitude in length- and time-scales to feed to the “chemistry-informed” ML algorithms to develop design rules that will help tame the complexity of crystallization pathways.

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Ten Most Relevant Publications Supported by BES 2023-2025

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Grain Boundary Engineering by Electro-Nano-Pulsing (ENP)

Eugene Olevsky (PI) and Wenwu Xu (co-PI), San Diego State University

Keywords: Electro-Nano-Pulsing, Grain Boundaries, Dislocations, Tailoring

Research Scope

The primary objective of this project is to develop an innovative electric current-assisted materials processing method that enables nanoscale control and tailoring of grain boundaries (GBs) and interfaces in materials. This approach focuses on the application of ultra-intense nanopulsing electrical current, delivered in nanosecond (ns) pulses, through conductive samples using a custom-designed nanopulsing system¹⁻⁴.

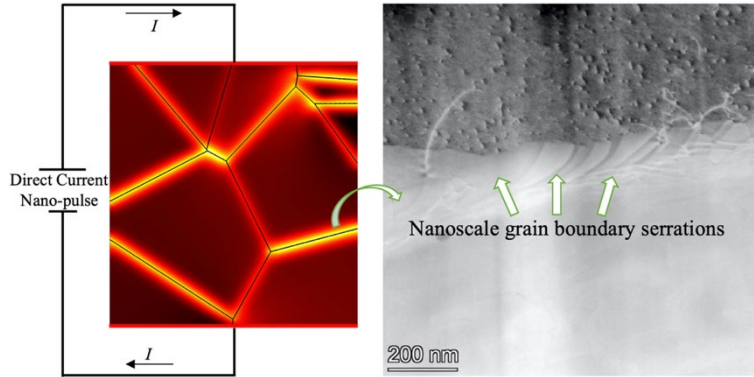


Fig. 1. Electro-nano-pulsing (ENP) processing generates highly localized thermal and nonthermal effects to material heterogeneities, enabling nanoscale tailoring of grain boundaries and interfaces.

These extremely short-duration, high-density direct current pulses are expected to generate highly localized Joule heating within the material. Due to the differences in electrical and thermal properties at GBs and particle interfaces, we anticipate concentrated heat accumulation in these regions. This results in steep temperature gradients across GBs, while the surrounding grain interiors remain relatively unaffected. As shown in Fig. 1(left), our numerical finite element calculations show significant heat concentration along GBs¹.

The central hypothesis is that, at the atomic scale, GBs undergo transient structural disruption. This may include local disorder or even partial melting, leading to atomistic-level reconfiguration. Because each pulse lasts only a few nanoseconds, atomic diffusion and thermal effects are confined to the immediate vicinity of GBs or interfaces. Consequently, structural changes are localized, and the bulk microstructure of the material remains largely unchanged. Fig. 1(right) presents an example of formation of nanoscale GB serrations after the ENP processing in a Ni-based superalloy¹.

This non-equilibrium, highly localized processing approach presents new opportunities for engineering grain boundaries and interfaces with exceptional precision. By systematically adjusting nanopulsing parameters such as current density, pulse duration, and frequency, this technique can be used to selectively modify GB structure, chemistry, and properties^{1,2}. The method holds promise for advancing the design of next-generation materials with enhanced performance across a range of applications.

Recent Progress

Our recent progress establishes electro-nano-pulsing (ENP) as a transformative method for defect engineering in metals. By achieving dislocation densities that rival or exceed those found in heavily deformed materials, ENP offers a promising pathway for tailoring mechanical, thermal, and

electrical properties in structural and functional materials. These findings pave the way for future explorations into rapid, non-thermal microstructural modification strategies. Minimal oxidation was observed in the sample interiors due to the high oxidation resistance of Ni-based superalloy and the extremely short pulse duration. Elemental analysis using energy-dispersive X-ray (EDX) analysis showed that oxidation was confined to the outermost surface layers, and the internal compositions remained stable post-treatment³.

We conducted finite element modeling to simulate the stress distribution during nanopulsing³. As shown in Fig. 2, our results confirmed that stresses introduced at GBs propagate into grain interiors within hundreds of ns, generating conditions suitable for dislocation formation throughout the material. The simulations support our hypothesis that the non-thermal electron wind-induced stress plays a more critical role than Joule heating in driving dislocation formation during ENP.

Quantitative analysis of the dislocation density was performed using stereological methods applied to multiple representative transmission electron microscope (TEM) images, resulting in estimated densities of $\sim 8.7 \times 10^{15}/\text{m}^2$ and $\sim 11.6 \times 10^{15}/\text{m}^2$ in different regions³, which are at the microscale length scale, meaning dislocations are $\geq 1\mu\text{m}$. Furthermore, as shown in Fig. 3, HRTEM analysis identified nanoscale dislocations (a few to a few tens of nm) and atomic-scale screw dislocations with densities as high as $\sim 8.3 \times 10^{17}/\text{m}^2$. These values are among the highest ever reported for bulk metallic systems and surpass previously documented limits achieved through prolonged current stressing or confined nanoscale geometries.

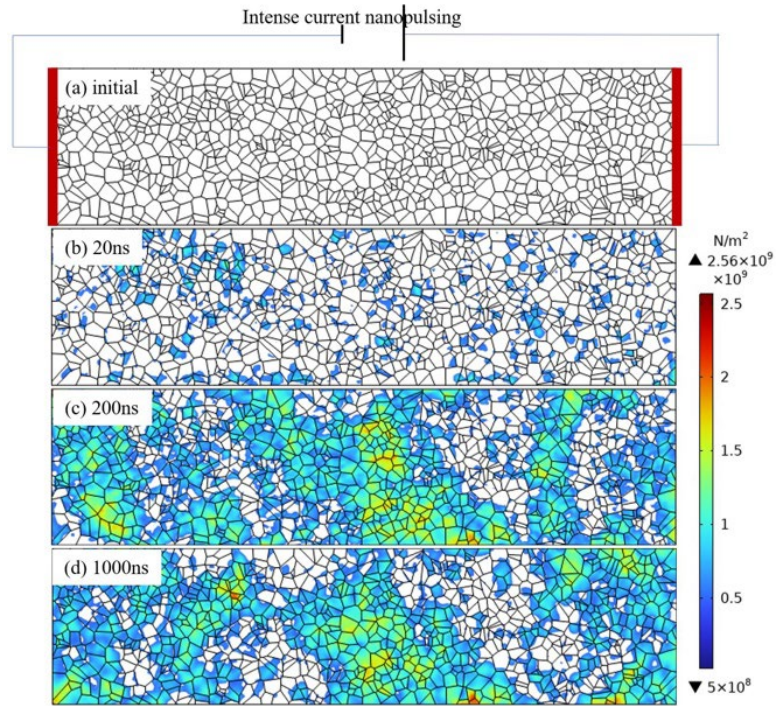


Fig. 2. (a) Initial microcrystalline structure; (b)-(d) distribution of von Mises stress at varied instances during the nanopulsing processing.

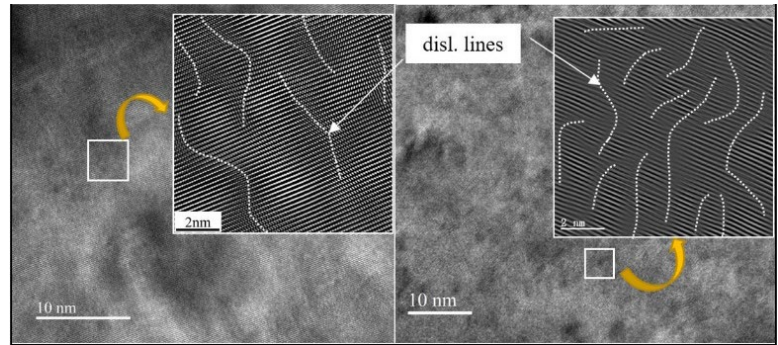


Fig. 3. Representative HRTEM images of the Nichrome samples treated by ENP processing showing significant formation of screw type dislocations.

Also, we noticed that the dislocation orientation is influenced not only by the electron current direction but also by the intrinsic crystallographic slip systems of the FCC lattice. Dislocations are commonly aligned with or inclined to the current direction, reflecting a complex interaction between external stress fields and crystallographic constraints³.

The mechanism behind this dramatic increase in dislocation density is attributed to the significant localized stresses induced by electron wind forces during ENP. These stresses are particularly intense at grain boundaries, where the electrical resistivity is orders of magnitude higher than in grain interiors. Consequently, GB regions experience transient but extreme shear stresses, estimated up to 500 MPa, that exceed the critical resolved shear stress of the superalloy at elevated temperatures. These forces promote lattice shearing and the rapid generation of screw dislocations³.

In summary, in our most recent work, we have demonstrated that ultra-intense ENP processing can produce unprecedentedly high dislocation densities in metallic materials such as the Nichrome-80 superalloy. This technique utilizes nanopulses of electric current at densities exceeding a few 10^{10} A/m², with pulse durations on the order of ns to microseconds. Through this approach, we observed dislocation densities reaching $\sim 10^{18}$ /m² at the nanoscale, significantly surpassing those produced by conventional cold-working methods, which typically max out around $\sim 10^{14}$ - 10^{15} /m².

Future Plans

Building on our recent demonstration of ultra-intense ENP processing as a powerful tool for inducing extreme dislocation densities and microstructural changes, our upcoming research will focus on disentangling the coupled thermal and non-thermal effects of ENP at the atomic scale. This work will deepen our understanding of how ENP parameters influence GB behavior, dislocation formation, and chemical reactivity, enabling strategic control over microstructural evolution in metals.

Future Research Objective 1: Disentangling thermal and non-thermal effects of ENP at the atomic scale

A central goal of our future research is to isolate and characterize the distinct contributions of Joule heating and non-thermal electron wind forces in driving atomic-scale transformations during ENP. To achieve this, we will integrate large-scale reactive molecular dynamics (MD) simulations with multilayer experimental architectures designed to modulate thermal gradients and electric current exposure independently. Our ENP experiments will utilize tri-layer samples that spatially separate the effects of direct current conduction and thermal diffusion. These will be complemented by advanced electron microscopy techniques, specifically HRTEM and scanning TEM (STEM) imaging, along with diffraction-based structural analysis such as X-ray diffraction (XRD), to reveal atomic-level distortions, GB morphology changes, and defect structures. By systematically comparing ENP-treated regions with conduction-heated control samples, we will identify microstructural features that are uniquely attributable to electric field-driven, non-thermal processes. The insights gained will enable the rational tuning of ENP parameters to optimize defect generation and GB restructuring for targeted applications in high-performance materials.

Future Research Objective 2: Unveiling the effects of electron wind and localized heating on dislocation structures

In parallel, we will investigate how ENP influences dislocation behavior, including nucleation, motion, interactions, and pattern formation in metallic systems. Dislocations are central to mechanical strength, plasticity, and defect-mediated transport, and their manipulation via ENP presents a transformative opportunity for materials engineering. Using reactive MD simulations, we will model dislocation dynamics across a range of current densities and temperature conditions representative of ENP exposure. These predictions will be validated experimentally through ENP treatment of metallic samples followed by multiscale characterization using TEM and XRD. We will analyze dislocation density, distribution, and configuration as a function of pulse frequency, amplitude, and duration, and critically compare these results against conduction-heated references. This approach will allow us to isolate the role of electron wind forces in promoting non-equilibrium dislocation structures and to identify ENP conditions that selectively enhance or suppress specific dislocation types. The resulting framework will support the design of ENP-enabled processes for tailoring dislocation-driven properties such as strength, ductility, and conductivity.

Future Research Objective 3: Determining ENP's influence on oxygen diffusion and reactivity at grain boundaries

Finally, we will explore the chemical aspects of ENP processing, specifically the interaction of oxygen with GBs under high-current, short-duration pulsing. Understanding the mobility and reactivity of oxygen in ENP-activated materials is critical for assessing stability, corrosion resistance, and the potential for oxidation-assisted microstructural engineering. Through reactive MD simulations, we will examine how electric fields influence oxygen transport, oxide nucleation, and bonding dynamics at the atomic scale. Experimentally, we will use bicrystal samples exposed to oxygen-containing atmospheres during ENP treatment and analyze them using combined TEM/STEM imaging and spectroscopy methods such as electron energy loss spectroscopy (EELS) and EDX to quantify oxygen distribution and oxidation states at GBs. By benchmarking these results against conduction-heated samples, we will determine whether ENP accelerates oxygen infiltration, alters oxide growth mechanisms, or enables new oxidation pathways. These findings will not only clarify the interplay between electrical and chemical driving forces in ENP but also inform new strategies for leveraging oxygen reactivity to engineer protective or functional GB phases.

Together, these future research objectives will advance our fundamental understanding of ENP as a versatile, non-equilibrium processing tool. By revealing how thermal and non-thermal stimuli influence microstructural and chemical transformations at GBs and other crystallographic defects and within bulk materials, we aim to establish a comprehensive framework for ENP-based GB and defect engineering in metals.

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Temperature-Time-Transformation Diagrams for Predictive Solid-State Ceramic Synthesis

Wenhao Sun, University of Michigan Ann Arbor

Keywords: Predictive synthesis, *ab initio* thermodynamics, CALPHAD, liquidus, metastability.

Research Scope

Temperature plays a fundamental role in solid-state synthesis, but there are currently no mechanistic theories to predict which temperature is best to carry out a solid-state ceramic reaction. It is often difficult to deconvolute whether temperature affects non-equilibrium phase evolution because of thermodynamics, $\Delta G = \Delta H - T\Delta S$; or kinetics, $k = k_0 \exp(-E_a/k_B T)$. This Early Career Award set out to elucidate the fundamental thermodynamic and kinetic principles for how temperature determines the reaction sequence, onset temperature, liquid formation, and metastable intermediates in a solid-state reaction. Specifically, we aimed to build a theoretical framework that unifies classical thermodynamics, nucleation, diffusion, and crystal growth theories to calculate Temperature-Time-Transformation (TTT) diagrams for predictive solid-state ceramic synthesis.

Recent Progress

Since the 2023 DOE Synthesis and Processing Science PI meeting, we have published two major papers, one in *Nature Synthesis* and one in *Nature Physics*. Both of these manuscripts pushed the frontiers of computational materials science, nucleation and growth theory, and solid-state chemistry. As this Early Career Award comes to a close, we are wrapping up our two biggest publications, where first we predict and characterize a transient metastable liquid phase in mediating interdiffusion in the early stages of materials synthesis; and the second where we have built efficient and scalable algorithms to evaluate liquid free energies in a way that can be readily combined with high-throughput DFT convex hulls such as from the Materials Project.

“Navigating phase diagram complexity for robotic inorganic materials synthesis”

Jiadong Chen, Sam Cross, Lincoln Miara, Eric Wang, Wenhao Sun*, *Nature Synthesis* (2024)

Efficient synthesis recipes are needed to streamline the manufacturing of complex materials and to accelerate the realization of theoretically predicted materials. Often, the solid-state synthesis of multicomponent oxides is impeded by undesired by-product phases, which can kinetically trap reactions in an incomplete non-equilibrium state. Here we report a thermodynamic strategy to navigate high-dimensional phase diagrams in search of precursors that circumvent low-energy, competing by-products, while maximizing the reaction energy to drive fast phase transformation kinetics. Using a robotic inorganic materials synthesis laboratory, we perform a large-scale experimental validation of our precursor selection principles. For a set of 35 target quaternary oxides, with chemistries representative of intercalation battery cathodes and solid-state electrolytes, our robot performs 224 reactions spanning 27 elements with 28 unique precursors, operated by 1 human experimentalist. Our predicted precursors frequently yield target materials with higher phase purity than traditional precursors. Robotic laboratories offer an exciting platform for data-driven experimental synthesis science, from which we can develop fundamental insights to guide both human and robotic chemists.

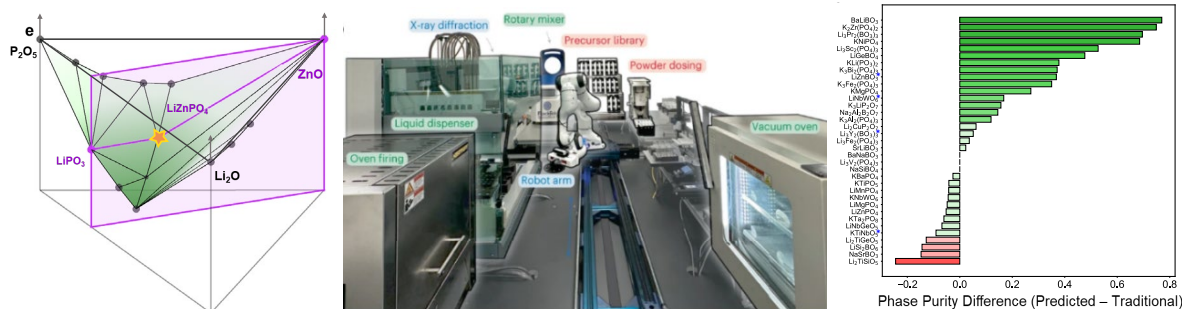


Figure 1. In our *Nature Synthesis* paper, we examined how different pairs of precursors on a higher-dimensional convex hull intersect the target phases with different reaction driving forces. We hypothesized that precursors that offer larger thermodynamic driving forces provide more effective kinetic pathways to synthesize target materials. This hypothesis was validated by a robotic synthesis laboratory at Samsung Semiconductor in Cambridge, MA, where for a diverse set of materials we were able to obtain higher phase purities in a solid-state reaction than from traditional precursors.

Quasicrystal stability and nucleation kinetics from density functional theory

Woohyeon Baek, Sambit Das, Shibo Tan, Vikram Gavini, Wenhao Sun*, *Nature Physics* (2024)

The aperiodic order of quasicrystals bridges the amorphous and crystalline regime, so it has remained unclear whether quasicrystals are metastable or stable phases of matter. Density functional theory (DFT) is often used to evaluate thermodynamic stability, but quasicrystals are long-range aperiodic and their energies cannot be calculated using conventional *ab initio* methods. Here, we perform first-principles calculations on quasicrystal nanoparticles of increasing sizes, from which we can directly extrapolate their bulk and surface energies. Using this technique, we determine with high confidence that the icosahedral quasicrystals $\text{ScZn}_{7.33}$ and $\text{YbCd}_{5.7}$ are ground-state phases—revealing that translational symmetry is not a necessary condition for the $T = 0$ K stability of inorganic solids. Although we find the $\text{ScZn}_{7.33}$ quasicrystal to be thermodynamically stable, we show on a mixed thermodynamic and kinetic phase diagram that its solidification from the melt is nucleation-limited, which illustrates why even stable materials may be kinetically challenging to grow. Our techniques here broadly open the door to first-principles investigations into the *structure-bonding-stability* relationships of aperiodic materials.

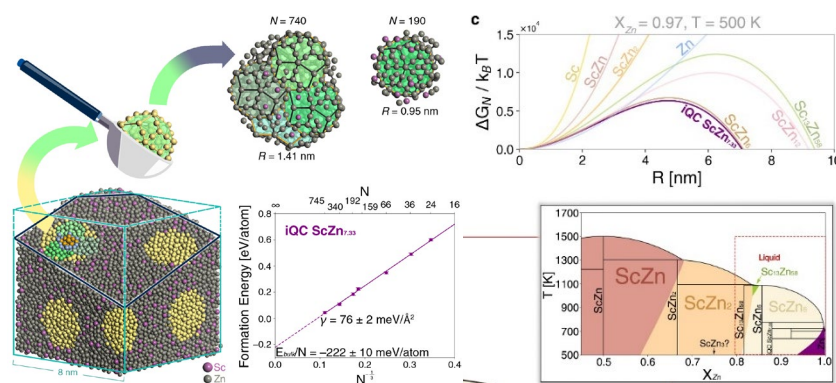


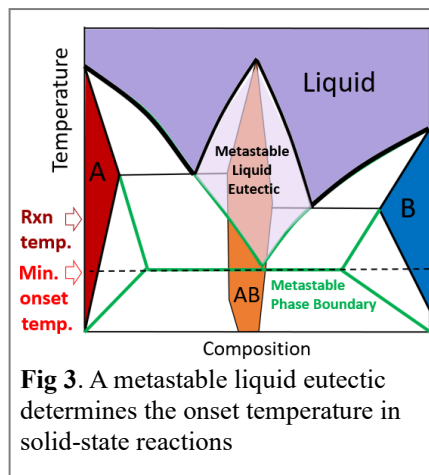
Figure 2. Sampling quasicrystal nanoparticles from a 30,000 atom enables us to characterize quasicrystal bulk and surface energies. Bulk energies confirm convex hull stability of quasicrystals; whereas surface energies allow us to evaluate nucleation kinetics during solidification from the liquid.

The DFT calculations in this work used DFT-FE (DFT Finite Element), led by Prof. Vikram Gavini at University of Michigan, which was code developed also through the DOE-funded PRISMS program. The calculations were performed on the *Frontier* supercomputer at Oak Ridge, and these are arguably the first exascale DFT calculations ever performed.

Origin of the reaction temperature in solid-state materials synthesis

Shibo Tan, Gabrielle Kamm, Karena Chapman, Wenhao Sun, et al., *In Preparation* (2025)

Temperature plays a crucial role in solid-state materials synthesis, but there is currently no mechanistic theory to explain or predict what temperature is best to carry out a solid-state reaction. Reactions between powder precursors are conventionally assumed to be slow diffusion-limited processes, however recent *in situ* experiments show that solid-state reactions can complete in minutes above a critical onset temperature. Here, we show evidence that a transient liquid phase forms above the metastable eutectic temperature, and that this non-equilibrium liquid serves as a fast diffusion media to intermix precursors and initiate a solid-state reaction. This mechanism is agnostic to the structure or chemistry of the reactants, meaning that this thermodynamic principle should be broadly applicable in predicting reaction temperatures for the synthesis and manufacturing of complex materials.



This is the primary output of my DOE Early Career Award, and is the culmination of 4 years of efforts to characterize a transient metastable liquid phase and its role in solid-state materials synthesis. We led the thermodynamic modeling and prediction of the metastable eutectic temperature, Karena Chapman at Stonybrook University led the *in situ* synchrotron X-ray diffraction characterization of the reaction progress (funded through the DOE Genesys EFRC), Ashwin Shahani at University of Michigan (also in the DOE Synthesis and Processing program) led X-ray nanotomography characterization of reaction diffusivity, and Robert Hovden (who won the DOE Early Career Award in 2024) led *in situ* transmission electron microscopy of the reaction. We are preparing the work for submission to *Science*.

Efficient *ab initio* prediction of liquidus curves in new alloy systems

Joshua Willwerth, Shibo Tan, Abrar Rauf, Mario Plata, Julia Chan, Wenhao Sun, *In preparation* (2025)

The liquidus curve captures the high-temperature eutectics, peritectics, congruent melting and incongruent melting regions of a phase diagram. Being able to predict liquidus curves in novel alloy spaces would enable *ab initio* guidance of materials processing temperatures, as well as the design of new alloys for operation in extreme high-temperature environments. Liquidus curves are available in databases like Thermocalc or Factsage, but their coverage of chemical spaces is often limited. Here, we present a CALPHAD-inspired approach to reference liquidus curves from ASM phase diagrams to DFT convex hulls from the Materials Project DFT database. Using our

technique, we fit non-ideal liquid mixing free-energies on a 70×70 matrix of binary alloy phase diagrams. By machine-learning these liquid mixing free energies, we can interpolate from binary liquidus curves to multicomponent liquidus surfaces. We can also extrapolate liquid free energies to novel unexplored alloy spaces, where predicted liquidus curves have been experimental validated.

[\(Link\) 70x70 Matrix of DFT-Referenced Liquid Free Energies](#)

[\(Link\) Interpolation of 3 binaries to a ternary liquidus surface](#)

All of the projects in this DOE Early Career Award crucially relied on liquid free energies, but there are currently no scalable and efficient ways to compute the liquid free energy. Thrust 2 of this award aimed to predict liquid free energies by referencing liquidus curves from ASM phase diagrams against DFT convex hulls from the Materials Project. This will enable predictive synthesis capabilities broadly across various chemical systems.

Future Plans

Crystal growth of bulk single crystals greater than 5 mm in size are needed for a variety of scenarios in materials science and engineering. For example, large single crystals enable 1) more detailed refinements of crystal structure and magnetic structure by X-ray or neutron diffraction; 2) characterization of quantum materials properties by angle-resolved photoemission spectroscopy (ARPES); and 3) measurement of fundamental ionic and electronic conductivities of defect-free materials for electrochemical applications like Li-ion batteries and catalysts. Finding an optimal **flux composition is an essential design parameter** in flux growth. A second key parameter is the undercooling temperature for crystal growth, which should low enough to maximize the growth kinetics of step-edge attachment, but not so low such that nucleation of secondary crystallites consume solute nutrient that was intended for the target crystal.

For the DOE SPS renewal, we propose a design hypothesis and a computational framework to predict flux chemistries and processing temperatures for flux crystal growth. This proposal leverages theoretical and computational developments from the DOE Early Career Award, including the capability to predict both liquidus surfaces across broad chemical spaces, as well as nucleation and growth rates from a liquid melt. Using these tools, we will broadly screen high-component liquidus surfaces for optimal flux compositions, and interrogate optimized growth temperatures that balance the kinetics of diffusion, nucleation and growth. Our predictive tools will reduce the tedious trial-and-error experiments needed to optimize the bulk crystal growth of materials important to DOE BES missions.

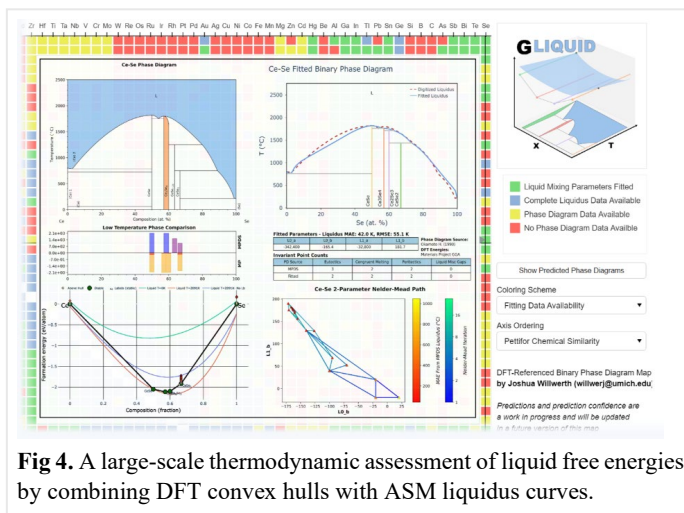


Fig 4. A large-scale thermodynamic assessment of liquid free energies by combining DFT convex hulls with ASM liquidus curves.

Publications (from last 2 years)

Led by PI Wenhao Sun

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Controlling Kinetics to Synthesize Metastable Compounds with Targeted Structures

David C. Johnson, University of Oregon

Keywords: Synthesis, dichalcogenides, heterostructures, metastable compounds, reaction intermediates

Research Scope

The goal of this project is to discover experimental parameters required to direct a reacting system through the energy landscape to a targeted metastable compound, avoiding stable compounds as reaction intermediates. We prepare precursors by sequentially depositing elemental layers, which creates new experimental parameters (layer thicknesses, the ratio of layer thicknesses and the sequence of layers) that can be tuned to control the reaction pathway. Information gained by investigating the evolution of binary A|B, A|C, and B|C diffusion couples as a function of layer thickness and composition enables us to design ternary A-B-C layer sequences that avoid the formation of binary compounds at reacting interfaces. In these ternary precursors, the local structure and composition control what compounds nucleate. By creating more complex layer sequences, specific compounds in a homologous series can be synthesized. As elemental layer thicknesses in precursors are increased, the evolution of the composition profile at interfaces as a function of temperature and time determines which compound nucleates first at the reacting interfaces. We are developing experimental approaches to measure interfacial composition profiles using a combination of techniques. A scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDS) map is collected on a precursor is used to measure the average change in composition across an interface. This is used as a starting point to refine by X-ray reflectivity data collected on the precursor. The precursor is repeatedly annealed and refined using the previous refinement as a starting model.

Recent Progress

We have investigated the following binary systems (Pb-Se, Sn-Se, Fe-Se, Nb-Se, Mo-Se, ZnSe) and the large differences in the composition profiles in the as-deposited precursors is shocking. Fe diffuses through 50Å of Se to form an amorphous Fe-Se alloy until a 1:1 ratio is present, at which point depositing additional Fe forms a layer of Fe metal on top of the alloy. Nb does not diffuse far into Se, so Nb|Se bilayers have Bragg reflections from modulation in electron density even when the bilayer thickness is 7Å. Pb, Sn and Zn are like Fe in their interdiffusion with Se while Mo behaves similarly to Nb. Our current hypothesis is that if the metal's highest oxidation state in a Se matrix is 2+ or less, then significant interdiffusion occurs during the deposition process. The limited prior literature reports are consistent with this hypothesis. Cu, which is always monovalent in chalcogenides, diffuses rapidly through Se. Cr forms Cr₂Se₃ which

contains Cr^{3+} cations in a rhombohedral structure (space group: $R\bar{3}$) based on the NiAs-type structure with ordered vacancies. Bensch and coworkers reported that sequential deposition of Cr and Se will result in layered precursors containing alternately Cr rich and Se rich layers.^{ref} Mn is always divalent in compounds with Se, as MnSe_2 has the pyrite structure, which contains Se_2^{2-} dimers in a rock salt like structure with Mn^{2+} . We expect it will behave similarly to Fe, forming a homogenous amorphous alloy for samples containing more Se than Mn.

Our investigations of the binary Nb-Se and Sn-Se systems resulted in several surprises. Only NbSe_2 was observed to nucleate and grow during the annealing amorphous Nb-Se intermediates with compositions close to the stoichiometries of the 6 known binary compounds. Amorphous intermediates with compositions that differ significantly from the 1:2 Nb:Se stoichiometry of NbSe_2 remained amorphous even when annealed to 500°C. We showed that NbSe_2 is the only compound that nucleates and grows at Nb-Se interfaces, but only if the interface composition gradient has regions with compositions that include the stoichiometry of NbSe_2 . Nucleation is clearly the rate limiting step in the formation of crystalline niobium selenides, but composition of the amorphous intermediate alone is not enough to control what nucleates. This points out the need to develop experimental parameters that can be used to lower nucleation energies of targeted structures. In the Sn-Se system, we observed the nucleation and growth of Sn and SnSe for films with compositions that are Sn rich. Both cubic and orthorhombic SnSe are formed, and we are in the process of determine what controls which structure is formed. Films that are Se rich interfuse during the deposition to form amorphous intermediates. Annealing these amorphous precursors results in the formation of either the known 1T structured SnSe_2 or a new Sn-Se compound. We are currently working to determine the structure of this new compound. We continue to be surprised at the amount that is not known about simple binary systems.

The data on the evolution of binary M-Se systems has enabled us to extend the composition range of alloy formation relative to the bulk phase diagram, make new ternary compounds with layers having structures not found in equilibrium phase diagrams, and make homologous series of heterostructures. In our previous granting period, we showed that annealing designed Pb-Fe-Se precursors resulted in extending the range of substitution in the $\text{Pb}_{1-x}\text{Fe}_x\text{Se}$ alloys and enabled us to prepare the first ternary Pb-Fe-Se compounds ever prepared. Conventional synthesis approaches only resulted in the formation of known binary compounds, consistent with the known phase diagram. The new ternary Pb-Fe-Se compounds are homologous members of the $(\text{PbSe})_m(\text{FeSe}_2)_n$ series, where the structure of the FeSe_2 layers in the heterostructures have a hexagonal 1T layered structure rather than the pyrite structure found in the bulk phase diagram. Iron is octahedrally coordinated in the Se-Fe-Se trilayer structure.

We are currently probing whether the confinement of a 2D Fe-Se layer between any adjacent pair of layers is sufficient to form the 1T structured FeSe_2 layer(s) or whether the PbSe interface has an additional role stabilizing the 1T structured FeSe_2 layer(s). Towards this end, we have prepared Nb-Se-Fe-Se and Mo-Se-Fe-Se precursors targeting the formation of $(\text{FeSe}_2)_m(\text{TSe}_2)_n$ heterostructures with $\text{T} = \text{Mo}$ and Nb . We expected to observe the initial formation

of MoSe₂ and NbSe₂, creating an amorphous Fe-Se layer that may or may not form FeSe₂. This behavior was observed for the Mo-Se-Fe-Se precursors, with FeSe₂ nucleating and growing as annealing temperature is increased. At ~300°C, the FeSe₂ layer loses Se and converts into an FeSe layer while maintaining the heterostructure nanoarchitecture. For the Nb-Se-Fe-Se precursors we did not see a heterostructure form. Fe_{1-x}Nb_xSe₂ was the initial crystalline phase formed during the deposition. This alloy also formed when specific x values were targeted by preparing precursors with a Fe|NbSe sequence of layers, each containing the number of atoms required to form a specific Fe_{1-x}Nb_xSe₂ compound. Our attempt the synthesis of 3 predicted ternary Fe-Nb-Se compounds with energies only slightly above the energy hull of mixtures of binary compounds by preparing precursors with the correct ratio of atoms in a Fe|Nb|Se sequence of ultrathin layers was not successful. Only mixtures of known compounds and alloys formed.

Future Plans

While continuing the investigations described above, we will begin to investigate the Sr-Se and La-Se binary diffusion couples and use the resulting information to probe the formation of 5 ternary compounds predicted to be stable that cannot be prepared using conventional synthesis approaches. Based on our findings on these systems, we will explore the synthesis of other ternary and quaternary compounds using the additional synthesis variables of diffusion distances, local composition, and controlled nanoarchitecture provided by the sequential deposition of layers to avoid known binary compounds as reaction intermediates. We will also explore the concept of confined 2D volumes as an approach to prepare new layer structures within designed heterostructures.

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Unraveling Grain Refinement Mechanisms in Multi-Principal Element Alloys

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Keywords: Massive transformation, Grain refinement, Multi-principal element alloys (MPEAs), Directed energy deposition (DED), Powder bed fusion (PBF)

Research Scope

This research aims to advance our understanding of the relationship between composition, processing, and mechanical properties in the additive manufacturing (AM) of multi-principal element alloys (MPEAs). Our focus is on the effect of solidification pathways, specifically the formation of intermediate phases, on microstructure and mechanical properties. Using a co-design approach, we integrate experimental and computational methods to guide the development of novel alloys with tailored performance.

The major goals of this project are as follows:

- Establish the link between metastability and microstructure by investigating phase formation and transformation pathways during solidification in AM.
- Evaluate the mechanical properties of AM-processed alloys, particularly how phase stability influences strength, ductility, and overall performance.
- Develop composition-processing guidelines to optimize alloy design for fine-grained microstructures and enhanced mechanical properties.

As a case study, Fe₃₀Mn₅₀Co₁₀Cr₁₀ exhibited significant grain refinement in directed energy deposition (DED) due to a BCC-to-FCC massive transformation during solidification. In contrast, higher cooling rates in powder bed fusion (PBF) suppressed this transformation, resulting in coarser grains, highlighting the importance of composition-process co-design. To generalize this approach, we computationally screened several MPEAs, atomized selected compositions, and conducted synchrotron experiments. Future work will refine design principles and implications on mechanical properties.

Recent Progress:

Our prior work has shown that massive phase transformation is a key contributing factor to the observed grain refinement in the FeMnCoCr system printed using directed energy deposition (DED) technique [1]. Scheil plots for Mn₄₀, Mn₄₅, and Mn₅₀ compositions (Fig 1. (a-c)) exhibit a BCC-to-FCC transition during solidification. Grain refinement was observed in Mn₅₀ (Fig1. (f)) due to its specific composition, which favors diffusionless massive phase transformation under rapid solidification conditions [2]. The BCC phase fraction in Scheil simulations increases progressively from Mn₄₀ to Mn₄₅ and Mn₅₀. The higher intermediate BCC fraction in Mn₅₀ suggests greater phase stability, which facilitates massive transformation. Additionally, Mn₅₀ has single phase FCC crystal structure (Fig1. (i)) indicating that the intermediate BCC phase has fully transformed into FCC during solidification [3].

Intermediate BCC phase stabilization in Mn50 can be influenced by the cooling rate of the manufacturing process. Grain refinement is only observed in the DED process (Fig 2. (b)), where relatively lower cooling rates enable intermediate metastable phase formation and stabilization during solidification (Fig 3. (c)). In contrast, the high solidification rates in the powder bed fusion (PBF) process, combined with solute trapping effect, shift the primary solidification phase from BCC to FCC, suppressing the massive transformation and hindering grain refinement (Fig 2. (d)) [4].

We hypothesize that by screening Scheil solidification simulation results of multi-principal element alloys (MPEAs) it would be possible to explore other systems that exhibit grain refinement through possible massive transformations or compositional effects using DED process. We screened the MPEAs containing Al, which generally stabilizes BCC phase formation, and those that exhibit BCC-to-FCC or FCC-to-BCC phase transformations. Quaternary and quinary combinations of Al, Co, Cr, Fe, Mn, Ni, Nb, and Ti were considered for Scheil simulations. The materials systems containing sigma or laves phases in the Scheil solidification simulation were excluded from the screening process. We analyzed the results and selected two new MPEA systems (AlCoCrFeNi and AlCrFeMnNi) which include three compositions with low, intermediate, and high BCC fractions and the freezing range of smaller than 400 °C. We made the pre-alloyed powders of MPEAs using

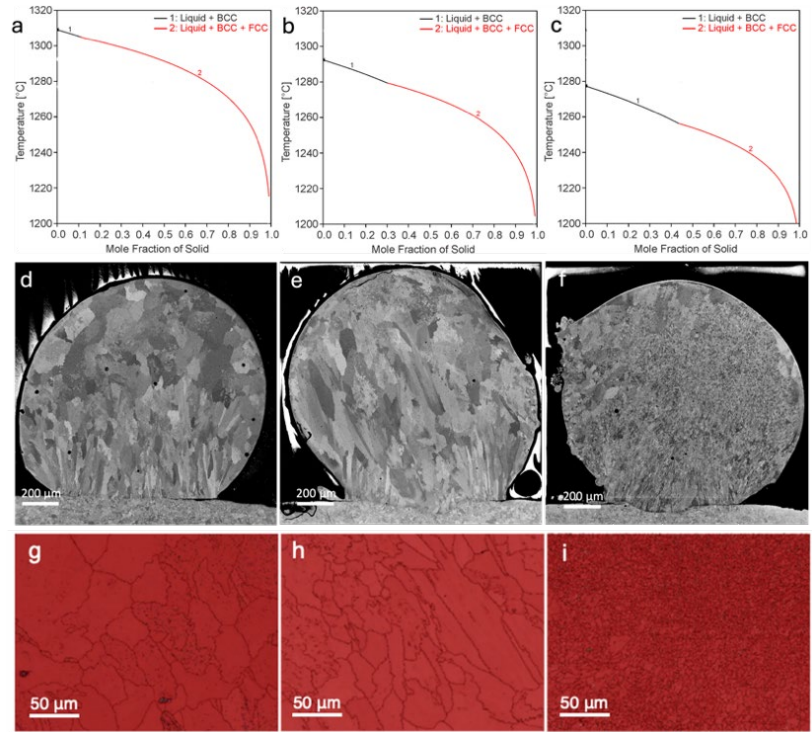


Figure 2. Scheil solidification plots and microscopy images of FeMnCoCr system; (a-c) Scheil solidification simulations results for Mn40, Mn45, and Mn50, respectively, (d-f) BSE images of single DED-printed bead of Mn40, Mn45, and Mn50, respectively, (g-i) EBSD-phase maps of Mn40, Mn45, and Mn50, respectively.

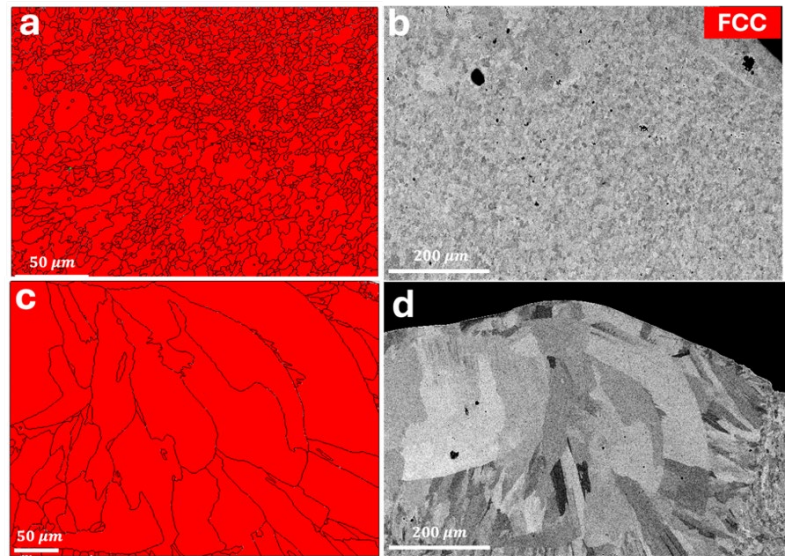


Figure 2. Microscopy images of FeMnCoCr (Mn50); (a) EBSD-phase map of Mn50-DED, (b) BSE image of Mn50-DED, (c) EBSD-phase map of Mn50-PBF, (d) BSE image of Mn50-PBF.

ultrasonic atomizing technique and printed the single bead structures using a custom printer setup integrated to the Cornell High Energy Synchrotron Source (CHESS). Beads were printed using DED process (200 W power and 5 mm/s scan speed) while in-situ XRD data were captured at every stage of additive manufacturing process such as melting, solidification, and cooling. We expected to observe grain refinement in microscopy images and intermediate phases in synchrotron XRD data of the compositions with high BCC fractions.

Grain refinement was observed in AlCrFeMnNi sample with highest BCC fraction (Fig 3. (g,h)). Additionally, bimodal grain size distribution was observed in AlCoCrFeNi sample with intermediate BCC fraction (Fig 3. (d,e)). Time-resolved XRD data showed BCC–B2 and FCC–L1₂ peaks in both samples at the final frame, Unlike Mn50, all of the peaks corresponding to FCC and BCC phases appear at solidification stage and remain till the end of cooling process (Fig 3. (f&i)) indicating coexistence of phases in the new MPEAs. In both samples, we observed dual phase ordered microstructures (Fig 3. (d&g)) accompanied by grain refinement (locally in Co2).

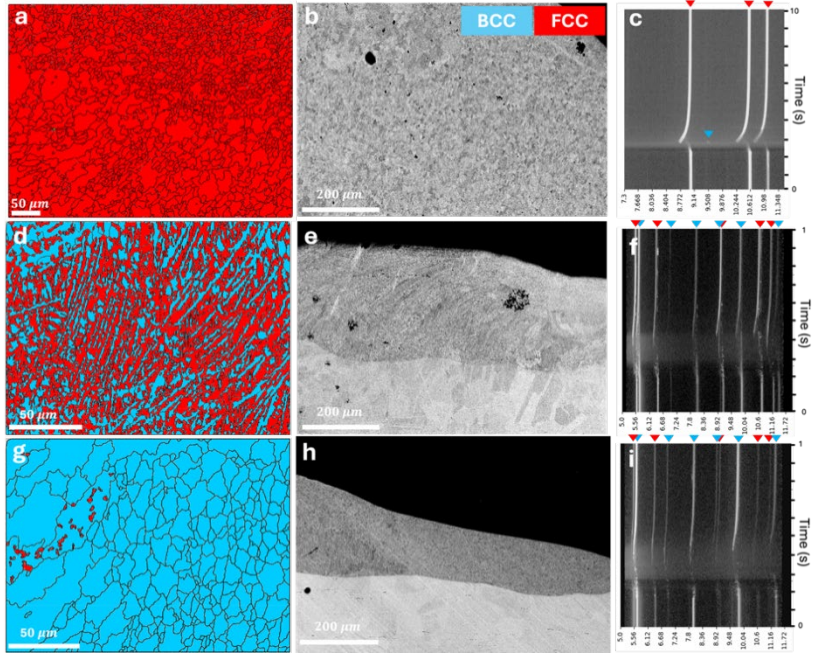


Figure 3. Microscopy images and Time-resolved XRD plots for samples exhibiting grain refinement; (a) EBSD-phase map of FeMnCoCr (Mn50), (b) BSE image of FeMnCoCr (Mn50), (c) Time resolved XRD plot of FeMnCoCr (Mn50), (d) EBSD-phase map of AlCoCrFeNi, (e) BSE image of AlCoCrFeNi, (f) Time resolved XRD plot of AlCoCrFeNi, (g) EBSD-phase map of AlCrFeMnNi, (h) BSE image of AlCrFeMnNi, (i) Time resolved XRD plot of AlCrFeMnNi.

Future Plans

Since there are dual phase microstructures in the new systems, massive transformation is probably not the main mechanism causing the grain refinement. Additionally, presence of ordered phases in AlCoCrFeNi and AlCrFeMnNi microstructures adds another layer of complexity to unraveling the solidification process and grain refinement mechanism in these new dual phase microstructures.

For future work we will:

1. Investigate the different solidification modes in each of the new material systems. Compositional changes can alter the final microstructure, however, rapid solidification in additive manufacturing processes can also introduce new pathways to conventional solidification mechanisms expected in typical manufacturing techniques. Synchrotron X-ray diffraction data

collected from different detectors will be incorporated with advanced post-process refinement/analysis techniques to study solidification pathways. We hypothesize that different microstructures observed in all new compositions can be the result of various fast phase formations/transformations, and specific elemental segregations.

2. Unravel grain refinement mechanisms in AlCoCrFeNi and AlCrFeMnNi through multi-scale microscopy analysis (SEM, EBSD, EDS, TEM), operando synchrotron XRD data and CALPHAD-based simulations.

3. Explore the presence and effect of ordered phases (BCC-B2 and FCC-L12) on final microstructure, phase morphology, and mechanical properties of additively manufactured MPEAs through multi-scale microscopy techniques and operando synchrotron XRD data.

4. Multilayer printing and mechanical properties; All compositions will be printed using an industrial scale DED printed (Formalloy) to enables us to explore their mechanical properties (deformation and strengthening mechanism). Mechanical testing and multi-scale microscopy analysis (TEM, SEM) will be utilized to exhibit differences in deformation modes and correlate them to the microstructures and the solidification pathways.

5. Explore the effect of process parameters (power and scan speed) in additive manufacturing on solidification pathway, final microstructure, and phase morphologies in AlCrFeMnNi system through multi-scale microscopy techniques and operando synchrotron XRD data.

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Acknowledgment

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analysis and microscopy) and by the National Science Foundation CAREER Award #CMMI-2046523, A.M. (conducting operando experiments). A.W. acknowledges a graduate fellowship through the NASA Space Technology Graduate Research Opportunities [Grant #80NSSC20K1199, AW]. This work made use of the Cornell Center of Materials Research Shared Facilities, which are supported through the NSF MRSEC program [DMR-1719875]. This work is based upon research conducted at the Center for High Energy X-ray Sciences (CHEXS), which is supported by the National Science Foundation [DMR1829070]. W.X. acknowledges funding from the National Science Foundation CAREER Award [CMMI 2047218, W.X.]. N.S. acknowledges a graduate fellowship through the NASA Space Technology Graduate Research Opportunities [Grant # 80NSSC19K1142, N.S.]

2. Akane Wakai , Atieh Moridi. Role of grain refinement and phase metastability on deformation behavior of additively manufactured FeMnCoCr multiprincipal element alloys, Materials Science & Engineering A 916 (2024) 147348.

Acknowledgment

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Collaborative:

3. Kaushalendra K. Singh, Akane Wakai & Atieh Moridi, Advancements in operando X-ray techniques for metal additive manufacturing, Communications Materials | (2024) 5:258.

Acknowledgment

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Acoustic-Field Driven Nanoparticle Organization in Semi-Crystalline Polymer Matrix

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Keywords: Polymer Nanocomposite, Acoustic Field, Sonication, NP ordering, Laser Zone Annealer.

Research Scope

This project aims to create hierarchically ordered polymer nanocomposites and polymer blends by leveraging external field-assisted crystallization. Building upon our prior DOE-funded work, which demonstrated that quiescent, isothermal crystallization can drive nanoparticle (NP) organization into the amorphous interlamellar regions of semicrystalline polymers such as polyethylene oxide (PEO) and polyethylene (PE) ¹⁻³, the current research explores how external drivers—acoustic, and thermal fields—can further accelerate and control this ordering.

The key parameter controlling NP organization in semicrystalline polymers is the Peclet number (Pe), defined as the ratio of the time scale for NP diffusion ($\tau_D = a^2/D$) to that for polymer crystallization ($\tau_G = a/G$), where a is the lamellar spacing, D is the NP diffusion constant, and G is the crystallization rate. At $Pe \approx 1$, NPs optimally segregate into the amorphous interlamellar regions; at higher Pe, particle mobility is insufficient for ordering within the interlamellar regions. Currently, the critical crystallization rate is too slow for scalable processing. Previous work in hydrogels demonstrated that acoustic radiation forces provide significantly enhancing NP diffusivity.⁴ Thus, the practical objective is to use external fields to increase D , increase critical crystallization rate, G_c , thus opening the processing window to create organization at lower temperature and shorter times. The more fundamental objective is to combine theory and experiments to understand the mechanisms that control external field, kinetically driven, non-equilibrium, processes to create hierarchical, layered nanocomposites for advanced applications.

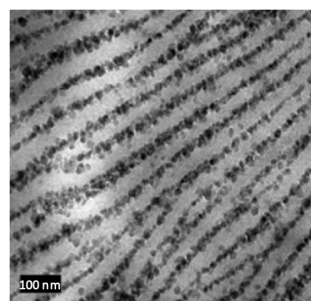


Figure 3: Ordered 15nm Silica / PEO Nanocomposite

Two main hypotheses drive this work: (1) External fields (e.g., acoustic vibration) enhance NP or polymer diluent mobility, enabling faster and more extensive directional organization. (2) Combining directional crystallization and external fields can be extended to sustainable polymer mixtures to create interlamellar multilayered materials with improved mechanical properties.

Recent Progress

Our current work focuses on validating the use of acoustic fields to enhance nanoparticle (NP) mobility during isothermal crystallization, and on constructing a zone annealing platform compatible with external field application.

Acoustic Field-Enhanced Nanoparticle Ordering: We conducted a systematic study to evaluate the impact of low-intensity, unfocused acoustic signals on NP mobility and resultant ordering in silica-PEO nanocomposites. Nanocomposite films were prepared via solution casting using

silica nanoparticles (diameters: 15 ± 4 nm) at loadings of 20 wt% in a 38 kDa polyethylene oxide (PEO) matrix. Differential scanning calorimetry (DSC) was used to characterize crystallization kinetics. SAXS measurements were performed to evaluate the degree of NP ordering, with 2D anisotropic patterns azimuthally integrated over a 25° wedge centered at the scattering maxima using PYFAI library in python. TEM was used to look more locally at morphology. The contrast between crystalline lamellae and the nanoparticles results in a first order SAXS peak, if ordering occurs. The corresponding q value of the peak (q^*) when inversed over 2π in neat samples is the distance between 2 crystalline lamellae (Long period) but in our case is the interparticle spacing which is the center-to-center distance between 2 nanoparticles.

At 55°C , PEO required 180 minutes for complete isothermal crystallization, and some NP organization was observed (prior work found significant ordering at 56°C and 8 hours). In contrast, at 52°C , crystallization occurred in just 25 minutes, and SAXS showed no ordering. Based on this, 54°C was selected as a critical temperature: it offered an intermediate crystallization time (65 minutes), but did not exhibit NP ordering in the absence of external stimuli—ideal for testing the effect of acoustic activation.

Isothermal crystallization experiments were conducted at 54°C under varying sonication amplitudes (0–35%) using an unfocused probe in a stirred water bath to ensure

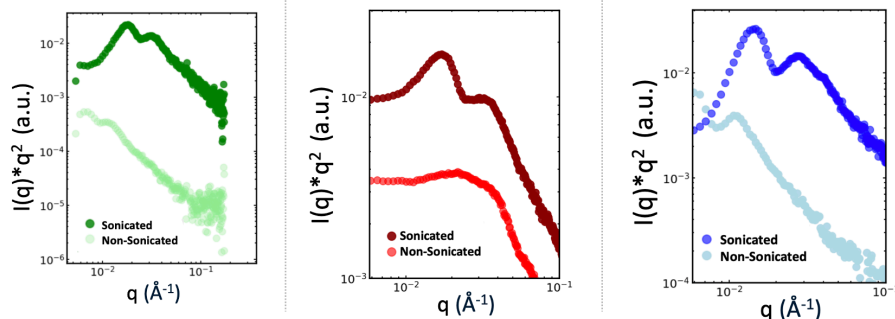
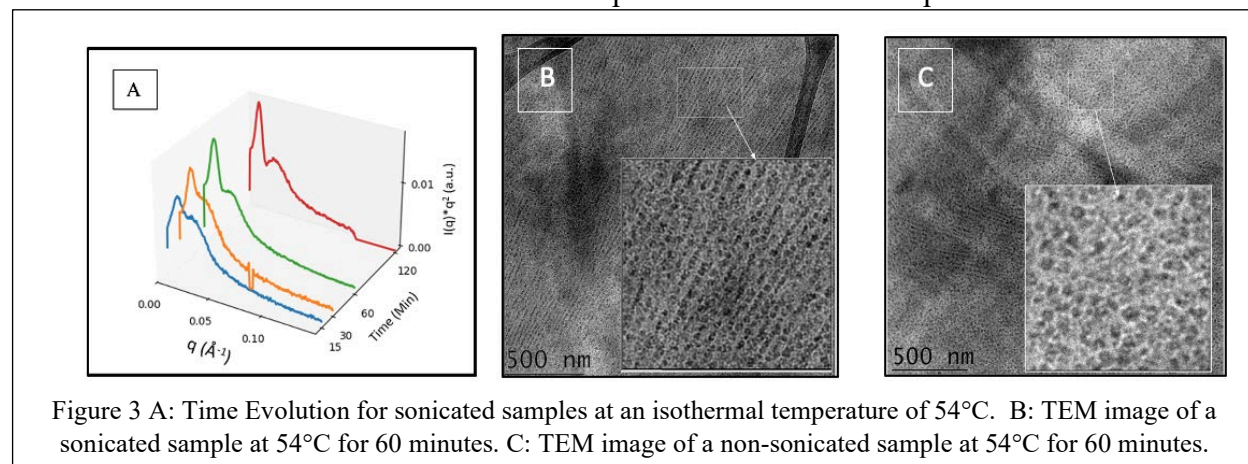


Figure 2. Shows the difference between sonicated and non-sonicated samples for a fixed duration of 1 hour at temperatures of 53,54 and 55°C respectively.

temperature stability ($\pm 0.25^\circ\text{C}$). Samples were collected at 15, 30, 60, and 120-minutes. At lower sonication amplitudes, no significant organization was observed—the SAXS profiles resembled those of non-sonicated controls. At 35% amplitude, distinct first-order peaks emerged in the scattering data, indicating the formation of layered NP morphologies (Figure 2) at three different temperatures (53°C , 54°C , 55°C) for sonicated samples. For a similar time frame, no first order peaks were observed in non-sonicated samples indicating that the particles are well dispersed and not organized. These results clearly show that the acoustic field increased D, enabling organization at a crystallization rate previously above G_c .

The time evolution of structure under sonication at 54°C is shown in Figure 3A. NP ordering is evident by 30 minutes. There were no visible changes between the neat sonicated and control samples, indicating that the acoustic field is not increasing the pure polymer crystallization rate.

These results support our hypothesis that an external unbalanced acoustic field can effectively shift the critical crystallization rate by increasing NP mobility. The TEM images (Figure 3B&C) show the difference between the sonicated samples and the control samples over a fixed duration



of time further validating the hypothesis. The interparticle spacing matched that obtained by SAXS.

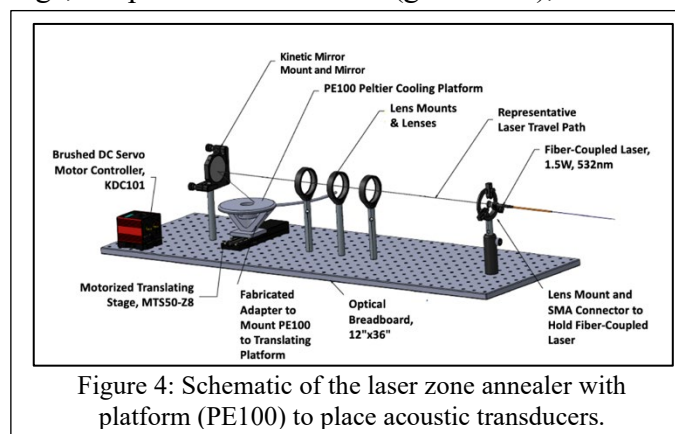
Zone Annealing System Development with Field Coupling Capability:

To facilitate combined thermal and acoustic processing, we are constructing a laser-based zone annealing (ZA) platform using a 532 nm green laser for localized heating, chosen for its proven effectiveness in long-duration annealing applications such as block copolymer alignment.⁵ The laser beam is directed onto the sample via a 3D-printed optical mount, while the substrate rests on a temperature-controlled Linkam PE100 stage. The entire assembly is placed on a motorized translation stage, allowing precise control over crystallization front velocity (Figure 4).

The zone annealing setup is enclosed within a nitrogen-purged chamber to eliminate oxidation during processing. This controlled environment also minimizes spatial fluctuations in thermal gradients and ensures reproducible sample cooling.

To integrate acoustic fields with directional crystallization, we are incorporating a 5 MHz contact-mode transducer mounted on a wedge, coupled to the substrate (glass slide), and driven using a function generator and amplifier. The wedge geometry enables acoustic wave delivery directly into the melt region during zone annealing. This configuration allows for concurrent spatially localized heating and acoustic field application.

This setup also opens the possibility of processing semicrystalline polymers



with higher melting points, extending the generalizability of our approach to new sustainable material systems.

Future Plans

In the short term, we aim to:

- Perform crystal growth rate experiments with PLOM attached with cross-polarizers under isothermal conditions to check if there is any effect of sonication on the crystal growth rate.
- Construct a setup for measuring change in diffusivity of nanoparticles in the semicrystalline melt to quantify D values using XPCS.
- Validate alignment along both parallel and perpendicular directions relative to the annealing front. Investigate the interaction between directional crystallization and NP diffusion under field activation.
- Determine how NP size, density, and surface grafting affect acoustic response during ZA.
- Benchmark resulting materials using SAXS and mechanical testing.

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Directional Crystallization (Zone Annealing) of Polymer Blends

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Keywords: Polymer Crystallization, Polymer Blends, Polymer Reprocessing

Research Scope

Over the last 60 years, plastics have been the largest man-made materials due to their design potential, diversity, flexibility, low cost, and durability. However, only 5% of the plastic waste generated was recycled; the rest was either discarded in landfills or combusted. There is thus a pressing need to sustainably upcycle/reprocess these materials. Moreover, a majority of these plastics are semicrystalline (layered crystalline and amorphous domains) in nature. Directional crystallization (zone annealing) of polymers, demonstrated by Lovinger and Gryte and many other workers in the 1960s, is a promising pathway to the reuse of end-of-life polymers, specifically of multi-layered plastics (containing semicrystalline polymers). To this end, recent efforts include studies on the directional crystallization (or zone annealing) of semicrystalline polymers and semicrystalline-glassy blends, and report the preferential orientation of the crystallizable component in the direction of the imposed temperature gradient. However, a clear molecular mechanism of crystallization at the zone annealing front and the resulting microstructure (and consequent material properties) is still unclear. In this project, we propose to sequentially study directional crystallization of semicrystalline polymer systems, followed by miscible polymer blends, and finally immiscible polymer blends (frequently encountered in multi-layered plastics). To begin with, the role of nucleation on zone annealing of polyethylene oxide (PEO), and the resulting material will be explored. Further, we study model miscible semicrystalline-amorphous blends, namely - (PEO/PMMA(poly(methyl methacrylate))), PEO/PVAc (polyvinyl acetate)). In our recent work, we show that at accessible velocity of zone annealing, the PMMA segregates interlamellar (length scales of nm) in the blends. Previously, Runt, etc, have shown that in isothermally crystallized PEO/PVAc blends, the PVAc diffuses into the interfibrillar zone (length scales of nm - μm). We hypothesize that zone annealing of PEO-rubbery PVAc should greatly influence the morphology of the final material. These differences in morphology (PEO/PMMA vs PEO/PVAc) are consequential in determining the mechanical response of these materials. Then, we move to immiscible semicrystalline polymer blends such as PEO and PCL (polycaprolactone). PCL is shown to not develop oriented spherulites when subjected to thermal gradients. The resulting morphology corresponds to commercial multilayered materials, and directly validates the zone annealing protocol as a promising method of reprocessing. This research thus, opens up multiple avenues that can be explored, for example, to reprocess multi-layered immiscible plastics.

Recent Progress

In the current work, we are investigating the directional crystallization of PEO (semi-crystalline)/PVAc (rubbery amorphous) blends to understand the role of a mobile diluent in a semicrystalline structure. It has been shown that PEO and PVAc are melt miscible, and weakly interacting ($\chi \sim 0$), with the PVAc being rubbery ($T_g \sim 35$ °C) during processing (crystallization). We subject the blends of concentrations – PEO (85): PVAc (15) and 70:30 to zone annealing in our in-house zone-annealer (setup details provided in the attached reference) at a velocity of 0.1 $\mu\text{m/s}$. The chosen velocity has been shown to induce directionally oriented crystals for neat (pristine) PEO. The processed samples are post-facto characterized using techniques such as small-angle X-ray scattering (SAXS) for temporal distribution of the diluent; tensile testing to study their mechanical properties, such as modulus and toughness. Further, the samples were locally probed using a transmission electron microscope (TEM) to study the lamellar morphology resulting from zone annealing. The results are summarized and discussed below.

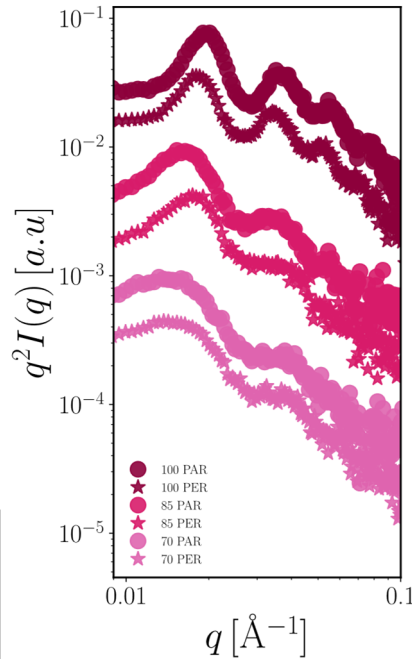
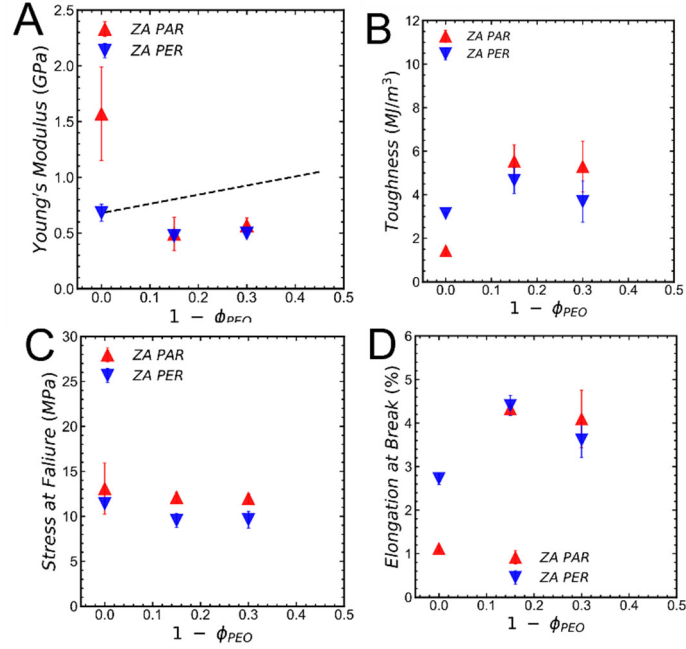


Fig 1: Scattering patterns for different compositions of PEO/PVAc blends zone annealed at 0.1 $\mu\text{m/s}$.

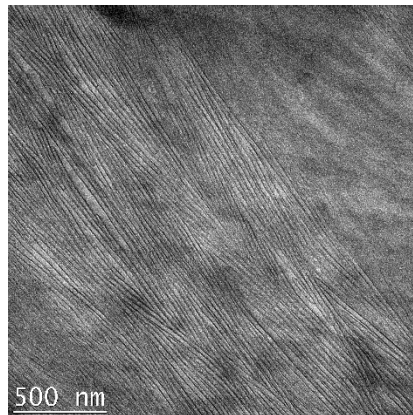
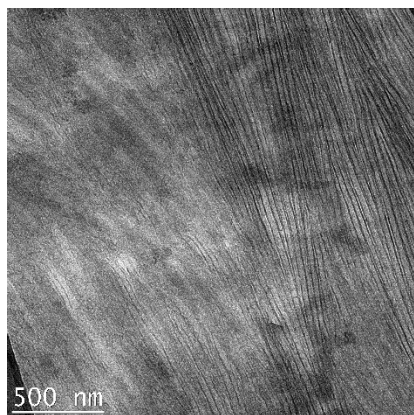
The scattering patterns for the blends are shown in Fig 1. The long period increases as the concentration of PVAc. Qualitatively, the first order peak successively smoothens out, indicating multiple populations of lamellar/crystal thickness in the sample with an increase in PVAc. This is likely due to the PVAc segregation at different crystallization fronts. As a first approximation, the increase in long period can be correlated to the amount of PVAc segregating interlamellar. For example, from Fig 1, the long period of neat PEO is ~ 31.4 nm, and for the 85:15 sample it is ~ 34.9 nm. Assuming all the PVAc segregates interlamellar, the long period ought to be ~ 36.9 nm. This indicates clearly, not all the PVAc is interlamellar. This is in agreement with previous findings. More rigorous analysis (using correlation function) should yield accurate numbers, however should not alter the conclusions. This result is distinct from our recent work, where for the PEO/PMMA system, all the PMMA segregates interlamellar (1-10 nm). However, as shown,

preliminary scattering results suggest that in PEO/PVAc blends, the PVAc only partially segregates interlamellar, with some of the PVAc diffusing interfibrillar scale which spans all the way out to the μm scale. Thus, while the PEO/PMMA morphology appears homogeneous on the μm scale, the PEO/PVAc blends do not. We now discuss the mechanical properties of these PEO/PVAc systems. In the following section, “parallel” refers to the direction of tensile testing parallel to the oriented lamella, and the “perpendicular” indicate the direction of pulling perpendicular to oriented lamella.

Fig 2: Mechanical properties of zone annealed PEO/PVAc blends



The mechanical properties are displayed in Fig 2. In Figure 2A, the Young's modulus (extracted from the linear stress-strain regime) is shown. The overall modulus decreases with addition of PVAc, which is expected due to the rubbery diluent. Surprisingly, the parallel and perpendicular samples show no differences at all compositions. A possible explanation is that the stress is transmitted through the rubbery PVAc in the sample which has no orientation, and hence orientation independent modulus. Figure 2B shows the toughness (the total area under stress-strain curve). The parallel and perpendicular samples overlap, again indicating perhaps the materials fails in the segregated PVAc regions (interfibrillar regions). These results motivate for locally probing the samples using TEM, which are shown below.



The TEM images (70:30 ZA, left– parallel, right – perpendicular) display the distinct crystal (bright regions) and amorphous (darker regions) domains in a local area in the sample. The TEM images show no apparent macroscopic segregation of PVAc. However, it does a bimodal lamellar thickness distribution which is indistinguishable in the X-ray scattering patterns. Further work is in progress to compare the above with isothermally crystallized blends. Furthermore, since the TEM is local (nm scale), these images do not cover/represent the PVAc segregation (μm scale).

Future Plans

As discussed, the PEO/PVAc blends shows macroscopic temporal differences. We hypothesize that these large-scale heterogeneities can be analyzed at a XPCS in beamline (Argonne National Laboratory) with an in-situ zone-annealing setup, mapping of the solid-melt interface, allows us to study the interfacial dynamics of the non-crystallizing component (PVAc) responsible for the resulting morphology (A proposal for the same has been submitted). Parallely, the effect of nucleation density will be studied systematically by controlled incorporation on nucleating agents in PEO, followed by ZA at different velocities. These experiments will elucidate the role of crystallization kinetics in determining the post-processed morphologies. As discussed above, representative immiscible polymer blends (PEO/PCL) will be investigated. These experiments should provide sufficient evidence for using directional crystallization as a scalable means for plastic reprocessing.

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Put the list of publications in the recent 2-years SUPPORTED BY BES here. **If more than 10 publications, list only the 10 most relevant.**

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Chiral Control of Nanocluster-Fiber Architectures via Confined Evaporative Assembly

PIs Richard Robinson (Cornell) and Steven Weinstein (RIT)

Keywords: Chirality, evaporative assembly, UV polaritons, magic-sized clusters, scalable nanomaterial processing

Research Scope

We have identified a materials system and processing method that creates large-scale chiroptic films from fibrous inorganic-organic nanoclusters^{1,2}. The method uses meniscus-guided evaporative assembly in confined geometries to produce high fidelity organization. This collaborative research program aims to develop a fundamental understanding of chiral nanocluster-fiber assembly processes using confined evaporative assembly techniques. By exploring the physical mechanisms that drive solidification, fluid dynamics, and the emergence of chirality at multiple length scales, this work seeks to bridge the gap between microscopic molecular forces and macroscopic material architectures. Inorganic nanoclusters present a unique opportunity for hierarchical chiral assembly, enabling optical properties like linear dichroism and circular dichroism (CD) that combine functionality with scalability. These optically active, multiscale materials hold transformative potential for applications in photonics, energy harvesting, and advanced sensors. Despite their importance, understanding how chirality propagates during synthesis and assembly remains elusive, particularly for metallic and inorganic systems, which lag behind their organic counterparts in processing science frameworks.

The primary motivation for this work is to understand pathways to unlock scalable, cost-effective methods for creating these chiral materials by leveraging meniscus-guided evaporative assembly. Recent advancements have revealed that fluid mechanics—especially the interplay between solvent evaporation, meniscus geometry, surface tension gradients, and fiber deposition—serve as critical variables governing chirality formation. The research focuses on developing predictive models to capture these relationships while addressing variability issues arising from stochastic pinning effects and assembly contingencies. The ability to refine processing techniques can enhance optical activity across measurable length scales, bridging nanomaterials to scalable deployment in roll-to-roll manufacturing systems.

This program focuses on three aims: (1) characterizing the relationship between chiroptical properties and fiber solidification dynamics; (2) developing robust predictive processing models that account for fluid mechanics and solidification physics under confined geometries; and (3) investigating meniscus-directed fluid dynamics. Together, these aims will produce a deeper understanding of the fundamental mechanisms behind confined evaporative assembly, enabling scalable processing methods for hierarchical materials optimized for energy applications and optical functionality. The scalability of this process suggests great potential for incorporation into

roll-to-roll manufacturing methods, making it suitable for applications across optics, electronics, and manufacturing fields.

Recent Progress

I. Modeling Efforts

The modeling progress during this reporting period focused on understanding the fundamental mechanisms driving chirality during evaporative assembly. Two key components were developed: one addressing the dynamics of the wetting line during drying, and the other predicting how the drying process impacts chirality formation in deposited solid fibers.

The first phase of the model explores solvent evaporation in confined geometries, where high vapor pressure necessitates including convective contributions to mass flow in the gas phase. Contrary to conventional assumptions of dilute diffusion, dimensional analysis revealed evaporation-induced creeping flow dynamics—a result that simplifies theoretical approaches for predicting wetting line evolution. Using a quasi-steady-state approximation, these models predict the wetting line's dynamical shape throughout evaporation, and the results align favorably with experimental observations. Python-based implementations allow real-time manipulation of model parameters to match experimental geometries. **Figure 1** shows a typical comparison between experiment and theory.

The second phase of the model incorporates steric interactions between depositing fibers that, when coupled with the drop drying model results, provides a prediction of the observed angle between the drop meniscus wetting line and the deposited line patterns. Our current theory is that chirality is directly related to this angle based on a mechanism set forth in a recent collaborative paper by the PIs². The theoretical framework leverages insights refined in a recent collaborative study by the PIs and formalizes the underlying mathematics to connect meniscus shapes and chirality. Experimental comparisons continue validating favorable model predictions, including correlations between drying speeds and fiber band angles. Early results suggest that local drying rates, material properties, and fiber deposition dynamics contribute synergistically to the emergence of chirality (see **Figure 2**).

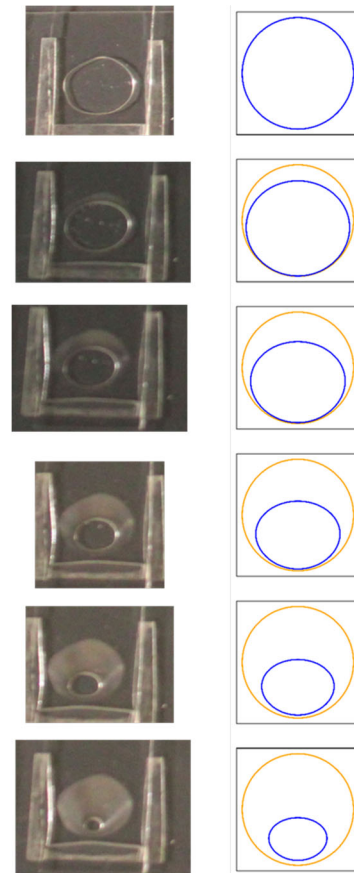


Fig. 1: Typical comparison of observed (left) and predicted (right) drying shapes. A parallel plate geometry made of glass microscope slides is used. Here, a view of the geometry from a top view is examined. In the theoretical predications, the red curves are the shape of the wetting line (assumed circular) at time $t=0$. The blue curves correspond to theoretical predications at later times.

Finally, recent investigations introduced small non-parallel plate angles into the experimental geometries, improving reproducibility and refining theoretical assumptions. Modeling now incorporates local contact angle hysteresis and receding contact angle effects, which impact wetting line motion. These modifications aim to stabilize the drying interface and enhance predictability.

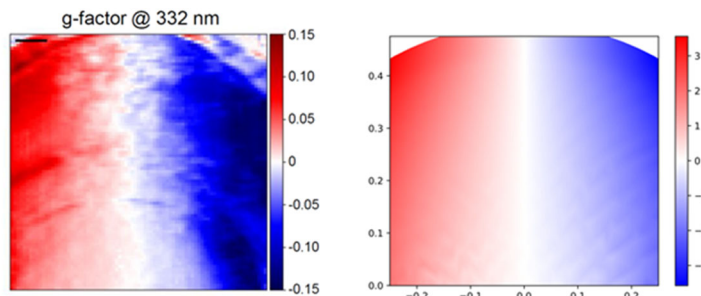


Fig. 2: Comparison of: (left) experimentally measured g-factor (figure of merit for chirality) for thin films assembled with meniscus guided evaporation, and (right) the predicted angle between the wetting line and dried solid bands at various locations. (right) The indicated units and color scale in are the length in mm and the angle in degrees, respectively.

II. Experimental Progress

Significant strides were made to refine experimental techniques and characterize the controlled self-assembly of chiral nanocluster-fiber materials. Meniscus-guided experiments demonstrated the creation of chirality-controlled materials using MSC solutions, and efforts focused on transitioning from narrow, lab-scale geometries to scalable methods suitable for manufacturing.

One of the primary challenges addressed was the stochastic pinning of wetting lines during evaporation, which interferes with reproducibility. Geometry adjustments, such as transitioning to slight angle differences between experimental plates, have improved control over material deposition. This change stabilizes fluid dynamics along the wetting line, aiding the creation of consistent solid banded structures.

A critical question in understanding the chiral banded phenomenon is: what is the length of a typical fiber unit in solution? While it is known that the solidified bands are centimeters long and micrometers wide, we are still examining whether these centimeter-long fibers exist in solution before deposition, or if the fundamental units are much smaller and self-organize into larger fibers during the deposition process.

To address this, we examined the effect of sonication on the solutions for various durations, followed by spin coating the material into thin films on a glass substrate. This approach proved successful in producing smooth, uniform films. Subsequently, using simple solution processing, we were able to embed these smooth films into mirrored Fabry-Pérot (FP) cavities. We excited the cavities with light to create CdS MSC exciton-polaritons in the UV (**Fig. 3**). The MSCs

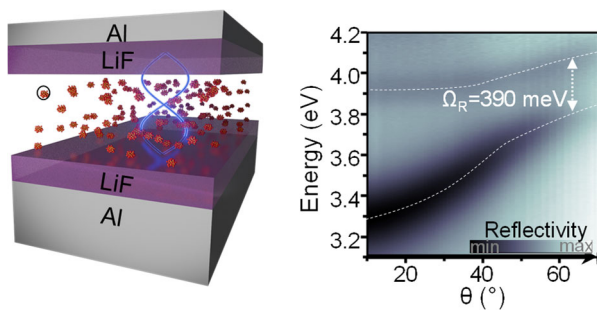


Fig. 3. Processing Magic Sized Clusters (MSCs) into Polariton Gain Media. left) Model of a cavity used to form polaritons using MSCs. (right) Angle resolved reflectivity plot displaying characteristic splitting of upper and lower polariton branches. [adapted from *ACS Nano* **19**, 16438 (2025)]

demonstrated a square root dependence of Rabi splitting on chromophore concentration, reaching values as high as 390 meV. Emission from polariton states spanned the near-UV range from 3.07 eV (403 nm) to 3.64 eV (340 nm). When normalized by excitonic line width, this system rivals high-performing visible-light systems and surpasses previously reported UV polariton systems. The strong UV absorption and stability of MSCs provide a robust platform for developing tunable polaritonic devices in the near-UV spectrum³.

Preliminary experiments also demonstrated the scalability of chiral self-assembly using open-faced droplet geometries instead of confined plate configurations. This receding meniscus technique revealed strong chiroptical signals, suggesting that drying rates combined with meniscus recession can overcome geometric constraints. Initial smearing experiments further indicate compatibility with roll-to-roll manufacturing methods like blade coating, dip coating, or slot die coating—each demanding careful matching of drying rates and meniscus motion to manipulate fiber assembly.

Future Plans

We are currently working towards assembling a publication for our current experimental and modeling efforts. One issue we are trying to examine is the sensitivity of the experiments to initial conditions, which often display stochastic pinning of the contact line. Observations of exceptional chirality have thus far been limited to these drop geometries which are prone to these pinning effects. The parallelism of the plates has recently been found to be the controlling factor for directing the solidification. We are improving the modeling by overlaying the results closely with time-series experimental data. Once thoroughly tested, we expect the experimentally verified model to guide the enhancement of chiral formation in this system—and enable the scale up to larger systems, including roll-to-roll coating methodologies available in RIT PI Weinstein's lab.

Moving forward we plan to transition from the lab-scale techniques used previously for processing of the chiral films to scalable roll-to-roll techniques such as blade coating, dip coating, and/or slot die coating, utilizing the more rapid rate of assembly granted by sonicated solutions. All necessary equipment is available in lab or through the Cornell Center for Materials Research (CCMR).

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Automated Workflow for Coarse-Grained MD Simulations of Block Copolymer Self-Assembly

Qiang Wang, Colorado State University

Keywords: Automated workflow, Molecular dynamics simulation, Block copolymer self-assembly, Self-consistent field calculations.

Research Scope

There are several general-purpose and commonly used packages for molecular dynamics (MD) simulations; none of them, however, is easy to use for researchers who have very limited or no computational background. The PDF version of LAMMPS¹ manual, for example, has about three thousand pages, and that of HOOMD-blue² is not much shorter. While such documentation is essential, it is not easily understood by beginners. Also, although the force fields in coarse-grained polymer models are simple, the chain architecture can be rather complex; we note that there are general tools³ designed to address this problem. Last but not least, an individual researcher or a research group typically uses MD simulations in a specific project for a particular system. So instead of asking each new student to learn how to use a MD package and then to perform repetitive simulation tasks manually, we have developed an automated workflow that can greatly increase the student's work efficiency and productivity, eliminate human error, and be customized to various projects.

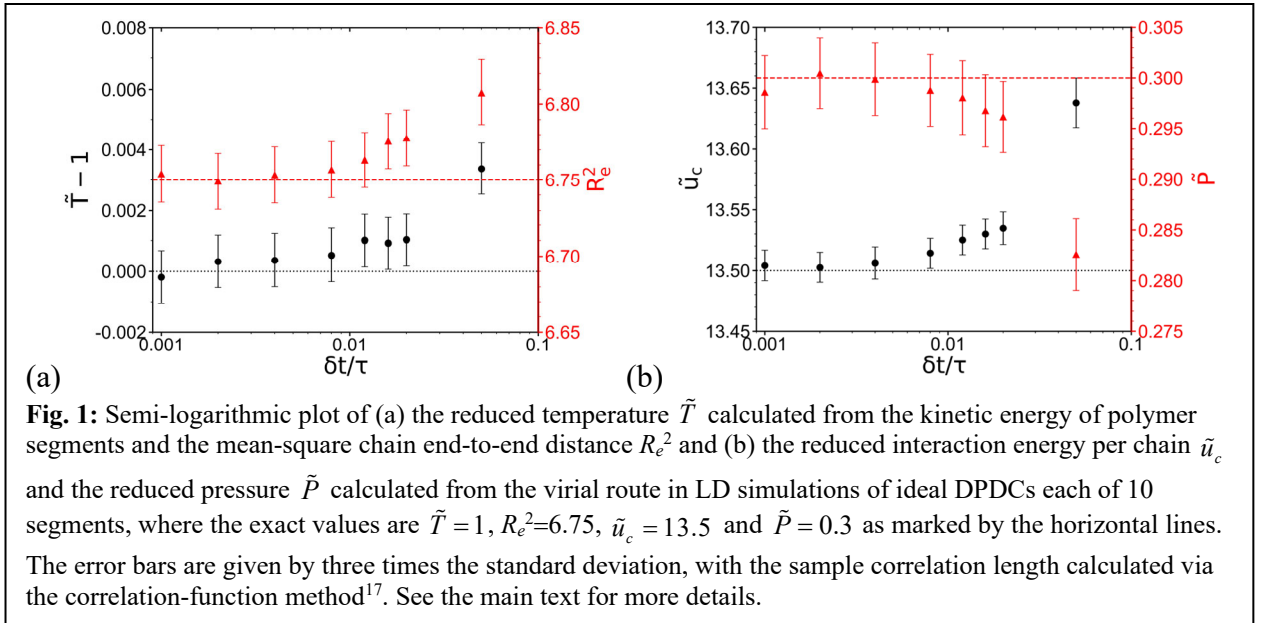
Our specific research here is about finding the bulk period of self-assembled structures of block copolymers. It is well-known that such structures have bulk period L_0 that minimizes the free-energy density of the system.⁴ In the widely used self-consistent field (SCF) calculations⁵, L_0 must be found for each ordered phase, otherwise the constructed phase diagram is incorrect. Finding L_0 , however, has rarely even been attempted in molecular simulations.⁶⁻¹⁴ In most cases, people just use a cubic simulation box with fixed and arbitrarily chosen length. This is partly because computing the free energy in simulations is much harder than in the SCF calculations. A few years ago, our group proposed that for one and two-dimensional structures properly oriented in the box, L_0 is found when Δ_D quantifying the difference among the diagonal elements of the pressure tensor vanishes.¹⁴

For the above project, we use the discrete Gaussian chain model with the dissipative particle dynamics (DPD) non-bonded potential, referred to as the dissipative particle dynamics chain (DPDC) model¹⁵, in both SCF calculations⁵ and MD simulations, enabling direct comparisons between them without any parameter-fitting to unambiguously quantify the effects of fluctuations/correlations inherently neglected in the former.¹¹

Recent Progress

We have made the following progress:

- (1) Using Python, we have integrated two widely used MD simulation packages (HOOMD-blue² and LAMMPS¹) with our in-house FORTRAN 90 code for efficient data analysis. This workflow not only allows automated determination of several critical simulation parameters (*e.g.*, timestep δt , equilibration time t_{eq} , sampling frequency t_{out} , and the total number of samples M to be collected after equilibration; see below for details), but also enables efficient simulation case planning and submission by automatically generating the input data files for the MD simulations and summarizing the important simulation results (*e.g.*, ensemble averages and statistical errors) of various cases into a specified worksheet of an Excel file. Users therefore work mostly with Excel and only need to execute a single Linux command (*i.e.*, `submit Excel_filename worksheet_name`) to run multiple MD simulation cases in parallel.
- (2) Our Langevin dynamics (LD) simulations of ideal DPDCs show that HOOMD-blue² gives excellent temperature control; but δt should not be larger than 1% of $\tau \equiv \sqrt{\beta m \sigma}$, where $\beta \equiv 1/k_B T$ with k_B being the Boltzmann constant and T the thermodynamic temperature of the system (set as 1), m is the mass of each polymer segment (set as 1), and σ is the cut-off distance of the DPD potential (set as 1); this is shown in Fig. 1 below.
- (3) We incorporated in our workflow the Python code recently developed in Ref. 16, which uses the Marginal Standard Error Rule to automatically determine t_{eq} .
- (4) To properly choose t_{out} and M , we divide the simulation into pilot and production runs. The correlation-function method¹⁷ shows that the square of estimated error of the ensemble average of an output quantity, denoted by σ_A^2 here, is proportional to the statistical inefficiency (or sample correlation length) g_A and inversely proportional to M . As different quantities have



different correlation lengths, we focus on the so-called key quantity A (e.g., the mean-square chain end-to-end distance R_e^2 in the above case of ideal DPDCs). The pilot run is used to obtain a good estimate of g_A . Since it is roughly inversely proportional to t_{out} , we then use it to choose the proper value of the latter to be used in the production run such that the collected samples are nearly uncorrelated. The production run is finally used to ensure that $\sigma_{\bar{A}}$ is smaller than its pre-specified error criterion by choosing the proper value of M .

- (5) Table 1 clearly shows that the SCF theory⁵ always overestimates L_0 of an ordered phase formed by the DPDC model of diblock copolymer A-B melts, regardless of the phase being lamellae (not highlighted), cylinders (highlighted in yellow), or spheres. Note that for lamellae and cylinders we use Δ_D , while for spheres we use the dimensionless excess Helmholtz free energy per chain (with the dimensionless excess chain chemical potential calculated via the Rosenbluth method), to find L_0 .

- (6) Similar result is also found for the [8.8.4] and (3.3.4.3.4) tiling patterns formed by the ABC miktoarm star triblock terpolymers¹⁸ of symmetric interactions, where the repulsions between different types of segments are the same. We note that L_0 of these structures has not been determined in MD simulations before.

Table 1: Quantitative comparison of the bulk period L_0 of an ordered phase (unhighlighted rows are for lamellae, rows highlighted in yellow are for hexagonally packed cylinders, and the last row is for the body-centered cubic spheres) formed by the DPDC model of diblock copolymer A-B melts given by MD simulations and the corresponding SCF calculations, where N denotes the copolymer chain length, N_A the A-block length, N/κ and χN the two parameters¹¹ controlling the DPD interaction between all segments and that between different types of segments, respectively, and ρ_0 the segment number density. See the main text for more details.

N	N_A	N/κ	χN	$\rho_0 \sigma^3$	L_0/σ	$L_{0,\text{SCF}}/\sigma$
10	5	50	30π	3	6.10	6.4757
		50π	30π	3	6.49	6.9057
		50π	20π	5	6.10	6.3627
	4	50π	30π	3	6.49	6.8927
		50π	25π	3	6.23	6.6465
		50π	20π	5	5.72	6.3445
	3	50π	30π	3	6.81	7.2646
		50π	20π	5	6.43	6.6771
16	2	50	200	3	7.2	8.4650

Future Plans

As proposed in the Specific Aim 3 of our funded project, we plan to incorporate the well-tempered metadynamics (WTM) simulations^{19, 20} in our automated workflow, perform WTM simulations of selected Frank-Kasper phases formed by the DPDC model of conformationally asymmetric diblock copolymer A-B melts, and directly compare our SCF and WTM results without any parameter-fitting to unambiguously quantify the system fluctuation/correlation effects neglected by the SCF theory.

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Metallic Glass Nanoparticles Synthesized via Flash Joule Heating

Mo Li, Georgia Institute of Technology and André Taylor, New York University

Metallic glasses (MGs) are a class of amorphous metal materials with remarkable properties. By leveraging an abundance of uncoordinated active sites that can serve as catalytic regions, MGs can have high catalytic activity and long-term stability as compared to their crystalline counterparts.¹ Conventional synthesis methods cannot produce nanosized MGs with precise control over composition, phase, and morphology. Our work has explored flash Joule heating (FJH) as a novel one-step approach to synthesize fully amorphous MG nanoparticles while enabling unprecedented control over their composition, phase, and morphology (Fig.1).² The rapid heating (up to 2505 K/s) and ultrafast cooling rates (up to 1485 K/s) during FJH surpass the critical rates required for glass formation in metal-phosphide alloys like Pd-P, Pd-Ni-P, and Pd-Cu-P, preventing crystallization. Characterization techniques such as SAED, XRD, and XPS have confirmed the amorphous nature and metallic states of the nanoparticles.

FJH has allowed precise tuning of ternary alloy compositions spanning wide ranges from Pd-rich to Ni/Cu-rich regimes, closely matching designed precursor ratios. The technique significantly expanded the glass formation region compared to conventional methods, accessing previously unattainable compositions like binary Pd₃P. Moreover, FJH enabled control over particle size from 2.33±0.83 nm to 36.5±10.1 nm with narrow distributions by optimizing precursors, thermal profiles, and alloy chemistries. Incorporating multiple elements facilitated smaller nanoparticle formation due to enhanced entropy, reduced melting points, and decreased surface tension.

The amorphous MG nanoparticles exhibited outstanding electrocatalytic performance and remarkable stability, superior over their crystalline counterparts. For the oxygen evolution reaction (OER), Pd-Ni-P MGs displayed ultra-low onset potentials ~300 mV below pure Pd and retained stable activity over 60 hours, contrasting rapid deactivation of crystalline samples of the same composition within 1 hour. Pd-Co-P MGs for methanol oxidation showed high reaction rates and resilience against activity decline during accelerated durability testing, unlike the rapidly decaying crystalline counterparts. This FJH synthesis approach unlocks new opportunities to realize the full potential of MGs by expanding the compositional space of alloy systems with precise control over MG properties, unlocking potential future transformative catalysts.

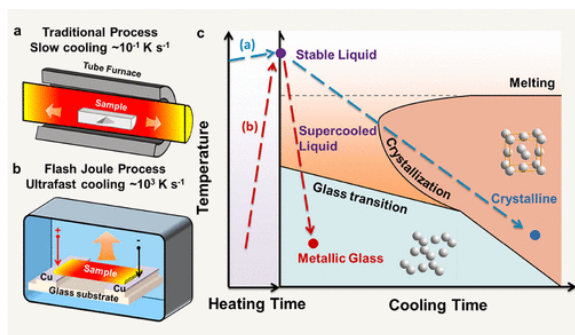


Figure 1. FJH processing and phase transformation with crystallization or glass formation during cooling. Schematics for (a) a traditional heating-cooling process. The cooling rate for a conventional laboratory tube furnace is $\sim 0.1 \text{ K s}^{-1}$ and (b) the FJH process with a cooling rate of $\sim 1000 \text{ K s}^{-1}$. (c) Illustration of temperature vs time diagram of supercooled liquid alloys and glass transformation. Red and blue arrows represent the thermal profiles of the traditional heating in (a) and FJH processes in (b), respectively.

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Novel internal chemical vapor infiltration (CVI) densification using in-built channels in a C/C composite

Hema Ramsurn, The University of Tulsa (Principal Investigator); Michael W. Keller, The University of Tulsa (Co-Investigator); Sanwu Wang, The University of Tulsa (Co-Investigator); Matthew Ryder, Oak Ridge National Laboratory (Co-Investigator)

Keywords: Carbon/carbon composites, densification, chemical vapor infiltration, porosity, density

Research Scope

Carbon/Carbon (C/C) composites' synthesis is complex, intricate, and costly. The performance of C/C composites is superior to other high-temperature materials and are hence used in aerospace and military applications because of their mechanical and physical properties, such as increased oxidation/ablation resistance, mechanical strength, and lower density¹. In fact, C/C composites are the most promising lightweight materials for hypersonic leading edges and engine components. Most of the enhancement in C/C composites fabrication is based on improving the densification step through chemical vapor infiltration (CVI)², pitch infiltration with intermediate³ or by impregnation/pyrolysis of the pre-densified preform with pitch⁴. Here, we propose a novel CVI densification by taking advantage of in-built channels in the composite.

Recent Progress

To enable internal densification, a carbon/carbon (C/C) composite with an internal channel was fabricated using our published method⁵. This densification approach is a novel technique proposed in this study where

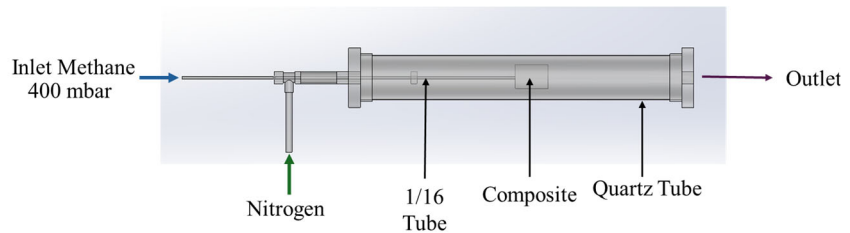


Figure 1: Experimental setup for novel internal CVI

Table 1: Optimized densification cycle for internal CVI.

Temperature (°C)	Dwell time (hours)	Flow rate (sccm)
1000	15	10
1000	15	5
1000	10	5

methane is used as the precursor gas for the chemical vapor infiltration (CVI) process (see Figure 1 for the set-up). Liquid infiltration cannot be used as the channels will be clogged. The experiment was conducted at a temperature of 1000 °C and a pressure of 400 mbar. Methane gas was introduced directly into the internal channel of the composite using a 1/16" stainless steel tube, while nitrogen gas was flowed around the outer

surface to maintain an inert atmosphere. The gas flow rate was optimized specifically for this setup, as shown in Table 1. The flowrates have been chosen so that the tubing and channel do not get clogged with time, and densification continues. The internal CVI experiment was initially carried out for 40 hours, as outlined in Table 1. After each cycle, the density and porosity of the sample were measured and compared with a reference sample (with no channels) processed using the traditional isothermal CVI technique.

As illustrated in Figure 2, in the novel internal CVI method, a thermal gradient is created from the inner channel (cooler) to the outer surface (hotter) of the composite. This gradient helps the reactive gas diffuse toward the hotter regions near the surface, where deposition begins, and proceeds inward into the cooler, porous interior. This promotes more uniform densification throughout the structure. In contrast, traditional isothermal CVI has a uniformly hot surface where the gas deposits quickly on the outer layers, forming a dense barrier that blocks further gas diffusion and prevents efficient pore filling deeper inside the material. The comparison between traditional isothermal CVI and the novel internal CVI highlights the improved performance of the proposed internal densification method for carbon/carbon composites. In the traditional isothermal CVI process, methane was introduced at a flowrate of 50 sccm, and the experiment was conducted for 40 hours so that it could be compared with the novel method. The results are shown in Figure 3. Over time, with the traditional CVI, the density of the composite increased and reached approximately 1.55 g/cc by the end of the 40 hours. However, the reduction in porosity slowed

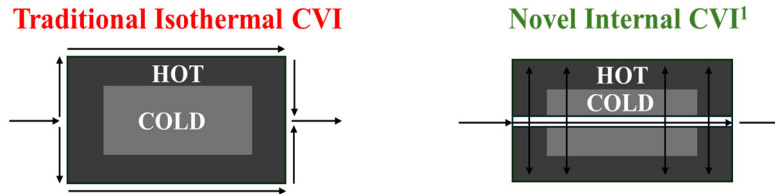


Figure 3: CVI densification comparison of isothermal and novel internal.

down significantly at around 20 hours, indicating that further densification was becoming less effective. This is likely due to excessive carbon deposition on the hot outer surface of the composite, which blocked the pores and restricted gas diffusion into the interior, leaving the inner regions under-densified. In comparison, the novel internal CVI technique used a 5 times lower methane flowrate (10 sccm) and introduced the gas through an internal channel in the composite. This created a thermal gradient and allowed the gas to diffuse outward from the cooler interior to the hotter surface. As a result, the porosity decreased gradually and consistently over time, with no signs of stagnation. Despite using a lower flowrate, the final density achieved was

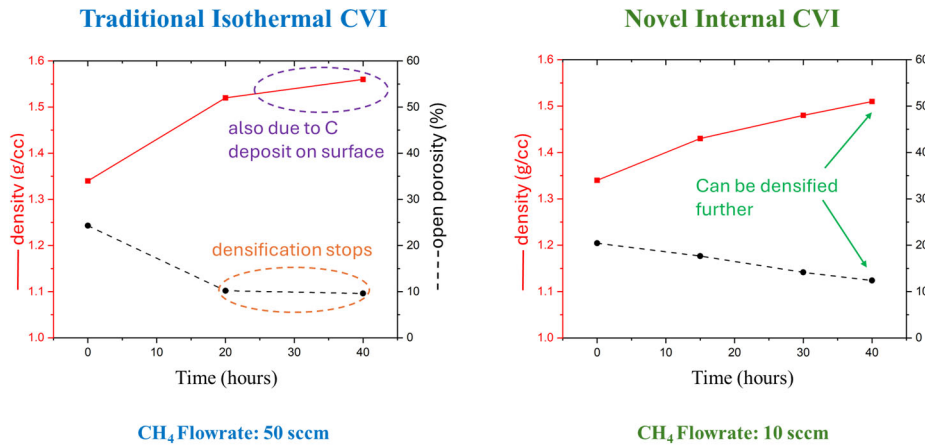


Figure 2: Density and porosity comparison of Isothermal and Novel Internal CVI.

the inner regions under-densified. In comparison, the novel internal CVI technique used a 5 times lower methane flowrate (10 sccm) and introduced the gas through an internal channel in the composite. This created a thermal gradient and allowed the gas to diffuse outward from the cooler interior to the hotter surface. As a result, the porosity decreased gradually and consistently over time, with no signs of stagnation. Despite using a lower flowrate, the final density achieved was

comparable to the traditional method, showing that internal CVI can achieve better densification more uniformly. The ability to continue densifying without surface blockage demonstrates the effectiveness of this novel approach in producing well-densified C/C composites.

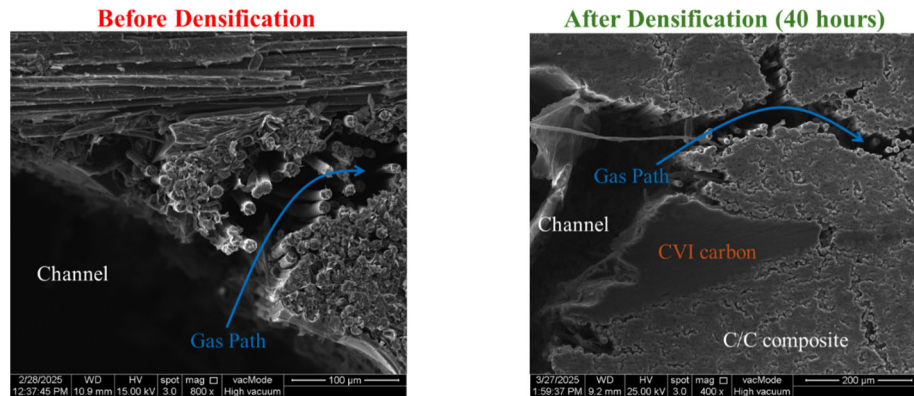


Figure 4: SEM images illustrating the internal CVI densification process near the embedded channel.

SEM analysis was performed on the composite cross-section before and after a 40-hour CVI cycle to validate further the potential for extended densification using the internal CVI technique. As shown

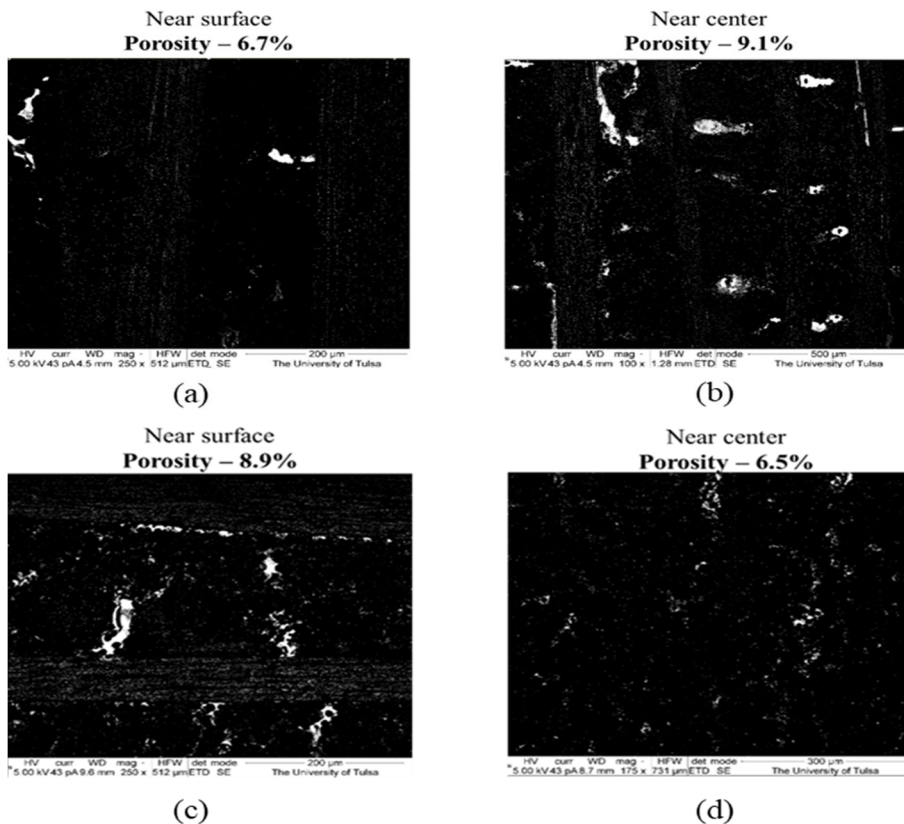


Figure 5: Porosity distribution in C/C composites: (a) surface region under traditional isothermal CVI; (b) center region under traditional isothermal CVI; (c) surface region under novel internal CVI; (d) center region under novel internal CVI.

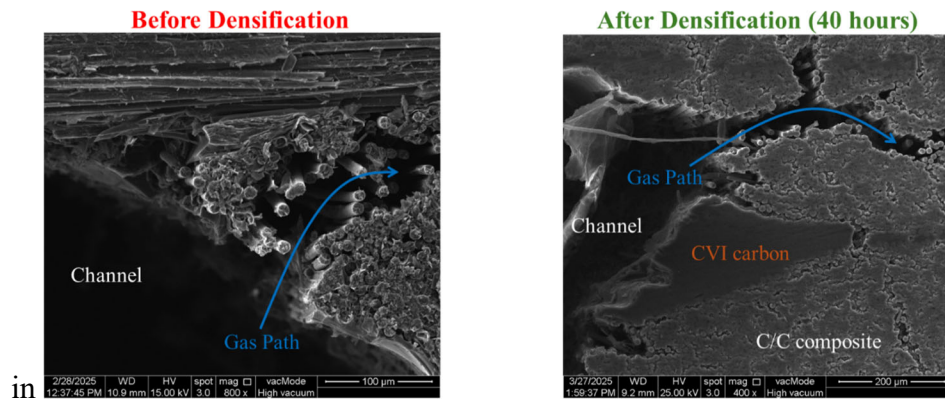


Figure 4, the structure before densification exhibits significant open porosity with a clear gas path from the internal channel into the porous region of the composite. After 40 hours of densification, a noticeable amount of CVI carbon has been deposited, partially filling the pores. However, the SEM image clearly shows that continuous gas pathways remain open, indicating that gas can diffuse deeper into the structure. This suggests that the densification process is incomplete and can be extended further to achieve even lower porosity and higher density. The presence of CVI carbon throughout the cross-section and the remaining porosity demonstrates the progressive nature of internal CVI and its ability to densify the composite more uniformly over time without early pore blockage. Further analysis was conducted using SEM imaging at the surface and the center of samples prepared by traditional isothermal CVI and the novel internal CVI technique. The SEM images were processed using ImageJ software to calculate porosity as a fraction of the total area. In the case of the traditional CVI method, porosity increased from the surface (Figure 5a) to the center (**Error! Reference source not found.b**). This supports the observation that once the hotter surface is sealed by carbon deposition, gas diffusion into the inner regions becomes restricted, preventing effective densification at the core. In contrast, the sample prepared by the novel internal CVI method showed decreased porosity from the surface (**Error! Reference source not found.c**) to the center (**Error! Reference source not found.d**). This trend confirms that the internal CVI technique enables gas to reach and fill interior pores more effectively, demonstrating its advantage in achieving deeper and more uniform densification within the composite.

Future Plans

Densification of the composite for more hours (cycles) will be performed to observe when the porosity reaches a plateau with this new CVI method and the corresponding porosity that can be achieved. Our goal is to produce a very dense C/C composite as close to 1.9 g/cc. This work is intended for publication by the end of this year.

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Investigating Multilayer Anti-oxidative coatings on carbon-carbon (CC) composites for High Temperature applications

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Keywords: anti-oxidative, silicon carbide, self-healing, packed cementation, CVD

Research Scope

In literature, there is no study on which technique and/or type of coating should be used first or last or which sequence of coating techniques should be used to optimize the number of anti-oxidative layers. In this work, we progress from mono- to bi- to multilayer coatings with SiC-PC (with and without boron), CVD (SiC from HMDS, as pioneered by previous work in our lab¹), and slurry (ZrB₂-SiC) layers. These layers are synthesized, characterized and tested to understand the interaction between them and the substrate, assess the performance of multilayers, and find the most efficient ordering of the different methods. Boron is expected to react with the carbon in the powder mixture to create B₄C which can create oxides (B₂O₃) at moderate temperature, stabilizing the packed cemented coating until critical silicon oxides can form at higher temperatures. The effectiveness of the boron addition to the pack cementation mixture was analyzed in conjunction. All the samples underwent oxidation testing in an air atmosphere at 1000 °C until failure with periodic weight measurements to evaluate oxidation resistance. SEM (scanning electron microscopy), EDS (Energy-dispersive X-ray spectroscopy), and XRD (X-ray diffraction) were used to analyze surface morphology, elemental composition, and identification of crystalline phases both before and after oxidation. This study aims to develop an optimized multilayer SiC-based coating system that provides superior oxidation resistance with minimal thickness by systematically assessing the role of layer quantity, order, and composition. The findings will offer valuable insights into improving the performance and longevity of C/C composites in extreme high-temperature environments.

Recent Progress

A commercially available C/C composite was cut into smaller samples for coating purposes. The sample size depends on the desired oxidation testing (TGA: 5 x 5 x 3 mm vs muffle furnace: 25 x 15 x 3 mm). Multilayer coatings were developed using a combination of pack cementation, chemical vapor deposition, and slurry as described in the following sub-sections. The sequence of methods and number of layers (from single to multilayer) were varied (refer to Table 1). Two different pack cemented coatings were prepared: with and without boron. It is to be noted that the mixtures without boron were strictly used to produce a SiC and are termed as PC-SiC, while the other mixture, which included B to produce B₄C alongside the SiC, is referred to as 5BPC-SiC with 5 representing the weight percent of added B. A high boron content can lead to an increased amount of liquid B₂O₃ causing coating failure, while a lower content may result in insufficient B₄C formation. Therefore, a base percentage of boron of 5 wt% was chosen, which allows for the formation of both SiC and B₄C. Additionally, the low amount of boron can be beneficial during the intermediate temperatures, reacting with O₂ to form B₂O₃, filling any cracks that may form,

while not hindering the coating once the B_2O_3 volatilizes at higher temperatures. Both coatings (with and without B) were separately prepared based on our previous work¹. For CVD, the precursor for the SiC coating was hexamethyldisilane (HMDS) and was directed towards the samples via an injector and bubbler setup with slow heating to allow the SiC to deposit into any pores or cracks (from previous coatings, if any), increasing the overall density and effectiveness of the coatings. Finally, a ZrB_2 -SiC self-healing coating was prepared using a slurry coating technique with ZrB_2 powder, SMP-10 (a SiC polymeric precursor) as the binder, and THF as a solvent.

The coating design evolved from single to four-layer systems to improve oxidation resistance methodically and compare layer-by-layer mass loss, as shown in Table 1.

Table 1: Comparative Analysis of Oxidation Resistance in B-Modified and Regular Multilayer Coatings Based on Mass Change

Number of layers	B-Modified		Mass loss (%)		Regular	
	Time	Sample Name	B-Modified	Regular	Sample Name	Time
1	60	5B-PC	59	63	PC	60
				90	CVD	4
				85	Slurry	24
				86	Slurry (2)	24
2	24	5B-PC+CVD (1)	62	70	PC+CVD (1)	12
	24	5B-PC+CVD (2)	63	67	PC+CVD (2)	12
	24	5B-PC+S (1)	-1	-3	PC-Slurry (1)	24
	24	5B-PC+S (2)	-2	-4	PC-Slurry (2)	24
3	60	5B-PC+S+CVD	40	57	PC+S+CVD	60
	60	5B-PC+CVD+S (2)	-5	-4	PC+CVD+S (3)	60
	60	5B-PC+CVD+S (3)	-7	-3	PC+CVD+S (4)	60
4	60	5B-PC+CVD+S+CVD	8	59	PC+CVD+S+CVD	60
	60	5B-PC+CVD+S+CVD	21	51	PC+CVD+S+CVD	60

CVD and Slurry as a first layer did poorly, losing all the C/C mass with only the SiC coating shell remaining. Pack cementation (PC) and boron-modified PC (5B-PC) were used to optimize the first layer; 5B-PC performed better because of its self-healing capabilities through the creation of B_2O_3 . Figure 1 shows the phase compositions of PC, 5B-PC, CVD, and slurry single-layer coated C/C composites before oxidation. With a temperature of 1900 °C, the PC coating exhibits significant α -SiC peaks, indicating a thermodynamically desirable transition from cubic to hexagonal SiC. Due to the porosity, graphite peaks are also evident along with residual Si because of partial conversion and/or melting of Si during heat treatment. While the 5B-PC coating has a phase composition of B_4C and α -SiC, indicating a multifunctional architecture, the slurry coating is rich in ZrB_2 . Since the CVD coating is deposited at lower temperatures of 800–1000 °C, where the cubic structure of SiC usually occurs, it displays distinctive β -SiC peaks. Figure 2 presents the

isothermal oxidation behavior of the single-layer coated samples in air at 1000 °C. The CVD-coated sample experienced complete mass loss within the first few hours, indicating poor oxidation resistance as a single first layer. Similarly, the slurry-coated samples also failed to retain the mass of the composite, as only the coating shell (representing around 15% of their original mass) was left after oxidation. This happened mainly because of the coefficient of thermal expansion (CTE) mismatch of the Slurry and C/C composite, which initiated cracks during oxidation. In contrast, PC and 5B-PC coatings performed significantly better as single layers, stabilizing after an initial drop and

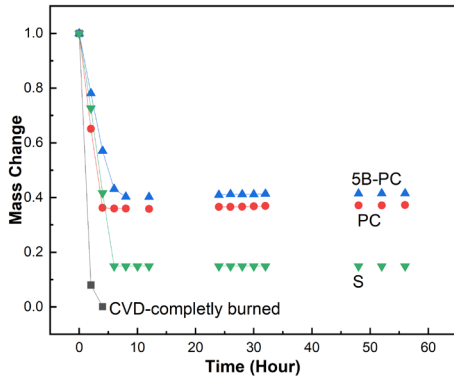


Figure 2: Mass change behavior of single-layer coated C/C composites under oxidation at 1000 °C

SiC peaks are prominent, along with minor SiO₂, suggesting a synergistic barrier effect where SiC is converted to its oxides. These results reinforce the improved stability of the 5B-PC coating due to its tailored phase composition and structural design.

It was clear from mass loss and XRD that PC should be the first layer on a C/C composite due to its strong adhesion to the substrate. Following the evaluation of single-layer coatings, where pack cementation (PC) demonstrated superior oxidation resistance compared to CVD and slurry coatings, multilayer configurations were investigated to assess the effectiveness of the second-layer coating. Over the PC first layer (with and without B), the second layer applied was either slurry or CVD. Slurry, as the outer layer, outperformed the CVD outer layer. Figure 2 shows that samples coated with slurry as the top layer (PC+S and 5B-PC+S) exhibited exceptional oxidation stability, maintaining

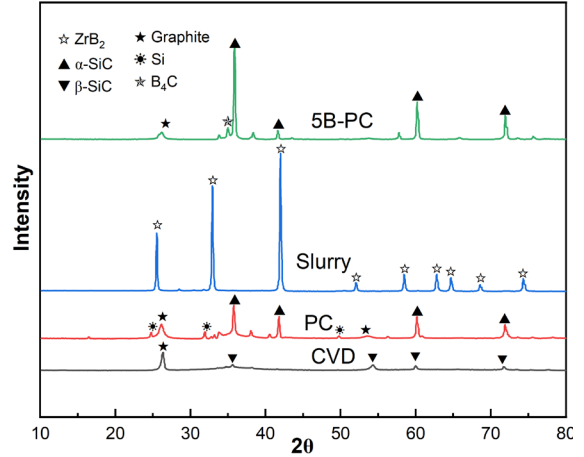


Figure 1: XRD patterns of the surface of single-layer coatings before oxidation.

retaining mass changes of around 0.37 and 0.41, respectively, suggesting that the boron modification (5B-PC) enhanced oxidation resistance over regular PC. The initial mass loss is attributed to the lack of SiO₂ formation, and over time, once sufficient SiO₂ is formed, the mass stabilizes, even increasing slightly due to oxygen absorption by oxide formation (confirmed by XRD). The mass loss rate of 5B-PC was lower than that of regular PC due to the formation of B₂O₃, which has better self-healing properties. XRD analysis on the PC, slurry, and 5B-PC coated samples after oxidation at 1000 °C for 60 hours shows that the PC coating retains some prominent peaks of α-SiC. The slurry-coated sample shows a rich composition of ZrO₂, including peaks of ZrB₂. In the 5B-PC sample, α-

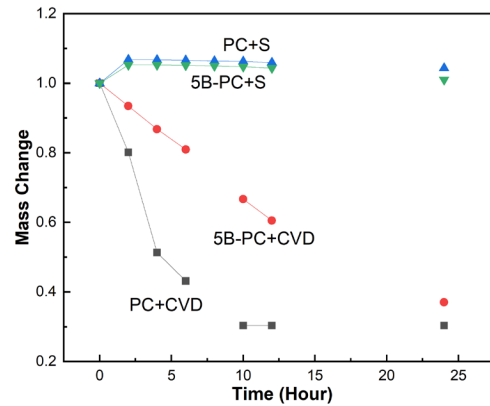


Figure 3: Mass change behavior of bilayer coatings: comparison of slurry and CVD as outer layers under oxidation at 1000 °C.

nearly complete mass retention throughout the 25-hour isothermal exposure at 1000 °C. In contrast, configurations using CVD as the second layer (PC+CVD and 5B-PC+CVD) showed a significant decline in mass, indicating inferior oxidation resistance, attributed to the coating thickness (20 μm) and porous nature. Furthermore, the 5B-PC+CVD combination performed better than PC+CVD, highlighting the beneficial role of boron modification in the base layer as expected and seen with single-layer oxidation results (Figure 2). For the two-layer anti-oxidative coatings, the slurry-based outer coatings outperformed the CVD coatings, suggesting that the slurry acts as a more effective barrier layer, likely due to its dense and crack-sealing characteristics shown in XRD analysis. Therefore, slurry is identified as the most suitable second-layer (outer layer) coating, particularly when applied with a PC or 5B-PC base layer. This trend can be observed with three-layer coatings where CVD on the exterior had reduced oxidation protection, while placing slurry as the last (outermost) layer in three-layer systems resulted in the maximum mass retention. For the triple-layer coatings, each coating method was utilized exactly once, where the base layer is kept as either 5B-PC or PC, and the second and third layers were interchanged. As seen in Figure 4, both configurations where CVD is the second layer and slurry as the external layer had exceptional mass retention over the 60-hour testing period. However, both samples had significant mass loss when the slurry was the second layer, and CVD was the external layer. The difference in performance can be attributed to the location of the slurry layer. Slurry as an external layer through three coatings allows for the crucial formation of oxides to be more readily available due to the layer's exposure, increasing oxidative protection. On the other hand, when CVD was the external layer, it prohibited the slurry from readily reacting with the oxygen, limiting the oxide formation and allowing the oxygen to reach the sample. This is especially apparent when comparing slurry performance as a second layer in the double layer coating results (Figure 3) with the triple layer coating with CVD as the third outer. However, the CVD-SiC layer in between as the second layer enhances the protection when used as an intermediate, likely due to filling the pores of the underlying PC coating, limiting oxygen diffusion overall. It is interesting to see that the double layer (5B-PC+S) fares as well as the triple layer (5B-PC+CVD+S) when oxidized for 60 hours.

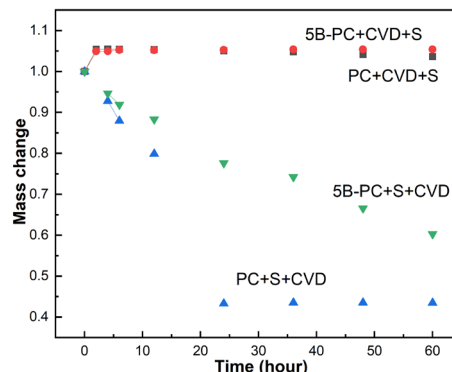


Figure 4: Mass change behavior of tri-layer coated samples: comparison between PC+CVD+S and 5B-PC+CVD+S coatings under oxidation at 1000 °C

Future Plans

For future work, it is intended to continue the oxidation tests for longer hours to validate the stability of the different multilayer coatings and add some more characterization (XRD, SEM) to explain the oxidative behaviors of the coatings. This work is intended for publication by the end of this year.

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Anomalous Effects of Dilute Phosphorus Alloying on Diffusion and Phase Transformations in the Fe-Ni System

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Keywords: Ordered Phases, Vacancy-Defect Pairs, Phase Transformations, Dilute Alloying

Research Scope

The $L1_0$ ordered tetragonal phase of Fe-Ni is the only known earth-abundant system with the potential to rival the magnetic energy product of the rare-earth element permanent magnets, which are central components in many current and emerging technologies, yet suffer brittleness, susceptibility to corrosion, and severe strategic supply limitations of national concern. The tetragonal phase occurs naturally and stably within meteoric samples, but after over five decades of study terrestrial production of bulk tetragonal has proved elusive. This is due to the combination of a diminutive thermodynamic driving force for the transformation, as the energy is very similar to the chemically disordered face-centered-cubic (FCC) parent phase (Figure 1), and diffusion rates on the order of single atomic jumps per million years at the limit of tetragonal's stable temperature range. In a surprising finding published in 2022 and since partially retracted [1], a research group claimed to have produced $L1_0$ -FeNi tetragonal during conventional casting of several phosphorus-modified compositions. While there were errors in their initial analysis, notably concerning the percentage and character of the ordered phase, it is clear that the addition of phosphorus induces some type of ordered tetragonal FCC-type phase (potentially $L1_0$) that may open up a new viable synthesis pathway. Phosphorus is notably present at significant concentrations within the meteoric samples known to contain tetragonal, but to date Fe-Ni-P alloys have only rarely been synthesized or characterized as phosphorus generally has a negative impact on many other physical properties.

The research scope of this project explores the unique roles phosphorus additions play in the Fe-Ni alloy system that may be able to drive the synthesis of Fe-Ni $L1_0$ ordered tetragonal permanent magnets. The core hypothesis is that the presence of phosphorus greatly accelerates diffusion kinetics in Fe-Ni through a fast diffusion mechanism driven by vacancy-phosphorus pairs. Moreover, it is believed that actively segregating supersaturations of phosphorus produced by annealing rapidly quenched Fe-Ni-P alloys can critically increase local atomic scale diffusion several orders of magnitude further than the vacancy-pair mechanism alone, enabling the formation of energetically favorable ordered phases that would normally be kinetically prohibited from forming at lower temperatures. Experiments in the first phase of this project have concentrated on producing and characterizing the behavior of numerous Fe-Ni-P alloys in the largely unexplored compositional space believed to be optimal for $L1_0$ formation. These samples provide the backbone of both an ongoing transmission electron microscopy diffusion couple study investigating the limits of the vacancy-phosphorus pair fast diffusion mechanism, and are

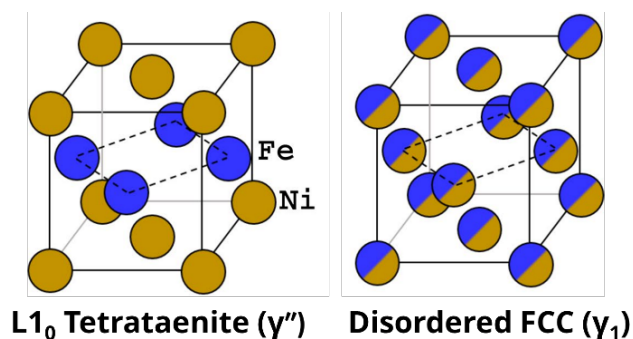


Figure 1. $L1_0$ ordered FeNi tetragonal (left), and the disordered FCC solid solution (right)

providing critical yet unestablished ternary phase diagram boundaries that will be essential for quenching in phosphorus supersaturations for the final project phase.

There is existing experimental evidence that dilute additions of phosphorus substantially increase the diffusion rates in Fe-Ni, and this discovery previously led the cooling rate of meteoric material to be revised upward by two orders of magnitude (Figure 2) [2]. Ascribing this behavior mechanistically to vacancy-phosphorus pairs as a fast diffusion mechanism might seem counterintuitive as vacancies associating strongly to phosphorus atoms would reduce the number of vacancies freely available to migrate for diffusional processes. Ab-initio calculations on FCC nickel, which has an electronic structure similar to Fe-Ni, help to explain the discrepancy. The formation of a vacancy-phosphorus pair provides an energetic barrier to dissociation, but it also significantly modifies the successful jump frequency by lowering the barrier for other diffusional exchanges [3]. While a jump leading to dissociation of the pair (ω_3 , Figure 3) has a much greater energy barrier than for an unbound vacancy, it is offset by a greatly reduced barrier for both vacancy-phosphorus exchange hops (ω_2) and vacancy pair rotational hops (ω_1). This provides a fast dilute solute diffusion mechanism through cycles of exchange and rotation of the solute-vacancy pair, similar to the Johnson mechanism for self-interstitial dumbbell configurations. Computational work predicts that the addition of 1 at% P could accelerate long-range diffusion rates in pure Ni by a factor of 2×10^4 at 300°C. Viewing the limited experimental

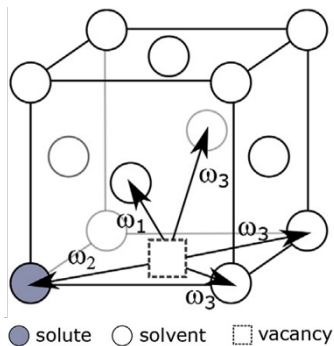


Figure 3. Jump frequencies for dilute FCC, solute P and solvent Fe-Ni

the magnitude of the diffusion rate enhancement, pair dissociation temperatures, and any more complex and unpredicted phenomena related to ordering are completely unknown as a function of both P and Ni concentration outside of the range of meteoric samples. What is known about the trends with increasing P and Ni, combined with observed short-range ordering due to defect migration in the Fe-Ni-P system at Invar compositions (36 at% Ni, outside the $L1_0$ ordered region) during electron irradiation [4], is highly promising for promotion of the ordered phase.

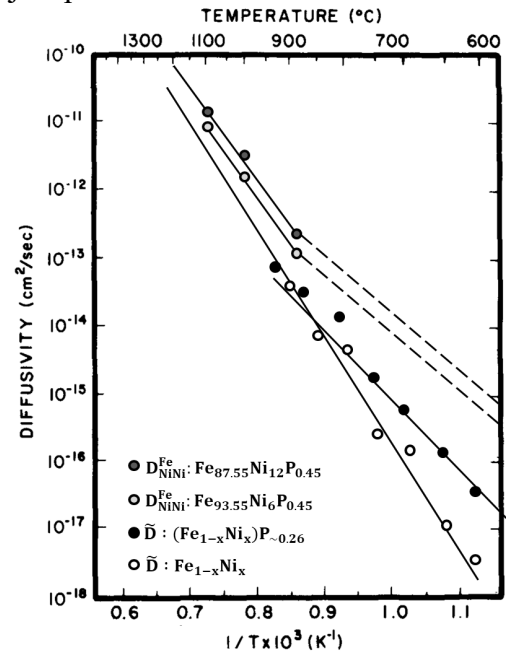


Figure 2. Diffusion rates from Fe-Ni-P diffusion couples, P increases the kinetics in the temperature regime vacancy-P pair formation is predicted to be prevalent. [2]

diffusion rate data in light of the proposed vacancy-phosphorus pair mechanism, several important research questions can be readily identified. Due to the slow diffusion rates requiring experimentally intensive transmission electron microscopy diffusion couples, a low temperature diffusion series is only available at the low 0.26% P level, and the enhanced diffusion appears to end around 900°C which is in the expected range for high temperature dissolution of the vacancy-phosphorus pairs [3]. Increasing the P concentration has been found to yield greater diffusion in the regime pairs are primarily dissociated but the effect at lower temperatures is completely unknown. Greater Ni concentrations also appear to increase diffusion rates in Fe-Ni-P, but Ni compositions have only been tested well away from the ideal 50:50 composition for $L1_0$ and not at low temperatures. Consequently,

Recent Progress

Fe-Ni-P samples have been cast in matrix of compositions (37.5, 40.0, 42.5, 45.0, 46.5, 50.0, and 52.5 Ni%, with 0.00%, 0.25% and 0.50% P additions), followed by homogenization and quenching to lock in the desired metastable solid solution FCC phase. Both the as-cast and homogenized conditions have been fully characterized via scanning electron microscopy and X-ray diffraction. Each of these samples is the first Fe-Ni-P alloy ever reported in its compositional range. Dilatometric studies of the Fe-Ni-P samples produced an unexpected result during preliminary analysis, where homogenized samples with 0.5% P show a highly anomalous sharp drop in their coefficient of expansion near 900°C during heating, which is significant enough to completely arrest thermal expansion temporarily at the 47.5% Ni composition (Figure 4). Upon cooling and reheating this sharp transition is replaced by a different sharp valley-peak anomaly pair in the same temperature range. This behavior is not observed for the more dilute 0.25% P compositions tested (which are comparable to the only complete diffusion study of Fe-Ni-P seen in Figure 2), where the only feature is a loss of the magnetically driven Invar effect above the Curie temperatures ranging between 300°C -500°C.

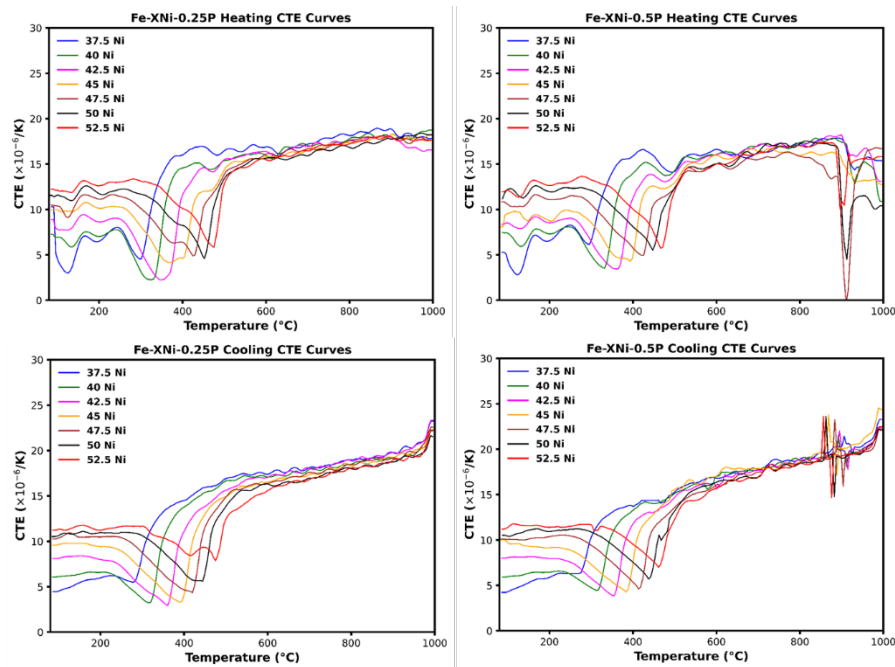


Figure 4. Fe-Ni-P coefficients of thermal expansion via dilatometry, heating and cooling rates of 5°C/min.

The 900°C temperature coincides with the range that the phosphorus pairs are expected to dissociate. While this explains the hysteresis between heating and cooling, since the homogenized and quenched state will have a supersaturation of vacancies to release upon heating that will not return, other features of the anomalies remain unexpected and highly informative. The sharpness in the dissociation and reassociation transition is remarkable, as density function theory models on pure Ni have the transition occurring much more gradually over a range of hundreds of degrees. This suggests that in Fe-Ni alloys the phosphorus-vacancy pairs interact strongly with their local environments and have a deeper and more constrained energy potentials due to interactions with the binary matrix. The phosphorus-vacancy pairs interact with Fe-Ni in a manner that local Fe and Ni pairings with the defects cannot be treated as equal.

This anomalous behavior is most prominent at 47.5% Ni (approximately the ideal L1₀ forming composition, which from the phase diagram appears slightly below equiatomic) followed by 50.0% and 52.5%, and shows a strong dependence on Ni composition away from equiatomic. That excitingly suggests that the presence of phosphorus-vacancy pairs promotes some form of chemical ordering near the Fe-Ni equiatomic compositions. Whether this ordering is of L1₀ type, L1₂ type, or a more complex possibility where the P orders in addition to the Fe and Ni, will require in situ neutron diffraction studies due to the very low scattering contrast present between Fe and Ni in XRD (which makes even complete ordering difficult to detect). The anomalous behavior being markedly stronger near equiatomic concentrations is highly indicative that phosphorus-vacancy pairs promote L1₀ type ordering. Any type of pronounced chemical ordering, however, can serve as nuclei for the L1₀ phase to form and would lower an important kinetic barrier.

Future Plans

Portions of the homogenized Fe-Ni-P samples have been cut and bonded into an extensive series of diffusion couples that are undergoing long-term aging anneals this summer at four different temperatures to map out the effects of P content and Ni content on Fe-Ni interdiffusion. Transmission electron microscopy samples of the couple boundaries will be produced via focused ion beam liftout due to the fragile nature of the interfaces, and the diffusion profiles analyzed via energy dispersive X-ray spectroscopy to assess the diffusion rates

Ternary phase diagrams in the dilute P regime using a CALculation of PHase Diagrams (CALPHAD) approach with CompuTherm's Pandat software have been optimized over the last few months to include more experimental data to improve their accuracy in the dilute P regime near equiatomic FeNi compositions, which was found to be underdeveloped in commercially available off-the-shelf databases. Fe-Ni-P samples are being aged and characterized to provide experimental verification of the FCC to FCC + (Fe,Ni)₃P boundary of critical importance to the synthesis and processing of Fe-Ni-P, which currently has no experimental verification and is important processing information to successfully quench in high supersaturations of phosphorus.

The Fe-Ni-P samples created for the diffusion study have already had their magnetic properties measured by vibrating sample magnetometry in both the as cast and homogenized conditions. Neither the as-cast or homogenized states exhibit any appreciable coercivity, though this is expected behavior for the relatively dilute P concentrations (max 0.50 at% P) in these initial samples. Magnetic measurements will continue to more promising compositions with higher P content (1-5% P) over a tighter range of Ni compositions.

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Understanding Nucleation and Film Growth Processes of Solution-Processable Renewable Energy Materials Printed from Confined Volumes

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Keywords: Printing, nucleation, crystallization, thin-film growth, capillary action

Research Scope

The major goals of this project are to answer three interrelated questions: (1) How does the high surface area-to-volume ratio of the substrate/superstrate and ink influence the nucleation and growth in solution-processed thin films? (2) Can a model for thin film growth from solution be developed that is analogous to the Structure Zone Model for thin film growth from vacuum deposition? and (3) How do the surface energies and chemistries of confining surfaces influence crystal nucleation and growth as well as the resultant film morphology?

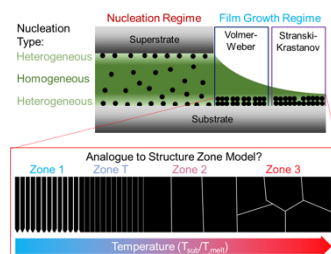
To answer these questions, we are using our in-house developed manufacturing process, restricted area printing by ink drawing (RAPID). In RAPID, the ink is confined between—and in contact with—a parallel superstrate and substrate separated by tens of microns. This confinement provides three key differences compared to conventional printing techniques such as slot-die coating: (1) the evaporation of the solvent is inhibited since most of the surface area is in contact with impermeable solids; (2) the thickness of the printed wet film has similar dimensions as the gap between the superstrate and substrate which enables higher printing speeds according to the viscocapillary theory; and (3) the surface chemistry/energy of the superstrate can be readily tuned, which will influence the flow interactions and meniscus shape and likely affect the crystallite nucleation and film growth.

Recent Progress

We have focused on using *in situ* photoluminescence to measure crystallite growth rates and automation of capillary bridging measurements so that angles and forces can be directly computed from videos of droplets between plates during extension and compression cycles. In addition to these efforts, we have also focused on measuring the viscosities of a range of solutions, which will later be correlated with growth rates and domain sizes in films as a function of multiple printing parameters, including but not limited to print speed and acceleration (shear rate), superstrate/substrate temperature, and time spent in confinement.

In Situ PL to Determine Growth Rates

To gain insight into the nucleation and growth of perovskite crystallites, we employed *in situ* photoluminescence (PL) spectroscopy to monitor the radiative recombination of charge carriers as a function of real experimental time. During the early stages of the experiment, as perovskite crystallites grow in solution, a distinct regime emerges in which the peak photoluminescence (PL) emission energy exceeds that of the bulk semiconductor. This deviation is attributed to quantum confinement of excitons within the semiconductor crystallites, which emerges when the spatial dimensions of semiconductor crystallites are near the bulk exciton Bohr radius.¹



Using confined volume printing, we aim to better understand crystallization and thin-film growth dynamics in printed films.

For semiconductors, the exciton Bohr radius, a_B , can be expressed in terms of the Bohr radius of the 1s electron in the hydrogen atom, a_0 (Equation 1):

$$a_B = \epsilon_r \left(\frac{m_0}{\mu_{ex}} \right) a_0 = \frac{4\pi\epsilon_r\epsilon_0\hbar^2}{\mu_{ex}e^2} \quad (1)$$

where a_B is the Bohr radius of the 1s electron in the hydrogen atom a_0 , ϵ_r is the relative dielectric constant of the semiconductor, m_0 is the electron mass, μ_{ex} is the effective reduced mass of the exciton, ϵ_0 is the permittivity of free space, and e is the elemental charge. Example published exciton Bohr radii for MAPbI₃ and MAPbBr₃ are 4.6 and 3.8 nm, respectively.²

In the quantum confinement regime, the deviation of the emission energy, $E_g(R)$, from the bulk value, $E_{g,bulk}$ can be approximated using the Brus equation, which models the exciton as a hydrogen-like quasiparticle confined within a spherical quantum well, with its kinetic energy governed by the reduced effective mass of the electron-hole pair (Equations 2, 3):³

$$E_g(R) - E_{g,bulk} = \frac{\hbar^2}{8R^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\epsilon_{pvsk}\epsilon_0 R} + E_{pol} \quad (2)$$

$$E_{pol} = \frac{e^2 \left(\frac{\epsilon_{pvsk}}{\epsilon_{env}} - 1 \right)}{2\pi R^2 \epsilon_{pvsk} \epsilon_0} \int_0^R \sin^2 \left(\frac{\pi r}{R} \right) \sum_{k=1}^{\infty} \frac{k+1}{\left(\frac{\epsilon_{pvsk}}{\epsilon_{env}} + 1 \right) k + 1} \left(\frac{r}{R} \right)^{2k} \quad (3)$$

where $E_g(R)$ is the deviation of the emission energy from the bulk value, $E_{g,bulk}$, R is the particle radius, $\hbar$ is Planck's constant, ϵ_{pvsk} is the dielectric constant of the perovskite crystallite, and ϵ_{env} is the dielectric constant of the surrounding medium. The first term on the right-hand side of Equation 2 represents the kinetic energy of both the electron and the hole, accounting for their confinement within the spherical crystallite of radius R . The second term represents the Coulomb attraction between the negatively charged electron and positively charged hole. The final term accounts for the polarization energy arising from the introduction of charged particles into the dielectric-confined potential well. This interaction can be interpreted as the Coulombic coupling between a charge and the surface polarization field induced by its counterpart.³ This last term is typically small compared to the electron-hole kinetic energy and Coulomb potential, especially in solvents with high dielectric screening. It is worth noting that the truncated form of the Brus equation—comprising only the kinetic and Coulombic terms—has frequently been misrepresented in literature, which may contribute to erroneous interpretations and conclusions in recent studies. The effective mass of the electrons and holes—necessary inputs to solve Equation 2—are challenging to determine experimentally, typically requiring cyclotron resonance for accurate measurements. In practice, effective masses are more reliably determined using first-principles methods such as density functional theory (DFT), where they are extracted from the curvature of the electronic band structure near the valence band maximum (VBM) and conduction band minimum (CBM).⁴ The effective mass of the electron and hole can be evaluated from the band structure by computing the curvature around the conduction band minimum (CBM) and valence band maximum (VBM), respectively (Equations 4, 5):

$$\frac{m_e}{m_0} = \hbar^2 \left[\frac{d^2 E_{CBM}}{dk^2} \right]^{-1} \quad (4)$$

$$\frac{m_h}{m_0} = \hbar^2 \left[\frac{d^2 E_{VBM}}{dk^2} \right]^{-1} \quad (5)$$

where $\frac{d^2 E_{CBM}}{dk^2}$ and $\frac{d^2 E_{VBM}}{dk^2}$ describe the curvature around the conduction band minimum (CBM) and valence band maximum (VBM).

Using this methodology, we determined average effective masses for MAPbI₃ of $0.138m_0$ for the electron and $0.118m_0$ for the hole, respectively at the PBE+SOC level of theory. These effective charge carrier masses translated into a Bohr exciton radius of 6.24 nm, slightly larger than other reported values.⁴ Using our computed effective masses and a relative dielectric constant of 7.5 for MAPbI₃, we converted the peak energy of each steady-state PL snapshot into an effective crystallite radius via Equation 2, incorporating 20 terms of the summation inside the polarization energy integral. Each radius was determined by numerically solving the nonlinear relationship between crystallite size and peak emission energy using Brent's root-finding method.

As a demonstration of this approach, we investigated the impact of amino acid aliphatic chain length on the growth kinetics of MAPbI₃ crystallites by computing the crystallite radius from *in situ* PL data for precursor solutions containing 1 mol% (w.r.t. lead) amino acids. Interestingly, transforming the peak emission energy into effective crystallite radii revealed the presence of three distinct growth regimes, suggesting temporally separated stages of growth. The first regime was attributed to initial organization and nucleation of small crystallites in the wet films while the second regime was rapid growth due to the initiation of annealing. The final regime appeared to show dramatic slowing down of growth. Exponential functions were fit to these growth regimes and the derivatives were taken to determine the radial growth rate of these crystallites and significant differences were observed in the second regime.

Capillary Bridging

Capillary bridging experiments are being used to understand impacts of surface energy and chemistry on the liquid film/substrate interface. We built an in-house system capable of monitoring sub-microliter droplet shape and extracting surface forces from contact angles and droplet curvature. We perform geometric fitting in a multi-step process using Python in a user selected region of interest (ROI) which is a box centered on the droplet with top and bottom edges corresponding to the top and bottom substrate surfaces.

We use the “Segment anything Model (SAM)” developed by Meta to identify the left-side and right-side contours to the droplet for each frame in the video. Our python script uses openCV's robust fitting algorithm to fit a generalized ellipse to the water droplet edges and calculates the droplet-surface contact angles and all other necessary geometric information. It then computes the mean curvature from the fitted ellipse. Finally, it calculates the capillary force on from the contact angles at each contact point, and mean curvature (Equation 6):

$$F = -2\pi\gamma \left(y(x_i) \sin \theta_i - \frac{H}{2} y^2(x_i) \right) \quad (6)$$

Where the subscript i denotes either 1 (top plate) or 2 (bottom plate), γ is the liquid-air surface tension of the drop liquid, θ_i is the contact angle, $y(x_i)$ is the location of the solid-liquid-gas interface (or contact point), and H is the mean curvature of the droplet contour.⁵

Future Plans

In the future, we will focus on connecting the results from the various characterization approaches we have been developing. Specifically, we intend to connect how the solution rheological properties and surface tension correlate with crystal growth. We will incorporate our *in situ* photoluminescence measurements with direct monitoring of crystal (or island) growth from solution via optical microscopy. We also intend to correlate this work with *in situ* GIWAXS and GISAXS measurements; we have a current proposal for beamline 17-2 use at SLAC and will apply for time in the next scheduling period; concurrently, the lead graduate student on this project has submitted an application for the DOE Office of Science Graduate Student Research program to work at SLAC for 6 months to integrate our printer into beamline 17-2 and answer the following questions with multiple metal halide perovskite formulations:

1. How do solvent properties and ink formulation govern evaporation kinetics—thus nucleation density—in confined volume printing?
2. How does altering the surface energy and chemistry of the substrate and superstrate influence crystal growth and orientation?

We will also measure domain sizes in our films using a python package, “Segmenteverygrain,” which uses a patch-based convolutional neural network to create a first pass segmentation mask that can then make use for training the neural network for quicker, more accurate segmentation than approaches typically used in literature. We have been training this model on both SEM and optical microscopy images and are confident in its accuracy. We will correlate the size of domains—and potentially boundaries between them—to the solvent systems and surface chemistries used to better understand the interactions between solvents and surfaces in film growth.

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Atomistic Information Theory of Materials Synthesis and Free Energy Landscapes

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Keywords: predictive synthesis, atomistic simulations, thermodynamic entropy, information theory, generative modeling

Research Scope

Materials synthesis is dominated by a complex interplay of thermodynamics and kinetics that hinders their predictability. Within computational materials science, characterizing and sampling free energy surfaces is one of the major limitations to rationalizing synthesis. In principle, full knowledge of free energies could inform anything phase stability, processing conditions for solidification, or the kinetics of phase transformations. Nevertheless, there are major computational bottlenecks to produce an accurate description of free energies or sample reaction pathways and interfaces relevant to synthesis. This project develops new methods to simulate and navigate free energy pathways in atomistic simulations by accelerating the quantification of entropy in equilibrium and out-of-equilibrium conditions. Specifically, our main goal is to create a theoretical framework grounded on information theory to sample, analyze, and rationalize free energy landscapes and phase transformations from a computational perspective.

Recent Progress

This project started in FY24-25 and has so far produced two publications (plus one in preparation). The main outcomes of the project include: (1) establishing an information-theoretical framework that relates information entropy to thermodynamics and synthesis, (2) using information theory to improve outlier detection in atomistic simulations, and (3) creating generative models that relate “information matching” to modeling of grain boundaries of materials. This progress is summarized below.

Connecting information theory to atomistic simulations: Free energy calculations are notoriously slow to converge and compute, especially for systems where the potential energy landscapes are not well-understood. Borrowing from the field of machine learning interatomic potentials (MLIPs), we

have proposed that atomic descriptors and information theory recover important aspects of thermodynamic entropy directly from molecular dynamic (MD) simulations.¹ First, we proposed atom-centered representations that can be efficiently computed over systems with tens of millions of particles or long timescales. Using this descriptor, we then quantified a probability distribution to atomistic simulations based on a density estimation over the representations (**Fig. 1**), which showed multiple useful applications within atomistic machine learning (ML), including model-

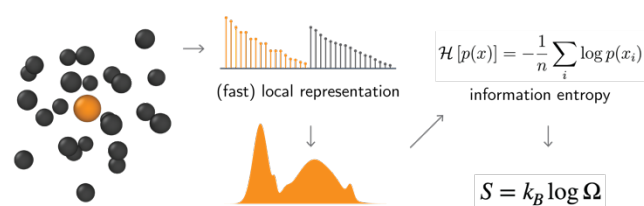


Fig. 1: Overview of our method. Thermodynamic entropies are estimated from probability distributions of atomic environments obtained from simulations.

free uncertainty quantification or measuring dataset completeness. The parallels between Shannon's theory of information, Gibbs' thermodynamics formalism, and atomistic ML also allowed us to show that the information entropy of this distribution is a useful surrogate to thermodynamic entropy across multiple systems. For instance, the method was used to predict high-temperature, high-pressure phase transformations with competitive accuracy with respect to thermodynamic integration (TI) approaches (**Fig. 2a**), but at a fraction of the computational cost. Furthermore, the theory and computational implementation provided a tool to measure information contents within out-of-equilibrium simulations. Though entropy can be ill-defined in out-of-equilibrium settings, our information entropy approach was able to describe transformation rates during nucleation and growth across solidification trajectories (**Fig. 2b**). The functional derivative of information entropy also showed discontinuous-like behavior during the phase transition, mirroring the behavior of heat capacity within phase transformations.

Information theory recovers the classical nucleation theory: The framework of the classical nucleation theory (CNT) is typically employed in synthesis science given its useful description of phase

transformations in materials. However, an accurate description of CNT within atomistic simulations depends on the effective modeling of cluster size distributions and other assumptions. Typical algorithms used to perform phase classification analysis fail to predict any clusters within supercooled liquids, and thus cannot be used to explore the limits of CNT within solidification approaches. We relaxed the phase classification hypothesis within the CNT and recast the problem as a continuous overlap between probability distributions. The approach used our information-theoretical formalism to define the probability space,¹ and treats clusters as atomic environments with high mutual overlap between the liquid and solid phases. We demonstrated this definition recovers the CNT in archetypical homogeneous nucleation trajectory sampled with classical MD simulations with quantitative accuracy. **Figure 3** shows that the information-theoretical analysis correctly defined the onset of nucleation and its corresponding nucleus, and captured the fluctuations of the largest

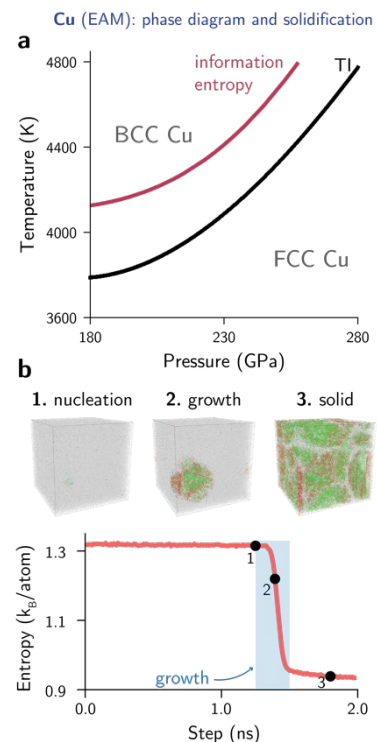
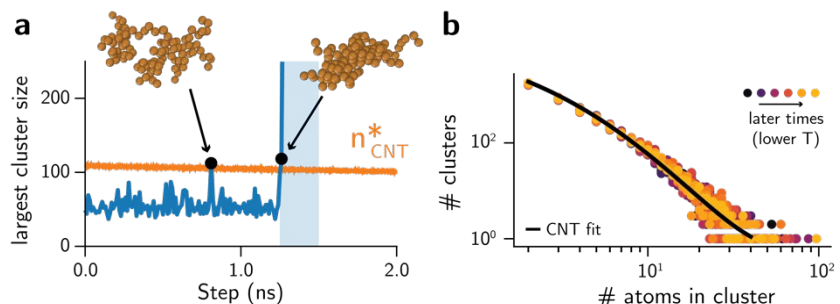


Fig. 2: information entropy analysis of **a**, phase stability and **b**, out-of-equilibrium MD simulations of a copper melt

Fig. 3: our information analysis recovers the CNT predictions of **a**, largest cluster sizes and **b**, cluster distributions. The methods create a continuous classification strategy of solid clusters within a liquid phase.

cluster size across the simulation. Though the behavior from the CNT continuum model is reproduced, non-classical mechanisms explanations (e.g., spherical clusters) are not necessarily observed (**Fig. 3a**). This agreement suggests that our methodology can be used to describe other phase transformation mechanisms and determine when non-classical nucleation can dominate over classical nucleation.

Developing algorithms for rare event detection in large atomistic datasets: Within computational synthesis science, atomistic simulations can be performed at large length and time scales to sample

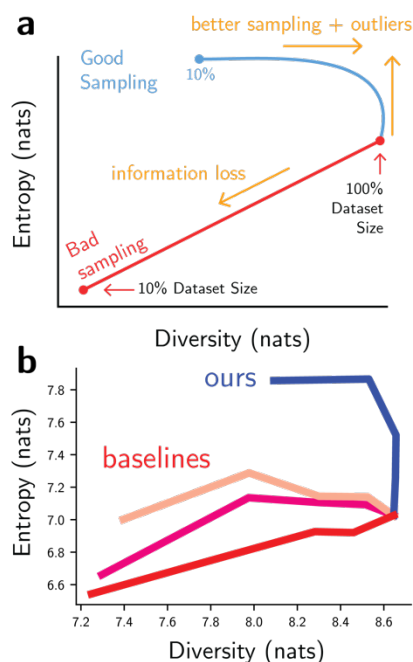


Fig. 4: **a**, information entropy is used to subsample atomistic datasets. **b**, our method outperforms all baselines in retaining outliers.

quantities of interest such as thermodynamic entropy or allow phase transformations to take place. While exascale-grade computational infrastructure is increasingly available, analyzing and subsampling rare events in very large dataset sizes is challenging. Specifically, even if one were able to save and analyze all snapshots of large nucleation/growth trajectories in materials at the atomistic scale, finding rare events within these datasets is an extremely time-consuming task. Typical data compression algorithms and unsupervised learning analysis employed in atomistic ML struggle to capture rare events in atomistic trajectories (such as the onset of phase transitions) due to their sparsity, and thus lose important information when subsampling (**Fig. 4a**). Therefore, there is a need for low-cost tools to perform outlier detection in atomistic datasets. We built on our work in information theory to propose an algorithm that subsamples atomistic datasets by solving the minimum set cover problem over the space of atomistic environments. The set cover analysis ensures that points with highly redundant environments with respect to the entire distribution of environments are discarded before others, thus maximizing the retained information. Across multiple

examples of datasets, our algorithm preserved outlier environments, retained the long tail of distribution of forces, and maximized the information entropy of the datasets (**Fig. 4b**), outperforming other dataset compression methods. The method can be used to automate the detection of rare events in large-scale atomistic simulations and accelerate the study of phase transformations, solidification, and kinetic phase diagrams.

Information matching for generative interfacial modeling: Synthesis phenomena emerge not only from the thermodynamics of idealized bulk structures, but also from microstructures, defects, and structural heterogeneity. For instance, modeling interfaces at the atomistic scale is critical to understand heterogeneous nucleation, but sampling stable interfaces between solid phases using computational methods is challenging not only due to the cost of generating and simulating structures, but also because of the number of degrees of freedom required to sample interfaces. We

developed a generative diffusion model to sample materials interfaces by training them only to bulk structures (**Fig. 5a**).² As a model system for interface prediction, grain boundaries (GBs) exhibit multiple degrees of freedom, metastable structures, and aperiodicity, and influence a range of multiple mechanisms of nucleation and growth. The generative model used an information-matching approach to sample the interfaces, where atoms are denoised to best approximate bulk-like configurations in the training data. Generated structures often led to lower energies than those obtained from direct optimization (**Fig. 5b**) and showed excellent agreement with simulation and characterization data from the literature even for more complex GBs such as Al_2O_3 (**Fig. 5c**).

Future Plans

Within the scope of methodological development, sampling, and free energy landscapes, our goals for the next year will focus on improving the theoretical foundations of our atomistic information theory and employ its direct use in simulating phase transformations in materials. Short-term research goals include improving the formalism of predicting thermodynamic quantities from descriptor distributions, as well as using entropy in enhanced sampling methods to actively sample reaction pathways in solid-solid and liquid-solid transformations without prior knowledge of potential energy landscapes. We will also extend the simulation methods to machine learning interatomic potentials that will be used to more accurately sample phase transitions. Finally, we will use our generative framework to model other interfaces, setting the stage for simulation of heterogeneous reactions.

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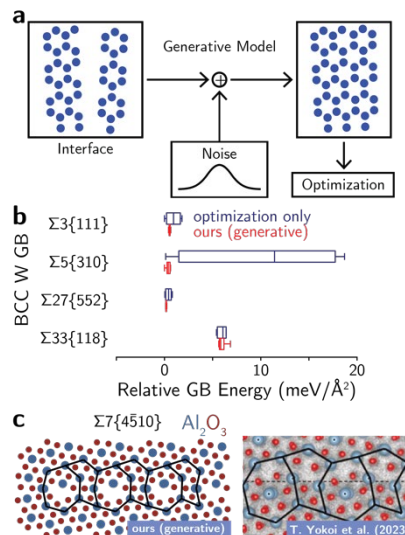


Fig. 5: a, generative framework for sampling grain boundaries. Our method samples b, low energy configurations (e.g., in BCC tungsten) and c, reasonable GBs for ceramics such as Al_2O_3

Fundamental studies of hydrogen arc plasmas for high-efficiency and carbon-free steelmaking

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Keywords: thermal plasma, reduction kinetics, phase transition, surface chemistry

1. Research Scope

Iron and steelmaking is one of the most energy-intensive industries in the US. The dominant industrial energy requirement in iron and steelmaking originates primarily from coke-based reduction required to drive the iron-ore reduction process. Hydrogen plasma smelting reduction (HPSR) is a promising new technology that can improve the efficiency and raw-materials flexibility of ore reduction with the use of hydrogen and electrified industrial heat. The role of the hydrogen plasma is to enhance the kinetics of the reduction and to provide thermal energy to melt and separate the molten iron from the oxide gangue. However, the plasma arc that is integral to this strategy generates extreme environments (temperature $\sim 10,000$ K), involves capital-intensive equipment and operations, and comes with significant scale-up challenges. In this project, we develop a first-principles theoretical understanding of HPSR through high fidelity simulations and novel time-resolved experimental measurements. Our objective is to elucidate fundamental physicochemical processes to overcome knowledge gaps in the foundational science of hydrogen plasmas for energy efficient and electrified iron ore reduction and melting. We address basic science questions associated with the physical processes of hydrogen thermal arcs, interaction of plasma with solid and melt surfaces, transport of active hydrogen species in gas/solid/melt phases, and the kinetics of iron ore reduction. We deploy a multi-scale approach that couples fundamental molecular-scale models to mesoscale (phase field, pore transport) and macroscale (plasma fluid dynamics, heat/mass transfer) models. Together with data-driven scale bridging and in-situ/ex-situ experimental measurements of chemical compositions in plasma/solid/melt phases, our project will develop a comprehensive theory of hydrogen-plasma iron-ore interactions, that will accelerate the scale-up and transition to steelmaking via HPSR. The objective of this project is to close fundamental research questions related to characteristics of hydrogen plasmas and their roles on the mechanisms of reduction and melting of iron-oxides. Specifically, we aim to answer the questions:

- *What is the structure and dynamics of hydrogen containing arc plasma discharge when coupled with multiphase ore reduction process?*
- *What is the thermal and chemical environment presented by the hydrogen arc at the iron ore surface to facilitate ore reduction and ore melting?*
- *What are the mechanisms for gas species transport at the mesoscale within the pores of the iron ore that control the plasma-arc reduction process?*
- *What are the thermochemical processes that lead to ore reduction and phase transitions?*

2. Recent Progress

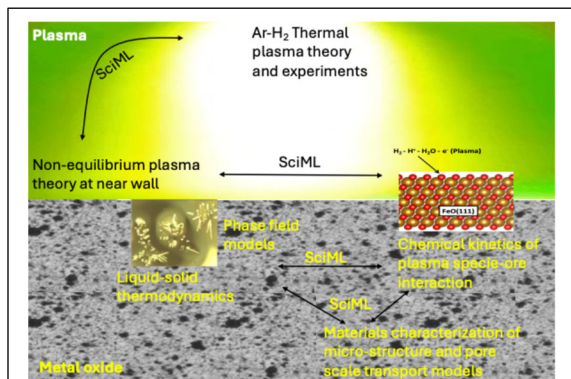


Figure 1: Various physicochemical phenomena addressed in this project

This project involves a laboratory scale experimental campaign with electrical and optical emission measurements along with characterization of the iron ore samples post partial and complete reduction. Computational modeling for thermochemical structure of the hydrogen arc and gas species transport through porous media will be used to validate with the experimental measurements. Atomistic scale models using ab initio Density Functional Theory (DFT) and Molecular dynamics (MD) are used to quantify reduction mechanisms at the surface from various plasma species alongside solid-liquid thermodynamics and melt free energies. These models inform kinetic and

transport parameters within the phase field model that tracks the iron ore reduction and corresponding phase changes. Finally, both the plasma and the solid liquid reacting phase models will be complemented by a surrogate model developed through machine learning (ML) that is informed by experimental and high-fidelity model data. In principle, an accurate and fast surrogate model will enable process space exploration, process optimization, and discovery. The team has organized itself into subtasks as indicated in Figure 1. The progress in these subtasks are as follows:

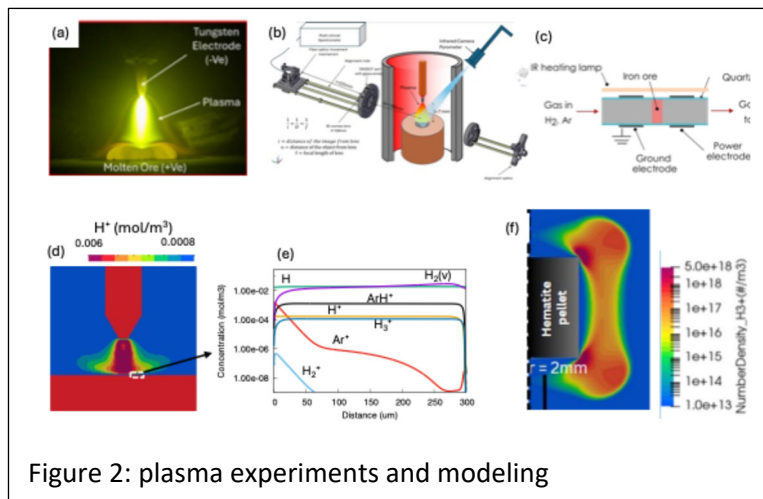


Figure 2: plasma experiments and modeling

2.1 Experiments on plasma assisted reduction: The plasma arc reduction experiments are performed in a lab-scale plasma smelter with Ar-H₂ mixtures, as shown in Figure 2a. The team has equipped the plasma smelter with in-situ optical emission spectroscopy and thermal camera to measure the gas phase species, characteristic plasma parameters, such as gas temperature, and the iron ore temperature (Figure 2b). Plasma modeling efforts from

task 2.2 has indicated significant non-equilibrium effects at the plasma-ore interface. Therefore, to decouple the contributions of heat and non-equilibrium plasma species, the team has also developed a nanosecond (NS) pulsed plasma reduction setup (Figure 2c) where lower gas temperature, higher electronic contributions and non-equilibrium chemical processes will provide information on the reduction process for computational models and understand how the reduction mechanism changes as a function of plasma parameters. Our initial results show that doubling H₂ concentration leads to faster reduction yields and kinetics. For instance, at an arc current of 200 A and 5% H₂ concentration, complete reduction of 10 g of iron ore is achieved within 15 minutes of plasma exposure. In contrast, under similar current conditions but with only 1.25% H₂

concentration, approximately 50% of the oxide remains unreduced even after 30 minutes of plasma treatment. Baseline measurements using a non-plasma thermal hydrogen reduction process has already provided novel and valuable insights into mass transport and iron formation microstructures, summarized in a publication from this team [1].

2.2 Plasma discharge model:

2.2.1 Thermal plasma model for argon-hydrogen arc: We have developed a local-thermodynamic equilibrium (LTE) based 3D plasma model that solves bulk fluid flow, heat transfer including radiation, and electromagnetic equations. Figure 2(d) shows the H^+ concentration for a transferred arc at the experimental conditions of 95% Ar/5% H_2 and 100 A current, that captures the bell-shaped plasma plume and peak temperatures $\sim 15,000$ K in the bulk of the plasma. We observe that the flux of hydrogen ions increases with current, whereas the flux of hydrogen radicals does not change significantly.

2.2.2 Non-equilibrium plasma model: In order to quantify important species close to the ore surface, a near-wall non-equilibrium model [2] was developed, that utilized LTE conditions predicted from task 2.2.1 as the boundary condition. Figure 2(e) shows species concentrations in a $300\text{ }\mu\text{m}$ near wall region indicating significant presence of vibrationally excited H_2 , H radicals, H_3^+ and ArH^+ ions. These conditions are used in task 2.3 for developing detailed surface chemistry models. Due to importance of non-equilibrium plasma chemistry in the near wall region, we continued our efforts on a low temperature plasma model for a nanosecond pulsed discharge for experiments planned in task 2.1 (Figure 2(c)). Figure 2(f) shows a snapshot of anode directed streamers produced from a cylindrical ore pellet held at -5 kV in a pure H_2 environment indicating significant H_3^+ concentrations.

2.3 Materials characterization and microstructure scale models: Figure 3(a) illustrates the effect of arc current and hydrogen concentration. Complete reduction at 200 A and 5% H_2 is

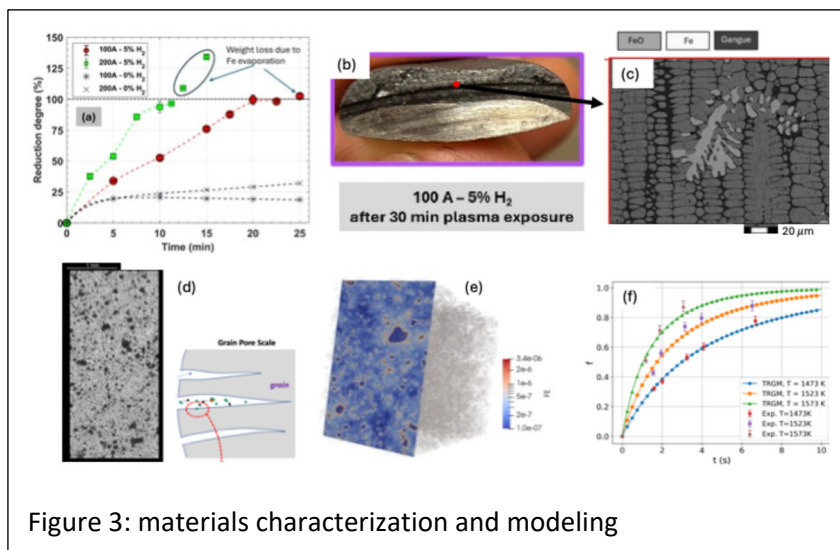
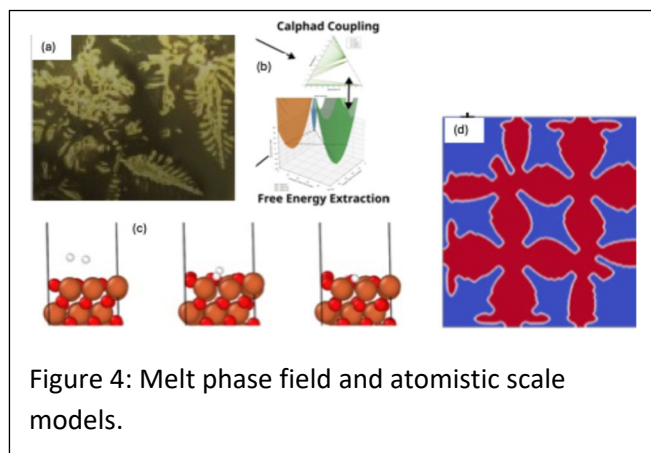


Figure 3: materials characterization and modeling

used for phase-field model (task 2.5) validation. X-ray computed tomography (XCT) imaging of ore pellets (Fig. 3(d)) indicate a complex pore structure, that are directly imported into our open-source transport-reaction solvers (Fig. 3(e)) to study heterogeneity in Fe formation. A Transient Reactive Grain Model (TRGM) [3] was also developed for simulating the reduction process that are validated with experimentally predicted reduction degrees (Fig. 3(f)). Results reveal species concentration gradients with a diffuse reaction zone, and enhanced hydrogen diffusion at the grain

outer surface due to evolving porosity.



2.3 Surface chemistry model: We have completed a machine-learned force field-assisted ab initio MD study of surface reaction kinetics using hydrogen plasma species (H_2 , H , H^* , H^+ , H_2^+ , and H_3^+). Figure 3(c) shows the interaction of H_2^+ with FeO surface. Our calculations, e.g., species sticking coefficients, will feedback into the plasma models and pore-scale transport/phase-field models.

2.5 Liquid-solid chemistry and thermodynamics: In this work, we employed SLUSCHI [4] to drive DFT–

MD simulations of oxygen transport in FeO, with the explicit goal of quantifying atomistic mass-transport mechanisms across liquid phase and directly comparing to the in-situ measurement. Our simulations reveal that oxygen diffusivity in liquid FeO rises by roughly 60% between 1300°C and 1500°C and then levels off beyond 1500°C, indicating that thermal activation becomes the primary driver of reduction kinetics, which has been observed experimentally.

2.6 Solid-liquid phase model: To investigate Fe precipitation via dendrites during reduction, a phase-field model is developed that is being validated with experimental images (Fig. 4(a)). This model leverages CALPHAD data (Fig. 4(b)) to incorporate free energies and atomic diffusion coefficients. Figure 4(d) shows a snapshot of dendrite formation and evolution that qualitatively match experimental images. Thus, this framework offers deep insight into the mesoscale mechanisms driving phase evolution and morphological changes during hydrogen reduction, bridging the gap between atomistic processes and macroscopic observations.

3. Future work

As our models mature, we plan to use SciML techniques for connecting multi-scale models, optimization and parameter sensitivity studies. For example, our near-wall non-equilibrium model will be converted to a surrogate for coupling with the thermal plasma model. As part of multi-fidelity modeling, we have been working on a bridging SciML model that corrects the missing physics and dimensionality of a 1D arc discharge model that runs in ~ 5 mins as opposed > 2 days for a full 3D arc model. The objective is to obtain an accurate computational framework for obtaining quantities of interest, while having the computational cost of the 1D model.

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Mississippi EPSCoR: Developing an autonomous closed-loop copolymer materials discovery platform at USM

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Keywords: Block copolymer self-assembly, High throughput experimentation, Machine learning, Closed loop discovery, Synchrotron scattering

Research Scope

The University of Southern Mississippi's EPSCoR research grant named “Data-driven Rein vigorated Advanced Materials for Energy Application (DREAM)” will establish a world-leading research, education, and technology platform in the southeast region with the goal of advancing **data-driven polymer materials design** to address various challenges faced by the Department of Energy in its energy applications. What makes the DREAM seed grant unique is its comprehensive approach to materials discovery, which combines high-throughput materials synthesis through non-covalent interaction, high-throughput computational simulation, and advanced morphology and property characterization. By integrating these techniques, the team's long-term goal is to solve current challenges in energy materials for the national's growing energy demand, which have so far remained elusive. To achieve our goal, the team will leverage the intellectual breadth of the University of Southern Mississippi, Iowa State University, and Lawrence Berkeley National Laboratory. The center will be the first to create a complete data-driven materials discovery platform for polymeric materials, enabling a synergistic and convergent approach to develop new autonomous data-driven experimental and computation facilities to address various energy challenges within the DOE's core mission.

The overarching goal of this research is to leverage data science for the rapid screening and development of novel polymeric materials with applications in energy. To achieve this goal, three major objectives are being pursued, as illustrated in **Fig. 1**:

- **Objective 1:** To rapidly generate a large library of copolymer materials by utilizing non-covalent interactions derived from end-functionalized homopolymers. This approach aims to accelerate the creation of diverse copolymer compositions.
- **Objective 2:** To construct a comprehensive database of new copolymer structures, processing parameters, and morphologies. This is achieved by employing high-throughput material processing, advanced morphology characterizations, and integrated analysis and simulation techniques.

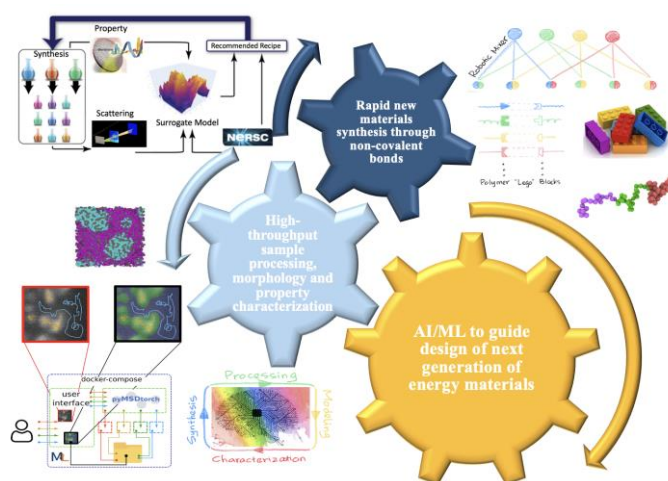


Figure 1. leveraging the data science to enable rapid screening and developing of new polymeric materials for energy applications.

This is achieved by employing high-throughput material processing, advanced morphology characterizations, and integrated analysis and simulation techniques.

- **Objective 3:** To develop an AI/ML (Artificial Intelligence/Machine Learning)-guided closed-loop materials discovery platform. The ultimate aim of this platform is to efficiently identify and optimize the desired phase behavior of copolymer thin films for specific applications.

Recent Progress

1. Development of New Hydrogen-Bonded Homopolymers:

A crucial step in high throughput polymer synthesis involves the development of new hydrogen-bond functionalized polymers. This innovation enables the rapid construction of hydrogen-bonded block copolymers (**Fig. 2**). The strategy employed is modular synthesis, which utilizes click-reactions to precisely incorporate hydrogen bonding groups onto homopolymers. This modular approach provides flexibility and efficiency in tailoring homopolymer structures. We first synthesized 34 telechelic homopolymers. Then BCPs were fabricated by physically blending the DAT/Thy-homopolymer precursors using a liquid-handling robot, in a combinatorial approach at 1:1 molar ratio for hydrogen functional group. Based on those initial 34 homopolymer polymers, we successfully obtained 273 distinct BCPs (**Fig. 2**). The formation of BCPs was confirmed by ^1H NMR and further verified through temperature-dependent measurements. The combinatorial chemistry allows rapid access to a large library of copolymers.

2. High-Throughput Sample Processing and Characterization:

USM has successfully implemented high-throughput sample processing capabilities with the acquisition of a robotic sample formulation and processing system (**Fig. 3a**). This system automates thin film sample preparation by pipetting, mixing, and stirring homopolymers and additives, then transferring the formulated ink to silicon substrates for spin coating. User-defined Python scripts control processing conditions like mixing ratios, liquid transfer volumes, spin-coating speeds, and post-deposition thermal annealing parameters. This automation allows for the preparation of thousands of samples per day, which is at least 100 times faster than manual processing. High-throughput thin film morphology characterization has been achieved through collaborations with LBNL/BNL, utilizing their synchrotron Grazing incidence X-ray scattering and microscopy facilities. An improved sample stage and a robotic arm, controlled by a Python script, automate the exchange of samples mounted on aluminum bars (**Fig. 3b**), achieving throughput rates of 500 samples per day, which is about 10 times higher than previous methods.

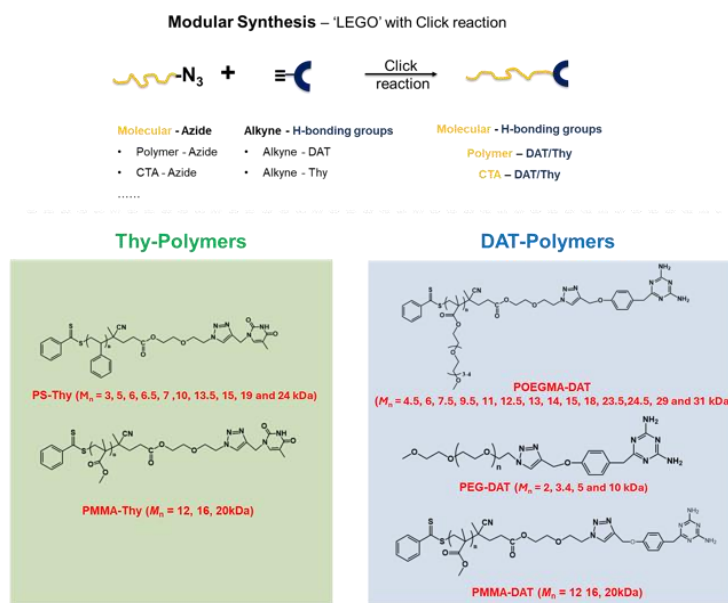


Figure 2. Modular synthesis based on the click-reactions to add hydrogen bonding group to homopolymer. Chemical structure and molecular weights of DAT/Thy-functional polymers.

The team also collaborated with Dr. Paul Ashby to develop automated AFM measurements for multiple BCP thin films, leveraging the Jupiter AFM's programmable platform. A specialized substrate holder (Fig. 3c) can accommodate up to 52 samples with pre-registered positions for automated imaging. An overview of the high-throughput AFM image analysis process for extracting grain size is presented in Fig. 3.

Morphological features, including domain spacing, FWHM, and grain size, extracted from GISAXS data and AFM

images, have been curated into the MaterialsMine database. Each entry in the database includes comprehensive composition, formulation, processing, and morphology information. This data is accessible via SPARQL queries or a graphical user interface and can be downloaded in various formats for analysis and ML model training (Fig. 4). Efforts are also underway to curate raw GISAXS and AFM images into the database for direct exploration of BCP morphology.

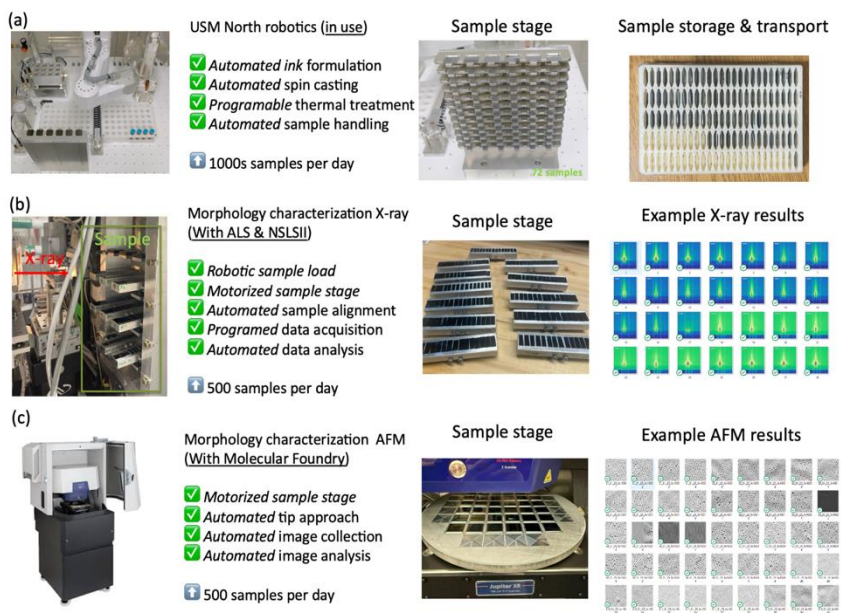


Figure 3. (a) Image of the sample processing robot from North Robotics, commissioned at USM. (b) Example of a high-throughput X-ray scattering tool used to analyze sample morphology, including the sample stage and representative X-ray scattering images. (c) Picture of Jupiter high-throughput AFM, AFM sample holder and corresponding microscopy

3. Machine Learning Model Development:

With a robust dataset based on 202 BCP thin films, the team has successfully developed ML models. These models are designed to predict BCP thin film morphological features

based on various processing conditions, including solvent ratio, additive type, and additive ratio. As an illustrative example, Fig. 5 presents a plot of predicted versus actual domain spacing using a random forest regression model. Fig. 5c displays a bar chart of the mean SHAP values, which provide insights into the importance of different features in the model's predictions. Additionally, Fig. 5d shows a SHAP dependence plot specifically for additives, illustrating how the model's output changes with varying additive concentrations.

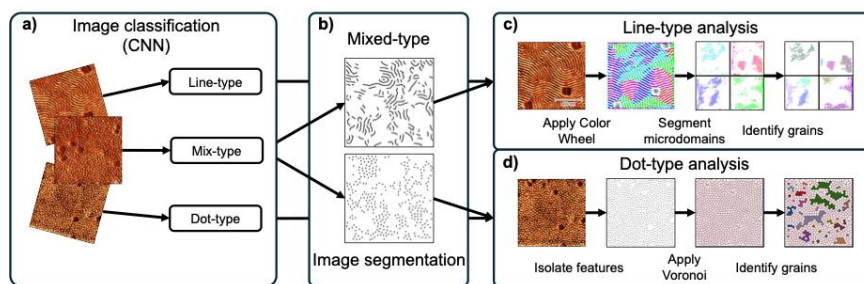


Figure 4. Overview of the high throughput AFM image analysis process for extracting grain size.

4. High-throughput Morphology Simulation:

Our team employed a generic bead-spring coarse-grained model, comprising two distinct bead types, to investigate the self-assembly and morphological behaviors of AB diblock copolymers using molecular dynamics simulations (Fig. 6). Specifically, we focus on the effects of segmental incompatibility associated with interfacial interaction strength ($\epsilon_{(A,B)}$), interaction range ($r_{c,(B,B)}$), and degree of polymerization (N) on the system morphology. By systematically varying these Lennard-Jones parameters governing intermolecular interactions, we quantify the resulting morphologies using domain spacing (D), the peak intensity of the structure factor $S(q^*)$, and the correlation length (ξ_{fit}). Our results reveal that enhanced B-block cohesive interactions by increasing the range of intermolecular interactions ($r_{c,(B,B)} \geq 2.0$) stabilizes lamellar structures by suppressing curvature-induced instabilities and preserving domain periodicity, even at high miscibility between the A and B blocks. Correlation analysis further reveals that longer chain lengths and extended cohesive interaction ranges synergistically enhance long-range ordering and interdomain connectivity. Building upon our CG modeling efforts, we have generated a dataset comprising over 1000 image-based entries derived from diverse molecular parameter sets of CG simulations. We are currently applying these CG modeling derived imaging data and machine learning (ML) techniques to predict morphological features of BCPs. These efforts have demonstrated the feasibility of integrating multiscale modeling and data-driven approaches to explore complex polymer morphologies.

Future Plans

The current seed grant will conclude in September 2025. During the remaining two months, our efforts will focus on drafting and submitting manuscripts. Five papers are currently in preparation. A follow-up proposal has been submitted to request additional funds. If the renewal proposal is awarded, the next phase of work will concentrate on demonstrating closed-loop morphology discovery, both at the ALS beamline and at USM.

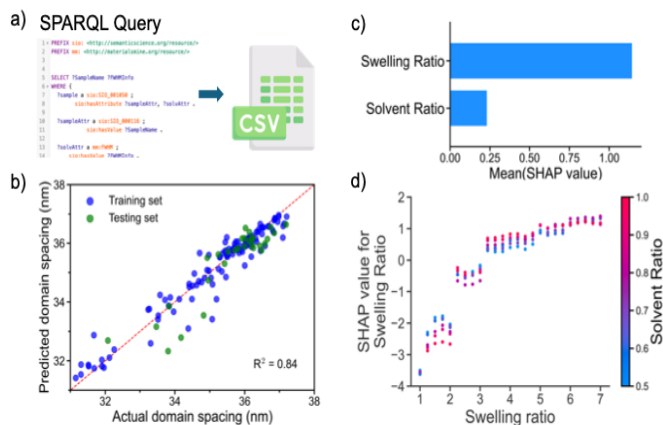


Figure 5. a) Schematic of accessing data via SPARQL query, b) predicted vs. actual domain spacing with random forest regression model, c) bar chart of the mean SHAP values, and d) SHAP dependence plot for additives

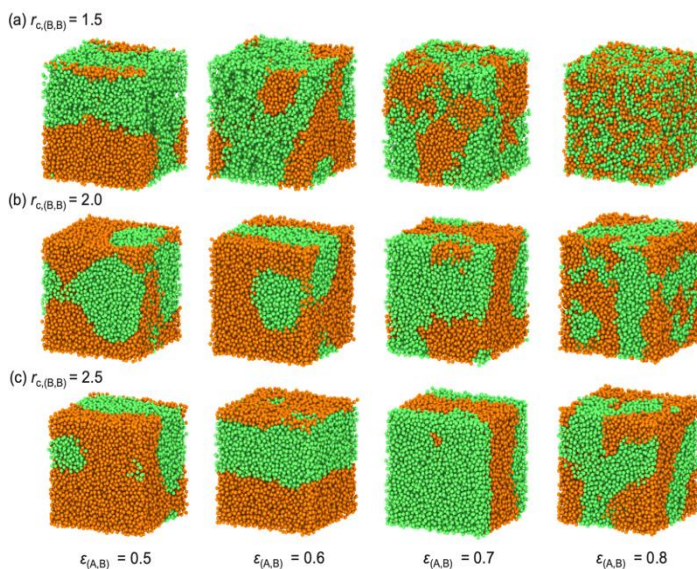


Figure 6. Coarse-grained modeling of BCPs with varying intermolecular interactions strength and range of interactions, forming different morphologies.

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Data-Driven Synthesis Science

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Keywords: predictive synthesis, machine learning, autonomous experimentation, solid-state, sol-gel

Research Scope

Materials synthesis remains difficult to predict and control due to the complex interplay of thermodynamics, kinetics, and nucleation processes that govern phase formation. The Data-Driven Synthesis Science (D2S2) program seeks to overcome these challenges by establishing a predictive, AI-augmented framework for inorganic materials synthesis. We focus especially on solid-state and sol-gel synthesis routes, which dominate the landscape of bulk inorganic materials synthesis. Our approach integrates thermodynamic models (*e.g.*, reaction free energies, phase diagrams), kinetic and transport descriptors (*e.g.*, nucleation barriers, diffusion constraints), and machine learning (ML) trained on text-mined data from historical synthesis literature. These models are tested and refined using closed-loop, autonomous experimental platforms.

Recent Progress

Over the current funding period, D2S2 has established a foundational framework for rationalizing and predicting solid-state reaction pathways using a combination of thermodynamic and kinetic descriptors. One major theoretical advance is the quantitative validation of the “max- ΔG ” hypothesis, which predicts that the first phase to form in a solid-state reaction will be the one that maximizes the local decrease in Gibbs free energy. Across 37 ternary oxide systems, we showed via in-situ XRD that when the free energy difference between competing first-formed phases exceeds 60 meV/atom, the reaction pathway is thermodynamically controlled; below this threshold, kinetic factors predominate [1]. This insight provides a quantitative threshold separating thermodynamic and kinetic control in powder reactions.

We also developed several tools to incorporate kinetic effects into reaction modeling. A cellular automaton framework, ReactCA [2], simulates phase evolution under spatial constraints and predicts intermediate product sequences by considering local interface reactions. We further extended our modeling to include mass transport through reaction product layers, using ML-predicted ion transport coefficients derived from ab initio molecular dynamics and atomic cluster expansion potentials. These theoretical advances are being validated through comparisons to experimental systems with known kinetic constraints, such as Ba-Ti-O reactions where sluggish ion diffusion explains the absence of predicted phases under certain conditions.

In tandem with theory development, we expanded our infrastructure for synthesis data curation. Using modern large language models (LLMs), we extracted over 80,000 synthesis recipes from the literature, including more than 18,000 phase-impure syntheses. These “negative” results provide critical training and test data for synthesis prediction models. We validated that impurity phases in these records tend to have higher reaction energies than target phases, supporting the hypothesis that they often represent early-forming, kinetically accessible phases.

Our experimental efforts centered on characterizing and controlling synthesis pathways using autonomous laboratories and advanced diagnostics. The A-Lab platform, designed and operated at LBNL, now automates powder dosing, mixing, reaction, and XRD analysis, and has been used to synthesize 58 compounds, 41 of which were achieved without human intervention [3]. Autonomous control has been extended to include SEM/EDS analysis via an ML-enhanced pipeline capable of compositional phase clustering.

In sol-gel synthesis, we investigated BiFeO_3 as a model system and revealed that precursor solution chemistry (*e.g.*, ligand coordination environment) determines the formation pathway [4]. DFT modeling and reaction network analysis showed that a dimer-mediated pathway is energetically favorable over conventional solvation mechanisms. In parallel, we demonstrated that nanoscale precursors in solid-state synthesis lead to pure BiFeO_3 , while micron-scale precursors yield competing phases, reinforcing the critical role of diffusion and particle size in pathway selection [5]. TEM studies confirmed that intermediate phases like $\text{Bi}_{12}\text{FeO}_{39}$ form via interfacial diffusion at early stages, highlighting the mechanistic basis of precursor-dependent outcomes.

Our team also made progress on broader platform capabilities. The AutoBot system enables combinatorial sol-gel synthesis screening, and has been used to study crystallization pathways in DRX cathodes and the role of chelating agents in precursor sol stability. Within the A-lab, a newly integrated Anton Paar diffractometer enables high-throughput in-situ XRD of synthesis reactions at rates of up to 10 runs per day.

Future Plans

Moving forward, D2S2 will enhance both the intelligence of our algorithms and the capabilities of our autonomous platforms. On the AI front, we will investigate reinforcement learning (RL) agents to optimize synthesis conditions in real-time. Additionally, we plan to explore contrastive representation learning to bridge different synthesis methods. By learning shared latent representations of synthesis trajectories, our models will be able to transfer knowledge across experimental modalities. On the experimental side, we will upgrade A-Lab and AutoBot to further close the loop between prediction and validation. New *in situ* diagnostic tools, including an automated furnace-XRD system and robotic sample handling for sequential measurements, are being integrated to observe reaction progress continuously at high throughput. We will also incorporate automated electron microscopy (with sample prep and EDS analysis) to capture morphological and compositional outcomes, enriching the feedback to our models. These

improvements will yield an unprecedented multimodal dataset of synthesis pathways, against which our theoretical models (incorporating diffusion limitations, multi-step reaction networks, etc.) can be rigorously tested and refined. Ultimately, D2S2's future efforts will converge on demonstrating a fully autonomous discovery workflow: the AI will hypothesize a synthesis plan, execute it via robotics, analyze the outcome, and update its strategy in a continual loop.

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Autonomous synthesis with pulsed laser deposition: integrating *in situ* diagnostics and machine learning

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Keywords: pulsed laser deposition, *in situ* diagnostics, AI/ML, automation, 2D materials

Research Scope

Our project aims to address key research priorities in synthesis and processing science by developing *in situ* diagnostics-guided autonomous synthesis and characterization platforms to understand growth mechanisms and control non-equilibrium processes for capturing novel states of matter in nanomaterials. A central challenge in 2D materials and heterostructure growth is the understanding of the vast and complex synthesis parameter space. Our approach combines *in situ* diagnostics, automated deposition platforms, and machine learning to both efficiently explore this space and traverse it with real-time control over synthesis to accelerate the discovery of metastable quantum phases in 2D materials. The overarching goal is to reveal the crystalline pathways and interactions that govern the intermediate states and metastable phases in the formation of functional quantum nanostructures, specifically atomically thin 2D quantum materials that are crucial to DOE's energy mission. This is achieved through three aims: (1) Understand how confinement and strain influence the nucleation and growth pathways of 2D materials. (2) Reveal the mechanisms of phase transformation in 2D materials driven by non-equilibrium processing, and (3) Accelerate the mapping of the energy landscapes for the directed synthesis of desired phases. Our pulsed laser deposition (PLD) and chemical vapor deposition (CVD) platforms incorporate real time feedback, adaptive control and machine learning (ML) to implement autonomous synthesis. In parallel, multiscale *in situ* diagnostics and *ex situ* characterization inform mechanistic models and guide experiment design.

Recent Progress

Our project is building a foundation for autonomous synthesis that integrates *in situ* diagnostics with machine learning to accelerate the navigation and optimization of the exponentially large synthesis parameter space for discovering new materials and phases. *In situ* diagnostics are essential to capture real-time feedback on material growth, enabling intelligent control of synthesis conditions while ML is the key to identify and optimize parameter space through unbiased analysis. Accelerating characterization—both *in situ* and *ex situ*—is critical to inform models and provide atomic-level insights to close the synthesis loop. So here we illustrate two complementary efforts: *in situ* diagnostics-guided PLD, which enables real time observation of materials evolution and forms the basis of our first demonstration of autonomous synthesis; and

ex situ atomic-resolution characterization of bilayer heterostructures to understand mechanisms of hyperthermal implantation by resolving dopants and defects layer-by-layer.

Encapsulation and implantation by kinetic energy tuned PLD with *in situ* diagnostics.

We developed a strategy to enable damage-free encapsulation of monolayer 2D materials with amorphous boron nitride (a-BN) using PLD by tuning the kinetic energy (KE) of growth species. Ion probe and ICCD diagnostics revealed plume splitting into fast and slow components (**Fig. 1a**). We moderate the KE of growth species arriving at the substrate to < 1 eV/atom to achieve “soft landing” conditions by introducing Ar background gas. The drag model analysis of the ion probe data reveals that scattering with the background causes the incident KE to decrease exponentially with increasing pressure. *In situ* Raman spectroscopy (**Fig. 1b**), revealed that high-KE conditions correlate with rapid defect generation and amorphization while low-KE deposition preserves graphene integrity. a significant new result is that ~ 1 – 2 nm of a-BN deposited at low-KE is sufficient to protect the graphene from further damage, even under high-KE deposition.

To improve film quality without damaging the 2D layer, we developed a hybrid deposition method, starting with low-KE deposition followed by high-KE deposition—yielding smooth, dense films. Extending this approach to monolayer MoS₂ (**Fig. 1c**), we showed that a-BN encapsulation improves thermal stability and enhances photoluminescence (PL) intensity via oxygen-mediated passivation of sulfur vacancies during annealing. Overall, this work demonstrates a general strategy for damage-free PLD encapsulation layers on 2D materials, enabling new possibilities for thin-film integration, defect control, and functional tuning in next-generation devices.

Twist angle-dependent Se implantation in bilayer WS₂. Building on prior work converting monolayer TMDs into Janus structures via hyperthermal Se implantation,¹ we investigated twist angle effects in bilayer WS₂. We found that Se incorporation is twist-angle

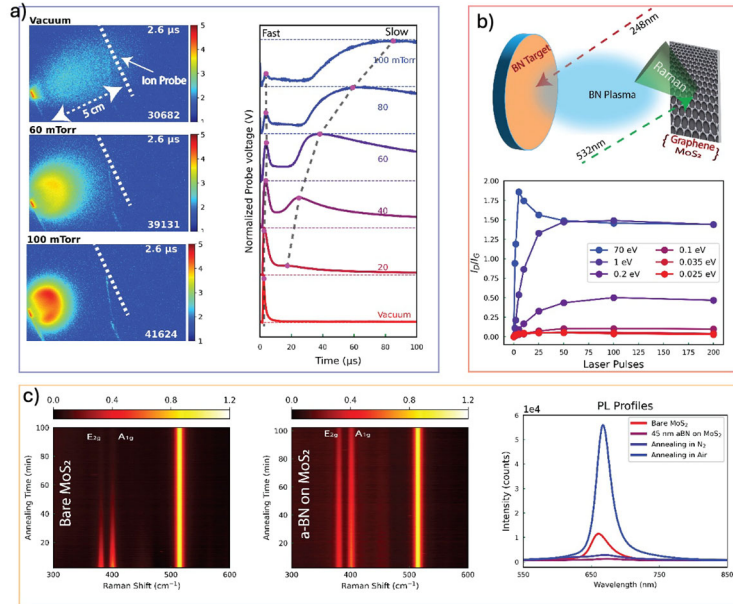


Figure 1. Encapsulation of 2D materials by kinetic energy controlled PLD. (a) ICCD images and ion probe signals of the a-BN plume at varying Ar background pressures during PLD reveal the ‘fast’ and ‘slow’ plume components to minimize the damaging fast plume component. (b) Schematics of the plume interaction with 2D materials, with *in situ* Raman characterization for defect detection. The I_D/I_G ratios of monolayer graphene quantify defect generation relative to kinetic energy of BN species. (c) *In situ* Raman collected during annealing at 250°C of both pristine and a-BN encapsulated MoS₂ shows that the encapsulation protects the monolayer MoS₂ with minimum decay rate, compared to the rapid degradation of the non-encapsulated MoS₂. (Submitted)

dependent and limited to the top layer, with implantation efficiently varying below the 40 eV/atom threshold. We hypothesized that the local electronic modulation from moiré lattice would influence the Se site substitution probability, but the moiré interference pattern made it impossible to locate Se atoms via high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging experiments. To address this, we developed a deep learning model, Gomb-Net, capable of layer-resolved dopant identification from moiré images (Fig. 2).² Using Gomb-Net, we found that Se atoms substitute randomly at chalcogen sites in top layer without clear preference for specific moiré lattice locations. This suggests that local energetic or electronic modulations are too small relative to the KE of the incident Se atoms for the substitution site to be influenced by moiré lattice. This is a notably different mechanism that is predicted/observed for doping of moiré materials in near-equilibrium synthesis methods like CVD. Overall, this study reveals how van der Waals interactions and moiré superlattice effects influence atomic implantation and recrystallization in 2D bilayer systems, offering new insights into layer-specific transformation processes in twisted heterostructures.

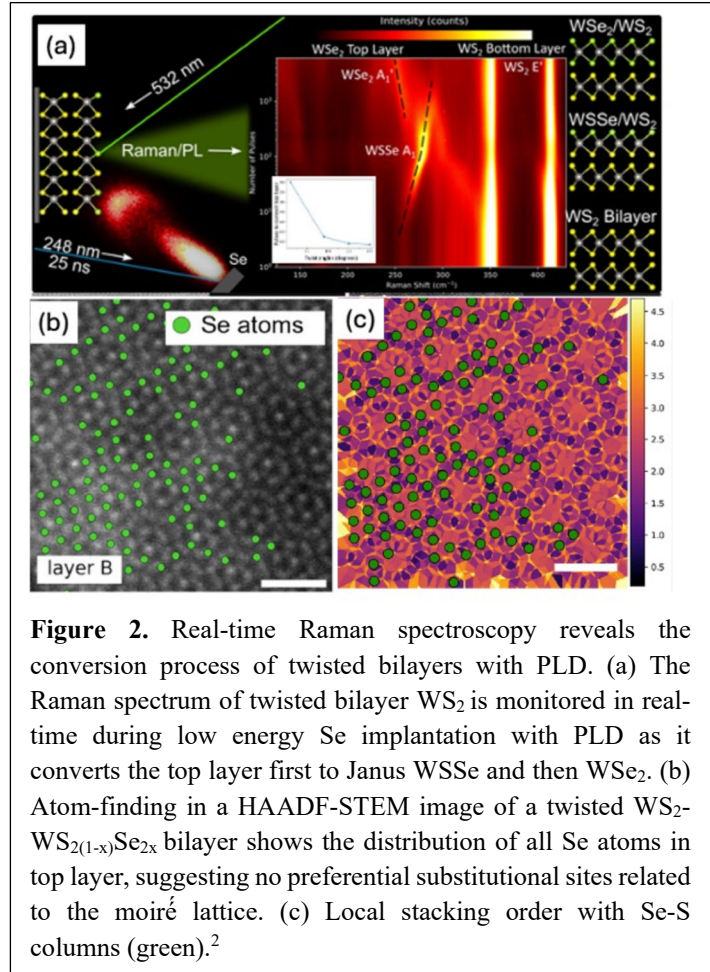


Figure 2. Real-time Raman spectroscopy reveals the conversion process of twisted bilayers with PLD. (a) The Raman spectrum of twisted bilayer WS_2 is monitored in real-time during low energy Se implantation with PLD as it converts the top layer first to Janus WSe_2 and then WSe_2 . (b) Atom-finding in a HAADF-STEM image of a twisted WS_2 - $\text{WS}_2(1-x)\text{Se}_{2x}$ bilayer shows the distribution of all Se atoms in top layer, suggesting no preferential substitutional sites related to the moiré lattice. (c) Local stacking order with Se-S columns (green).²

Machine learning-guided pulsed laser deposition: Accelerating discovery and enabling real-time control. We developed a fully autonomous pulsed laser deposition platform (Auto-PLD, Fig. 3a) that integrates multimodal *in situ* diagnostics - Raman, PL, and reflectivity, for the growing film on substrates along ICCD imaging and ion probe measurements for the plasm plume-with various machine learning methods to intelligently guide thin film synthesis to understand fundamental growth mechanisms. We pushed the state-of-the-art in AI-driven materials synthesis by demonstrating three distinct capabilities: active learning for intelligent design of experiments, deep learning for predicting growth kinetics from non-trivial features of the growth environment, and real-time, physics-informed feedback control of film growth trajectories. In our first study, we demonstrated fully autonomous synthesis for PLD of WSe_2 by exploring a 4D parameter space (background pressure, substrate temperature, and dual-target fluences). Using Bayesian optimization with a Gaussian process surrogate model, Auto-PLD

autonomously synthesized 125 samples ($\approx 0.25\%$ of the 50,625 possible combinations) and successfully identified optimal growth window (**Fig. 3b**)³. This approach achieved $\sim 10\times$ faster discovery compared to manual PLD and uncovered two distinct growth windows associated with different plasma plume dynamics. In addition, we trained a deep neural network on time-resolved ICCD plasma-plume images to predict both synthesis conditions (e.g., chamber pressure, laser fluences) and growth kinetics (extracted from *in situ* reflectivity), enabling accurate, real-time monitoring of the synthesis environment (**Fig. 3c**).⁴

Finally, we integrated a physics-based thin film nucleation and growth model with *in situ* laser reflectivity for real-time control of 1T'-MoTe₂ by PLD (**Fig. 3d**). Using an online Bayesian direct filter, the system estimated nucleation and growth rates in real-time, with uncertainty bounds, down to as low as $\sim 15\%$ monolayer coverage, allowing adaptive control of the growth trajectory.⁵ Together, these advances deliver within-experiment adaptivity, continuous multimodal feedback, and deep mechanistic insight, capabilities not previously realized in thin film synthesis. By combining high-throughput exploration with mechanistic modeling, and real-time adaptivity, auto-PLD enables rapid discovery and precise control of complex materials, establishing a new paradigm for autonomous materials discovery and manufacturing.

Future Plans

We will extend our autonomous synthesis framework to a newly developed robotic CVD platform to explore reaction kinetics and crystallization dynamics during flux-assisted and encapsulated growth of 2D materials. Automated control and *in situ* diagnostics will be adapted to CVD for real time monitoring and ML-informed process optimization. At the atomic scale, we will investigate crystallization and phase transitions using laser and thermal processing within TEM/STEM, providing direct insight into transformation pathways. The long-term vision of our program is to couple synthesis and characterization through ML to enable autonomous discovery of functional quantum materials. By integrating diagnostic-guided synthesis, rapid characterization, and intelligent feedback, we aim to establish a scalable and generalizable strategy for accelerated materials design across PLD, CVD, and laser-processing platforms.

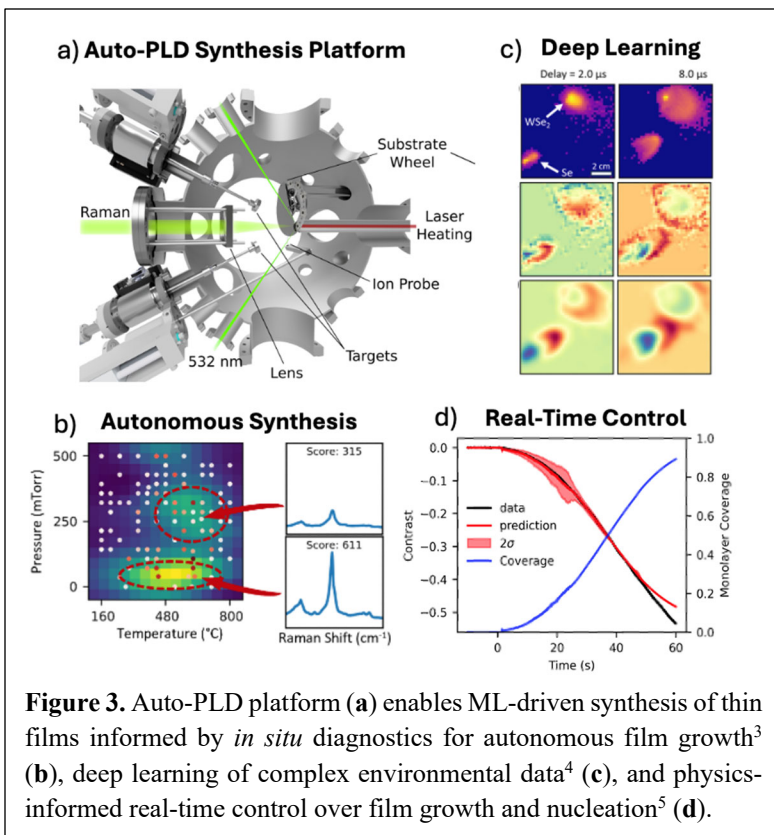


Figure 3. Auto-PLD platform (**a**) enables ML-driven synthesis of thin films informed by *in situ* diagnostics for autonomous film growth³ (**b**), deep learning of complex environmental data⁴ (**c**), and physics-informed real-time control over film growth and nucleation⁵ (**d**).

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PLENARY:

“The Never-Ending Frontier in Advancing T_c to New Heights at Ambient”

Paul C. W. Chu

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University of Houston

Superconductivity is one of the oldest fields of study but remains full of vigor since its discovery more than a century ago for its unusual scientific interest and technological potential. To raise the superconducting transition temperature T_c has served as one major driving force for these long sustaining efforts. This is particularly evident in the last half-decade by reports of near room temperature superconductivity in hydrides under extreme pressures. Unfortunately, the great potential of superconductivity science and technology cannot be fully realized until the burden of extreme pressure is released. At TCSUH, we have adopted a novel approach to over-come the extreme-pressure dilemma by first taking advantage of pressure to generate a metastable phase in a compound with a high T_c and then retain this phase at ambient without pressure following our pressure-quench protocols (PQP). A new record ambient-pressure T_c of 149 K in HBCCO has thus been achieved. In this presentation, I shall present our experimental results and discuss future promises and challenges for PQP, after briefly reviewing events leading to this development.

Directed Assembly of Metastable States for Harnessing Quantum Effects

Rongying Jin (University of South Carolina) and William A. Shelton (Louisiana State University)

Keywords: metastable states, magnetism, topological materials, directed assembly, quantum effect

Research Scope

This research project is designed to explore new states of matter through combined experimental (PI) and computational (co-PI) efforts. By exploiting complex chemistry and extreme environmental conditions, we aim to identify hidden stable or metastable states of matter that cannot form under ambient conditions. With the complementary expertise in materials synthesis (PI) and simulation/modeling (co-PI), single crystals of technologically relevant materials (superconductors, magnets, topological materials) are synthesized and studied for understanding the underlying synthesis and processing science, which will turn to guiding principles for directed assembly of states to predefined configurations.

The overarching goal of this project is to uncover mechanisms and hidden correlations between synthesis conditions and resultant physical properties, leading to desired materials properties via synthesis, growth, characterizations, simulations, and modeling. Eventually, we can address one of the grand challenges of materials science: how do complex phenomena emerge from simple ingredients?

Recent Progress

This project has been funded for two years (Aug. 14, 2023-present). Multiple approaches have been employed to advance our understanding of materials synthesis and processing science. What presented below are a few highlights.

*A superconducting state stabilized via extremely small amount of Li insertion in semiconducting SnSe₂ through an **electrochemical process**:* From both fundamental interest and technological application point of view, superconductivity is the most important subject of materials physics. Establishing a superconducting state with the control-effective synthesis and processing is advantageous. Scientifically, we are interested in superconductivity in materials with the low dimensionality, in which unconventional superconducting mechanisms often occur. Through both first-principles calculations and experimental investigation, we find that SnSe₂ forms a layered structure with a semiconducting ground state. The

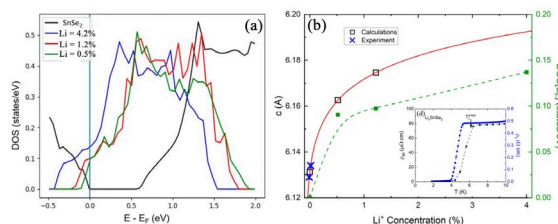


Figure 1: (a) Calculated DOS versus energy for different Li concentrations. (b) Calculated c -axis lattice parameter and $DOS(E_F)$ versus Li concentration. Inset: Zero resistivity observed in both the ab plane and c axis.

unique feature of SnSe₂ is that its Fermi level (E_F) is slightly below the minimum of a conduction band. Its physical properties are thus expected to be easily tuned. According to first-principles calculations shown in **Figure 1(a)**, there is the finite density of states (DOS) at E_F when introducing 0.5%-amount of Li into SnSe₂. Experimentally, we obtain Li_xSnSe₂ with the superconducting transition temperature $T_c \sim 6$ K for $x \sim 2 \times 10^{-4}$ (**Figure 1(b)**), which is *three orders* lower than the required superconductivity onset condition [1]. Our combined computational and experimental investigation provides critical information about material processing: (1) there is little energy barrier between semiconducting SnSe₂ and superconducting Li_xSnSe₂ if Li⁺ occupies the interstitial space, i.e., with little structure change; (2) the energy barrier is too high to overcome for expanding the interlayer spacing for Li⁺, and (3) the x value is extremely small which is estimated $\sim 2 \times 10^{-4}$ for changing the ground state.

Impact on the magnetic structure of MnBi₂Te₄ via *magnetic annealing*: The key ingredients for developing quantum materials with the *desired electronic and magnetic properties* lie with specific symmetries. Our goal is to identify these basic ingredients via the application of external stimuli. MnBi₂Te₄ is a well characterized magnetic topological insulator exhibiting many exciting quantum phenomena. At the ambient condition, MnBi₂Te₄ forms an A-type antiferromagnetic (AFM) structure at $T_N = 24$ K. Prior theoretical calculations predict metastable magnetic states with the energy slightly higher than the ground state [2]. Our hypothesis was that the magnetic field could stabilize some metastable states with different magnetic structures than that at the ambient condition. We thus performed magnetic annealing with the field up to 10 Tesla at 600 K. While the crystallographic structure remains unchanged after field annealing, there is drastic difference in its electronic and magnetic properties. **Figure 2** shows the temperature dependence of the in-plane (χ_{ab}) and c -axis (χ_c) magnetic susceptibilities for the as-grown (blue and black) and field-annealed (green and red) MnBi₂Te₄. Note that, for the field-annealed samples, χ_c (red) increases sharply and is much larger than χ_{ab} (green) below $T^* \sim 15$ K, showing an opposite trend to that (black curve) for the as-grown samples. Our investigation demonstrates that magnetic annealing is a powerful approach for manipulating magnetic materials properties.

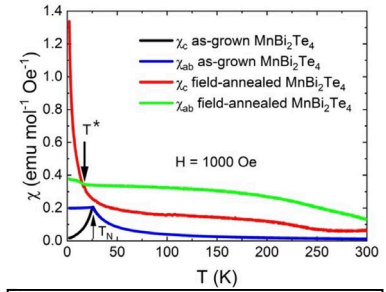


Figure 2: Temperature dependence of the magnetic susceptibilities of the as-grown and field-annealed MnBi₂Te₄ obtained by applying 1000 Oe along the ab plane (χ_{ab}) and c axis (χ_c), respectively.

Magnetochemical synthesis of MnBi₂Te₄: With the success of magnetic field annealing to modify the physical properties of MnBi₂Te₄, we believe that the magnetic field could stabilize some metastable states with different magnetic structures than that at the ambient condition. Especially, our first-principles calculations predict the canted (148.84 °C) AFM structure can be

stable as shown in **Figure 3(a)**. Guided by the computational results, we carry out MnBi₂Te₄ single crystal growth under a 9 Tesla magnetic field at National High Magnetic Field Laboratory. It turns out that the field-grown single crystals not only form the same crystal structure as those grown without field (as-grown) but also have better crystallinity as reflected by sharper x-ray diffraction peaks. More remarkably, the temperature dependence of the magnetic susceptibility shows ferromagnetic (FM) characteristic below $T_C \sim 15$ K (**Figure 3(b)**). As $\chi_c > \chi_{ab}$, the magnetic moment is more easily aligned along the c direction as demonstrated in the inset of **Figure 3(b)**. Given that the saturation moment at high fields is much less than the expected value, our field-grown MnBi₂Te₄ may exhibit canted spin structure as predicted by first-principles calculations.

To understand the spin structure in the field-grown MnBi₂Te₄, we carry out magnetic torque measurements up to 35 T at 0.4 K, which is shown in **Figure 3(c)**. At each angle, we find four anomalies at H_1 , H_2 , H_3 , and H_4 (see indications for $H//c$ (0°)). These represent the threshold fields for spin reconfigurations. Note that (1) the $\tau(H)$ curve for $\varphi = 0^\circ$ is distinctly different from that for $\varphi \neq 0^\circ$ with the opposite field dependence at $H > H_1$, (2) the peak intensity of $\tau(H)$ at H_2 is the highest for $\varphi \sim 30^\circ$, and (3) $\tau(H_3)$ and $\tau(H_4)$ reveal a minimum for $\varphi \sim 60^\circ$. These features suggest that there is field-induced spin structure change. In the as-grown MnBi₂Te₄, the magnetotransport reveals anomalies as well when spins are reconfigured [3]. **Figure 3(d)** shows the field dependence of the in-plane resistance (R_{xx}) at 0.4 K for field-grown MnBi₂Te₄. Surprisingly, R_{xx} increases smoothly with increasing field at $H > H_1$ at each angle. Above H_3 , $R_{xx}(H)$ increases linearly without any sign of saturation up to 35 Tesla. Given the linearity occurs at low temperatures, it likely reflects the intrinsic property of the system when approaching the quantum limit.

Future Plans

With knowledge gained from studying MnBi₂Te₄, we would like to apply similar

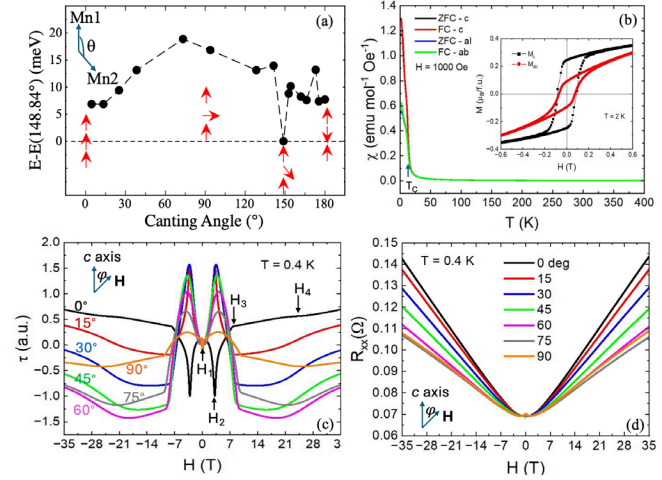


Figure 3: (a) Energy for different spin structures plotted as the $E-E(148.84^\circ)$ versus canting angle between neighboring Mn along the c direction. (b) Temperature dependence of the magnetic susceptibility of field-grown MnBi₂Te₄ for field (1000 Oe) applied along the ab plane and c axis, respectively, in both ZFC and FC conditions. Inset: Field dependence of the magnetization along the ab plane and c axis taken at 2 K. (c) Field dependence of the magnetic torque (τ) at 0.4 K with the field applied at indicated angles (φ) as defined in the inset. At each applied field direction, four anomalies are identified as marked by H_1 , H_2 , H_3 , and H_4 . (d) Field dependence of the in-plane resistance (R_{xx}) at 0.4 K with the field applied at indicated angles (φ) as defined in the inset.

approaches to its sister compound MnSb_2Te_4 , seeing the impact of magnetic field to its magnetism. Compared to MnBi_2Te_4 , MnSb_2Te_4 is expected to have weaker spin-orbit coupling (SOC), which may impact the magnetic field effect [4]. The outcome will allow us to elucidate the relationship between the synthesis and growth conditions and the inherent interactions such as SOC.

We plan to insert Fe to SnSe_2 through multiple approaches such as solid-state reaction, electrochemical process, and/or magnetic field. It is motivated by the recent publication [5] that proposes the coexistence of superconductivity and ferromagnetism. The preliminary first-principles calculations show the stability of Fe_xSnSe_2 with antiferromagnetic ordering. We will examine the actual system for its synthesis and growth conditions and elucidate the influence of external stimuli to the magnetism of Fe_xSnSe_2 . Most importantly, we will find out if we can stabilize a system with alternated superconducting and magnetic layers.

We are currently designing and making coils for generating magnetic field for the laser floating-zone growth of proposed materials.

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Plasmon Mediated Deposition of Single Atom Transition Metal Catalysts

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Keywords: Single atom catalysts; Transition metals; Titanium Nitride; Plasmonic; Synthesis

Research Scope

The goal of this work is to develop a noble synthesis method for stable single atom catalysts on metallic supports using plasmon enhanced photodeposition method under mild condition. We have successfully developed a visible light mediated synthesis method to deposit transition metal single atom catalysts such as platinum (Pt) and nickel (Ni) atoms on refractory plasmonic metallic-like transition metal nitride nanomaterials such as titanium nitride (TiN) support. We could vary the size of nanocatalysts from single atoms to few atom clusters to nanoparticles by varying the light intensity and wavelengths. Single-atom and few atom clusters transition metal catalysts are promising systems to enhance different catalytic reactions including CO₂ reduction, hydrogen generation, and solar energy conversion. The development of a simple and effective method for the synthesis of single atom catalysts is a prerequisite for achieving wide scale applications for these high-performance catalysts. Refractory plasmonic transition metal nitride nanostructures are emerging as promising support for single atom catalysts due to their high temperature stability and favorable electronic interactions with the transition metal catalysts.(1) Additionally, these plasmonic supports can efficiently absorb and concentrate light at the nanoscale to generate intense electromagnetic fields.(2) The photoexcited electrons can undergo nonradiative decay, generating highly energetic electrons. We developed a simple mild synthesis method using light where single atom of transition metal catalysts can be deposited on metallic (plasmonic) host by reducing metal precursor salts with the photo-excited electrons generated on the host. Importantly, deposition of catalysts on plasmonic supports allows us to develop active single atom catalysts as the support can absorb light and transfer the energy or photo-excited charge carriers to catalysts to drive reactions. We are conducting transient absorption spectroscopy studies to compare relaxation dynamics of titanium nitride nanomaterials with oxidized titanium nitride nanomaterials for understanding the efficiency of titanium nitride to generate hot electrons. We combined experimental and theoretical study to understand interactions of dopant metal atoms with the anchoring surface atoms of metallic host to predict the favorable deposition sites and stability using density functional based theoretical calculations and experiments. We studied the deposition rate as a function of light wavelength and intensity to provide insights into the mechanism. The catalytic properties of the single atom catalysts are compared with that of the nanocatalysts using both experimental and theoretical studies. We found in comparison to nanoclusters Pt-TiN, single atom Pt-TiN can enhance the reduction reaction of nitrobenzene better. Spin-polarized density functional theory (DFT) calculations were utilized to investigate the efficacy of Ni-based single-atom on titanium nitride (TiN) for methane pyrolysis reactions. It was found that single-atom Ni-

TiN was expected to resist coke formation on its surface. However, these Ni single-atom catalysts can sinter, aggregate into a small cluster, and form a coke layer from the highly exothermic reaction pathway that the cluster takes despite the facile reaction pathway.

Recent Progress:

In past two years, we used both theoretical and experimental investigations to make major progress in following aspects: (i) developed an understanding of the mechanisms of plasmon enhanced deposition of transition metal atoms on plasmonic supports and used the insights to deposit Pt or Ni nanocatalysts with size varying from single atoms to few atom clusters on titanium nitride nanostructures supports; (ii) characterized the optical and electronic properties of Pt or Ni deposited on the titanium nitride nanostructures; (iii) investigated their stabilities and catalytic properties of single atom Ni-TiN and single atom Pt-TiN. The following are the details of our accomplishments in the past year.

Structural and optical characterizations of plasmonic hosts titanium nitride:

The morphology of TiN nanoparticles characterized using high-resolution transmission electron microscopy (HRTEM) as shown in Fig. 1 (a) and 1(b). TiN nanoparticles develop 1-2 nm thick self-passivating oxide layer on the surface (Fig. 1(b), 1(c)). However, as shown in the previous papers from our group, this thin oxide layer has negligible effect on the optical properties TiN nanoparticles.(3, 4) evident by the UV-Vis

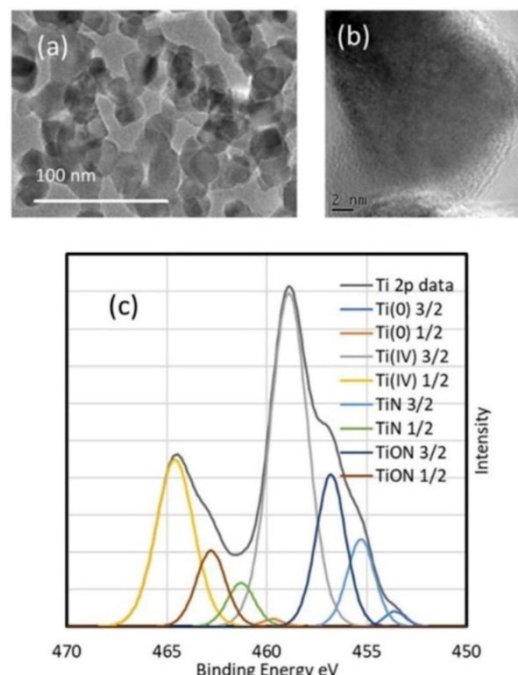


Fig. 1: (a) HRTEM of TiN nanoparticles (b) magnified image to show amorphous oxide layer on the surface of TiN nanoparticles. (c) XPS Ti2p data analysis of TiN samples.

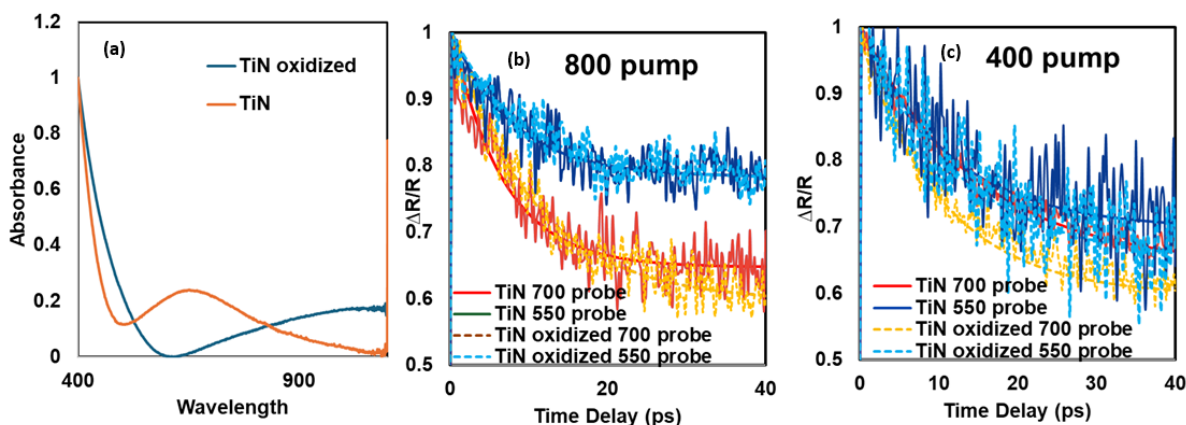


Figure 2: (a) UV-Vis absorbance of 20 nm TiN nanoparticles and the nanoparticles after oxidized by annealing in air at 350^o C for 20 minutes. Normalized decay kinetics of nanoparticles probed at different wavelengths excited by 800 pump (b) TiN nanoparticles. (c) oxidized TiN nanoparticles.

absorbance peak of TiN nanoparticles which show usual plasmonic peak around 650 nm (Figure 2(a)). XPS analysis confirmed that the surface layer is a mixture of TiN (~18%), TiO₂ (~55%) and Ti_xO_yN_z (27%). (Fig. 1(c)) Formation of surface oxide layer on TiN can improve the lifetime of the hot electrons making it easier to harvest them for hot electron mediated reduction reactions. Additionally, the nanoparticles are rapidly oxidized at 350°C in the presence of air, which affects both their steady state and transient optical properties. By oxidizing the nanoparticles, the signature plasmonic peak for TiN diminishes and the amount of TiN goes down and the TiO₂ increases. We conducted transient absorption studies spectroscopy to address how does the relaxation dynamics of plasmonic nanoparticles TiN varies with oxidation. The transient absorption spectroscopy is conducted in the ultrafast laboratory at Center of Integrated Nanotechnologies (CINT) in Albuquerque. The relaxation dynamics of nanoparticles are observed by exciting them with femtosecond laser pulses 800 nm as well as 400 nm. We found that oxidizing TiN can influence its the electron-phonon decay times (Figure 2(b) and (c)). Excited with 800 nm pump and probed with 700 nm wavelength, we can only excite intraband transitions in TiN, and in that case the decay time for oxidized TiN is longer than decay time of TiN. This could be because of the higher thickness of TiO₂ on the surface of TiN can delay the recombination of photoexcited electrons.

Unravel the mechanism of plasmon enhanced deposition: We performed calculations for both Pt and Ni deposited on titanium nitride using spin-polarized density functional theory computations. Using the calculated binding and aggregation energies, we were able to determine the expected active sites and cluster size for the differing oxide conditions on the surface of TiN. In summary we found that both single atom nickel and single atom Pt will preferably deposit on either the TiO₂ on the surface of TiN nanoparticles or the N-vacancy sites. We have developed a method to deposit single transition metal atom Ni and Pt on titanium nitride using visible light and realized that the size can be tuned by tuning light intensities and wavelengths. This enables us to deposit different size ranging from single atoms to nanoparticles of Ni or Pt deposited on the surface of TiN (Figures (3(a),(b) and (c)). XPS analysis suggested the single atom Pt or Ni deposited on TiN are present at higher oxidation states.

Studying the Stability of Single Pt atoms Deposited on TiN: To understand the stability of single atoms deposited on TiN Influence of sintering Single atom at higher temperature, we exposed the sample to various sintering temperatures in argon environment. We studied the effect of sintering on single atom Pt using STEM imaging also hydrogen Temperature programmed Desorption

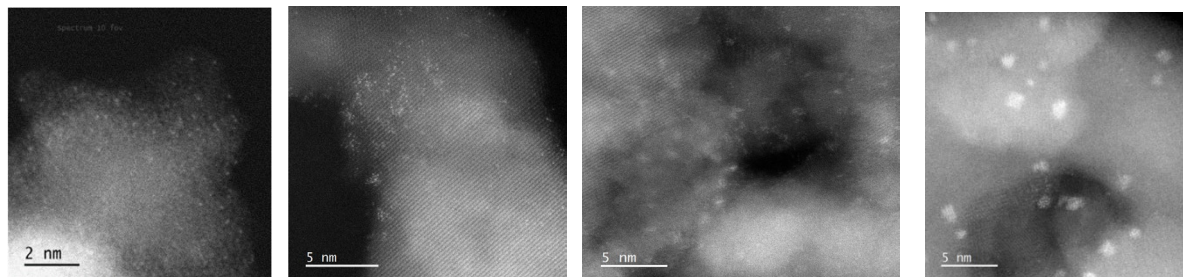


Figure 3: STEM images of a) Ni precursors reduced on TiN support under halogen lamp, intensity 384 mw/cm², showing mostly single atoms b) Pt precursors reduced on TiN support under 385nm light, intensity 50 mw/cm², showing mostly single atoms c) Pt precursors, reduced on TiN support under 575 nm light intensity 50 mw/cm², showing mostly Pt nanoclusters and d) single atom Pt deposited on Pt sintered in argon environment at 500 °C

(TPD) method. STEM imaging of single-atom catalyst (SAC) samples sintered at different temperatures shows that as we increase the temperature, more single atoms tend to form clusters (Figure 3(d)). At relatively lower sintering temperatures, higher adsorption capacity is observed for the Pt single atom sample, found using hydrogen Temperature programmed Desorption (TPD) method. This suggests that the surface retains a higher number of active sites capable of adsorbing hydrogen. As the sintering temperature increases, the adsorption capacity decreases due to sintering-induced aggregation of Pt atoms.

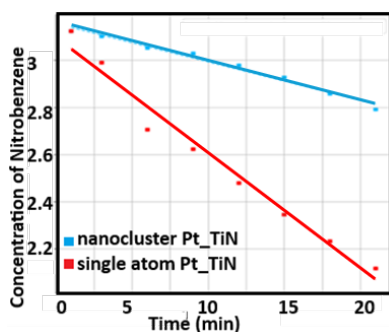


Figure 4: Nitrobenzene conversion in the presence of single atom Pt and nanocluster Pt catalysts.

Evaluating the Catalytic Performance of Pt or Ni Single Atoms Deposited on TiN:

To compare the catalytic performance of the single atoms Pt deposited on TiN with the Pt nanoclusters on TiN, we evaluated their performances towards the reduction reaction of nitrobenzene. (5) The Pt single atom samples performed better than the nanocluster samples for nitrobenzene conversion (Figure 4). We investigated the efficacy of nonprecious Ni-based single-atom and small-cluster catalysts supported on titanium nitride (TiN) for methane pyrolysis. Single-atom Ni catalysts exhibited moderate activation barriers (~ 1.10 – 1.31 eV) and a net endothermic reaction pathway, suggesting resistance to coke formation due to weaker adsorbate binding and thermodynamically unfavorable carbon deposition. In

contrast, Ni clusters demonstrated lower activation barriers (~ 0.88 eV), but may promote carbon coking. These findings indicate that while single-atom Ni sites offer coke resistance, they are susceptible to sintering.

Future Plans: Our plans include following tasks: (i) The relaxation dynamics of TiN nanoparticles with and without transition metal doping will be observed by exciting them with higher time resolution pump (~ 50 fs pulse width) to decipher the effect of transition metal doping on electron-phonon scattering in TiN. (ii) We will continue our calculations of electron-phonon couplings (EPC) in spin-polarized DFT using Quantum Espresso (QE) for both TiN and oxidized TiN systems to understand our experimental observations. (iii) We aim to extend the knowledge of plasmon enhanced deposition to deposit single atoms and nanostructures of gold and nickel on 2D MoS₂ materials, using its photocatalytic properties. (iv) In collaboration with Dr. Padmanabhan in CINT, we will study the relaxation dynamics of photoexcited electrons in MoS₂ with and without doping using transient absorption spectroscopy to determine how the metal doping affects the exciton dynamics in MoS₂.

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Project Title: Solution-Based Synthesis of Structurally Well-Defined Carbon Nanobuds

Lead PI: Dr. Yunxiang Gao, Prairie View A&M University

Co-PI: Dr. Yuemin Liu, Prairie View A&M University

Collaborating DOE PI and Laboratory: Dr. Di-Jia Liu, Argonne National Laboratory (ANL)

Project Overview

The goal of “*Solution-based Synthesis of Structurally Well-defined Carbon Nanobuds (CNBs) and Their Energy Applications*” is to create, at scale, a new generation of carbon nanobuds whose fullerene “buds” are precisely selected, uniformly distributed, and tethered to nano-carbon backbones (CNTs, graphene, etc.) by controlled sp^3 inter-lattice bonds formed entirely in solution under mild conditions. Achieving this will (1) eliminate the random bud sizes, low bud densities, and fullerene polymerization side-products that plague conventional CVD routes, and (2) furnish a high-surface area, curvature-engineered carbon support expected to enhance catalytic activity and durability in demanding electrochemical systems such as fuel-cell oxygen reduction, oxygen/hydrogen evolution, supercapacitors, and CO_2 reduction. To reach this goal, the project aims to address the challenges in synthesizing carbon nanobuds (CNBs) with high precision.

Traditional methods, such as chemical vapor deposition (CVD), have resulted in CNBs with random fullerene distributions, low bud density, and a wide range of uncontrollable fullerene species. The new approach focuses on solution-based synthesis to achieve better control over the fullerene bud species and density. Key strategies include:

- *Mixing Pre-existing Fullerenes and Nano-carbon Substrates:* This involves initiating direct inter-lattice sp^3 carbon crosslinking between highly curved fullerene carbon lattices and less curved carbon nano-substrates (such as CNTs or graphene).
- *Preventing Fullerene Polymerization:* The research will employ two synergistic strategies to overcome fullerene-fullerene polymerization. First, the project aims to increase the reactivity of the nano-carbon substrates through metal-free hetero-doping, which activates the C=C bonds in their graphitic lattice, thus lowering the energy barrier for nano-substrate/fullerene inter-lattice binding reactions. Second, it involves engineering design for maintaining individual fullerenes separated from each other to prevent aggregation and self-polymerization. We will employ two synergistic strategies to overcome fullerene-fullerene polymerization. First, the project aims to increase the reactivity of the nano-carbon substrates through metal-free hetero-doping, which activates the C=C bonds in their graphitic lattice, thus lowering the energy barrier for nano-substrate/fullerene inter-lattice binding reactions. Second, it involves preventing fullerene-fullerene aggregation, maintaining individual fullerenes separated via three possible options: 1. immobilizing individual fullerenes on solvated sacrificial micro-templates to prevent fullerene aggregation and self-polymerization 2. selective absorb oppositely charged small molecules on fullerenes and the other carbon substrate, respectively, to direct the fullerene/graphene, or fullerene/carbon nanotube self-assembly, and prevent fullerene aggregation via electric repelling force.

- *Depositing metal catalyst on the CNBs to test electrochemical process-based energy applications*, including oxygen reduction reactions, oxygen evolution reactions, hydrogen evolutions reactions, super capacitors, and CO₂ fuel conversions.

Current Research Progress

Theoretical Study: Surface-Reactivity Design Rules

In the last fiscal year, we completed a high-level MP2/NBO analysis of C₆₀. Key findings:

Highest-reactivity bonds are the 1.42 Å hexagon–hexagon junctions. Flanking with graphitic N atoms lowers the inter-lattice cross-linking barrier by 15 – 25 %. These benchmarks now steer our dual experimental strategy: (a) N- or B-doping of CNT/graphene to activate binding sites; (b) electrostatic or template isolation of fullerenes to suppress self-polymerization. We have also grafted these electronic parameters into QM/MM models that predict a 0.12 eV reduction in the first electron transfer barrier for CNB-supported CO₂ reduction compared with pristine CNTs.

Prototype CNB Synthesis:

Route A (Sacrificial Template Method):

We synthesized amino-functionalized silica beads with various size and surface morphology (20 nm – 500 nm, smooth vs mesoporous), followed by Immobilizing a monolayer of C₆₀ via aminolysis reaction; the C₆₀ coverage was tuned by reaction time and pore morphology. We then wrapped the monolayer-C₆₀ coated silica nanobeads with graphene oxide (GO) of controlled C/O ratio; optimized GO concentration for maximum dispersion stability of the GO-C₆₀ self-assembly. The GO-C₆₀ bonding was carried out both via photochemical processes and hydrothermal processes. Silica nanoparticles have been successfully removed from the GO-C₆₀-SiO₂ assembly to give the Graphene-C₆₀ carbon nanobuds (Figure 1).

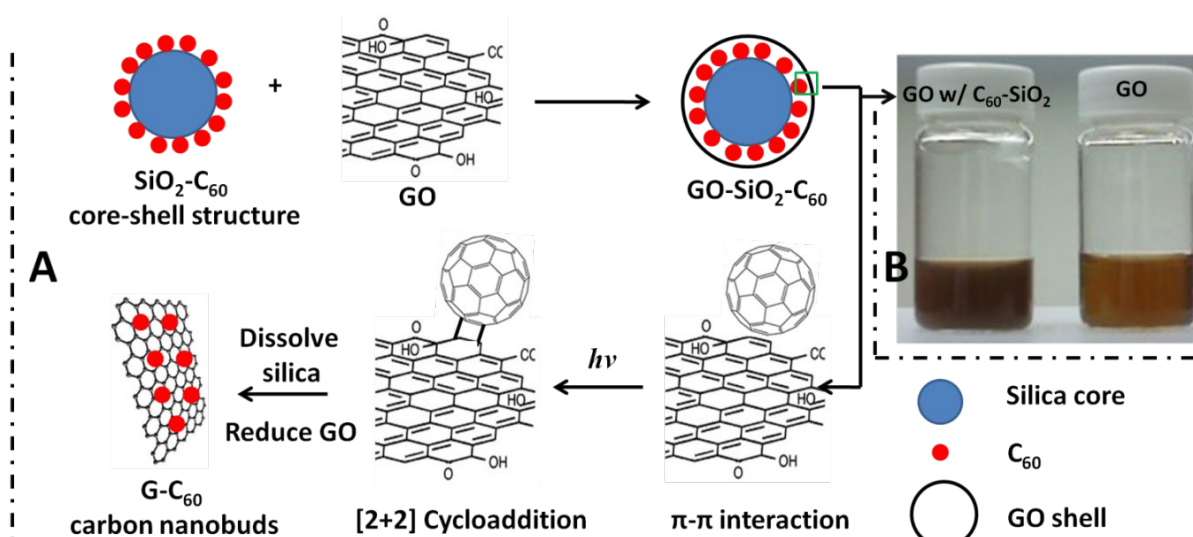


Figure 1. (A) Strategy for the photochemical synthesis of graphene-fullerene nanobuds in solution; (B) Photo image of the dispersion of GO-wrapped SiO₂-C₆₀ particles in water (stored overnight)

Electrochemical workstation scans (CV, LSV) indicated that comparing to GOs treated via the same procedure, the electrochemical activity of the Graphene- C_{60} CNBs performs show much lower reduction potential and provide higher current density in hydrogen evolution reactions (HER, Figure 2). More tests including CO_2 -fuel conversion applications and definitive fullerene-loading quantification is performed at Argonne National Laboratory.

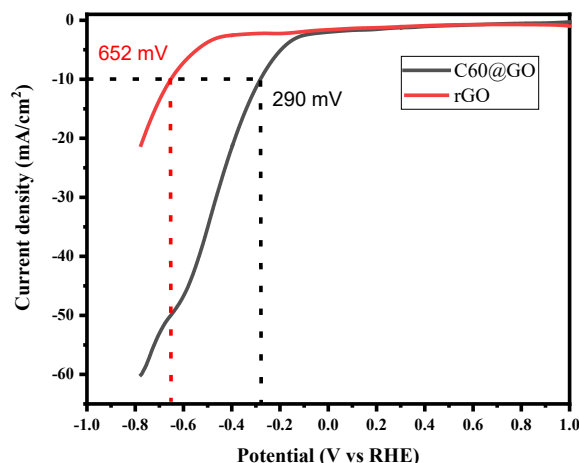


Figure 2. LSV curves of HER at -10 mA/cm^2 current density. Black trace: carbon nanobuds; red trace: reduced graphene oxide only.

Route B (Charged small molecule direct self-assembly):

We explored electrostatic interactions by first adsorbing oppositely charged small molecules onto fullerenes and carbon nanotubes (CNTs), then using those charge tags to drive fullerene-CNT co-assembly. Several complementary cationic and anionic dyes that bind selectively to each nano-carbon component have been identified, and we are now optimizing the assembly conditions.

Future Plans

During the next reporting period we will advance the project along several interconnected fronts:

- high-resolution characterization of carbon nanobuds (CNBs) using state-of-the-art equipment both on campus and at Argonne National Laboratory (ANL).
- expanded computational studies, supported by a new high-performance workstation.
- more rigorous energy-application testing.

On optimizing the Synthesis and Characterization of Carbon Nanobuds, we will:

- **Continued synthesis and optimization.** We will further refine our solution-phase protocol to obtain CNBs with highly uniform fullerene-bud densities and well-defined structures.
- **Comprehensive, high-resolution analysis.** Each optimized batch will be examined by FE-SEM, HR-TEM, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction

(XRD), and BET surface-area analysis to correlate morphology with surface chemistry and porosity.

- **Energy-application translation.** Once structural optimization is complete, the best catalyst recipes identified in our parallel screening on planar carbon will be transferred to the high-curvature CNB support for side-by-side electrochemical performance comparisons.

Publications:

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Electrocatalysis within nanoconfinement

Di-Jia Liu, Argonne National Laboratory and Yunxiang Gao, Prairie View A&M University

Keywords: Carbon nanomaterial, nanoconfinement, electrocatalysis

Research Scope

Argonne National Laboratory (ANL), as a subrecipient, is collaborating with Prairie View A&M University (PVAMU) to develop new carbon materials for energy applications, including hydrogen storage, fuel cells and electrocatalytic CO₂ reduction. PVAMU is leading the effort in design and synthesis of structurally well-defined carbon nanobuds (CNBs). ANL is supporting the performance evaluation of these materials using its existing material synthesis and characterization facility to study their structures as well as performances in energy related applications. In preparation for new carbon materials from PVAMU, ANL team tested two carbons with very different nano-porosities as the support for electrocatalytic conversion of CO₂ to multiple carbon chemicals. We found that nanoconfinement has a major impact on catalyst active site structure, which completely altered electrocatalytic reaction paths, leading to different product selectivity. Our result represents the first direct observation of influence on electrocatalyst performance by nanoconfinement of catalyst support.

Recent Progress

We recently studied the selectivity of electrocatalytic CO₂ reduction to multiple carbon compounds under different nanoconfinement environments. We applied our published amalgamated lithium metal synthesis (ALM) method [1] to prepare single atom copper catalysts over two commercial carbon supports, one is dominated by micropore and the other one is dominated by mesopore, respectively. ALM method is known to control the active site dimension from single atom to ultrasmall cluster by simply adjusting the metal loading in the molten lithium [2]. In this study, we applied the same low loading of Cu over the carbon supports with completely different porous structures so that their nanoconfinement effect can be clearly delineated in the study.

We discovered that nanoconfinement of carbon support can indeed play a critical role in controlling the selectivity of electrocatalytic CO₂ reduction reaction. For example, when single

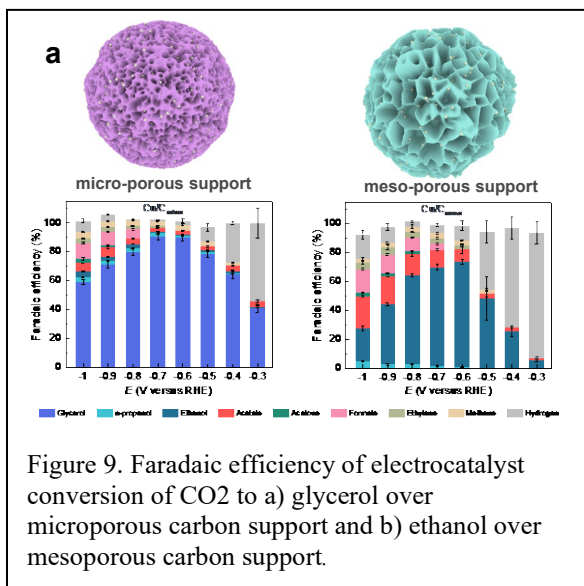


Figure 9. Faradaic efficiency of electrocatalyst conversion of CO₂ to a) glycerol over microporous carbon support and b) ethanol over mesoporous carbon support.

atom Cu is applied to carbon dominated by micropores, the conversion product was pivoted mainly to the formation of a C₃ chemical, glycerol (C₃H₈O₃), with a very high Faradaic efficiency (*FE*) of 89.9% at -0.7 V vs. RHE. (Fig. 1a). However, when the carbon support was switched to mesopore dominated carbon, the electrocatalytic conversion product was altered to mainly ethanol (C₂H₅OH) at 0.6 V (RHE) with *FE* > 70% (Fig. 1b). Clearly, the pore diameter of micropore (< 2 nm) versus mesopore (2 nm ~ 20 nm) changed the reaction pathway and conversion mechanism.

We further carried out a series of characterization studies to better understand the catalytic site-support-CO₂ interactions using the tools such as CO₂ adsorption isotherm, synchrotron x-ray absorption spectroscopy (XANES and EXAFS), *in situ* surface enhanced Raman spectroscopy (SERS), etc. Through these studies, we found that nanoconfinement in microporous carbon could significantly increase CO₂ adsorption enthalpy in comparison with mesoporous carbon, offering the foundation of high retention of electrocatalytic intermediates for enhanced C-C coupling to larger hydrocarbon molecules such as glycerol. XANES and EXAFS also revealed the influence of nanoconfinement to the coordination structure and oxidation state of Cu single atom, leading to a compression of Cu-O bond and blue-shift of Cu *1s* → *4p* electronic transition. Interestingly, a different sets of CO₂ reduction intermediates were found through *in situ* SERS in the catalyst prepared over microporous and mesoporous carbons, shedding the light on the electrocatalysis pathways affected by support's porosity. We are currently in the process of completing the data analysis and preparing a manuscript for submission.

Beyond the experimental study, we also produced an invited review article on electrocatalytic conversion of carbon dioxide to chemicals containing more than two carbon atoms early this year supported by this project. The PI also delivered an invited talk at the Spring annual meeting of American Chemical Society.

Future Plans

ANL's preliminary result on the impact of nanoconfinement to electrocatalytic selectivity opens up new route for the investigation of next-generation carbon nanomaterials such as carbon nanotube and nanobud currently under development at PVAMU. Going forward, we will utilize our ALM method to catalyze the next-generation nanomaterials through a joint ANL-PVAMU investigation. We continue our effort in preparing and testing high performance electrocatalyst by combining novel synthesis with new carbon material through a rational design approach under this project.

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Publications

1. S. Guo, J. Wang, H. Zhang, C. O. Iloeje,* D.-J. Liu*, *Direct Electrochemical Reduction of CO₂ to C₂+ Chemicals: Catalysts, Microenvironments, and Mechanistic Understanding*, ACS Energy Letter **10**, 600–619 (2025).
2. D.-J. Liu, “*Design and mechanistic study of highly selective electrocatalysts for direct CO₂ to C₂+ chemical conversions*” Invited Presentation at 2025 ACS Spring Meeting, San Diego, CA March 23 – 27, (2025)

Designing Architected Polymers and their Properties for Additive Manufacturing

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Keywords: Additive Manufacturing, Operando characterization, Nonequilibrium dynamics, Architected polymers

Research Scope: Additive manufacturing (AM) is growing in popularity due to its minimal waste in producing highly complex components. However, the polymers which are used in AM are derivative of legacy extrusion grades rather than purpose-built for the thermal, rheological, and kinetic constraints of high-throughput printers. Consequently, these printed parts deliver only a fraction of the strength, toughness, and dimensional fidelity attainable by conventional molding, chiefly because melt viscosity, interlayer diffusion, and residual-stress evolution remain coupled in ways that are not yet well controlled. Currently, there are no guidelines for the a priori design of polymers for high throughput AM that address these challenges.

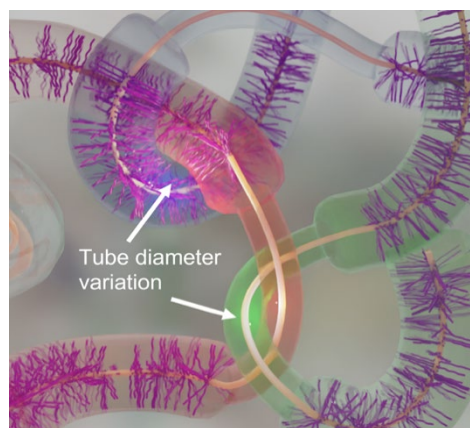


Figure 1. Variable mean-field depiction of branched, architected polymers.

This work seeks to establish first-principles design rules for AM directed macromolecules whose architecture can satisfy the competing demands of deposition flow and post-print performance. We target topologically complex systems which feature patterned (i.e., blocky) polymeric grafts (in comb and brush regimes) that expand chain dimensionality to unlock new controls over viscoelastic behavior and structure development (**Fig. 1**). Our central hypothesis is that altered topology of thermoplastic polymers can overcome the hurdles of residual stress and poor interlayer bonding by influencing the chain dynamics. Further improvements can be achieved by incorporating dynamic covalent bonding provide crosslinking throughout printed parts,

particularly across interlayer boundaries.

To test our hypothesis, we deploy multiple characterization and modeling tools along with novel synthetic approaches. Coarse-grained molecular dynamics and continuum fluid-mechanics simulations define the processing envelope, while small-angle scattering, solid-state NMR, nano-IR AFM, and time-resolved stress-relaxation experiments resolve the interplay of chain friction, bond exchange, and microphase evolution from the nanometer to the print scale. By integrating these approaches, we identify the architectural parameters that decouple flow from final properties and map a predictive pathway toward polymer chemistries expressly designed for the next generation of additive manufacturing.

Recent Progress: *Controlling dynamics through macromolecular structure.* The central synthetic challenge of this work is the introduction of distributed architectural features and functional groups that can be leveraged during processing to kinetically control order

formation. We hypothesized that by sterically frustrating the local structural environment of

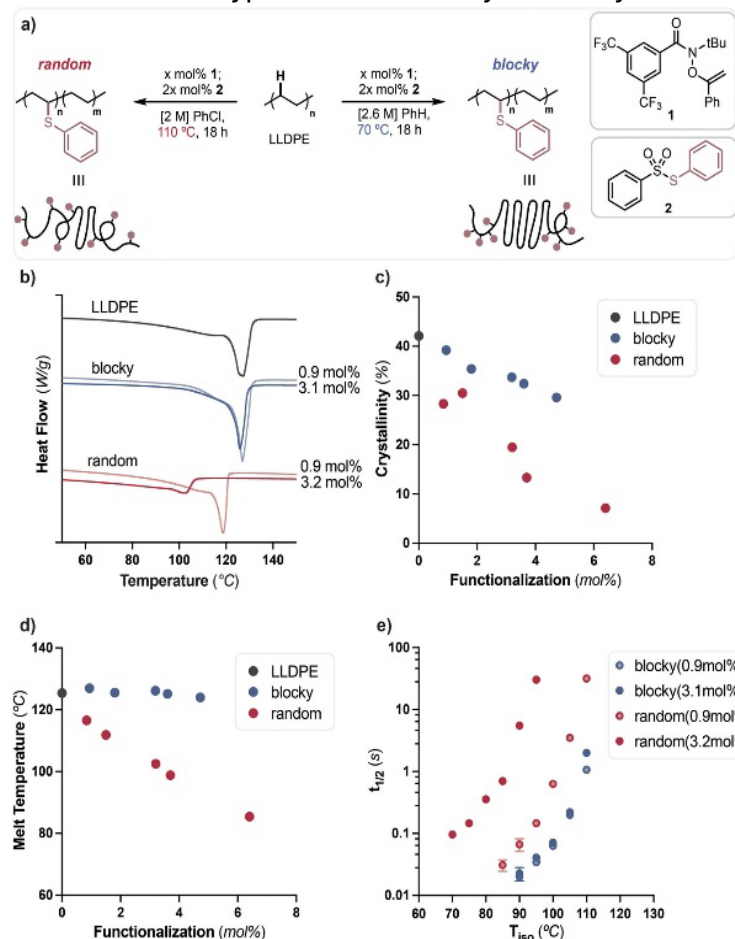


Figure 2. Functionalization-crystallinity relationships for blocky compared to random copolymers. a) Optimized conditions for blocky and random functionalization. PhCl, chlorobenzene; PhH, benzene. b) DSC thermograms for LLDPE, blocky, and random copolymers; data shown is taken from the second heating cycle at a scan rate of $10^\circ\text{C min}^{-1}$. c) Comparison of crystallinity percent as a function of functionalization determined from the enthalpy of melting by DSC. d) Comparison of T_m as a function of functionalization percent by DSC. e) Comparison of crystallization rate by fast

decoupled by partitioning functional groups into block-like segments of the polymer backbone while leaving long blocks of unfunctionalized polymer to crystallize unimpeded. The blocky functionalization resulted in functionalized polyolefins with a higher crystalline fraction and improved mechanical properties compared to their randomly functionalized analogues (**Fig. 2**). These findings prove the efficacy of this approach in controlling modified polymer structure.

We are extending the generalizability of these findings by measuring the reptation dynamics of structurally varied model systems using neutron spectroscopy and molecular dynamics (MD) simulations. Our MD simulation efforts address challenges in polymer processibility and interlayer bonding by elucidating critical grafting strategies to tune rheological behavior

entanglements, we can expand the kinetic window to access non-equilibrium microstates and enhanced solid state properties in the bulk. We recently demonstrated a scalable route to achieving these design features through a post-polymerization modification of polyethylene.(1) We envisaged that the development of selective post-polymerization C-H functionalization on the length scales of an extended polyolefin backbone (ca. 10–100 nm) would enable access to blocky copolymer microstructures that could circumvent many of the property tradeoffs associated with random functionalization. Selective placement of functional groups is particularly valuable for polymers with small enthalpy of fusion associated with crystallization results in disruption of weak interchain Van der Waals interactions by even a small number of functionalization sites, resulting in a large inhibitory effect upon crystallization. We anticipated that functionalization and crystallinity could be

in polymer melts. We developed a bottom-up, cross-scale modeling framework that integrates coarse-grained molecular dynamics (CGMD) and continuum-scale computational fluid dynamics (CFD) to quantitatively assess the effects of polymer grafting on flow dynamics for a range of branched polymers with systematic architectural variations.

Notably, the work has yielded a predictive framework for guiding the rational design of extrudable polymer materials with tailored topologies and showed polymers with concentrated grafted blocks exhibit significantly higher zero-shear viscosity than stochastically

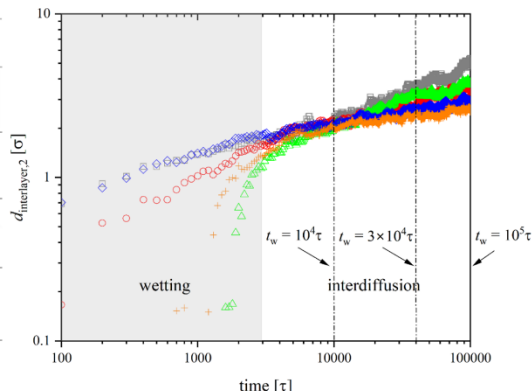
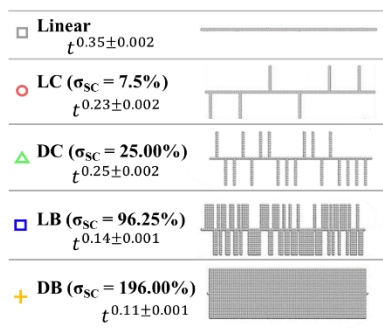


Figure 3. (Left) Architecture of simulated polymer chains and their fitted exponents from interchain diffusion distance simulation (right).

branched analogs while sidechain inertia drove longer relaxation times. Work exploring how polymer architecture influences interlayer bonding in model ungrafted and grafted polymer melts used CGMD simulation in tandem with in-lab characterization of linear and branched polymer systems. Through MD simulation, we showed diffusion controlled interdigitation follows a power law, with the exponent decreasing from 0.35 to 0.11 while grafting density increased from 0% to 196%, across five regimes: linear ($\sigma_{SC} = 0\%$), loose comb ($\sigma_{SC} = 7.5\%$), dense comb ($\sigma_{SC} = 25\%$), loose brush ($\sigma_{SC} = 96.25\%$), and dense brush ($\sigma_{SC} = 196\%$) (**Fig. 3**). While grafting reduced rates of interchain diffusion, both simulations and experiments indicated interfaces between polymers with higher grafting densities saturate the interdigitation threshold and achieve rupture strength parity to the bulk at shorter welding times. Furthermore, a tradeoff between interlayer diffusion and rupture strength became apparent with increased grafting density, while also transitioning from a more brittle-like failure mode to elastomeric type failure.

Tuning dynamic networks for interfacial welding. The addition of vitrimeric functionalities to otherwise thermoplastic polymer systems also address the challenge of poor interlayer adhesion and anisotropic mechanical properties while offering a counter to the strength losses displayed in blocky-branched architected polymers. Vitrimers offer a favorable solution by combining the advantages of crosslinked networks that endow thermoset-type strength, yet their dynamic covalent bonds allow facile reprocessability.

An epoxy–anhydride vitrimer, comprised of Bisphenol A Diglycidyl Ether (BADGE) and Methyl Nadic Anhydride (MNA), demonstrated the ability to chemically bond across interfaces when laminating multiple cured layers. Upon mild thermal treatment, the vitrimer layers crosslinked together at their interface, effectively unifying the laminate into a single monolithic piece. The resulting multi-layer composite maintained tensile strengths on par with a single-layer specimen, indicating minimal loss at the new interfaces. This interfacial welding is reflected in the favorable strength performance (40 MPa) which further increased (~70 MPa, tested 45° off the aligned fiber axis) when introducing reinforcing phases with surface functionalities that participate in bond exchange. The covalent fiber–matrix linkages both improved interlaminar shear stress and increased ductility four-fold (strain-to-failure >10% vs. ~2.5% for neat vitrimer), overcoming the embrittlement typically displayed in reinforced composites. The results underscore how vitrimer chemistry can produce strong, tough interfaces between dissimilar materials or printed layers. In an AM context, each layer of a vitrimer-based print can undergo bond exchange with underlying and adjacent layers to produce printed components that are more isotropic and robust than those made from standard thermoplastics. Varying epoxy and anhydride ratios promoted tunability of the thermomechanical performance of the vitrimer, decreasing rates of stress relaxation, and shifting T_g from 57.8 °C to 111.2 °C when increasing epoxy-to-anhydride ratio from 0.75:1 to 1.25:1 (Fig. 4).

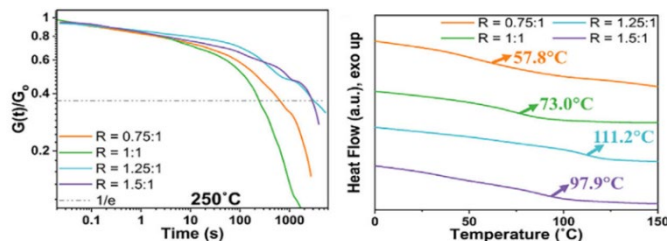


Figure 4. (Left) Controlled stress relaxation through vitrimer composition. (Right) DSC thermogram showing controlled T_g through vitrimer composition.

From standard stress relaxation experiments, T_v was calculated to be ~200 °C, closely aligning with previously reported ester-based vitrimers.(2-4) By comparison, we used low-field ^1H NMR time domain relaxometry and nano-infrared spectroscopy characterization techniques to further probe thermomechanical behavior. Using these methods, we showed that phase fractions remained stable up to 100 °C, where the rigid component dominates. Relaxation behavior shifts at higher temperatures with the bulk of the transition occurring between 125 °C and 160 °C, evidenced by the rise and fall of the mobile and rigid phase fractions, respectively (Fig. 5.ii). Similarly, T_2 relaxation times show the largest rates of increase near these temperatures (Fig. 5.i). Largely attributed to transesterification-based bond exchange, activation

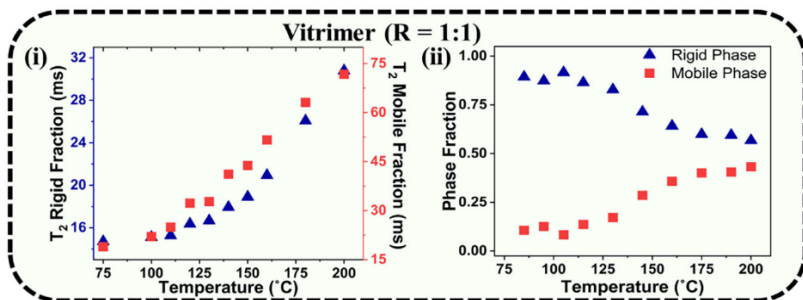


Figure 5. NMR relaxometry results. (Left) Increased T_2 relaxation times in the rigid fraction shows increased molecular mobility with temperature. (Right) Decreased rigid phase fraction and increased mobile phase fraction at 125-160 °C indicating thermal activation of

of bond temperatures occurred well below the rheologically determined T_v , occurring at ca. 150 °C. This work demonstrated a method for probing T_v with much higher fidelity. Viscoelastic probing through stress-relaxation tests to measure T_v are more strongly influenced by friction-controlled motions than the underlying chemical exchange. Moreover, the external load applied during such tests perturbs the network, shifting chain dynamics and the apparent activation barrier for bond exchange(5). These issues complicate the definition of T_v . As such, the work emphasized that factors which skew the balance between exchange kinetics and friction will distort the measured value of T_v , underscoring the need for complementary, chemistry-sensitive characterization methods. In our laminate tests, vitrimer composite panels were pressed and reformed above bond-exchange activation temperatures determined by NMR relaxometry (below stress-relaxation derived T_v), demonstrating the reliability of this method.

Future Plans. Dynamic covalent bonding schemes will be studied in phases segregating systems (e.g., block copolymers) to elucidate phase evolution and arrest through thermal activation and deactivation of bond exchange. Of particular interest are phase separation kinetics and phase stability as a function of dynamic covalent bond concentration, block structure, and processing history.

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2. S. S. Rohewal, N. Kanbargi, R. Young, L. T. Kearney, H. Hinton, L. Tetard, and A. K. Naskar, Fast relaxing sustainable soft vitrimer with enhanced recyclability, *Poly. Chem.* **15**, 714 (2024). DOI: [10.1039/D3PY01177A](https://doi.org/10.1039/D3PY01177A)
3. F. Leibfarth, E.K. Neidhart, M.E. Pomatto, C. Vasallo, E.R. Crater, J.W. Alty, P.P. Angelopoulou, E.J. Alexanian, L.T. Kearney, and R. B. Moore, Blocky Selective Post-Polymerization C–H Functionalization of Polyolefins. *Angewandte Chemie*, (2025) p.e202507687. DOI: [10.1002/ange.202507687](https://doi.org/10.1002/ange.202507687)

4. S.S. Rohewal, J.T. Damron, J. Seo, N. Kanbargi, S. Gupta, H.E. Humphrey, L.T. Kearney, J. Chang, L. Tetard, and A.K. Naskar. Hierarchically structured vitrimer biocomposites for sustainable manufacturing, *Small*, 2025, 2500721. DOI: [10.1002/sml.202500721](https://doi.org/10.1002/sml.202500721)
5. N. Kanbargi, S. Gupta, S. S. Rohewal, L.T. Kearney, and A. K. Naskar, Interfacial strength in hierarchical carbon fiber composites: Interplay of interphase modulus and roughness, *Adv. Mater. Interfaces*, 2025, 2500135. DOI: [10.1002/admi.202500135](https://doi.org/10.1002/admi.202500135)

Abstract not available yet for: Berton, Mariana, Arizona State University; Acoustic Modification of Crystallization and Dislocation Dynamics in Energy Materials to Reduce Carbon-Intensity

Molecularly Organized Nanostructured Materials

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Keywords: heteroepitaxy, layered heterostructures, van der Waals materials, in situ observation of nucleation and growth

Research Scope

The project aims to establish fundamental principles of interface-controlled nucleation and self-assembly that can be used to predict and control the synthesis of nanocomposite and layered materials that have structural ordering on multiple length scales. The foundational knowledge of interfacially controlled crystallization is being developed to address the challenge of developing scalable synthesis of nanocomposite and layered materials with structural control of sizes, crystallinity, morphology, surface, and interfacial chemistry. The project focuses on exploring the hypothesis that the dimensionality and crystalline structure of the materials can be controlled by interfacial energies and solvation structure in the interfacial region within a few nanometers of the substrate (nucleation interphases). Several key synthetic strategies are being developed in which interfacial energies can be systematically manipulated to gain insights into the effects of interfacial solvation, the polarity, and the topography (e.g., atomically flat vs Moiré patterned) of the substrate in controlling direct and remote epitaxy in layered materials with van der Waals, covalent, ionic, and metallic bonding between two-dimensional layers. By simplifying the systems down to ligand-free precursor solutions at well-defined surfaces, the most fundamental aspects of interfacial controls of crystal morphology, dimensionality, and architecture are revealed. A combination of state-of-the-art experimental and theoretical techniques are used to reveal nucleation mechanisms, nucleation pathways, and interfacial structures, and provide quantitative information about interfacial energies, growth kinetics, and solid–liquid interfacial band structure evolution.

Recent Progress

This project is demonstrating the potential of a general synthetic approach for multiscale structural control by manipulating the interfacial nucleation and growth pathways, developing an integrated theoretical and experimental approach, and developing and applying new in situ characterization tools. Recent studies focused on understanding the driving forces for the morphological and dimensionality control in solution synthesis of layered and porous heterostructures. We identified the role of interfacial dipolar interactions in directing the architecture and dimensionality of the growing inorganic crystals and hybrid heterostructures. The detailed studies of interfacial forces at electrified surfaces have revealed that these forces can be finely tuned by the applied electric potential to drive nucleation into the interphase region, enhancing the uniformity of the organic-crystal film and controlling its orientation on the substrate. These studies also revealed that the applicability of the classical theory of heteroepitaxy to van der Waals crystals is limited to materials with localized and semi-localized electron density.

Solvation Directed Morphological Control in Metal Oxide Nanostructures. Using advanced hybrid AIMD/classical DFT simulations and in situ electron microscopy, we showed that the development of structural hierarchy through heterogeneous nucleation is driven by dipolar and solvation forces [1]. Specifically, coupled simulations and experimental studies revealed that dipole build-up along the slow growth direction can trigger twinning and the development of branched architectures. Enthalpic solvation interactions were shown to either enhance or reduce the dipole moment of the nanoparticles and, thereby, control crystal morphology and architecture

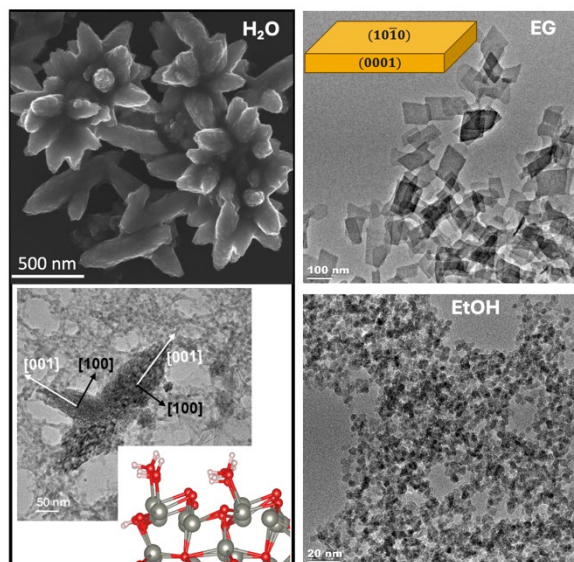


Figure 1. Solvation-directed morphological control of ZnO during homogeneous nucleation and growth in water, ethylene glycol, and ethanol, producing branched architectures, plates, and compact nanoparticles, respectively.

(Fig. 1). The systematic studies of chemical coupling between different solvents and undercoordinated surface atoms of the growing nanocrystals revealed the mechanism of dimensionality control and the development of structural hierarchy without ligands or structure-directing agents. These findings reflect the nanoscale nature of the particles during nucleation and early stages of growth, which, in the absence of the macroscopic dipole compensation mechanism, elevates dipolar forces to become the main interfacial drivers of morphological control. The extension of the finding for ionic crystals (e.g., ZnO) to other systems can provide a general pathway for ligand-free morphological control of nanoparticles during solution synthesis, enabling the synthesis of well-defined nanomaterials via a thermodynamically deterministic pathway.

Morphological and orientational control at interfaces. These concepts of morphological control were employed to direct synthesis of hybrid heterostructures. We demonstrated that at electrified substrates, nucleation can be driven to the interphase region. Then, the finding in 3D solution can be translated to solvent-directed morphological control in the interphase. The effect was demonstrated using representative ionic crystals (ZnO), layered van der Waals crystals (SnSe₂), and metal-organic frameworks (MOFs) at electrified metal surfaces. For example, by employing nucleation in the interphase at electrified surfaces, we demonstrated the growth of micron-sized platelets of conductive MOFs. Furthermore, by tuning the growth kinetics through the change in the applied potential, the orientation of the layered conductive MOFs on the substrate can be precisely controlled. We demonstrated that increasing the applied potential from 0.10 V to 0.15 V directs the change in Ni-HITP MOF orientation on ITO from edge-on to face-on.

Solvation forces also exert orientational control during heterogeneous nucleation. We showed that the structure of Ni-CAT-1 MOFs at a solid–liquid interface is controlled by varying the affinity of the solvent to the substrate [2]. As a fraction of DMF in a binary solvent mixture of water and

DMF increases, the arrangement of Ni-CAT-1 crystals changes from well-aligned nanorods perpendicular to the HOPG substrate to less ordered nanorods due to a decrease in π - π interaction between HHTP-linker and the HOPG surface in the presence of DMF. Similarly, modifying the interfacial dielectric and solvation properties with a polymer layer has been shown to direct the orientation of Zn plates at a metal surface during electrodeposition [3]. In this study, we used in-situ electrochemical atomic force microscopy to directly observe the interfacial evolution during Zn electrodeposition on Cu substrates in the presence of varying concentrations of ZnSO₄ and polyethylene oxide (PEO). Contrary to previous literature assumptions, which emphasize the binding to the growing Zn crystal surfaces or Zn²⁺ ions, our results demonstrate that PEO smooths Zn films by promoting nucleation of (002)-oriented Zn platelets through interactions with the Cu substrate (Fig. 2). Density functional theory simulations support this finding by showing that PEO adsorption on Cu modifies the interfacial energy of Zn/Cu/electrolyte interfaces, favoring the stabilization of Zn (002) on the Cu substrate, as well as confines Zn electrodeposition to a narrow near-surface region. These findings establish a novel design principle for 2D electrodeposition, highlighting the importance of the selection of polymer additives that exhibit an attractive interaction with the substrate but minimal interaction with the growing crystals.

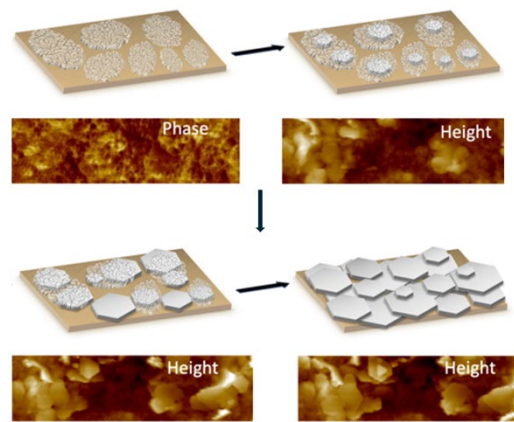


Figure 2. Mechanism of 2D electrodeposition in the presence of PEO. PEO creates a barrier to the electrodeposition of vertically growing Zn platelets, which are preferred in the absence of PEO, and promotes the layer-by-layer growth of flat-lying plates.

Polymer additives as structure-directing agents for the synthesis of 2D lateral heterostructure. Utilizing the principles of polymer-aided control of interfacial energy, we developed generalized strategies for solution synthesis of epitaxial core-crown heterostructures with controlled band alignment [4], overcoming significant challenges of existing approaches, which often suffer from poor reproducibility and scalability. Polyvinylpyrrolidone (PVP) was used as a structure-directing agent to reduce lattice mismatch between SnS₂ and SnSe₂ (10-10) surfaces and direct epitaxial growth of SnSe₂ crown on SnS₂ seed (Fig. 3). Additionally, PVP adsorption to the basal plane prevents van der Waals stacking and stabilizes 2D heterostructures during synthesis. Driven by interfacial thermodynamics, the formation of the core-crown heterostructure is highly reproducible, and the size of the 2D heterostructure and relative areas of

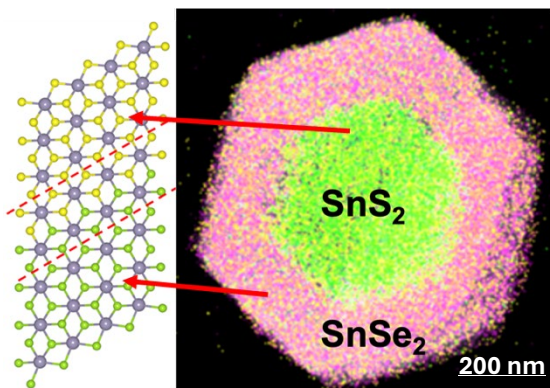


Figure 3. Interfacially-driven synthesis of two-dimensional core-crown SnS₂ /SnSe₂ heterostructure with an epitaxial relationship between the components.

the core and the crown can be precisely controlled in a two-step process by varying synthesis times for the seed and the crown. The identified growth pathway for 2D heterostructures provides a generalizable approach for synthesizing epitaxial heterostructures with a designer size, crystallographic alignment, and electronic structure.

Overall, these studies identified interfacial factors controlling the nucleation and growth of two-dimensional materials and their heterostructures and paved the way for the development of scalable solution synthesis of highly oriented functional materials.

Future Plans

Future research will continue to focus on understanding the principles of heteroepitaxy in van der Waals layered materials and the mechanisms of dimensionality control in solution synthesis of 2D layered heterostructures. We will further investigate the initial stages of nucleation and growth on distinct surface sites. Building on our preliminary work demonstrating the growth of 2D α - MoO_3 on N-doped graphene, we prepared graphitic and pyridinic nitrogen sites in a controlled manner on highly ordered pyrolytic graphite (HOPG) and characterized them using scanning tunneling microscopy and X-ray photoelectron spectroscopy. Moving forward, we will examine how different nucleation sites, such as graphene step edges, carbon vacancies, and pyridinic and graphitic nitrogen dopants, stabilize the initial $(\text{MoO}_3)_3$ building blocks and facilitate their incorporation as nucleation transitions to growth (Fig. 4). These studies will allow us to elucidate the kinetic and thermodynamic drives for the initial stages of heteroepitaxy. Using in situ STM, AFM, and the developed quantum capacitance measurements, we aim to elucidate the free-energy landscape and transition pathways to ascertain whether the growth of a new phase fits within the framework of classical heteroepitaxy.

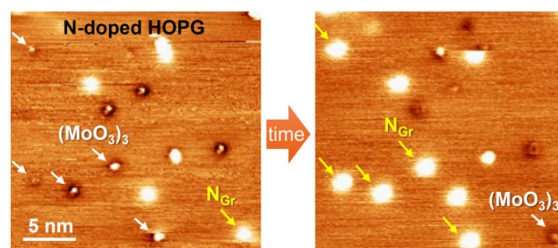


Figure 4. STM images demonstrating hopping of $(\text{MoO}_3)_3$ species between graphitic nitrogen (N_{Gr}) functional groups on graphene.

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Understanding and Controlling Nucleation in Atomic Layer Deposition for Materials Synthesis

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Keywords: Atomic Layer Deposition (ALD); Nucleation; Precursors; Transition Metal Dichalcogenides (TMDC); Surfaces

i) Program Scope

Atomic layer deposition (ALD) is a materials synthesis technique with potential to produce the precise, nanostructured materials needed in emerging energy conversion and microelectronics technologies. This research program aims to obtain mechanistic information about ALD materials synthesis. We use a strategy of employing a rationally designed series of precursors combined with careful control over surface functionality to separate and identify the precursor and surface properties that most strongly influence ALD nucleation. The research in this program focuses on understanding nucleation mechanisms in two technologically important materials systems: metal ALD on low surface energy dielectric substrates, and metal oxide ALD on transition metal dichalcogenides (TMDCs). We explore the use of precursor design, pre- and coadsorption of molecular species, and temperature to improve nucleation in ALD. New understanding will be used to develop deposition schemes in which better control over ALD nucleation can be achieved.

ii) Recent Progress

Our recent studies focused on two principal areas of study related to nucleation in atomic layer deposition (ALD): transition metal (Ru) ALD on low surface-free energy substrates, and metal oxide ALD on 2D transition metal chalcogenide (TMDC) surfaces.

Understanding nucleation mechanisms in ruthenium atomic layer deposition

Atomic layer deposition of Ru is of interest in applications ranging from catalysis to microelectronics, but it typically suffers from nucleation delays which result in non-uniform and inhomogeneous thin films, especially on low-surface free energy surfaces like SiO₂.

Recently, we investigated nucleation and growth enhancement observed in Ru ALD using the RuCpEt(CO)₂ precursor on SiO₂/Si substrates and compared it with the more commonly-used Ru(Cp)₂ precursor. RuCpEt(CO)₂ is of special interest because of its heteroleptic ligands that may engender smaller intrinsic nucleation delays. Two organometallic molecules—trimethylaluminum (TMA) and diethylzinc (DEZ)—were used to pretreat the substrate surface.

Without pretreatment, metallic Ru layers were deposited by ALD using RuCpEt(CO)₂ on SiO₂/Si with a growth per cycle (GPC) of 0.11 ± 0.01 nm/cycle, but the films were discontinuous and exhibited a nucleation delay of ~ 20 cycles. On the other hand, if one pulse of TMA or DEZ was

pre-dosed on the Si substrate prior to Ru deposition, nucleation and growth enhancement were achieved, and a shorter nucleation delay was seen. Despite the lower nucleation delay, the calculated GPC values for TMA-pretreated and DEZ-pretreated samples, once growth begins to occur, are 0.10 ± 0.01 and 0.09 ± 0.01 nm/cycle, respectively, similar to the GPC value observed for Ru growth on the non pretreated substrate. We quantify the nucleation enhancement via the enhancement factor (EF), defined as the ratio of Ru areal coverage on a treated substrate to Ru areal coverage on an untreated substrate, and show that pretreatments enhance the growth of the Ru films up to 3.2 times, for 40 ALD cycles, compared to the non pretreated substrates.

The trend in areal coverage observed with $\text{RuCpEt}(\text{CO})_2$ is consistent with that using $\text{Ru}(\text{Cp})_2$ as a precursor. However, significant differences are observed in the specific nucleation rates. Figure 1 summarizes the nucleation rates for both Ru precursors as a function of ALD cycle. First, the nucleation rate is ~ 7 times higher when using $\text{RuCpEt}(\text{CO})_2$ compared to Ru ALD using $\text{Ru}(\text{Cp})_2$ as a precursor, with either pre-treatment. Since the pretreated substrate surfaces are identical between the two systems (both employing saturation coverages of either TMA or DEZ), the difference in the magnitudes of the nucleation rate must be attributed to the differences in reactivity between the two Ru precursors. Second, the form of the nucleation rate trends differs, with the $\text{RuCpEt}(\text{CO})_2$ precursor exhibiting nearly constant nucleation rate but the $\text{Ru}(\text{Cp})_2$ precursor showing a strong variation of nucleation rate with cycle number. We attribute the different behavior to the availability of additional ALD reaction mechanisms for the $\text{RuCpEt}(\text{CO})_2$ precursor, stemming from loss of CO ligands and the presence of the ethyl group.

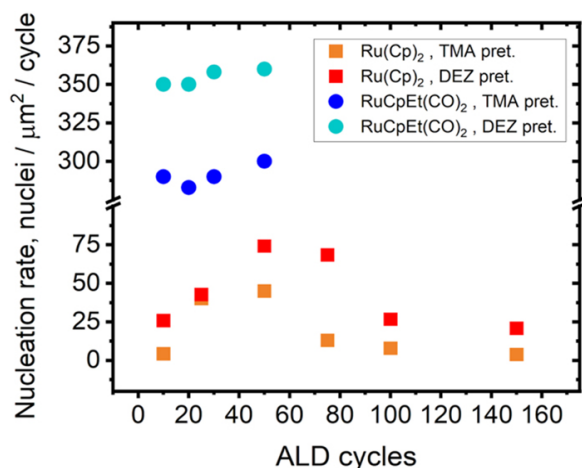


Figure 1: Nucleation rate vs. ALD cycles for Ru ALD using $\text{Ru}(\text{Cp})_2$ precursor with TMA (light squares) or DEZ (dark squares) as pretreatment and using $\text{RuCpEt}(\text{CO})_2$ precursor with TMA (dark circles) or DEZ (light circles) as pretreatment. The nucleation rates were calculated as the difference between the nuclei densities, which were normalized to the uncovered surface area, divided by the difference of the ALD cycles number for two adjacent points.

The role of ALD precursor chemistry on thin film nucleation on 2D TMDCs

Future use of two-dimensional (2D) transition metal dichalcogenides (TMDCs) in devices will require that they be interfaced with ultrathin, pinhole-free high- κ dielectrics. ALD holds significant promise for this high- κ dielectric integration, yet the inertness of 2D material basal planes poses a limitation for ALD nucleation, leading to island-like growth and poor material quality.

To improve ALD growth on 2D materials, we are exploring the ways how precursor selection and ALD process conditions can be used to impact nucleation of dielectric films on TMDCs. In particular, we investigate the mechanism by which physisorbed precursors enhance nucleation during metal oxide ALD on TMDC 2D materials. We have studied a range of alumina (AlO_x) ALD precursors to evaluate the impact of ligand size on physisorption potential and nucleation on 2D

MoS₂. Precursors include trimethyl aluminum (TMA), triethyl aluminum (TEA), triisobutyl aluminum (TIBA), and dimethyl aluminum isopropoxide (DMAI). We hypothesize that longer ligands in the Al precursor will improve van der Waals (vdW) dispersion interactions with MoS₂, increase the residence time on the surface, improve reactivity with the co-reactant, and ultimately elevate the nucleation rate.

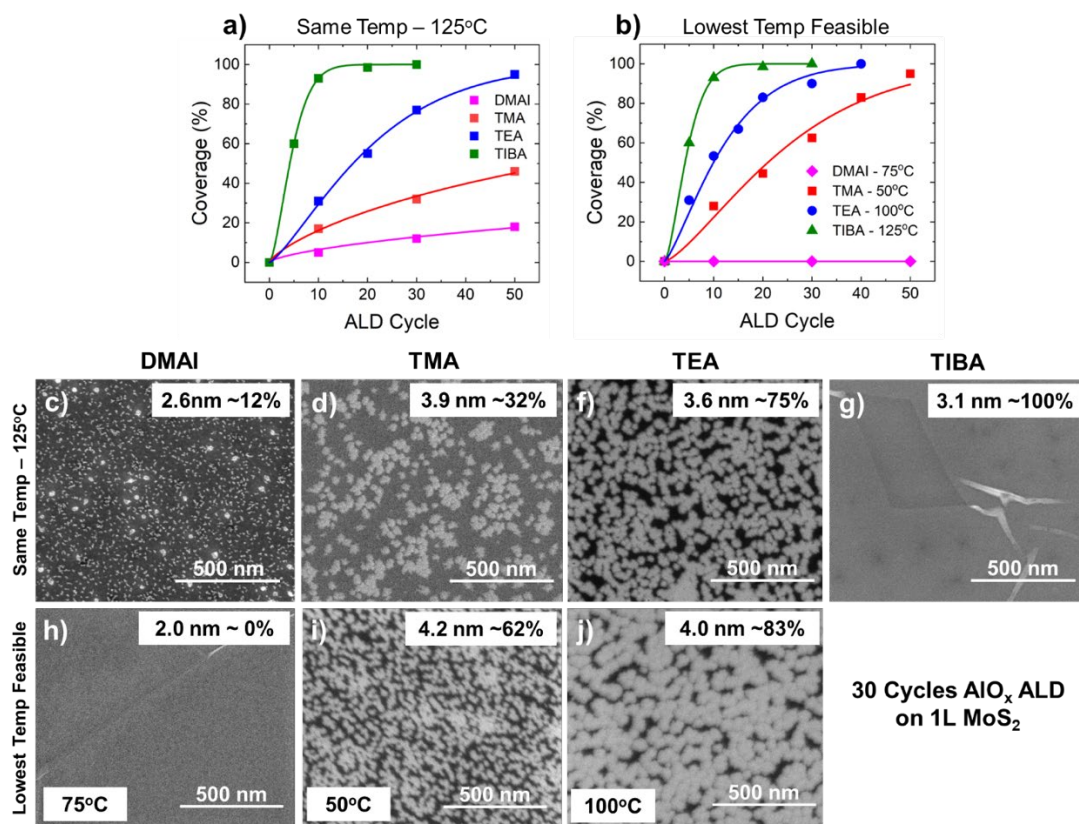


Figure 2. Nucleation study of each precursor on 1L MoS₂. Coverage of MoS₂ by AlO_x as a function of ALD cycle number for each precursor at (a) the same temperature – 125°C and (b) the LTF for each precursor. SEM of 30 cycles of AlO_x ALD deposited on 1L MoS₂ using (c, h) DMAI, (d, i) TMA, (f, j) TEA, and (g) TIBA as the precursor. The top row of SEM images ((c)-(g)) represents the experiments performed at 125°C, and the bottom row ((h)-(j)) represents the experiments performed at the LTF for each precursor. In the SEM images, the white/light grey regions represent the AlO_x, and the darker regions represent the 1L MoS₂. The thickness reported represents the thickness measured on SiO₂ by ellipsometry, i.e. the maximum thickness possible for the nuclei/film. The percentage shown represents the areal coverage of AlO_x on MoS₂.

After optimizing reactor conditions (temperature and purge times) to find the lowest temperature feasible (LTF) to obtain ALD, we can compare the nucleation and coverage behavior of each precursor on monolayer (1L) MoS₂ at the same temperature of 125°C, and at their respective LTF. The results (Figure 2) show that the coverage trends follow DMAI < TMA < TEA < TIBA, with TIBA achieving 100% coverage after just 30 ALD cycles, resulting in a maximum deposition of approximately 3 nm AlO_x on MoS₂. On the other hand, DMAI fails to provide much coverage at all, which we attribute to its tendency to dimerize, disrupting its ideal trigonal planar geometry, and hindering effective vdW interactions with the TMDC and its potential for physisorption. In contrast, the alkyl precursors (TMA, TEA, and TIBA) maintain their monomeric, trigonal planar conformation, facilitating better vdW interactions with MoS₂ and promoting physisorption. Their

highly reactive alkyl ligands further enhance nucleation kinetics. Our results show that precursors with longer ligands (like TIBA) that have higher vdW dispersion interactions permit operating the ALD process at high temperatures, thereby also improving the kinetics of nucleation.

We are also investigating the role of the substrate underlying the 2D material, which can significantly influence nucleation behavior. We have been studying physisorption-mediated ALD using Al precursors on MoS₂ exfoliated on Au and Ag surfaces.

iii) Future Plans

We plan to complete the studies on Ru ALD to understand how nucleation proceeds on substrates with different intrinsic surface free energies. For these studies, we will apply grazing incidence x-ray scattering (GISAXS) to track the Ru nuclei particle density and size at different substrate surfaces as a function of ALD cycle number. We will also continue our studies of physisorption-enhanced ALD of metal oxide insulators on TMDCs. We will complete our studies on the role of the TMDC substrate (including metals underlying the TMDC as well as other TMDCs) in influencing film nucleation and coverage, and we will expand our studies of metal oxide ALD on MoS₂ to other ALD precursors. In addition to film continuity, the role the insulator/TMDC stack quality plays on electronic properties will be explored.

v) Publications

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9. A. Rothman, L. Brandao, and S. F. Bent, “Influence of substrate crystallinity and surface functionalization on Ru nucleation and growth,” in preparation.

Science of Shape-Selective Nanocrystal Synthesis

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Keywords: Density Functional Theory, Molecular Dynamics, Metal Nanocrystal, Machine Learning, Assembly

Research Scope

A significant challenge in the development of functional nanomaterials is understanding the growth of colloidal metal nanocrystals. From a practical perspective, a knowledge of how to selectively synthesize desired metal nanocrystal sizes and shapes will be important in achieving a sustainable energy future. The proposed research targets several key gaps in the fundamental understanding of these syntheses (1) Understanding thermodynamic shapes of nanocrystal seeds using Parallel Tempering Molecular Dynamics (PTMD) and machine learning; (2) Understanding the hand-off between thermodynamics and kinetics as nanocrystal seeds grow and achieve kinetic shapes using accelerated molecular dynamics simulations based on hyperdynamics; (3) Understanding the growth of kinetic crystal morphologies, including crystals with high-index surfaces, using kinetic Monte Carlo simulations based on quantum density-functional theory (DFT); and (4) Advancing *ab initio* grand-canonical Monte Carlo simulations based on quantum DFT to understand the role of solvent and halides/halogens in controlling nanocrystal morphology.

Recent Progress

Themes in our research are (1) Understanding the growth, aggregation, and assembly of metal nanostructures mediated by organic molecules and halides; (2) Understanding Oriented Attachment (OA); (3) Understanding how reduction kinetics affect nanocrystal shape and phase; (4) Understanding the growth, structure, and transformations of nanocrystals in the single-nanometer size range; (5) Developing and deploying first-principles-based grand-canonical methods to describe gas-solid and liquid-solid interfaces; (6) Using kinetic Monte Carlo simulations to understand the non-equilibrium growth of metal nanocrystals from seeds.

For this abstract, we highlight our work on understanding the growth, structure and transformations of metal nanoparticles in the single-nm size range. This work utilizes advanced free-energy sampling techniques and machine learning (ML) to understand how nanocrystal shapes depend on temperature, size, and composition. These studies probed the shapes of Ag, Cu, and AgCu nanoparticles. We performed parallel-tempering molecular dynamics (PTMD) simulations to predict the temperature- and size-dependent equilibrium shapes of a series of Cu nanocrystals in the 100- to 200-atom size range, and we used Common-Neighbor Analysis (CNA) to provide descriptors of nanocrystal shape. **Figure 1** shows shape distributions of Cu nanocrystals with selected sizes as a function of temperature. From **Figure 1**, we see a major change in the shape distribution in going from 110 to 111 atoms, where the Ih is the most probable shape over a wide temperature range at $N = 110$, while for $N = 111$, the Dh is the most probable at low temperatures and the Dh-Ih is the most probable shape at high temperatures. The shape distribution

at $N = 111$ is largely held for $N = 112$ and $N = 113$, then there is a significant change in going from $N = 113$ to $N = 114$, where we see an Ih is the most probable shape at low temperatures and the Dh-Ih emerges as the most probable shape at high temperatures. As we increase the number of atoms from $N = 114$, there is a smoothly decreasing fraction of Dh-Ih accompanied by an increasing fraction of Ih until $N = 119$, where the Ih is the most probable shape for all temperatures below melting. Moving from $N = 119$ to $N = 120$, there is a dramatic change in the shape distribution and another significant shape change occurs in going from 120 to 121 atoms. Thus, we see an interesting trend of alternating gradual shape changes over certain size ranges, and dramatic shape changes with a size change of just one atom.

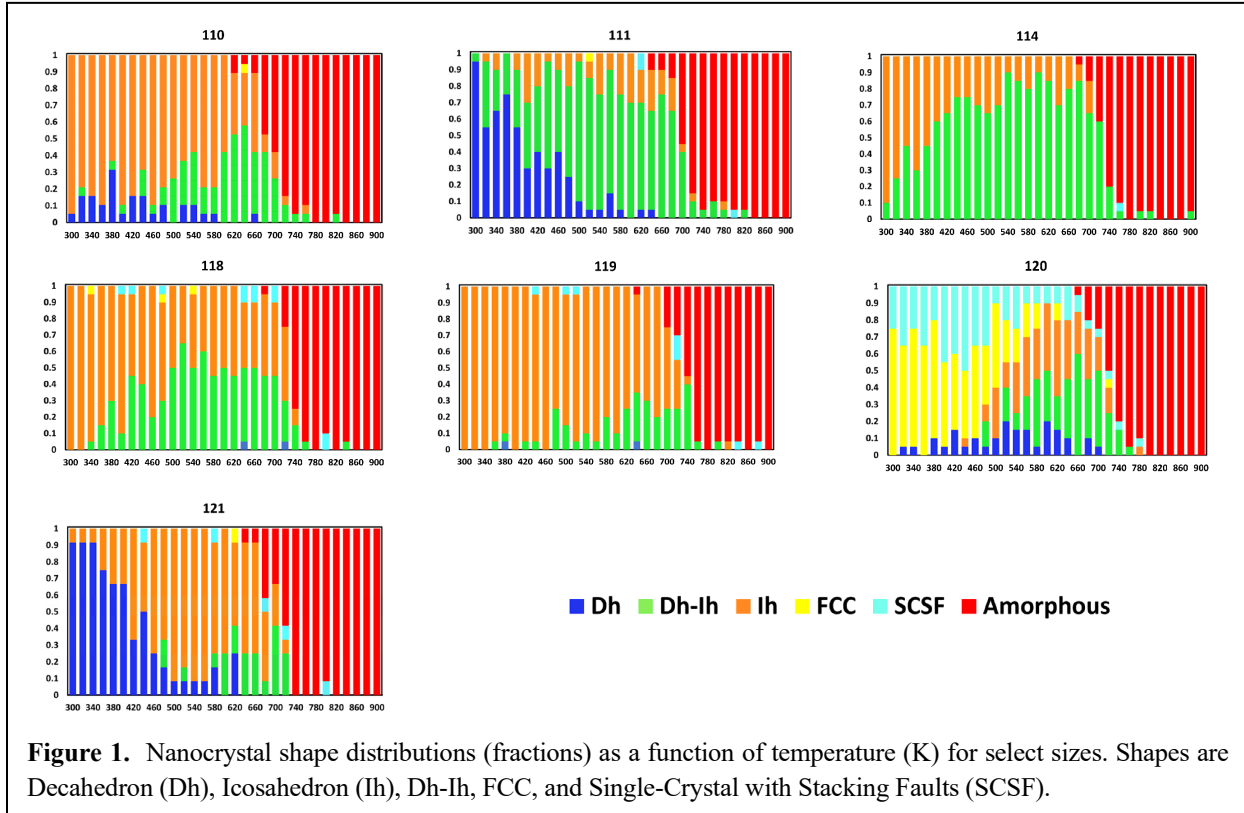


Figure 1 also shows the frequent occurrence of one shape being the most probable at low temperatures and another being the most probable at high temperatures. There are three shapes that appear to be favored by entropy (*i.e.*, they are not the most probable shape at low temperatures, but they become the most probable shape at high temperatures): Dh-Ih, Ih, and Dh. By calculating the vibrational entropies of the Dh, Ih, and Dh-Ih, we find $S_{vib,Dh-Ih} > S_{vib,Ih} > S_{vib,Dh}$, consistent with PTMD.

We used ML to quantify the shapes of the Cu nanocrystals. We constructed nanoparticle features using CNA, and we utilized Principal Component Analysis (PCA) to reduce the dimensionality of the CNA feature set. To sort the nanoparticles into structural classes, we employed both K -Means clustering and the Gaussian Mixture Model. We evaluated the

performance of the clustering algorithms through the gap statistic and silhouette score, as well as by analysis of the CNA signatures.

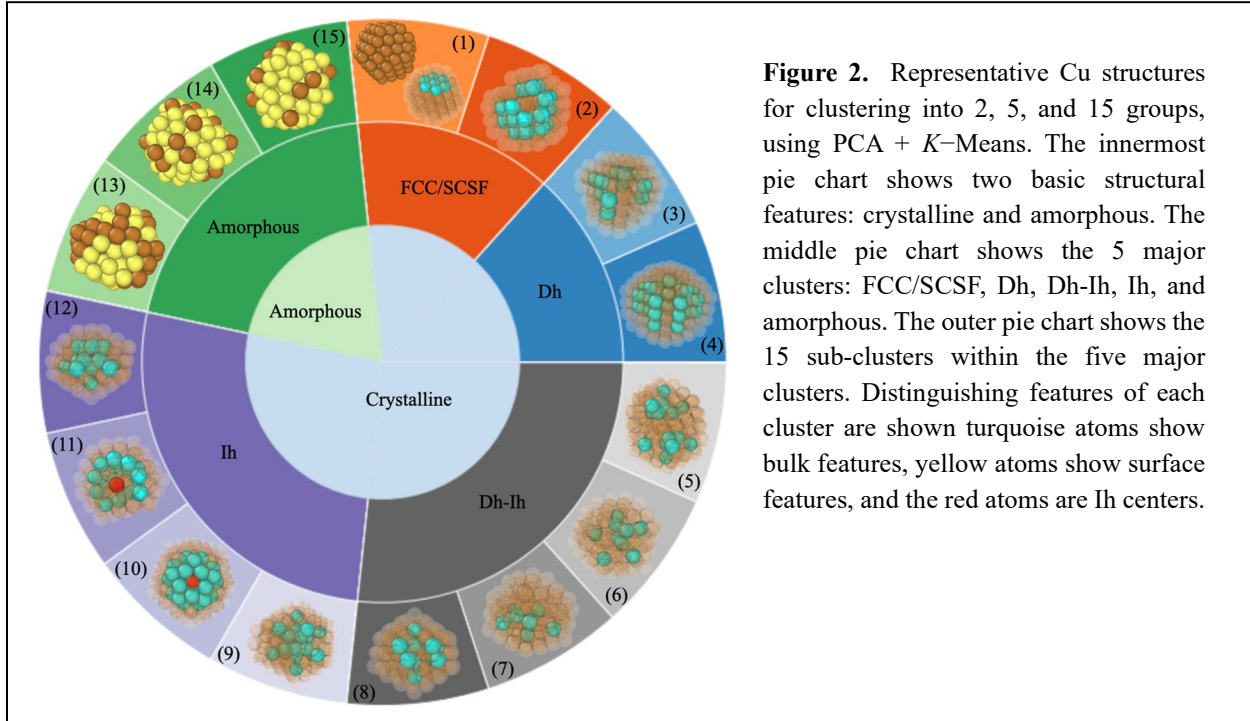


Figure 2 shows a chart of the nanocrystal shapes we found through ML classification. There are two broad classes (crystalline and amorphous), with five classes representing the major structural groups. These groups are the same as we found for manual structure classification (**Figure 1**), except ML groups FCC and SCSF structures as one structural class. This is significant because the CNA shape classification in **Figure 1** relied on “dictionaries” of CNA signatures and, for example, several CNA signatures associated with the Dh-Ih structure were not originally in the dictionary. As a result, this shape was considered amorphous in the first pass and the new CNA signatures had to be added to the dictionary. ML identifies structural classes without using a dictionary, which is a significant advantage.

In addition to the five major structural classes, ML yielded 15 detailed sub-classes, shown in **Figure 2**. Delving into the fine structural classes, the first two classes pertain to FCC structures: Class 1 consists of pure FCC single crystal structures and SCSF structures with one stacking-fault, while Class 2 consists of SCSF structures with multiple stacking faults. Classes 3 and 4 deal with Dh structures that differ in their surface atoms. Classes 5-8 pertain to various types of Dh-Ih structures and as can be seen in **Figure 2**, they differ in their internal twin structures. There are four classes for Ih structures. Class 9 is the only Ih class containing structures with a complete set of perfect Ih spines, with a number of atoms ranging from 150 to 160. Classes 10-12 contain Ih structures across the entire size range. The major difference between these classes is in their surface environments. Classes 13-15 are amorphous structures with different proportions of ordered atoms. Our results demonstrate that these ML methods are effective in identifying and categorizing

nanoparticle structures to different levels of complexity, enabling us to classify nanoparticles into distinct and physically relevant structural classes with high accuracy. This capability is important for understanding nanoparticle properties and potential applications.

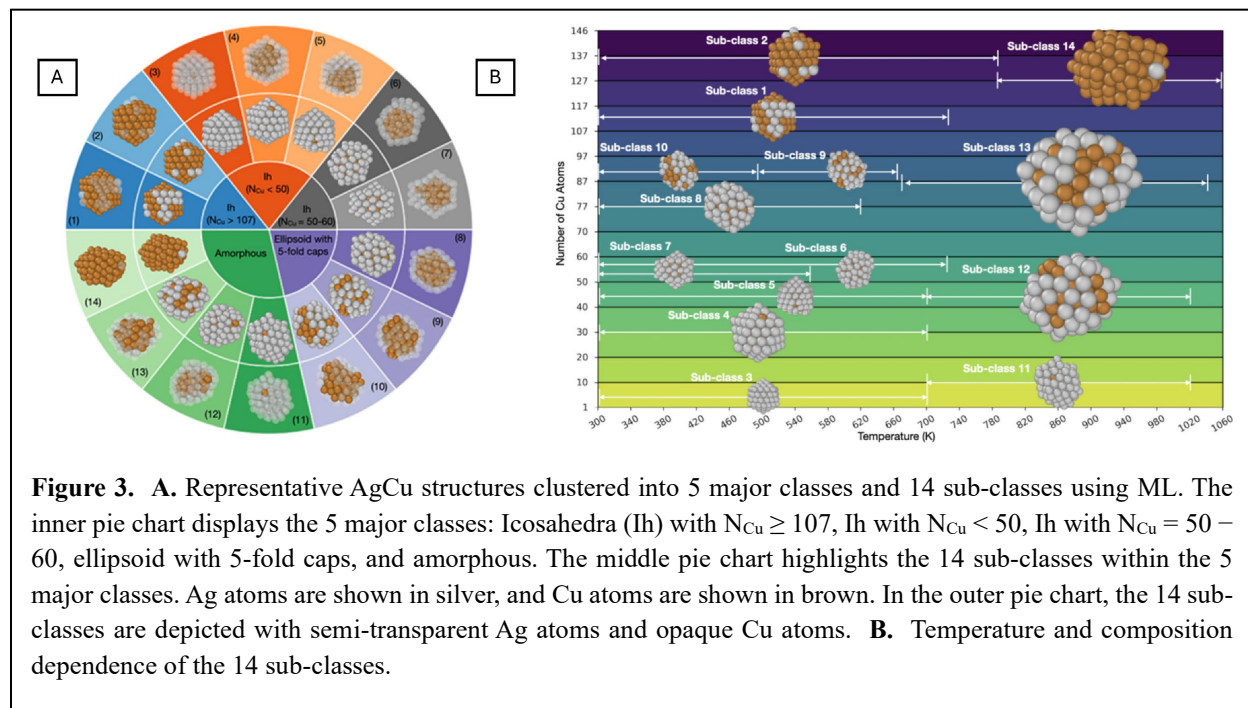


Figure 3 shows recent results from an invited paper on using ML to characterize bimetallic Cu-Ag nanocrystal shapes and composition distributions obtained using PTMD. As shown in **Figure 3A**, we classified 147-atom Ag-Cu nanocrystals of varying compositions into five different classes and 14 sub-classes, based on shape, Ag(Cu) content, and temperature (**Figure 3B**). We observed several morphologies relevant for catalysis: core@shell, single-atom alloy (SAA), and “patchy” alloy-like surface structures at equilibrium.

Future Plans

In the future, we will probe equilibrium bimetallic structures of Pt-Pd nanocrystals relevant for catalysis using PTMD and Machine-Learning Force Fields (MLFF). In ongoing work, we fit MLFF to describe the structures and energies of Pt-Pd nanocrystals and we can demonstrate that these are superior to Embedded-Atom Method (EAM) potentials, commonly used to describe metals. We have also been developing the capability to perform Time-Lagged Independent Component Analysis (TICA) – an ML tool to derive rates and transition mechanisms from nanocrystal MD trajectories. Similar to PTMD, TICA was first developed to characterize structural transitions of proteins. Our work will be the first to apply this technique to nanoparticles. We are also interested in characterizing the evolution of nanocrystal growth morphologies from equilibrium to kinetic as the nanocrystal size increases, considering growth phenomena such as single-atom additions to nanoparticles and nanoparticle aggregation.

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A Mechanistic Study of Ultrafast Sintering: Capillary versus Enthalpy and Entropy Driven Processes from Simple to Compositionally Complex Silicides

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Keywords: high-temperature processing, ultrafast sintering, induction ultrafast sintering

Research Scope

This basic research project aims at elucidating the general mechanisms of ultrafast sintering via developing and using a new *induction ultrafast sintering (IUS)* scheme. Our current research will answer the following open scientific questions: As it has been demonstrated that ultrahigh heating rates can enhance ultrafast sintering (Figure 1(a) vs. 1(b)) [1, 2], what are the underlying general mechanisms? In addition, what are the mechanisms of reactive ultrafast sintering of compositionally complex ceramics (CCCs)? Can ultrafast sintering produce non-equilibrium phases and unique microstructures?

This basic research project examines the two central scientific hypotheses: (i) Ultrahigh heating rates can alter the ratios of different kinetic processes to inhibit pore coarsening and coalescence to keep the sintering driving forces high in different schemes, serving as a general mechanism to promote both conventional and reactive ultrafast sintering. (ii) In addition, ultrafast sintering, along with large reactive driving forces, can alter phase formation and microstructural evolution. For our mechanistic studies, we proposed, and first realized in Year 1 of this project, new direct and susceptor heating induction ultrafast sintering schemes (see **d-IUS** in Figure 1(d) and **s-IUS** in Figure 1(e)). In addition, we plan to critically compare conventional and reactive ultrafast sintering in different kinetic pathways to establish generalizable mechanisms for ultrafast sintering.

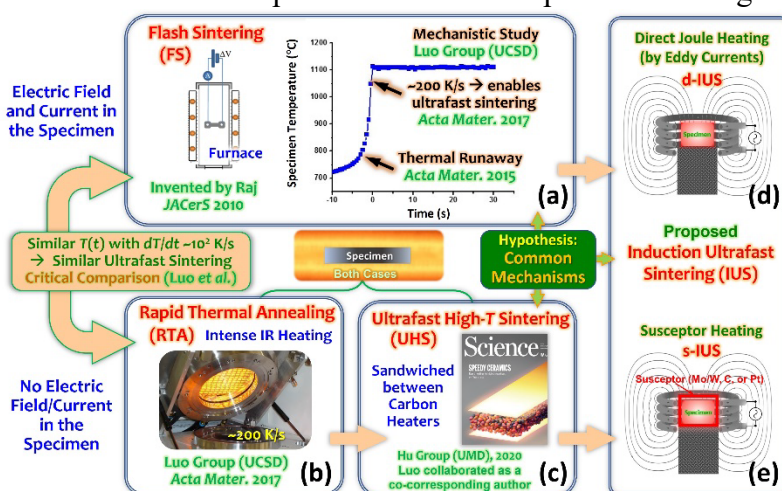


Figure 1. Overview of ultrafast sintering, including induction ultrafast sintering (IUS) originally proposed and first realized in this BES project. (a) *Flash sintering (FS)* [3] and a representative temperature profile, in which the flash was found to start from a thermal runaway [4]. (b) In 2017, PI Luo's group showed that *rapid thermal annealing (RTA)* using intense infrared heating can attain similar ultrafast densification rates as flash sintering with a similar $T(t)$ profile but without an applied electric field [1], revealing that ultrahigh heating rates of $\sim 10^2$ K/s promote ultrafast sintering. This new insight suggested the possibility of decoupling the electric response of a given material to develop (c) a general method of *ultrafast high-temperature sintering (UHS)* to sinter ceramics in seconds in a collaborative study [5]. *Induction ultrafast sintering (IUS)* with (d) direct (**d-IUS**) and (e) susceptor (**s-IUS**) heating, which was successfully demonstrated in Year 1 of this project.

Recent Progress

In this Basic Energy Science (BES)-supported research project, we first demonstrated *reactive synthesis and ultrafast sintering* of refractory compositionally complex alloy and compositionally complex carbide (RCCA-CCC) composites (Figure 2). We demonstrated that high heating rates of ~ 100 °C/s enable sintering of dense (~ 92 -95 % relative densities) bulk pellets of RCCA-CCC composites at ~ 1850 °C in ~ 70 s. These high-entropy metal matrix composites are composed of a continuous MoNbTaW-based primary (matrix) phase with a controllable amount of a reinforcing secondary carbide phase. Notably, this is the first report of ultrafast sintering of RCCA-based materials (representing a class of materials that are

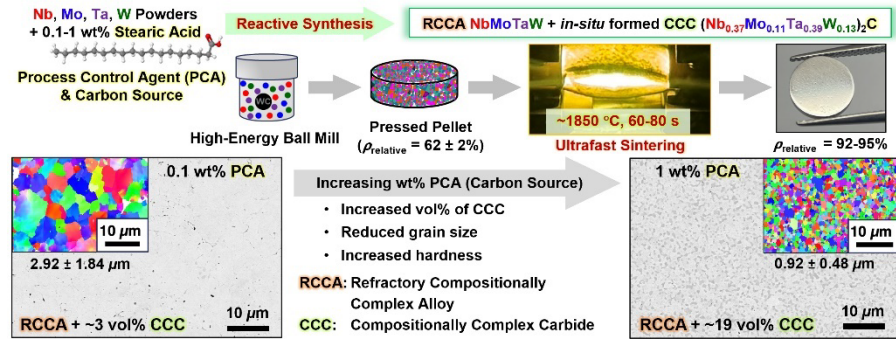


Figure 2. Reactive synthesis and ultrafast sintering of NbMoTaW based refractory compositionally complex alloy and carbide (RCCA-CCC) composites [Scripta Materialia 2025]. Stearic was used as a process control agent and carbon source to produce a controllable fraction (~ 3 -19 vol%) of carbides through reactive synthesis using high-energy ball milling. Ultrafast sintering was subsequently conducted at ~ 1850 °C for ~ 70 s to produce dense sintered pellets of ~ 92 -95 % relative densities. Furthermore, far-from-equilibrium ultrafast sintering led to the formation of a M_2C subcarbide phase (space group $P\bar{3}m1$) with expected favorite high-temperature mechanical properties. The amount of the secondary carbide phase(s) increases with increasing PCA addition, leading to improved hardness and decreased grain size.

generally difficult to sinter). Here, we demonstrated novel reactive synthesis and ultrafast sintering pathways to fabricate RCCA-CCC composites, with in-situ formation of a controllable amount of well-dispersed carbides through the use of a process control agent (PCA) as the carbon source. Furthermore, far-from-equilibrium ultrafast sintering enabled the formation of a $P\bar{3}m1$ subcarbide CCC phase, $(Nb_{0.37}Mo_{0.11}Ta_{0.39}W_{0.13})_2C$, which is expected to possess favorite high-temperature mechanical properties; in contrast, monocarbides were generally observed in more near-equilibrium spark plasma sintering. A thermodynamic model was developed to explain the observed Nb and Ta enrichments in the carbide phase. This study also supports our second scientific hypothesis that ultrafast sintering can alter the phase formation and microstructure. In summary, this study has demonstrated an innovative reactive synthesis and ultrafast sintering approach to fabricate metal-ceramic composites with favorable phase formation and microstructures. This BES-supported work has been published in *Scripta Materialia* in 2025.

In Year 1 of this project, we designed and built an induction ultrafast sintering (IUS) experimental setup capable of rapidly heating samples at >450 °C/s under direct induction heating (d-IUS) and >150 °C/s using susceptor heating (s-IUS). This experimental setup, shown in Figure 3, allowed us to realize IUS at heating rates on the order of $\sim 10^2$ °C/s to enable ultrafast sintering

in less than 2 minutes for the first time to our knowledge. Rapid heating to a maximum temperature of ~ 2500 °C was achieved in both d-IUS and s-IUS configurations. As schematically illustrated in Figure 3, temperature is recorded by a pyrometer, and the sample (a pressed pellet in d-IUS, or a Mo or C crucible/susceptor containing a pressed pellet in s-IUS) is placed inside a hot zone constructed of yttria-stabilized zirconia (YSZ). The present YSZ insulated hot zone allows continuous operation at ~ 2200 °C.

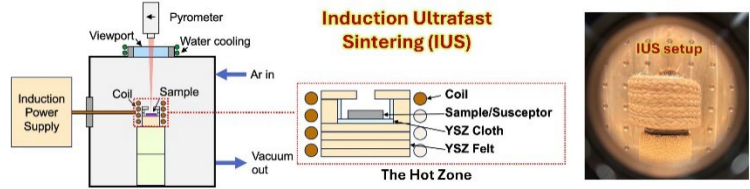


Figure 3. Schematic of our home-built experimental setup for induction ultrafast sintering (IUS) and a photo.

Using this home-built system, we have successfully demonstrated direct IUS (d-IUS) of Mo at ~ 2000 °C for 120 s (Figure 4). Heating and cooling rates as fast as 487.5 °C/s and 83 °C/s, respectively, can be obtained at 3 kW of input power (~ 30 % of the maximum induction power) at 131 kHz. Notably evident was a thermal hysteresis effect caused by the coupling of the sample to the applied radio-frequency field, leading to a temperature overshoot once the power is leveled off. Rapid densification (from ~ 69 % to ~ 94 % relative density in ~ 2 minutes) was achieved. Scanning transmission microscopy revealed a dense, sintered microstructure (Figure 4(c)). A ~ 150 μm thick porosity band formed at the specimen surface. Further mechanistic studies are in progress.

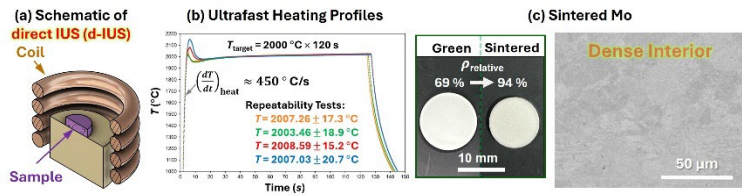


Figure 4. Demonstration of direct IUS (d-IUS). (a) Schematic of d-IUS. (b) The ultrafast heating profiles with ~ 450 °C/s heating rates with good repeatability. (c) Sintered Mo specimens.

In addition to d-IUS, we have demonstrated the broad applicability of IUS in a susceptor-heating mode (s-IUS). This s-IUS mode (Figure 5(a)) employs a molybdenum or graphite crucible as a susceptor which is rapidly heated by the induction and in turn heats the specimen to be sintered. This s-IUS mode enables ultrafast sintering of samples that are not electrically conductive or do not couple with induction power sufficiently for rapid heating. Rapid densifications of molybdenum (Mo, a model metal system) and 3 mol% Y_2O_3 -stabilized ZrO_2 (3YSZ, a model ceramic system) have been demonstrated. Specifically, s-IUS of Mo resulted in a sintered pellet with a ~ 93.4 % relative density, using a heating rate of ~ 100 °C/s and a ~ 120 s isothermal hold time at ~ 2000 °C. In addition, a green body of ~ 40 nm 3YSZ powders was sintered (s-IUS) to a relative density close to 97% at ~ 1570 °C in ~ 30 s with a ~ 75 °C/s heating rate.

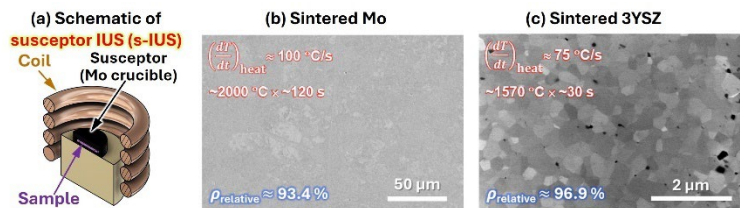


Figure 5. Demonstration of susceptor-heating IUS (s-IUS). (a) Schematic of s-IUS. Sintered (b) Mo and (c) 3YSZ specimens.

We have also demonstrated the initial feasibility of s-IUS of compositionally complex silicides (HES) using a graphite crucible as a susceptor, following the procedure outlined in Figure 6. Binary NbSi₂, MoSi₂, TaSi₂, and WSi₂ disilicides

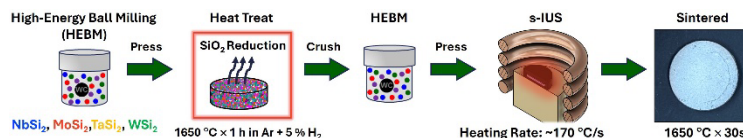


Figure 6. Initial demonstration of s-IUS of a compositionally complex silicide, (Nb, Mo, Ta, W)Si₂. Further powder processing optimization is underway to remove or reduce SiO₂ and secondary phases caused by the formation and evaporation of native oxides.

were used as the starting materials. We found that the presence of native oxides (SiO₂) in the starting powders makes rapid sintering of silicide materials challenging, with rapid evaporation of SiO₂ (or SiO) at high temperatures leading to bubbling or even explosion. Thus, we conducted high-temperature homogenization and reduction of SiO₂ in Ar + H₂. However, the reduction of SiO₂ came at the expense of silicon loss, resulting in precipitation of secondary phases (*e.g.*, monosilicides) following the silicon loss. We are currently improving powder processing methods to produce high-quality silicide powders to overcome this challenge.

Future Plans

We plan to use the IUS capabilities established in Year 1, along with an induction-heating dilatometer custom-designed in Year 1 to reach ~1950 °C (beyond the temperature capabilities of any other commercially available equipment) that will be installed in summer 2025, to conduct experiments to critically compare the effects of heating rates, particle sizes, and isothermal hold time, which can be conducted using simpler YSZ and Mo model systems. Furthermore, we plan to compare s-IUS and d-IUS using Mo as the primary model system. In addition, we will further improve the processing of compositionally complex silicides and subsequently use them as model systems to investigate reactive ultrafast sintering and compare ultrafast sintering in different kinetic pathways. If the powder processing optimization for silicides (to overcome the challenge of evaporative native oxides) cannot achieve ideal results, we will design alternative reactive sintering systems for our mechanistic studies, with the same goal of understanding reactive ultrafast sintering mechanisms. We also plan to test a couple of novel ultrafast sintering schemes.

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Electronic, Optical, and Electrochemical Properties of Doped Metal Oxide Epitaxial

Films and Interfaces

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Keywords: complex oxides, strain, defects, epitaxial thin films, in situ TEM

Research Scope

This project aims to *understand, predict, and ultimately control evolving lattice defects in well-defined heteroepitaxial oxide thin films and multilayers to achieve desired structure, stability, and functionality*. Complex oxides are of great interest due to their intricate structures, diverse properties, and wide-ranging applications, but their inherent complexity presents significant synthesis challenges. The premise of our research is that defects—both intrinsic and intentionally introduced—in epitaxial thin films, along with interfacial structural inhomogeneity, can modulate local lattice distortions and strain fields, which in turn govern phase stability and functional properties. We hypothesize that by systematically controlling these defect and interface characteristics, we can direct the emergence of metastable phases and enhance targeted material behaviors. In this project, we aim to address three identified knowledge gaps. 1) Which parameters can we use to effectively modify the dynamic evolution of lattice defects during epitaxial synthesis to selectively access and stabilize different competing phases? 2) How can we control defect evolution, particularly through ion intercalation and extraction, to modify functional properties and phase transition characteristics? 3) How can we leverage close contact, atomic registry, and structural inhomogeneity at epitaxial interfaces to facilitate efficient and robust charge and mass transfer? By combining precise thin film synthesis, in situ/operando structural and chemical characterization, and advanced computational modeling, we aim to reveal the structure–stability–property relationships in complex oxides. This will lay the foundation for the predictive synthesis of these materials and enable their use in energy harvesting, conversion, and storage, as well as advancements in microelectronics and solid-state ionics.

Recent Progress

To illustrate progress toward our central goals, we present three representative studies showcasing our integrated approach to study defect behavior in epitaxial complex oxides.

Topotactic phase transitions (TPTs) in vacancy ordered oxides under external stimuli.

Oxygen vacancies (V_O) play a central role in determining the functional behavior of complex oxides, with implications for catalysis, ion transport, and resistive switching. A persistent challenge remains in understanding how to order these vacancies, how to control their propagation, and how to control the transition between a potentially unlimited number of possible V_O orderings with

unique electronic signatures. At the core of this challenge is an inability to predictively initiate, track, and direct TPTs.

We demonstrated the ability to directly manipulate and visualize oxygen diffusion at an atomic scale through in situ transmission electron microscopy (TEM).¹ Brownmillerite $\text{SrFeO}_{2.5}$ (BM-SFO) thin films, grown via pulsed laser deposition (PLD) on various substrates, stabilized oxygen vacancy channels (OVCs) either parallel or perpendicular to the interface. Under electron beam irradiation, the created built-up electric field drives oxygen ions migration from the reducible substrates (Figure 1a), triggering the phase transition from BM-SFO to perovskite SrFeO_3 (P-SFO). Two diffusion pathways produced distinct $\text{SrFeO}_{2.75}$ intermediates: parallel OVCs enabled disruptive diffusion through both FeO_6 octahedral and FeO_4 tetrahedral layers, while perpendicular OVCs supported intercalation-only oxygen diffusion, yielding a metastable structure with alternating FeO_6 and FeO_5 layers (Figures 1b & 1c). Using in situ environmental TEM (ETEM), we also studied how water vapor interact with vacancy-ordered BM-SFO and BM- $\text{SrCoO}_{2.5}$ phases.² These results advance our understanding of TPTs and inform strategies for multi-state device design.

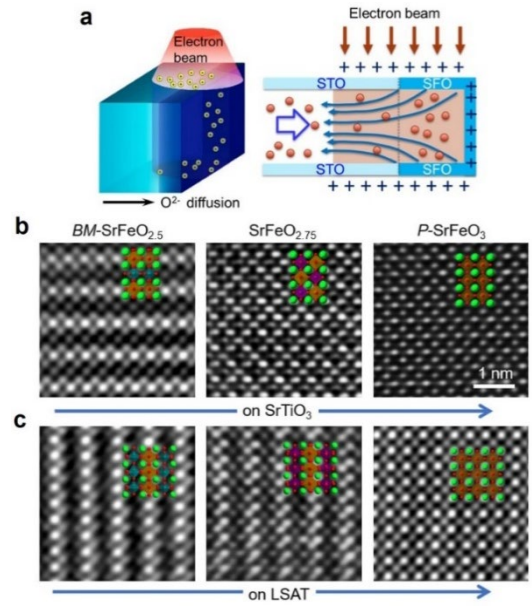


Figure 10. (a) Schematics of electron-beam induced electrical field generated during TEM imaging and its effect in promoting O^{2-} diffusion. (b,c) High resolution TEM images showing phase transformations of $\text{BM-SrFeO}_{2.5} \rightarrow \text{SrFeO}_{2.75} \rightarrow \text{P-SrFeO}_3$ in two different cases.

Unraveling Charge Transfer at $\text{LaNiO}_3/\text{LaFeO}_3$ (LNO/LFO) Heterointerfaces.

Understanding and controlling charge transfer at interfaces is crucial for harnessing the full potential of materials in advanced electronic and energy technologies. Over the past decade, LNO-based superlattices have attracted interest for their potential in high-temperature superconductivity, yet there is a lack of consensus regarding the direction and extent of charge transfer at heterointerfaces. For example, while O 2p band-alignment model suggests partial charge transfer from Fe to Ni for LNO/LFO heterointerfaces, the ionic bonding paradigm, which views Fe^{3+} in LFO as a highly stable $3d^5$ system with a half-filled 3d orbital, suggests no charge transfer.

Our combined theoretical and spectroscopic analysis provides clear evidence of charge transfer from Fe to Ni at LNO/LFO heterointerfaces.³ Calculations on a $(\text{LNO})_3/(\text{LFO})_1$ superlattice revealed a depleted Fe e_g -derived band and the downward shift of the FeO_2 layer's projected density of states (pDOS) relative to bulk LFO, alongside an upward shift of the NiO_2 layer's pDOS compared to bulk LNO (Figure 2a), indicating electron transfer from LFO to LNO. Molecular beam epitaxy (MBE)-grown LNO/LFO superlattices confirm this, showing that Ni oxidation state drops from Ni^{3+} to $\text{Ni}^{3-\delta}$ and Fe oxidation state increases from Fe^{3+} to $\text{Fe}^{3+\delta}$ (Figure 2b).

Quantitative analysis highlights up to 0.5 e⁻/interface transferring from Fe to Ni across the LNO/LFO heterointerface. Layer-resolved Fe L-edge electron energy loss spectroscopy (EELS) on a representative (LNO)₃/(LFO)₅ superlattice (Figure 2c) supports the direction of charge transfer, showing elevated Fe oxidation at the interface versus the bulk (Figure 2d). Moreover, we established a direct correlation between the interfacial charge transfer and the measured sheet resistance of the LNO/LFO superlattices, with LFO layer's thickness critically modulating interfacial charge redistribution and superlattices' in-plane transport properties.

Figure 11. (a) Calculated DOS projected on the BO₂ layers (green for NiO₂ and purple for FeO₂) and O 2p states (red) and the neighboring AO layers; Fermi level (E_F) marked by vertical black dash-dot lines and O 2p center (ϵ_p) by vertical red lines. (b) B-site cation formal charges as a function of m in (LNO)₃/(LFO) _{m} SLs. (c) HAADF-STEM image of the $m = 5$ SL with EDS maps. The black arrows point out which layer the corresponding EELS signal was taken from. (d) Fe L₃/L₂ ratio as a function of each Fe layer in the $m = 5$ SL.

Valence modulation and control in complex environment - from multicomponent to high-entropy oxides. Doping is a powerful way to tailor material properties, such as conductivity, magnetism, and catalytic activity. However, its impact on local structures, defect formation, and electronic states remain poorly understood. In oxygen-deficient $\text{SrFe}_{0.67}\text{Cr}_{0.33}\text{O}_{3-\delta}$ (SFCO) thin films synthesized by MBE,⁴ we observed species-selective charge modulation: Fe maintains Fe^{3+} throughout the film, while Cr exhibits layer-dependent oxidation states ($\text{Cr}^{3+}/\text{Cr}^{4+}$) (Figure 3a), indicating that Cr adapts more readily to local oxygen stoichiometry changes than Fe cations. Simulations indicate that Cr-O bond arrangements and the way V_O interact with Cr and Fe drive Cr charge disproportionation. We further studied Sr doping in epitaxial $\text{La}_{1-x}\text{Sr}_x(5\text{B})\text{O}_3$ (where $5\text{B} = \text{Cr}_{0.2}\text{Mn}_{0.2}\text{Fe}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}$) thin films.⁵ X-ray spectroscopies reveal that Sr doping preferentially promotes Cr oxidation from Cr^{3+} to Cr^{6+} , partially oxidizes Co and Ni, while leaving Mn^{4+} and Fe^{3+} unchanged (Figure 3b). Despite good structural quality for the $\text{La}(5\text{B})\text{O}_3$ film (Figure 3c), atomic-resolution energy-dispersive X-ray spectroscopy reveals pronounced Cr segregation (Figure 3d), with depletion at the film/substrate interface and enrichment at the film surface

(marked by aqua arrows in Figure 3d). These findings emphasize the need for careful doping design to control cation valence and prevent formation of unstable, toxic phases.

Future Plans

Our recent studies have clarified key mechanisms underlying defect evolution, charge transfer, and valence modulation in complex oxides, revealing how vacancy ordering, interfacial charge redistribution, and cation-specific oxidation behaviors govern phase stability and functional properties. These insights have highlighted the complexity arising from intertwined structural, chemical, and electronic factors, motivating a more targeted approach to disentangle multication interactions. Building on this, we will leverage the precise control afforded by MBE and PLD growth to design model heterostructures with simplified and well-defined cation arrangements, enabling systematic deconvolution of multi-cation coupling effects on lattice distortions, defect dynamics, and electronic structure. This will allow us to test specific hypotheses on how local chemistry and configurational entropy independently and cooperatively influence phase formation and metastability.

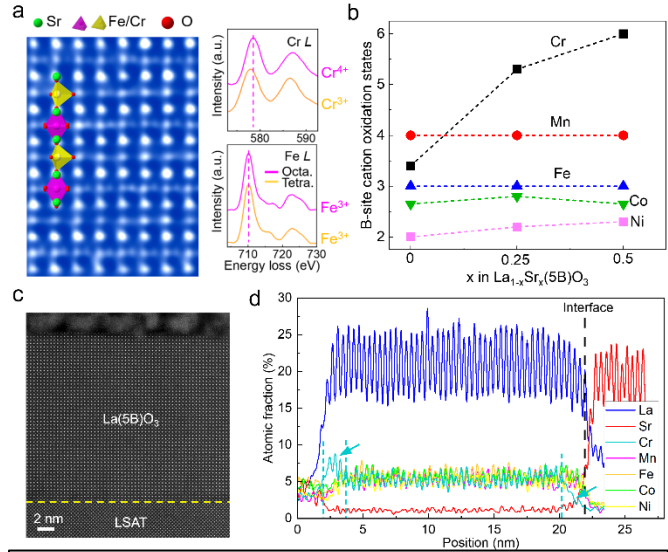


Figure 12. (a) STEM image showing a BM-like structure in Fe/Cr alloyed SFCO thin films with EELS revealing layer-dependent valence modulation of Cr and stable Fe^{3+} . (b) Spectroscopically determined average B-site cation oxidation states as a function of x in $\text{La}_{1-x}\text{Sr}_x(5\text{B})\text{O}_3$. (c,d) STEM image of the $\text{La}(5\text{B})\text{O}_3$ ($x = 0$) film and integrated line profiles of atomic fractions, indicating obvious Cr

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In Situ Studies of Charge Transfer Phenomena in Complex Oxide Heterostructures

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Keywords: Complex oxides, molecular beam epitaxy, iridates, X-ray spectroscopy, interfacial phenomena

Research Scope

Complex oxide thin films exhibit a wide range of unique phenomena that have been investigated for use in technologies ranging from renewable energy, data storage, and quantum information processing. Perovskite oxides with the formula ABO_3 represent a particularly interesting class of complex oxides because of the wide array of transition metal ions that can occupy the B site of the material. To date, most research has focused on $3d$ transition metals on the B site, such as cobalt. However, emerging work focused on $5d$ transition metal B site ions has shown that these materials exhibit stronger spin-orbit coupling and a wide array of correlated electronic phenomena. Many of these properties are modulated through charge transfer across epitaxial interfaces or between cations in ordered phases. In this EPSCOR-State/National Laboratory Partnership project, we are focused on the use of *in situ* techniques to examine the role of charge transfer processes in epitaxial oxide superlattices and ordered double perovskite thin films. Partners include Argonne National Laboratory and Brookhaven National Laboratory.

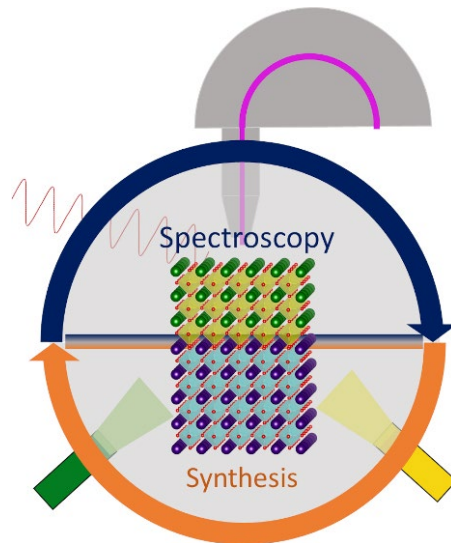


Figure 1: Feedback loop of in situ characterization of oxide thin films, providing feedback to improve the synthesis process. Taken from Thapa, et al.[1]

In this project, we employ hybrid metal-organic molecular beam epitaxy for the delivery of refractory tantalum and iridium cations and examine charge transfer to cobalt. Through systematic studies of interfaces and superlattices that combine the three B site cations, we are examining models governing charge transfer in oxide systems. Films and heterostructures synthesized in this work will also be examined to probe emergent electronic and magnetic topological phenomena. Collectively, this work will advance our synthesis capabilities and provide a fundamental understanding of interfacial charge transfer in complex oxides. Both results are key goals for the Department of Energy Basic Energy Sciences roadmap for development and control of new materials for quantum information technologies and renewable energy.

Recent Progress

In initial work on SrIrO₃ film growth, we explored how epitaxial strain affects the electronic transport properties of SrIrO₃ thin films. We found that applying compressive strain preserves metallic behavior, while even slight tensile strain drives the system into an insulating, gapped state. Through temperature-dependent resistivity measurements, we observed clear signatures of the Kondo effect, particularly in thinner films and those under reduced compressive strain. Because SrIrO₃ is known to have strain-dependent oxygen vacancy concentrations, our results

demonstrated that vacancies in SrIrO₃ are magnetically-active Kondo impurities that couple to free charge carriers. These results show that epitaxial strain serves as a powerful tuning parameter, enabling us to push SrIrO₃ toward a Kondo insulating regime and potentially access a strain-controlled quantum critical point in this correlated oxide system. They also show that electron and hole-doping of SrIrO₃ is a valuable way to tune quantum phenomena in the material.

Motivated by our interests in tuning of the electronic and magnetic properties of SrIrO₃ and the prediction of interfacial charge transfer, we grew a set of (SrIrO₃)_n/(SrCoO₃)_n (SIO/SCO) superlattices using plasma-assisted molecular beam epitaxy (MBE). We studied charge transfer phenomena tuned by a decreasing ratio of SIO:SCO (2:1, 5:3, 3:2 respectively). Scanning transmission electron microscopy confirmed the quality of the superlattices, and X-ray diffraction data indicated excellent crystalline quality of the films. We confirmed charge transfer using synchrotron-based polarization-dependent hard X-ray absorption spectroscopy on Co K and Ir L_{2,3} edges. Through collaborations with Prof. Boris Kiefer at New Mexico State University, we performed DFT calculations that suggest that charge transfer does not occur directly from IrO₂ layers into the CoO₂ layers but instead as Ir → O → Co, assisted by hybridization. We observed a stronger hybridization towards out-of-plane with the decreasing SIO:SCO ratio, and a directional

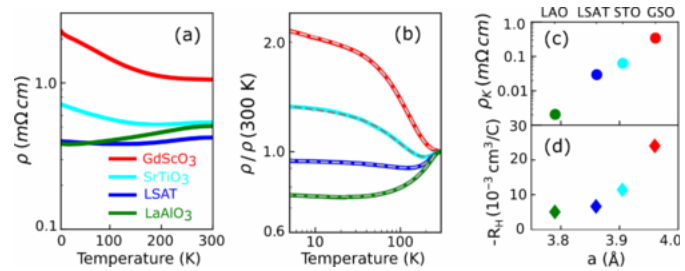


Figure 2: Transport behavior of 5-nm-thick SrIrO₃ films. Temperature dependence of (a) resistivity, and (b) resistivity normalized to the room-temperature value. The dashed lines in (b) show fits to the transport model defined in Eq. (1). (c) Kondo scattering term extracted from fits in (b). (d) Hall coefficient at 5 K.. Taken from Rimal, et al.[2]

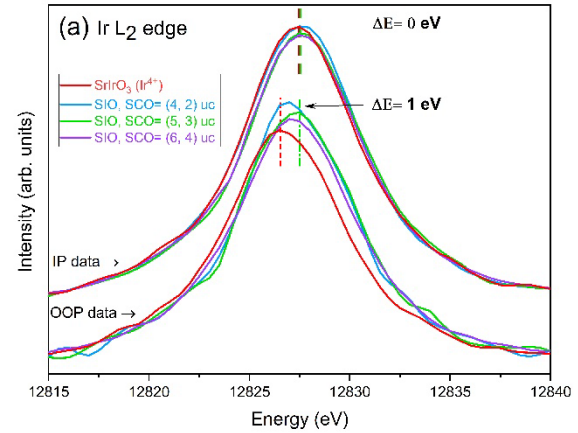


Figure 3: Ir L₂ edge X-ray absorption spectroscopy data for SIO/SCO superlattices showing higher Ir valence state for superlattices compared to strained SIO films. Taken from Ahammad et al. [4]

shift in hybridization was observed with changing layers ratio. An anisotropy between in-plane and out-of-plane hybridization was observed. Polarization-dependent Ir L₂ edge data indicated a strain-induced orbital polarization in SrIrO₃ layers in our superlattices. Electronic transport measurements show that by hole doping SrIrO₃, which suppresses free electrons and oxygen vacancy formation, we have eliminated the Kondo effect in the superlattices. This shows the tunability of the electronic phases of the material. Ongoing work focuses on understanding of magnetic phenomena in superlattices due to charge transfer via Co L edge X-ray absorption, magnetotransport measurements, and STEM-EELS layer-resolved measurements of the samples. Our findings offer a new perspective towards understanding and improving existing theories on charge transfer mechanisms in metallic transition-metal oxides, thus can help explore new physics and emergent phenomena that occur when spin-orbit coupling and strong-correlations coexist at an interface.

To explore the impacts of charge transfer on polar phenomena in complex oxides, the Jin group has employed ultra-fast spectroscopy to examine the impact of carriers in (Ba,Sr)TiO₃. SrTiO₃ can easily become ferroelectric under small perturbation, such as doping or mechanical stresses. For example, ferroelectric crystal Sr_{0.95}Ba_{0.05}TiO₃ has been tuned into a polar metal via electron doping. However, the microscopic picture of the ferroelectric transition remains unclear. In this project, using optical second harmonic generation (SHG) in the rotational anisotropy (RA) and pump-probe (PP) experiments, we investigate Nb-doped Sr_{0.95}Ba_{0.05}TiO₃ crystal. We have identified a ferroelectric phase transition at around 45 K that exhibit an order-disorder nature. In addition, at the temperature slightly above the transition temperature, we show that the population of polar regions can be manipulated by the polarization of pump laser pulses. The results provide important insight in modeling the ferroelectric transition of SrTiO₃ systems, which may shed light on intriguing physics in SrTiO₃ such as the link between ferroelectricity and superconductivity.

Future Plans

Having successfully demonstrated growth of SIO/SCO superlattices and measured their interfacial charge transfer, we are continuing to explore emergent phenomena in these systems, including modulation of magnetic phenomena in SrCoO₃, polar distortions at interfaces due to charge transfer, and topological electronic phases that may exist. We have conducted preliminary polarized neutron reflectometry experiments on select samples to determine interfacial magnetic states and intend to continue this work over the next year. Beamtime for X-ray magnetic circular dichroism at the Co L edge is scheduled for August 2025 at the Advanced Photon Source. With the return of capabilities at APS, we also plan to conduct *in situ* growth of SrCoO₃ on SrIrO₃ films while monitoring the Co K and Ir L₂ edges with XAS to examine changes in charge state due to interfacial charge transfer. Finally, second harmonic generation will be employed to study the effects of charge transfer on polar distortions at the interface in these samples.

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Synthesis of Thin Films Using Cryogenic MBE Processes

DE-SC0025017

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We explore thin film growth at cryogenic temperatures (< 20 K) using molecular beam epitaxy (MBE). At these low temperatures, atomic mobility is expected to be heavily suppressed, providing a unique opportunity to control disorder, stabilize metastable phases, and create abrupt interfaces. To understand how these kinetic limitations influence nucleation and film evolution, we use a combination of in-situ STM, RHEED, and XPS alongside ex-situ methods such as TEM, AFM, XRD, and electrical characterization.

Our initial studies focus on aluminum and tantalum thin films, materials whose superconducting critical temperatures are strongly affected by growth temperature. We use STM to directly observe the nucleation and interface formation of sub-monolayer films deposited on Si(111) 7×7 surfaces at cryogenic temperatures, with comparisons made to films grown at room temperature. By systematically varying coverage and substrate temperature, we aim to build a detailed picture of early-stage growth under suppressed kinetics.

Complementary TEM analysis reveals that aluminum films grown at 6 K exhibit polycrystalline morphology with partial (111) texture, in contrast to the fully textured, epitaxial Al(111) films obtained at room temperature. Notably, these cryogenically grown aluminum films appear yellow, an effect confirmed by ellipsometry, which likely reflects structural changes and increased disorder.

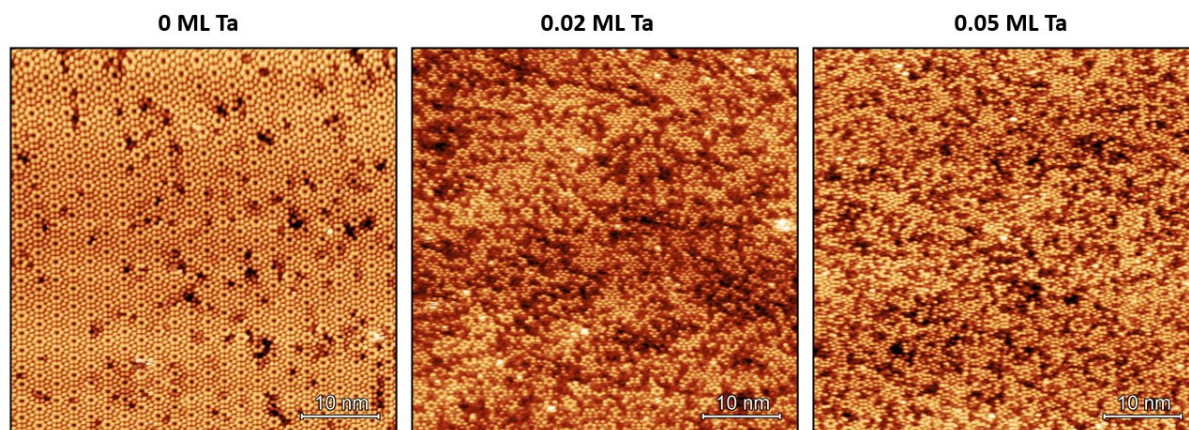


Figure 13: In-situ STM images of the Si(111) 7×7 surface before and after cryogenic deposition of 0.02 ML and 0.05 ML of Ta.

Understanding & Application of Flash Sintering for Highly Conductive High Temperature Ceramics

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Keywords: Flash sintering, high temperature ceramics, *in situ* characterization, synchrotron study, high entropy ceramics

Research Scope

In the past decade or so, many studies have been carried out on flash sintering (FS) of various oxides such as Y_2O_3 -stabilized ZrO_2 (YSZ), ZnO , and others. To carry out flash sintering, electrical current is forced through the sample, which leads to Joule heating. For oxides like YSZ that show a rapid (often “exponential”) increase in conductivity when temperature rises, Joule heating causes the sample resistance to drop. As a result, under the applied (often constant) voltage, reduced resistance causes current and heating to increase further, producing additional drop in sample resistance. The process becomes self-accelerating, which eventually leads to the *flash* or the drastic increase in current and power dissipation and rapid densification of ceramics within minutes or even seconds [1].

On the other hand, for highly conductive high temperature ceramics (HTC), their *bulk* conductivity behaves differently: it would *decrease* with increasing temperature, which, in principle, would *work against* the principle for flash sintering. Yet, flash sintering has been demonstrated for several highly conductivity HTC materials such as ZrN and WC , and the underlying mechanism is *not* clear.

The central objectives of this project are to ***investigate the fundamental mechanism for flash sintering of highly conductive high-temperature ceramic (HTC) materials using materials such as zirconium nitride (ZrN) as examples and reveal the interrelationships between those materials’ microstructure, defect and surface characteristics, transport properties, and their behaviors in flash sintering.*** The scope of the project will include (i) systematically characterizing the flash sintering behaviors for highly conductive HTC materials ZrN , (ii) revealing the origin for the observed flash sintering phenomena for these materials, and (iii) establishing the relationships between defects, materials transport properties (e.g., electrical conductivity), and observed flash sintering behaviors.

Recent Progress

In the past two years since the last DOE Synthesis & Processing Science PI meeting in July 2023, significant changes has occurred to the project, including the PI ZC’s relocation from Florida International University (FIU) to Colorado State University (CSU). Due to the various transitions, the project has been on pause since Aug 2024, and is waiting to be re-established at CSU. Nevertheless, the following briefly summarizes the progress made since 2023 in several areas.

- Finite element modeling of ZrN flash sintering behavior

As reported for the earlier PI meeting in 2023, experimental investigation of the flash sintering for highly conductive HTC of ZrN has been carried out, which captures the observed influence of various operating parameters such as applied voltage/electrical field, pressure, post-flash holding time, powder milling, repeated application, etc. on the ZrN flash sintering behavior.

To help understand experimental observations, finite element modeling (FEM) based on COMSOL® is used to simulate ZrN flash sintering behavior. As expected, many assumptions must be made for the modeling. Among them, assumptions about the electrical and thermal properties of the sample as well as the setup appear to play very critical roles. For example, regarding the

dependence of sample effective electrical conductivity σ_{sample} on temperature T , **Fig. 1(a)** shows some possible behaviors or assumptions that could be made, between room temperature (RT) and the estimated FS temperature (~ 2000 K) for ZrN. By choosing different assumptions about the $\sigma_{\text{sample}} - T$ relationship while keeping everything else the same, different current I versus time t behaviors would be obtained and compared with experiments. So far, the best appears to be the mid value between polynomial and exponential relationship (red short dash – dot line in **Fig. 1(a)**), which fits well with experiments (see **Fig. 1(b and c)**), for all DC voltage applied. The model displays the non-linearity in FS, i.e., the large increase in current with only small voltage increase. The model also demonstrates better match with experiments during incubation when using Mo electrode (instead of common graphite electrode) by introducing, between the sample and the electrodes, a more resistive layer (presumably oxides like MoO_x) whose conductivity increases exponentially with temperature.

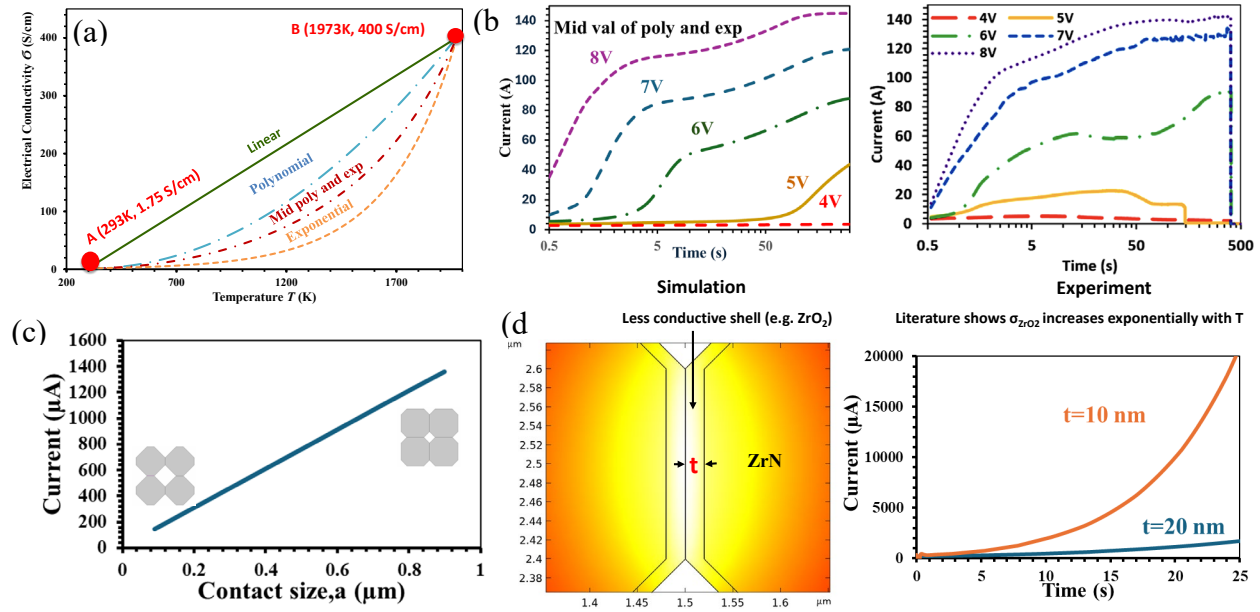


Fig. 1: Plots for finite element modeling of ZrN flash sintering, showing (a) different assumptions on ZrN sample effective electrical conductivity σ_{sample} vs T ; (b) simulated $I-t$ curves using the mid values of polynomial and exponential functions for σ_{sample} vs T and comparison with experiments for ZrN FS under different DC voltage; (c) effect of contact area/porosity on current under constant voltage; (d) effect of less conductivity shell thickness t on $I-t$ curve. The shell is assumed as ZrO_2 with exponential increasing σ_{sample} vs T

As to the reasons behind the non-linear σ_{sample} vs T behavior, possibilities include increasing contact area/drop in porosity between particles and the breakdown of less conductive shell with increasing T . To explore these further, models with closely packed particles (see **Fig. 1(c and d)**) are built, which show large increase in contact area does *not* adequate explain the drastic increase in current during flash (**Fig. 1(c)**). Meanwhile, adding a less conductive shell (possibly oxide) with exponentially increasing σ with T that around the particles seems to lead to the flash, faster for thinner layer shell (**Fig. 1(d)**).

- Application of reactive flash sintering for synthesizing new, high entropy ceramics

Apart from carrying out systematic investigation of the flash sintering mechanism for highly conductive, high temperature ceramics, flash sintering, especially reactive flash sintering (RFS) has been explored for the synthesis and processing of new, high temperature ceramics, potentially with unique properties.

For example, **Fig. 2** shows XRD patterns for AlN-NbN-TaN-TiN-ZrN five binary nitrides powder mixture before and after RFS with a post flash steady-state hold of ~300 sec. After RFS, the nitride powder mixture transforms into a largely single-phase, rock salt structured high entropy nitride (HEN) solid solution with a nominal composition of $(\text{Al}_{0.17}\text{Nb}_{0.17}\text{Ta}_{0.17}\text{Ti}_{0.32}\text{Zr}_{0.17})\text{N}$.

Examination by advanced characterization tools such as HAADF STEM and energy dispersive spectroscopy (EDS) elemental mapping confirms the crystal structure as well as the uniformity in elemental distribution, at least down to sub-micron scale (see **Fig. 3**). The formation process of the HEN phase *during* RFS was also studied in real time using *in situ* synchrotron XRD, as shown in **Fig.**

4(a). Starting from a mixture of five individual binary nitrides, the formation of the solid solution is largely complete right after the flash (at around ~55 sec), and the solid solution phase can be preserved after the system cool down to room temperature, indicating the thermodynamic stability of the newly formed HEN phase.

In addition, as shown in **Fig. 4(b)**, the high-pressure behavior and properties for the synthesized HEN powders are also studied in a diamond anvil cell (DAC) at room temperature. HEN with nominal composition of $(\text{Al}_{0.17}\text{Nb}_{0.17}\text{Ta}_{0.17}\text{Ti}_{0.32}\text{Zr}_{0.17})\text{N}$ maintains a stable NaCl structure up to 35.6 GPa, without showing phase separation or other phase transition, indicating the stability of the HEN material, and the obtained bulk modulus is 285 GPa, close to constitute binary nitrides (see Figure) as well as the ROM estimate

Future Plans

Future planned work for this project include: (i) characterization of the flash sintering behavior for the another highly conductive HTC material of ZrB_2 to understand the similarity and difference between different types of HTC materials; (ii) simulation and material electrical property and microstructure characterizations to understand the effects of materials intrinsic conductivity, powder packing/porosity/particle contact area, surface (oxide or other) shells, thermal insulation as well as other factors on the flash sintering behaviors for these HTC materials.

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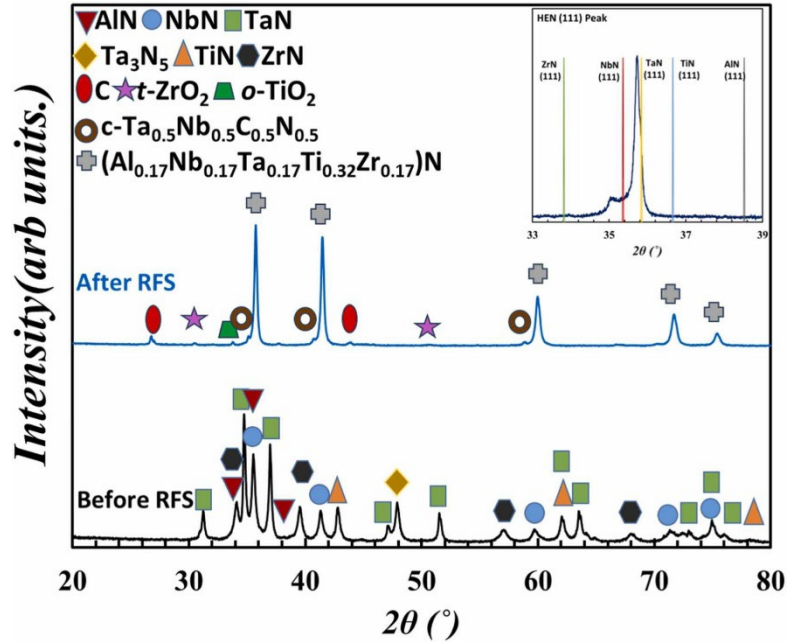


Fig. 2 XRD patterns of the AlN-NbN-TaN-TiN-ZrN powder mixture before and after reactive flash sintering (RFS). The insert is zoomed-in section showing the (111) diffraction peak, as well as the expected positions for the (111) peak of pure c-AlN, c-NbN, c-TaN, c-TiN and c-ZrN. From Das et al. *J European Ceram Soc* (2025)

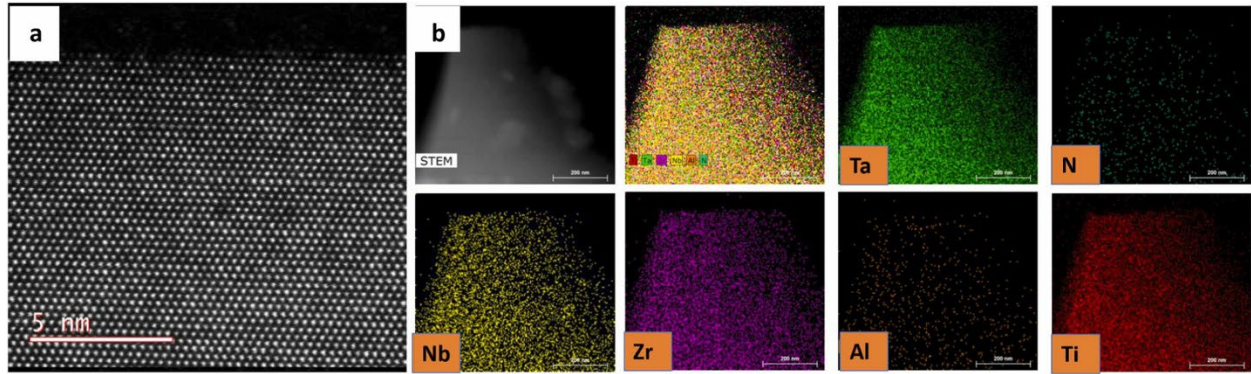


Fig. 3 High angle, annular dark-field scanning transmission electron microscopy (HAADF STEM) image (a) and EDS elemental mapping (b) of the reactive flash sintered $(\text{Al}_{0.17}\text{Nb}_{0.17}\text{Ta}_{0.17}\text{Ti}_{0.32}\text{Zr}_{0.17})\text{N}$ HEN sample (after grinding into powder), confirming the rock salt structure and showing relatively uniform solid solution formation down to at least sub-micron scale. From *Das et al. J European Ceram Soc (2025)*

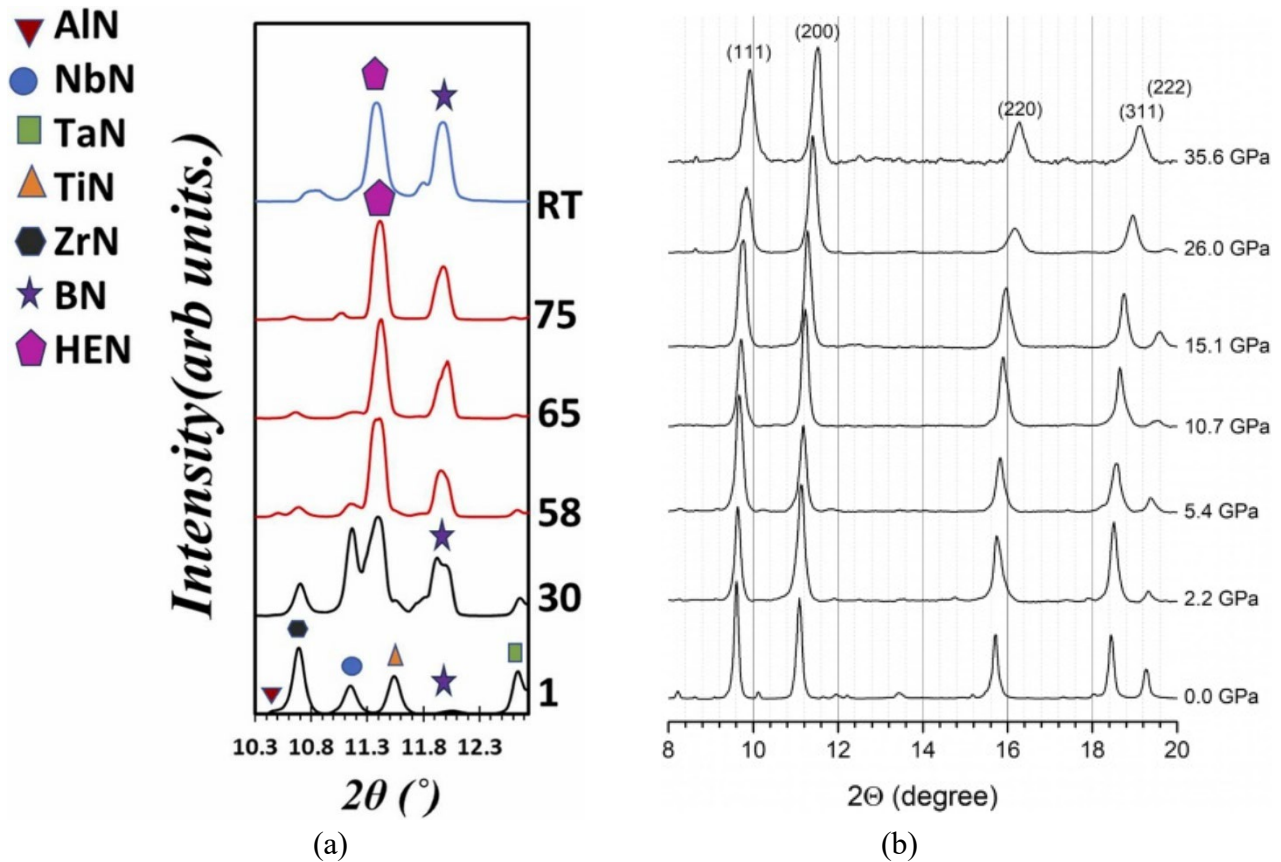


Fig. 4 (a) Selected integrated 1D *in situ* synchrotron (wavelength of 0.424590 Å) XRD patterns during RFS focusing on the (200) peaks for the binary nitrides as well as of the HEN targeting $(\text{Al}_{0.17}\text{Nb}_{0.17}\text{Ta}_{0.17}\text{Ti}_{0.32}\text{Zr}_{0.17})\text{N}$. The numbers on the right show time in seconds after the beginning of the RFS experiment. (b) Selected powder *in situ* synchrotron ($\lambda=0.424590\text{\AA}$) XRD patterns of $(\text{Al}_{0.17}\text{Nb}_{0.17}\text{Ta}_{0.17}\text{Ti}_{0.32}\text{Zr}_{0.17})\text{N}$ HEN collected at different pressures in a diamond anvil cell at room temperature (RT) From *Das et al. J European Ceram Soc (2025)*

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Toward Predictive PINN Models of Gas Hydrate Kinetics in Microfluidic Systems

(US DOE BES Award# DE-SC0022162 and DE-SC-0022161).

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Keywords: Gas hydrates, Physics-Informed Neural Networks (PINNs), Methane hydrate kinetics, Micro/nanofluidics, Crystallization modeling

Research Scope

Gas hydrates, particularly methane hydrates, play a dual role as a potential energy resource and a climate risk factor [1]. Accurate modeling of hydrate formation and dissociation under confined conditions is essential but remains computationally intensive and limited by data scarcity. In this work, we develop Physics-Informed Neural Networks (PINNs) to model methane hydrate kinetics in open microchannel systems using experimental data from thermoelectrically-cooled microreactors [2]. Our PINN framework incorporates heat transfer and crystallization kinetics equations, achieving high predictive accuracy ($R^2 = 0.9970$) and outperforming traditional Artificial Neural Networks (ANNs). Building on this success, we aim to extend the model to nanoscale systems using Anodic Aluminum Oxide (AAO) wafers, and eventually to CO₂ hydrate formation under similar conditions. This scalable PINN-based approach bridges data and physics, offering a powerful tool for hydrate research in energy and environmental applications.

Recent Progress

Our recent efforts have focused on developing a PINN framework to model methane hydrate formation and dissociation in microreactor systems. Using high-resolution experimental data from thermoelectrically-cooled microchannels, we incorporated physical constraints—derived from both conductive heat transfer and mixed mass-transfer-crystallization kinetics—directly into the learning process. This allowed the network to remain grounded in the underlying physics while maintaining high accuracy, even with limited data.

We systematically benchmarked the performance of our PINN models against conventional ANNs. While the ANN showed moderate predictive power ($R^2 = 0.68$; Figure 1) in predicting

methane hydrate propagation distances, the PINN incorporating the heat transfer equation achieved near-perfect alignment with experimental observations ($R^2 = 0.9970$; Figure 2).

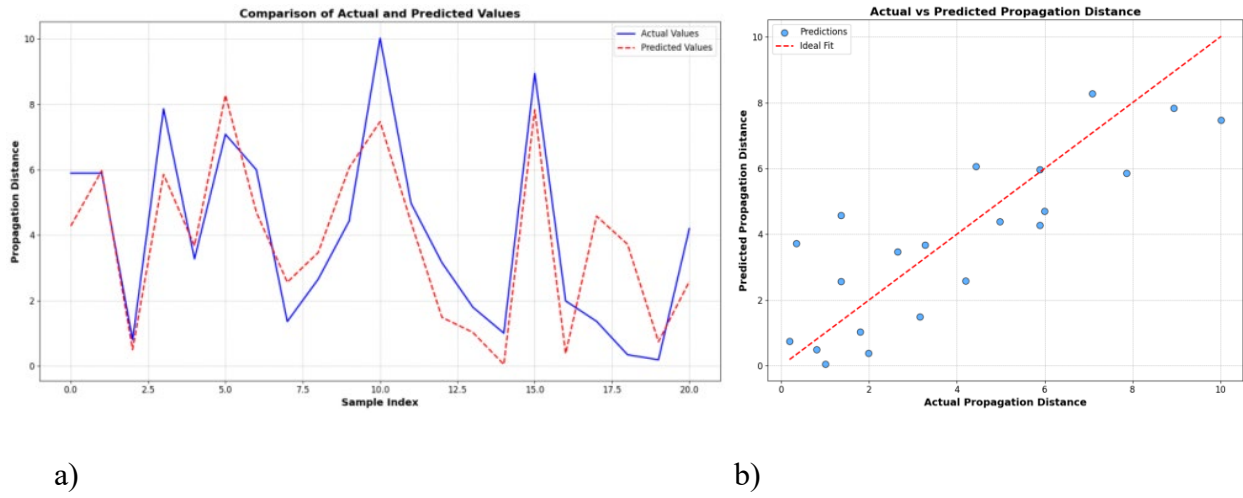


Figure 1: Comparison of ANN models. a) Time series plot showing predicted vs. actual propagation distances (μm) over the test dataset. b) Scatter plot of predicted vs. actual propagation distances with perfect prediction line (dashed).

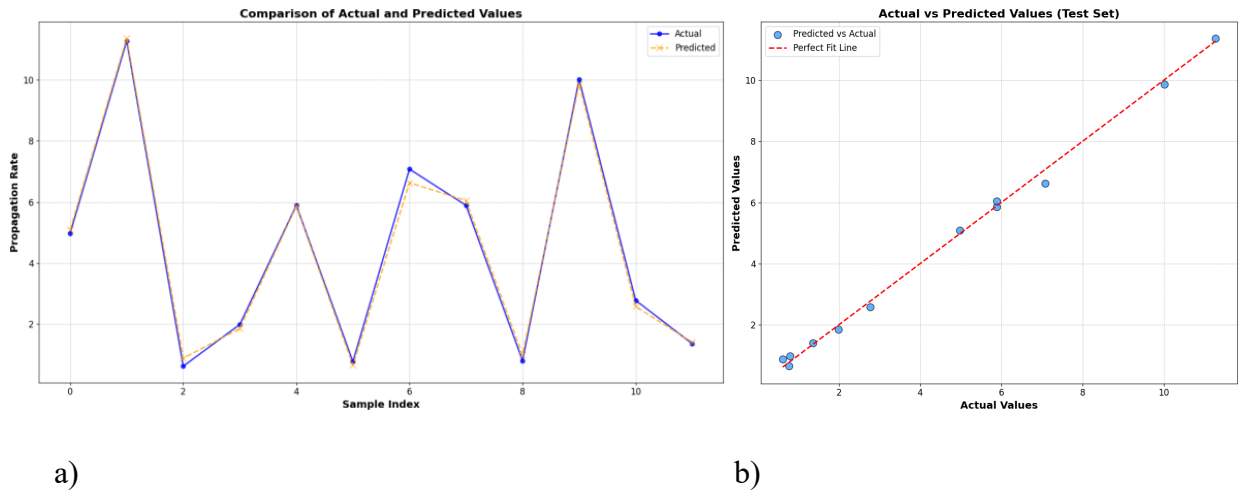


Figure 2. PINN model performance using heat transfer rate equation for methane hydrate formation. a) Time series comparison of predicted and actual propagation distances over the test dataset. b) Scatter plot of predicted vs. actual propagation distances (μm) showing near-perfect correlation ($R^2 = 0.9970$).

Additional models using crystallization kinetics alone, or in combination with heat transfer physics, also demonstrated excellent agreement with data ($R^2 \approx 0.9930$ – 0.9935), underscoring the versatility and robustness of the framework (Figure 3).

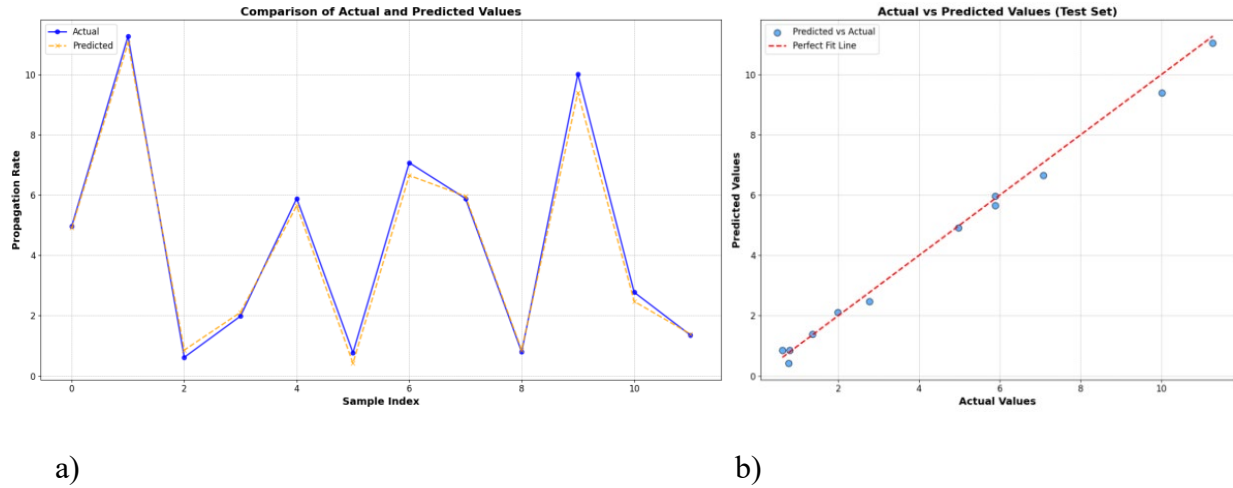


Figure 3. PINN model performance combining both heat transfer and mass-transfer–crystallization kinetics equations. a) Time series comparison of model predictions against experimental data. b) Scatter plot showing predicted vs. actual propagation distances (μm) with high correlation ($R^2 = 0.9935$).

This strategy was further extended to capture the dissociation behavior of hydrate films, with PINNs outperforming ANNs by a wide margin in predicting dissociation ratios ($R^2 = 0.99$ vs. 0.81 ; Figure 4 vs. Figure 5).

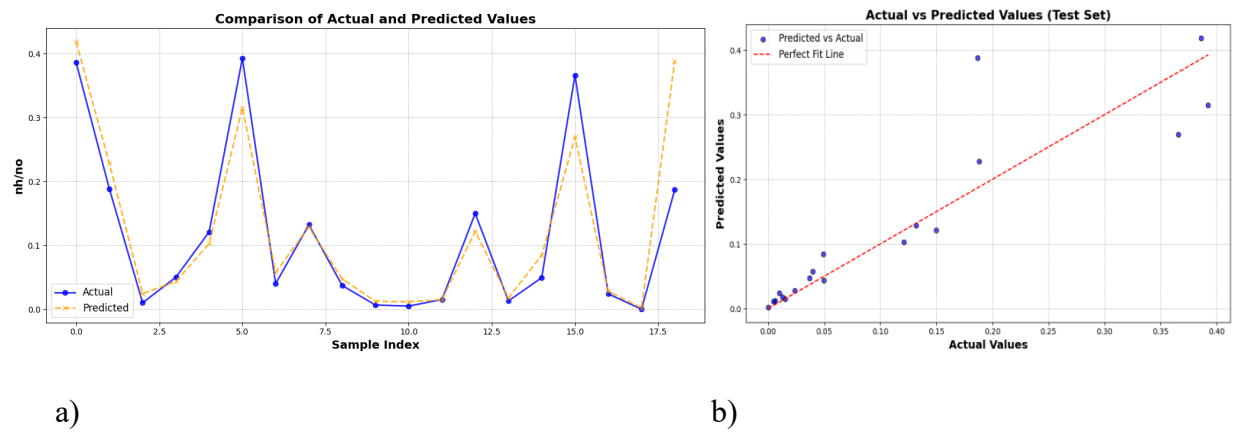


Figure 4. ANN model performance for methane hydrate dissociation kinetics. a) Scatter plot of predicted vs. actual dissociation ratios with correlation analysis ($R^2 = 0.81$). b) Time series plot showing predicted vs. actual dissociation ratios (n_d/n_0) over the test dataset.

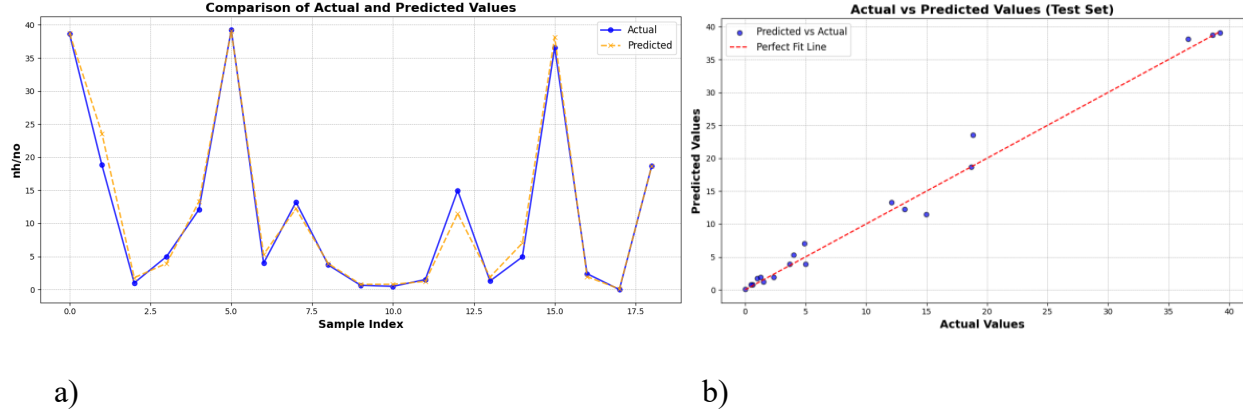


Figure 5. PINN model performance for methane hydrate dissociation incorporating kinetic constraints. a) Time series comparison demonstrating superior predictive accuracy of the physics-informed approach. b) Scatter plot of predicted vs. actual dissociation ratios showing excellent correlation ($R^2 = 0.99$).

Importantly, our PINN models adapt well to variations in film thickness, pressure, and sub-cooling, capturing transitions between kinetic- and heat-transfer-limited regimes. These findings validate the model's ability to simulate hydrate behavior across different physical regimes using interpretable, physics-consistent outputs. This foundation now enables us to expand the approach to more complex systems, including nanoscale hydrate formation within AAO templates—where confinement effects are dominant—and later to metal-catalyzed or semi-clathrate crystallization systems, where chemical surface interactions may further alter the kinetics

Future Plans

The PINN model that we developed for the methane hydrate system in microscale open channels will be applied to the methane and CO₂ open-system in AAO nanopores to study the molecular dynamics and to develop a crystallization kinetics model for metal-catalyzed and semi-clathrate catalyzed crystallization, based on the obtained experimental data. This next phase will allow us to explore hydrate behavior under nanoscale confinement, including the effects of catalyst type and pore geometry on nucleation and growth mechanisms. By combining targeted experiments with physics-informed machine learning, we aim to build a generalizable framework for predicting gas hydrate formation across multiple scales and compositions, supporting future advances in gas storage, separation, and climate-related applications.

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Field-Tailoring Science and Technology for Novel Materials Synthesis

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Keywords: Magneto-Synthesis, Magnetic Field, Laser.

Research Scope

This project explores a new paradigm for materials synthesis through **Field-Tailoring Technology (FTT)** -- an innovative, patented platform that couples a laser molten/floating zone furnace (up to 2200 C) with a superconducting magnet (up to 5T) (**Fig. 1**). The work is organized around two integrated thrusts:

1. **Development of FTT** for the synthesis of quantum materials that are inaccessible using conventional techniques.
2. **Fundamental studies** to understand the key physical mechanisms that underpin magneto-synthesis.

Recent Progress

While magneto-synthesis remains an emerging field, our approach demonstrates how even modest magnetic fields can significantly impact phase formation and crystal growth by exploiting the combined influence of:

- Lorentz force,
- Magnetic-field-induced modification of Gibbs free energy, and
- Strong spin-orbit interaction (SOI) coupled with magnetoelastic effects.

In a recent proof-of-concept study, we have observed dramatic field-induced changes in crystal structure and ground state, even under low magnetic fields. These findings, supported by our earlier experiments [1, 2], highlight the transformative potential of FTT in stabilizing novel quantum phases that are otherwise unreachable.

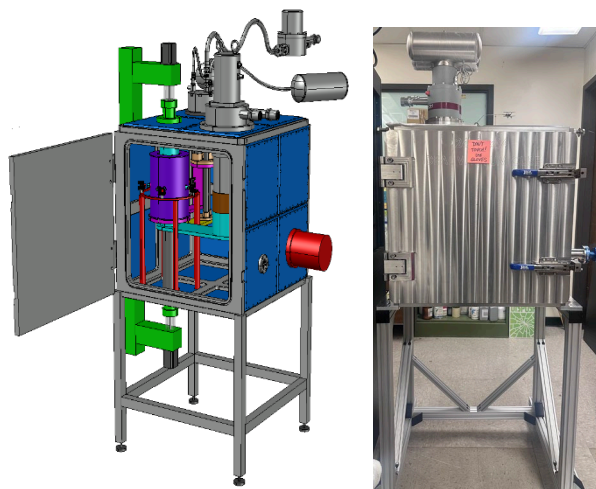


Fig.1. Left: FTT design. Right: FTT under development.

Future Plans

We aim to complete construction and commissioning of the FTT system by the end of 2025. Following optimization, we will initiate synthesis of targeted single crystals and investigate field-dependent pathways for materials design. These efforts will deepen our understanding of magneto-synthesis and expand the boundaries of accessible quantum/functional materials.

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Lattice engineered single crystal architecture in glass: early stages of formation and physical properties

PI: Himanshu Jain. Co-PI: Volkmar Dierolf. Lehigh University, Bethlehem, PA USA

Keywords: Radiation processing; lattice engineering; crystal growth atomistics; glass-crystal metastructures; surface probe microscopy

Research Scope

At the previous PIs' meeting, we reported a new type of laser-fabricated lattice-engineered single crystal-in-glass metamaterial fabricated by controlled processing of glass by suitable laser or electron beam. The lattice of such single crystal architecture in glass rotates in space, yielding a macroperiodic lattice with a periodicity of 10s of μm . The structural characteristics of the curved lattice were reported previously. These novel metamaterials dubbed as rotating lattice single (RLS) crystals have been fabricated in Sb_2S_3 glass, which is an emerging phase change material, but the basic concept of curved lattices has been demonstrated in several other compositions. Their characteristics originate from the solid-to-solid crystallization of glass, which can be engineered by varying laser parameters.

Sb_2S_3 is an emerging phase-change material whose optical and electrical characteristics offer a path forward for energy-efficient computation as memory, or computation elements as well as standalone platforms for integrated (optical/electrical) circuits. In addition to the glass $\leftrightarrow$ crystal two-state degree of freedom, the properties of an RLS crystal embedded in a glassy substrate could be tuned further to add new functionalities to a phase change element or integrated optical circuit. To establish the processing $\rightarrow$ structure $\rightarrow$ properties paradigm for macroperiodic RLS crystal architecture in glass, we have expanded our focus to characterize their functional electro-mechanical and electrochemical properties. Since their short dimensions and feature size are on μm scale, the measurements needed to be made with submicron or better resolution. Accordingly, we have determined local dielectric properties of RLS crystal lines using atomic force microscopy (AFM), validating their potential as an engineered metamaterial. We then sought to establish a correlation between local electrical characteristics determined by AFM-based techniques and macroscopic properties determined by impedance spectroscopy. We use this new methodology to show that electrochemical behavior can also be tuned into a phase change material with a curved lattice.

To further elaborate the fundamental processing science, we have continued atomistic simulations of seeded crystal growth (SCG) in glass. Specifically, we sought to develop an understanding of the very unexpected rotation of the crystal seed experimentally observed in situ in the very early stages of crystallization of glass. As reported at the last PIs meeting, X-ray or electron beam was used to induce crystallization as well as characterize crystal orientation by diffraction. We continued with molecular dynamics simulations of such observations, using LAMMPS code, in pure LiNbO_3 and binary $\text{LiNbO}_3\text{-SiO}_2$ glasses for which suitable potentials were well established. In order to compare it with our experiments we also simulated seeded crystal growth in Sb_2Te_3 that is close to Sb_2S_3 glass in structure and properties. The findings from this study complement our understanding of the mode of crystal growth (particle attachment in groups) with the atomistic origins of crystal rotation during early stages of growth. Recognizing the effect of glass structure on crystal growth, we explored the possibility of interaction between two seeds with varying misorientation and separation. Findings from this study would help us understand the development of the microstructure of glass-ceramics as well as optimum conditions for single crystal growth in a glass.

Recent Progress

1. Physical properties of lattice-engineered laser-written macroperiodic dielectric structures (Jack Kaman)

As mentioned above, highly anisotropic properties of lattice-engineered phase change materials such as Sb_2S_3 could offer additional functionality when crystal orientation and macroperiodicity of lattice are considered as degrees of freedom. Here, for the first time, we show that lattice engineering can be used to control the functional properties of a laser crystallized. Macroperiodic rotating-lattice Sb_2S_3 single (RLS) crystals in Sb_2S_3 display periodic electrical properties such as dielectric constant and conductivity. We have probed the dielectric properties using scanning Microwave Impedance Microscopy (sMIM). Further, only for crystalline, but not glassy, Sb_2S_3 , a large bias applied to the scanning tip is able to reversibly modify the observed capacitance of the tip-sample junction.

This effect bears some resemblance to the behavior of other highly defective semiconductors, where it has been attributed to charge trapping and defect migration. The relaxation of this rewritable capacitance additionally has different kinetics along the rotation of an RLS crystal (figure 1b). These experiments show that lattice engineering can be used to modify functional properties, which can be exploited with appropriate processing.

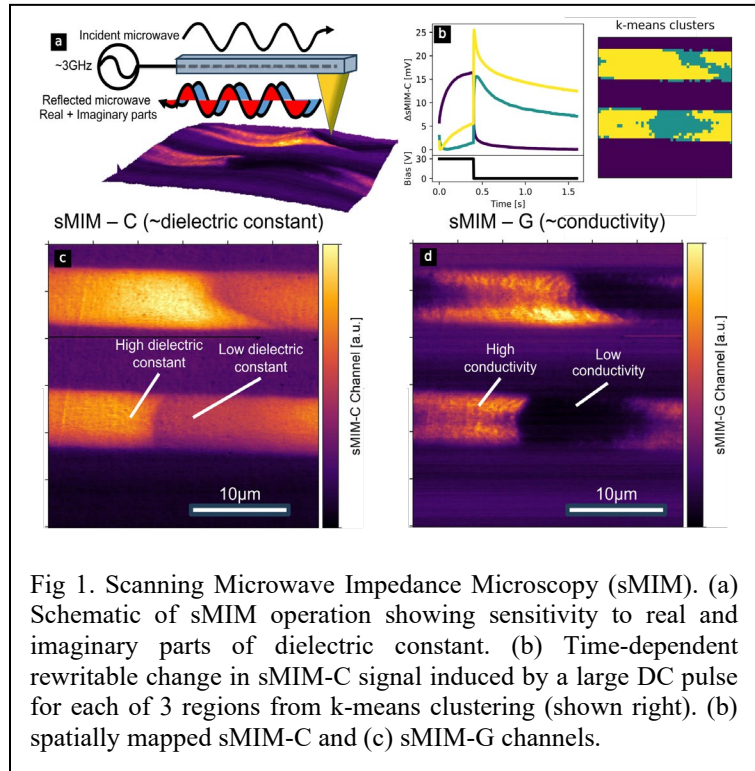


Fig 1. Scanning Microwave Impedance Microscopy (sMIM). (a) Schematic of sMIM operation showing sensitivity to real and imaginary parts of dielectric constant. (b) Time-dependent rewritable change in sMIM-C signal induced by a large DC pulse for each of 3 regions from k-means clustering (shown right). (c) spatially mapped sMIM-C and (d) sMIM-G channels.

2. Nanoscale electrochemical behavior of lattice-engineered Sb_2S_3 crystals (Jack Kaman)

Using a new method of analysis that bridges multiple macroscale and nanoscale techniques, we explored electrochemical/ionic transport phenomena in laser-crystallized macroperiodic Sb_2S_3 . Piezoresponse Force Microscopy (PFM), which is a scanning probe technique to measure the local piezoelectric effect with high spatial resolution, was used previously to study Sb_2S_3 [Varghese et. al. *Nano Lett.* 2012, 12, 2, 868–872]. We now show that the tip-sample electromechanical coupling in Sb_2S_3 originates from electrostatic attraction rather than the piezoelectric effect and corresponds

quite closely to the low-frequency electrical impedance. We show a relationship between local electrochemical behavior (AFM-IV, PFM) and traditional bulk electrochemical impedance measurements (impedance spectroscopy). Using this method of analysis, we reveal that the electrical response of crystalline Sb_2S_3 is dominated by diffusive capacitance and charge transport whereas glassy Sb_2S_3 is simply capacitive. Furthermore, the kinetics of interfacial charge motion changes as the lattice of a curved crystal rotates. This result serves to both demonstrate a new way to approach AFM-based electrochemical measurements and show an additional unexplored electrochemical aspect of phase change materials that could allow for new functionalities for phase change memory or computation devices.

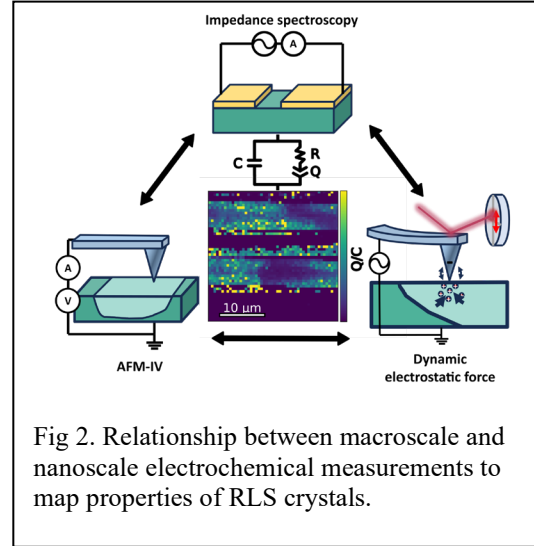


Fig 2. Relationship between macroscale and nanoscale electrochemical measurements to map properties of RLS crystals.

3. Atomistic description of seeded crystal growth in glass (Rajendra Thapa)

Molecular dynamics (MD) simulations were performed to model seeded crystal growth (SCG) in two different systems: LiNbO_3 and Sb_2Te_3 , glass. A crystal seed of 15 Å radius was embedded in respective glass of varying glassy structures as obtained by changing their thermal history. The sample was subjected to high temperature annealing, while maintaining NPT ensemble (simulating) at a temperature below the melting point, and the growth of the crystal was monitored. Early stages of the SCG were marked by the presence of a rotation of the seed, which ceased after the crystal became too large, as shown in Fig. 3. This rotation occurs mainly due to a torque on the crystal from the surrounding glass. It raises a fundamental question about the generally presumed isotropic, uniform nature of the glass. Our findings of seed rotation suggest that the glass cannot be considered as such in the crystal-glass interface region. However, as the crystal grows, these forces are not sufficient to provide enough torque to keep the crystal rotating. Fig. 3 shows the evolution of crystal rotation surrounded by glass of two different structures. A significant difference between the two curves indicates that the origin of seed rotation is in the glass structure outside the seed itself.

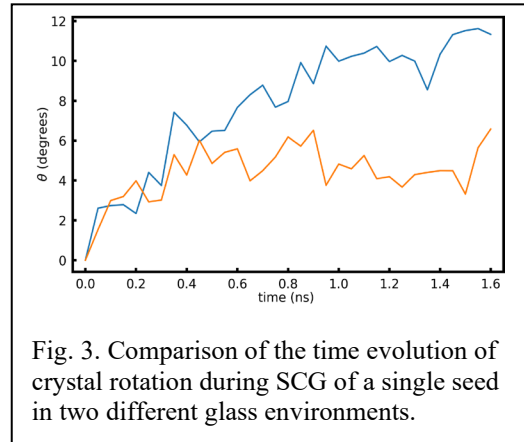


Fig. 3. Comparison of the time evolution of crystal rotation during SCG of a single seed in two different glass environments.

If surrounding glass can cause a seed to rotate, two neighboring seeds can also affect the growth of the other. To investigate this hypothesis, growth of two seeds of radius 15 Å inside a LiNbO_3 glass was modeled, which is a typical process in the glass ceramic industry. The system comprised about half a million atoms with varying seed separation (45 Å, 55 Å, 60 Å, 65 Å) and relative misorientation (0°, 10°, 30°, 60°). While the crystal growth rate does not show a trend with

respect to misorientation and separation, the relative alignment of two crystals was directly related to these variables, as shown in Fig. 4. Crystals grown from seeds sufficiently close (45 Å, 55 Å) and with low misorientations (0° , 10°) were found to become one single crystal. This finding is important because it shows the seeds rotating from an initially low misorientation (10°) into perfect orientation thereby facilitating single crystal growth akin to growth by particle attachment [De Yoreo *et al.*, *Science* **349**, aaa 6760 (2015). DOI: [10.1126/science.aaa6760](https://doi.org/10.1126/science.aaa6760)]. The

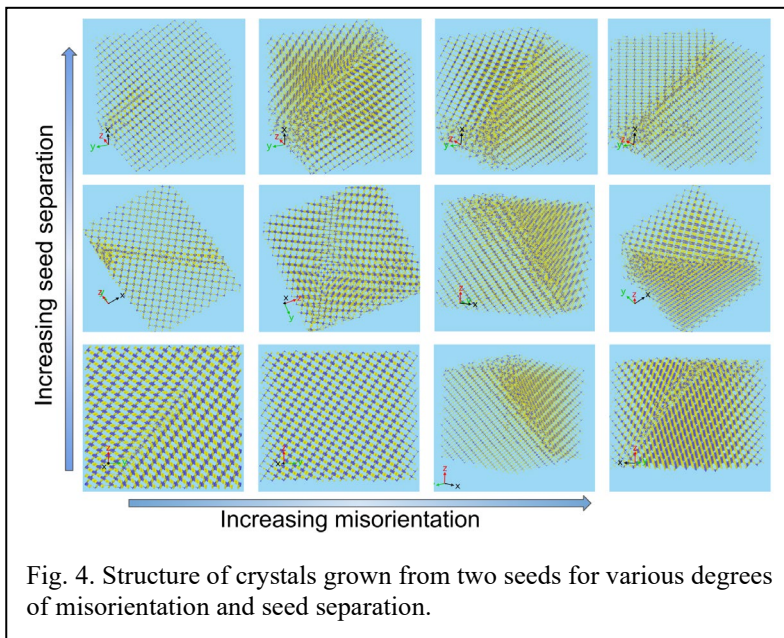


Fig. 4. Structure of crystals grown from two seeds for various degrees of misorientation and seed separation.

results suggest a strong interaction between two growing seeds. This interaction gets weaker when the seeds are too far (≥ 65 Å) when the final material becomes a polycrystal with a grain boundary.

Future Plans

To further the understanding of the mechanics of lattice curvature, crystallization of glass via solid-to-solid transformation, and potential applications of curved metamaterials, we ask the following question: What is the effect of confinement and lattice curvature on the ferroelectric response of a crystal? Dislocations and strain can strongly influence ferroelectric, flexoelectric, and electrical properties. Having shown strong electrical effects due to macroperiodic lattice rotation in Sb_2S_3 , next we propose to investigate local ferroelectric response, differentiating between the effects of lattice anisotropy and lattice curvature. With optical, electrical, and mechanical AFM techniques, ferroelectric polarization by PFM and changes in vibrational modes by tip-enhanced Raman Scattering will be probed with high spatial resolution. We also plan to study variations in these properties in the ongoing collaborations with Oak Ridge National Lab.

Having established that the growth of a crystal in glass is a highly interactive process involving surrounding glass and nearby seeds, next we aim to explore how the alignment of neighboring crystals can be improved by addressing the following questions: 1. What is the temperature dependence of the crystal alignment process? How similar or different is it from that of crystal growth rate and rotation observed during early stages of growth. The answer to this question will help design the protocol of crystallization of glass for a specific microstructure. 2. Cooling rates affect the structure, especially the openness (density) of the resulting glass, which would have an effect on rotation observed during early stages of crystal growth. Then, an important question is how do different cooling rates during glass formation influence the organization of crystal grains in the resulting glass-ceramic? 3. Often there is a preferred growth direction in crystals, which determines their resulting shape. So, a relevant question is: how does the shape of seeds affect their ability to rotate?

Publications 2024-2025

Full articles in archival journals

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Surface Structures Far from Equilibrium

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I. Program scope. As technologies rapidly evolve, materials with targeted properties become top priorities. This has generated a paradigm shift emphasized in the Synthesis and Transformative Manufacturing BRN reports: how on-demand modifications in atomic structure convert to pre-designed properties. The FWP goal is to build multi-component atomic scale structures with unusual precision, so structure-properties expectations are validated. The success hinges on placing atoms at specific locations and on tuning atomistic processes (diffusion, nucleation). Two projects are pursued: (i) intercalated metals under graphene on SiC (Gr/SiC) to synthesize 2-d quantum materials and control nucleation and growth on top by tuning the kinetic barriers with metals below[1-3]. Sub-surface metals can also order forming Moiré patterns, which is another way to modify the band structure, based on chemical bonding and not mechanical stacking[4-5]. (ii) to enhance the yield of on-surface chemical reactions and increase the length of Nanographenes (NGs) by synthesizing them on intercalated Gr/SiC or on metal oxides[6-7]. NG growth initially involves the deposition of precursors followed by their conversion to sp^2 -bonded nanomaterials. Both types of substrates are weakly coupled to NG so the intrinsic NG properties remain intact. However understanding growth on weakly interacting substrates is challenging and limited. The kinetic barriers are inherently low and require fine balance between competing atomistic processes. In both projects characterization is performed of the morphology with surface diffraction, STM, of spectroscopy with STS, of structure stability with DFT, within the FWP and in collaboration using ARPES.

II. Recent Progress.

Pb intercalated phases under Gr/SiC Quantitative growth studies using surface diffraction

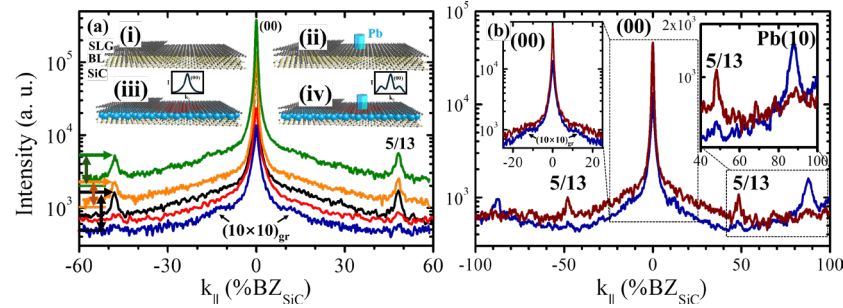


Fig. 1. (a) Five annealing profiles starting with clean graphene (black) until $(10 \times 10)_{gr}$ is observed (blue) when islands nucleate on top. (b) 1-d profiles that show both $(10 \times 10)_{gr}$ and Pb(10) appear at LN2 (blue) and become extinct at 250 °C (mauveine).

(SPA-LEED) and STM were carried out to determine the intercalation phases for Pb under Gr/SiC [9-13]. The transfer of atoms below is determined by monitoring the difference of a given spot intensity from its clean value, as a function of growth parameters (coverage, annealing temperature and time). The intercalated Pb can

order and a low intensity $(10 \times 10)_{gr}$ Moiré phase is observed, which shows that intercalation is promising as a new way to study Moiré physics. The growth of this phase is still an open question in the literature, so we identify protocols for the Moiré spot to grow reversibly. The spot is seen during low temperature deposition, shown in fig.1(a) (blue curve), when Pb(111) islands also grow on top, which indicates preferred Pb island nucleation on top of the $(10 \times 10)_{gr}$ domains[13]. Fig.1(b) shows the extinction of the $(10 \times 10)_{gr}$ and Pb(10) spots at 250 °C confirming their correlation. This most likely is a manifestation of “remote” epitaxy where the substrate and not graphene determines the growth of a metal deposited on top[14]. Besides the $(10 \times 10)_{gr}$ phase, a stripe phase is found of linear chains ordered 30° from the $(10 \times 10)_{gr}$ [15]. We have performed a joint theoretical and

experimental study to understand the coexistence of the two phases. If one half has compressive and the other half tensile strain, this results in the stripe phase with 2.3nm period. Sub-surface Pb occupies approximately SiC sites, which implies a compressed layer, since the SiC lattice constant is 12% smaller than the Pb(111) lattice constant.

Controlling the buried pristine graphene–SiC interface by the local electric field: The

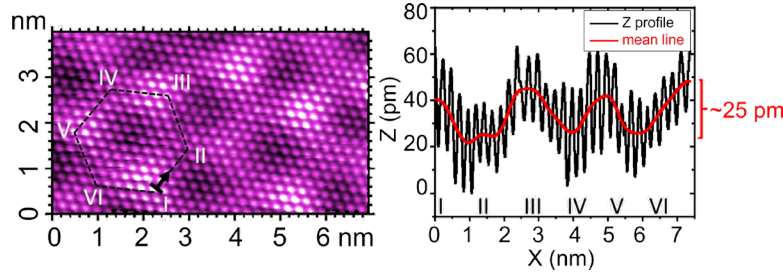


Fig. 2. (a) Image of pristine graphene showing the protrusions as the bright areas (b) 1-d profile around the black hexagon marking the protrusion height modulating the graphene periodicity.

quality of the graphene–SiC interface is important for performing controlled experiments like metal intercalation and NG growth. One poorly understood feature of graphene is the presence of nano-protrusions on top which are widely seen in the literature, but with their origin still unknown[8]. They are shown in fig.2 as the bright areas overlaid

with graphene, the smaller lattice of period 0.245nm on top. Because of the current interest to study targeted graphene-based heterostructures, it is important to understand these inhomogeneities. We show that these nano-protrusions originate from the broken sp^3 bonds at the buffer layer -SiC interface-due to charge redistribution. We show that these nano-protrusions can be manipulated, i.e, created or removed, by the electric field from the STM tip. The nano-protrusion density depends on the sign and magnitude of the applied electric field. As a result, their spatial distribution can be controlled by selecting where the electric field is applied.

SNOM studies of pristine Gr/SiC We report on a nano-infrared (IR) imaging and spectroscopy study of pristine Gr/SiC by using scanning near-field optical microscopy (SNOM)[16]. We revealed in real space micron-sized domains with distinct IR contrast. By analyzing both the nano-IR and atomic force microscopy (AFM) data, we concluded that the distinct IR contrasts are associated with single-layer graphene (SLG), bilayer graphene (BLG), and higher-doped BLG. With nano-IR spectroscopy, we found that graphene can screen the SiC phonon resonance. Mapping the screening across the sample offers a novel way to determine the distribution of graphene doping, since screening is stronger at regions with higher doping.

III.Future work

Controlling metal nucleation and growth on intercalated graphene Gr/SiC. Based on the Pb work completed and promising preliminary data, we plan to extend the range of questions about the system. Because atomistic barriers controlling the growth depend on the intercalated metal[17], we will study growth on top of intercalated Gr/SiC as a new way to tune nucleation. Pb growth on intercalated Gr/SiC shows that nucleation differs dramatically from growth on pristine Gr/SiC. This represents a single atomic layer version of “remote epitaxy” [14] which is a recent technique to grow homoepitaxial copies of films by using substrates draped with graphene. In addition, unusually strong Quantum Size Effects (QSE) and “magic” height Pb islands [18] of higher thermal stability are observed after Pb growth on Pb intercalated Gr/SiC. Intercalation poses unusual challenges for synthesis, i.e., to transfer the atoms below, to control their sub-surface location, to determine the coverage of the intercalated phase and even to realize long range order. This “under cover” chemistry is one of the most promising methods to grow 2-d materials based on chemical bonding and not simply mechanical stacking. Heterostructures based on intercalation

of graphene are of interest to maximize electronic effects (i.e., SO coupling [19], QSE [18], magnetism [20], ordered sub-phases [4]). As the preliminary Pb data show, the intercalated vs pristine areas become spatially patterned templates to control the energetic barriers experienced by deposited adatoms or precursor molecules to affect their nucleation and growth. This control becomes a new “knob” to engineer mass transport as emphasized in Transformative Manufacturing PRD *“Achieve precise, scalable synthesis and processing of atomic-scale building blocks for components and systems”*

Controlling nanographene (NG) growth on intercalated Gr/SiC and oxides The second FWP goal is to enhance the yield of on-surface chemical reactions and increase the length of NGs [21]. Since realizing the rich electronic phases of NGs requires decoupling from the substrate, we will perform synthesis on intercalated Gr/SiC and metal oxide surfaces, which are weakly interacting substrates. Graphene intercalated by metals [1-3] and transition metal oxide surfaces [6,7] were shown to be attractive substrates to tune growth. On-surface chemistry relies on organic molecular precursors with functionality embedded in their chemical structure, which results in NGs with exact atomic-scale compositions [6]. Understanding growth on weakly interacting substrates is a more general challenge, even for simpler systems grown by atom deposition, than by molecular precursors [21]. Their weakly interacting nature implies that all the kinetic barriers (adsorption, diffusion, atom attachment, etc.) are lower, by one order of magnitude, than the corresponding barriers on metals. The NG growth requires enhancing the rate of chemical reactions while suppressing the desorption of precursors. The growth is controlled by atomistic barriers, i.e., diffusion, preorganization, and activation of functional groups within the assembled structures. We will tune these barriers by choosing different intercalant metals. By varying doping levels and carrier type (whether n-doped or p-doped) we will selectively control the corresponding barriers to promote diffusion and conversion of the assembled structures to sp^2 bonded networks. The UHV chamber is already modified with the installment of graphene nanoribbons (GNRs) organic molecular precursors. The initial growth experiments on Au(111), a benchmark surface, have verified the formation of oligomeric chains and their conversion to sp^2 -bonded GNRs. We will deposit the same molecules on Gr/SiC to test their self-assembly and sp^2 conversion to GNRs on this new class of weakly interacting substrates for the first time.

Collective, non-random walk diffusion of the compressed intercalated Pb layer under Gr/SiC In practically all systems studied in epitaxial growth mass transport is by classical random walk diffusion. Discovering collective diffusion where atom motion is through correlated jumps of adatoms is rare and leads to faster $\sim t$ instead of $t^{1/2}$ time dependence. There is evidence that such unusual diffusion is present in the intercalated Pb layer under Gr/SiC. This is based on: the much faster intercalation/deintercalation kinetics for the large Pb atom at relatively low temperatures ($\sim 250^\circ\text{C}$); the increasing speed of the kinetics with increasing Pb sub-surface coverage; and real time LEEM studies in the literature [13]. These results indicate similarities to analogous kinetic effects observed in Pb/Si(111) in prior FWP work [22-24]. The collective motion in Pb/Si(111) was a result of the compressed wetting layer. Since the proposed models of the $(10\times 10)_{\text{gr}}$ Pb phase based on the SiC lattice have twice the Pb/Si(111) compression, it shows that the unusual type of diffusion is a more general phenomenon and present in intercalated metals.

z-V spectroscopy to determine buried interfaces under epitaxial graphene. The FWP is in close collaboration with the DOE Early Career Research Program (ECRP) project of M. Kolmer. The goals of the project are to study electronic phases and transport in nanostructures, especially connecting results from local to mesoscale probes. Using pristine and intercalated Gr/SiC are some of the proposed substrates, because of the extensive experience of the FWP in their predictive

growth under UHV. These capabilities complement the advanced measurements, using in situ multi-probe STM probe transport and high-resolution spectroscopy under the ECPR project. The FWP prepared and characterized in detail uniform pristine and intercalated Gr/SiC samples. Next we collected z -V and dI/dV spectra as a function of tip-sample voltage at constant current. Using the standing waves forming in the tip-sample gap it is possible to probe the electronic properties of the sample and the buried interfaces from such spectra. For tunneling into the sample and by extending the voltage in the field emission regime, we can probe the unoccupied states of the sample which can be mapped only by inverse photoemission. It will be a general method to map the buried interface beyond topographic STM capabilities, which are sensitive only to the top layer.

Moiré physics Since sub-surface metals can order and form supercells between metal and graphene, we plan to study their growth as a new platform for Moiré physics. Moiré systems are currently of high interest because they introduce a longer length scale in the graphene Hamiltonian, which results in replica Dirac cones generated at the smaller mini-BZs (Brillouin Zones) [4,5]. As the previous discussion showed sub-surface Pb has a relatively large $(10 \times 10)_{\text{gr}}$ supercell that required careful studies to identify the growth conditions. Optimizing the synthesis of the sub-surface Moiré lattices by extending their size, eliminating antiphase boundaries and defects will enable the placing of stronger replicas at pre-selected wavevectors in reciprocal space. After the Pb studies we plan to look for Moiré intercalated phases in other currently promising metals (Bi, In, Sn).

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INTEGRATED SYNTHESIS AND SIMULATION OF ZEOLITES: Engineering Order and Rapid Crystallization Via 3rd Route to Zeolite Formation

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Keywords: Zeolites, Crystallization, Raman, NMR, Fluoride, DFT, Machine Learning.

Research Scope. Zeolites represent a cornerstone of today's energy industry as the most used petrochemical catalyst in the world. However, the rational synthesis of zeolites with targeted framework structures, compositions, and defect properties, remains a grand challenge because of the complex interplay among synthesis parameters, and our poor understanding of zeolite crystallization mechanisms. Our research is shedding new and much needed light on how zeolites form in solution – opening the door to innovations that support new catalysis and separation technologies. Our research tightly integrates synthesis, spectroscopy, Monte Carlo simulations, and DFT calculation, and has provided unprecedented discoveries regarding the molecular building blocks that assemble to yield all-silica LTA (Si-LTA) zeolite. Below we highlight our research breakthroughs over the last two years of funding from Synthesis & Processing Science.

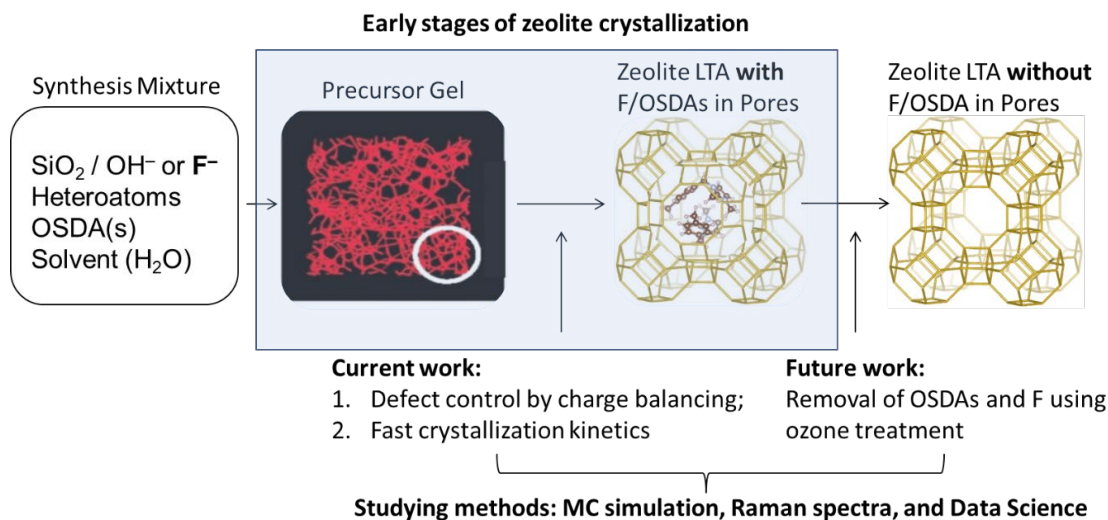


Figure 1. Project Scope – understanding early stages of zeolite crystallization for improved control over kinetics and ordering using our innovative 3rd route synthesis methods.

Recent Progress. Our work in the previous two years has yielded the following discoveries:

- **Reduced Synthesis Energy:** We have discovered how to efficiently calcine as-made zeolites using ozone instead of air at much lower temperatures, yielding defect-free zeolites through a cage-door opening/closing mechanism revealed by DFT.
- **Reduced Synthesis Time:** As-made zeolites have been rapidly produced with low defect densities using NH₄F as the mineralizing & charge-balancing agent, eliminating the use of HF and taking an order-of-magnitude less synthesis time, as well as reduced cost and energy.

- **Reduced Entropy:** Machine Learning analyses of Monte Carlo trajectories have shown that using a secondary OSDA speeds up zeolite formation via “pre-reduction” of silica network entropy, lowering free energy barriers to crystallization. This work suggests using controlled (not autogenous) pressures as a new parameter to speed up zeolite fabrication.
- **Building Blocks of Zeolite Formation:** Using three characterization methods assigned by Monte-Carlo-informed DFT, for the first time, we observed disorder-to-order transitions of each of the subunits in LTA: D4R by ^{19}F NMR, α -cage by Raman, and β -cage by ^{13}C NMR.
- **Eliminating Fluoride:** Using pre-formed D4R silica starting materials, we successfully carried out the first fluoride-free synthesis of high $\text{Si}/\text{Al} = 7.5$ zeolite LTA, yielding a new material that is promising for catalysis and that can be easily scaled up at low cost.

Here we detail key aspects of our DOE-supported research over the last two years.

1. Removing Fluoride from Double Four-Membered Rings Yielding Defect-Free Zeolites under Mild Conditions Using Ozone [T Wang, *et al.*, Chemistry of Materials 36, 870-880 (2024) [DOI](#)]

- *Objective:* Develop a milder post-synthetic process to remove synthetic additives such as OSDAs and fluoride ions from as-made zeolites. The typical approach (“calcining”) involves flowing air at 550 °C for 24 h. This is energy intensive and can produce defects.
- *Innovation:* The use of ozone at much lower temperature (**175 °C**), applying a battery of techniques including ^{29}Si NMR, Raman spectroscopy, and *ab initio* molecular dynamics to gain molecular-level understanding of ozone-treated zeolites.
- *Key Findings:* ^{29}Si NMR is silent in the Q₃ region indicating absence of defects after ozone treatment. *Ab initio* molecular dynamics (MD) predicts D4R door opening / closing mechanism for removing fluoride, and barriers consistent with a low-temperature process.
- *Significance:* Low-temperature ozone processing of zeolites (*i*) can save substantial energy considering the massive quantities of zeolites produced annually, and (*ii*) is subtle enough to produce defect-free structures.

2. Data Science Shows that Entropy Correlates with Accelerated Zeolite Crystallization in Monte Carlo Simulations [S. Hong, *et al.*, J. Chem. Phys. 161, 234708 (2024) [DOI](#)].

- *Objective:* Apply Machine Learning (ML) to analyze our previously published Monte Carlo (MC) simulations of zeolite formation, finding faster crystallization with 2 OSDAs that match the small and large LTA cage sizes, as opposed to only 1 OSDA. These predictions were confirmed by experiments but the origin of the speed-up remained unclear.
- *Innovation:* To reveal the key structural distinctions between 1OSDA and 2OSDA Monte Carlo trajectories, we applied ML to sort 1OSDA / 2OSDA structures and analyzed statistical and structural properties of the sorting algorithm. We applied a blend of supervised and unsupervised ML to graphically display the complex findings.
- *Key Findings:* We used 2-body and 3-body descriptors to encode structure and found that 2-body information is sufficient to provide an excellent segregation of 1OSDA / 2OSDA structures (AUC = 0.95, anything above 0.9 is a strong sort). We also found that fast (2OSDA)

trajectories exhibit less entropy than slow (1OSDA) ones. We then found that the 2-body entropy difference during crystal formation quantitatively accounts for the predicted speedup.

- *Significance:* Adding a second OSDA to the Monte Carlo has the effect of increasing pressure, suggesting that controlling pressure during zeolite synthesis (i.e., going away from autogenous pressure) can speed up crystal formation. Furthermore, our use of AI (real-space representations of supervised sorting) to unravel complex simulations opens the door to new understanding of computer simulations.

3. Rapid Crystallization of Zeolites with Controllable Defects: Disentangling Fluoride Concentration and pH Using NH₄F [M Shah, *et al.*, Crystal Growth & Design 25, 1821-1832 (2025) [DOI](#)].

- *Objective:* Zeolite synthesis is typically conducted under basic conditions or in neutral fluoride media using HF. However, the HF method often requires significantly longer crystallization times and involves the handling of dangerous HF. We sought syntheses that combine the benefits of OH and F, leading to fast crystallization and controllable defects.
- *Innovation:* We disentangled the roles of mineralizing agent and charge-balancing agent using ammonium fluoride (NH₄F) as an alternative to HF. Using NH₄F significantly reduced crystallization times for both pure-silica aluminum containing zeolites. Further, increasing NH₄F concentration in the synthesis also decreases defect densities of siliceous zeolites.
- *Key Findings:* Using NH₄F reduced crystallization times as follows: **6-fold** for Si-LTA (24 h → 4 h), **2.7-fold** for Al-LTA (96 h → 36 h), **40-fold** for ZSM-5 (240 h → 6 h), and **8-fold** for Si-*BEA (24 h → 3 h. Elemental analysis and ²⁹Si NMR show that syntheses with higher NH₄F concentrations yield zeolites with fewer defects.
- *Significance:* The major challenges in F-mediated zeolite synthesis are the long crystallization times and caustic HF. NH₄F is a safer reactant and it speeds up crystallization by as much as 40-fold, while allowing control of defect densities. Combining basic and F-media could produce faster zeolite production and improved control over structural properties.

4. Spectroscopy and Simulations Reveal Evolution of Specific Building Blocks During Zeolite Si-LTA Crystallization [M. Shah, *et al.*, JPC-C, in prep (2025)].

- *Objective:* Zeolite structures involve assemblies of building units such as D4R, α -cage, and β -cage in the case of the LTA zeolite. The question remains: can we observe the emergence of such building units during synthesis? We addressed this in the synthesis of Si-LTA, looking for distinct spectroscopic signatures of the three building units that comprise LTA.
- *Innovation:* (1) Using two OSDAs and F ions as spectroscopic reporters of the evolving structure of nearby silica; (2) Using Monte Carlo (RxMC) to generate databases of evolving structures that lead to LTA crystals, and extracting structures as inputs to DFT calculations of NMR and Raman spectra, for comparison with experiments. Our study represents the first application of RxMC to assign spectra associated with crystallization.

- **Key Findings:** Si-LTA crystals take 19 h to appear (Fig. 2a,b), but prior to this, we observed fluoride-filled D4R units (F/D4R) at 9 h using ^{19}F NMR (Fig. 2c,d) – the **first report** of F/D4R in the induction period of zeolite synthesis. Raman spectra and ^{13}C NMR (data not shown) reveal disorder-to-order transitions of α and β -cages as LTA crystals appear.
- **Significance:** This work reveals, for the first time, the emergence of each zeolite building block during assembly.

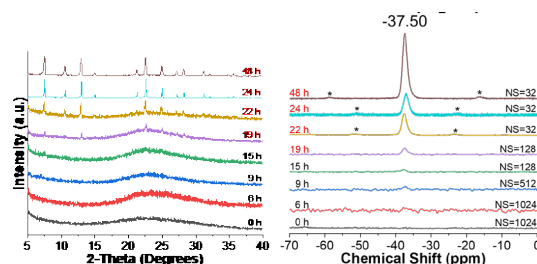


Fig 2. (a) XRD of Si-LTA at 0–48 hours (150 °C) shows LTA crystals at 19 h; (c) ^{19}F solid-state NMR shows formation of F/D4R in amorphous sample at 9 h, before crystals appear.

5. Synthesis of High Si/Al LTA Zeolite without Fluoride Using Pre-Formed Building Blocks as the Silica Source [S. Luo, *et al.*, Chemical Communication, in prep (2025)].

- **Objective:** To test the power of the insights gained thus far, we sought to make high Si/Al LTA without fluoride, which had not been done before.
- **Innovation:** Instead of using TEOS (tetra-ethyl orthosilicate) as the silica source (the standard approach), we used TMA-stabilized D4R crystals as the silica source.
- **Key Findings:** Using TMA/D4R as the silica source sped up crystallization by a factor of 3 (30 → 10 h) for Si-LTA; Si/Al of 7.5 was obtained **in the absence of F**. Standard silica sources cannot deliver this result.
- **Significance:** This approach will be studied in detail and extended to other zeolite frameworks in the next DOE funding period.

Future Plans

1. **Study the early stages of the synthesis reported above in Paper 5**, including both F-mediated and Al-containing syntheses of LTA, to answer the following questions:
 - Why is the F-mediated synthesis 3x faster with stab-D4R than with TEOS?
 - Why is a Si/Al ratio of 7.5 achievable with stab-D4R and not with TEOS?
 - To what extent do stabilized D4R species remain intact during these syntheses?
2. **Investigate how stabilized D4R as a silica source affects crystallization pathways of zeolites**, by varying stabilizing agents and OSDAs to address the following questions:
 - How many zeolites with D4R units can be made using stab-D4R as a silica source?
 - Can zeolites without D4R in their crystal structures be made using stabilized D4R?
 - Is stabilized D4R better at making zeolites using F-mediated or Al-containing syntheses?
 - To what extent do stabilized D4R species remain intact during non-LTA syntheses?
 - Can zeolite phase purity be controlled by tuning stabilizer and OSDA concentrations?

Answering these questions will usher in a new era of both understanding and control over zeolite synthesis and processing for advanced applications in catalysis and separations.

Publications

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Directing C and BN On-Surface

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Keywords: 2D materials, CVD, heterostructures, graphene, hexagonal boron nitride

Research Scope

When one- and two-dimensional materials are confined to a surface, their interactions with that surface profoundly affect their synthesis. New growth mechanisms arise. New opportunities for controlling synthesis with previously unobtainable precision emerge. As a result, novel materials behaviors can be obtained. With these opportunities come challenges: How do we understand these new synthetic mechanisms? How can we manipulate and control them to our benefit? To answer these questions, this project focuses on the chemical vapor deposition (CVD) based synthesis of graphene and graphene nanostructures and heterostructures (e.g., with hexagonal boron nitride, hBN) on substrates (e.g., Ge) that strongly and directionally influence their nucleation and kinetics. The project seeks to understand synthetic mechanisms unique to low-dimensional materials confined on surfaces and learn how to exploit them to control shape, size, aspect ratio, and crystallographic orientation – with atomic precision. Towards this end, the project concentrates on three Aims: (1) Directional growth in the nanometer-scale limit; (2) Precise heteroepitaxial growth in the strongly kinetically frustrated regime; and (3) Crystallographic orientational control of graphene monolayers and bilayers.

The project produces fundamental knowledge about the on-surface synthesis of low-dimensional materials by CVD – in regimes in which substrate interactions break symmetry and at the earliest, smallest, atomic-scale stages of synthesis. The project uncovers new mechanisms governing syntheses that bridge the worlds of organic chemistry and the CVD of materials. The project explores 2D materials heteroepitaxy in a kinetically frustrated regime that has the potential to enable exceptional control over materials dimensions and open the door to semiconducting, metallic, and insulating two-dimensional materials superstructures with novel electrical behaviors. At the same time, the research studies mechanisms and develops innovative synthetic approaches for realizing large-area, single crystals of graphene with controlled twist angle.

Recent Progress

- **Completed and submitted a manuscript on single-crystal graphene growth on Ge[1]**

An early breakthrough[2] reported the growth of single-crystal graphene on Ge(110). However, the graphene is not single-crystalline as originally reported. A second orientation, usually rotated by 30° with respect to the majority orientation, is observed (Fig. 1). Our recent publication[1] takes a big step towards solving this challenge. This study combines monolayer

graphene crystal growth studies with state-of-the-art LEED/LEEM characterization (by Michael Altman) to gain insight into why secondary graphene orientations form and to largely circumvent them.

Interestingly, the islands of graphene that initially nucleate on Ge(110) are indeed all crystallographically aligned with C–C bonds roughly parallel to Ge[11 $\bar{0}$] (called R0 domains). The original literature reported that these aligned islands then coalesce into a single-crystal. Our deeper analysis reveals that R30 domains (C–C bonds 30° from Ge[11 $\bar{0}$]) are present even in the “single-crystal” samples from the group of the aforementioned Ref. 2. Our work has discovered that the R30 domains are mostly a product of secondary nucleation. For reasons not yet understood, as the primary R0 domains grow, R30 domains nucleate from the R0 edges leading to polycrystallinity. The AFM data in Fig. 1d capture a R30 domain shortly after nucleating off the edge of R0, a typical secondary nucleation event.

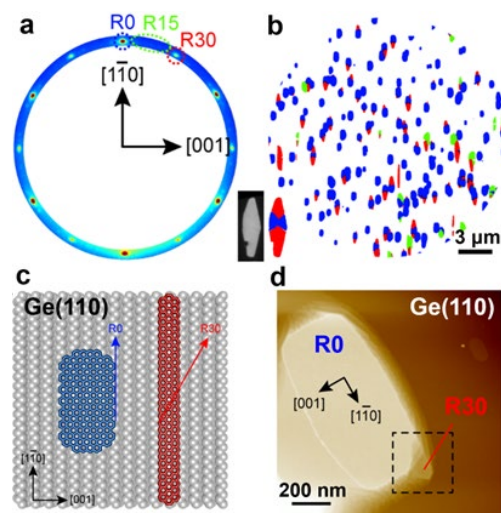


Figure 1. (a) LEED pattern on log-intensity scale evidencing a pronounced peak at the R30 orientation. (b) Corresponding color-coded DF-LEEM image. Most red R30 domains are found at the edges of blue R0 domains. (c) Schematic of orientations. (d) AFM height image of R30 domain nucleating off/near edge of R0 domain.

Empirically, we have observed that decreasing C supersaturation and growth rate (by decreasing CH₄ or increasing H₂) lowers the incidence of R30 secondary nucleation. Increasing the primary nucleation density moreover suppresses R30 secondary nucleation. We believe the latter indicates that the size of the R0 domains is an important factor – with R30 more likely forming only after the R0 domains have reached a critical size. By growing slowly at high nucleation density, we have achieved an R0 areal fraction of > 99.5%.

- **Achieved hBN synthesis on Ge from borazine for the first time, near single-crystal hBN on Ge(111), and 100 times reduction in pinhole defects[3]**

Little is known about hBN growth on semiconductors, and no reports have indicated the possibility of growing single-crystal hBN on semiconductor wafers. Our work demonstrates and characterizes the growth of high-quality hBN islands and monolayers on single-crystal Ge, vicinal Ge, and Ge epitaxial layers on Si. We have learned that the sublimation of Ge under high vacuum inhibits hBN growth, but this can be mitigated by decreasing Ge sublimation (e.g., by placing two Ge substrates face-to-face), enabling the growth of aligned hBN islands and monolayer hBN films. We have uncovered (a) the effect of Ge surface orientation on hBN domain orientation; (b) an exciting path toward single-crystal hBN on Ge(111); (c) how to measure and improve the quality/integrity of the hBN; and (d) how to grow hBN on Si using Ge epilayers. Particularly exciting is that while the six-fold-symmetrical Ge(111) surface was anticipated to produce two

anti-oriented hBN domains, our observations reveal that 95% of hBN domains align in the same direction (Fig. 2) – likely due to the asymmetric docking of hBN nuclei to Ge step edges as predicted by Yakobson. Another particularly noteworthy result is that we quantified the presence of pinhole defects in our hBN monolayers by dipping as-grown samples into a Ge etchant, FeCl_3 , as a method to label pinhole defects. Despite appearing as complete monolayers under SEM, AFM, and Raman analysis, these films surprisingly contained a high density of pinhole defects. Given the potential negative impact of pinholes, we addressed this issue by introducing a burst of borazine at higher partial pressure at the end of growth, leading to a $100\times$ reduction in pinhole density reaching as low as $0.7\ \mu\text{m}^{-2}$, close to densities observed in our highly optimized and state-of-the-art graphene grown on Ge. We are one of the few groups performing this kind of analysis, in this depth, on the quality of CVD hBN materials.

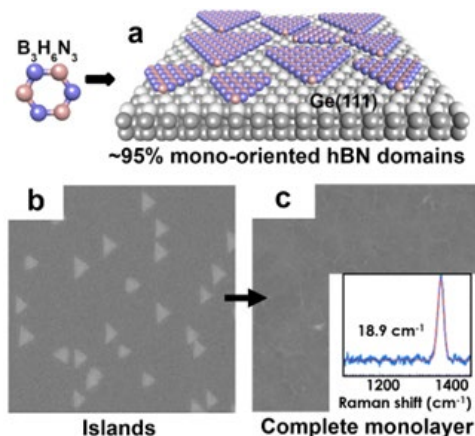


Figure 2. Nearly single-crystal hBN on Ge(111). (a) Schematic & (b) SEM evidencing > 95% islands oriented same direction. (c) SEM, Raman spectrum of monolayer.

- **Conducted *in situ* STM measurements of the behavior of PAH-based graphene nanoribbon seeds on Ge(001) (leveraging Argonne National Laboratory’s CNM user facility).[4]**

Our group pioneered the synthesis of graphene nanoribbons (GNRs) driven by anisotropic CH_4 CVD [5]. Small graphene-like molecules called polycyclic aromatic hydrocarbons (PAHs) are first deposited onto Ge(001) at relatively low temperature to act as seeds that initiate GNR synthesis with subsequent CH_4 exposure at high-temperature ($900\ ^\circ\text{C}$). The width growth rate is only $0.03\ \text{nm min}^{-1}$, affording excellent control over GNR width. Semiconducting armchair GNRs with mean normalized standard deviation in width as small as 11% ($3\times$ smaller than GNRs without seeds), aspect ratio as large as 30, and width as narrow as 2.6 nm (tunable via CH_4 exposure time) have been realized.

Our overarching goal in PAH-seeded GNR synthesis is to grow a single GNR from each PAH molecule. However, is this really happening? To assess, we conducted a follow-up study to track the behaviors of a prototypical PAH – perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) – on Ge(001).[4] Specifically, we tracked the conformation, diffusion, and clustering of PTCDA molecules in the time between their deposition onto Ge at room-temperature and the growth of GNRs from the edges of the seeds at $900\ ^\circ\text{C}$ with CH_4 exposure. We learned that small PAHs such as PTCDA are mobile and form multi-PAH clusters on Ge – and that these clusters are the seeds that start GNR growth. Initially, at $20 - 300\ ^\circ\text{C}$, the PTCDA molecules are indeed isolated (Fig. 3a). At $300 - 400\ ^\circ\text{C}$, the PTCDA molecules begin to migrate and pair (Fig. 3b). From $500 - 900\ ^\circ\text{C}$, progressively larger clusters form (Fig. 3c-e). Most of the clusters are located at steps or

holes in Ge. At 900 °C, the average cluster diameter is 1.7 nm, matching with the effective seed size extrapolated from CVD experiments.

- **Published 4 collaborative papers**

Three papers have been published with Jason Kawasaki (UW-Madison) on using state-of-the-art graphene grown in the Arnold lab for uncovering the fundamentals underpinning remote and vdW epitaxy. Another paper has been published showing that yttrium films react with and remove hydrocarbon residues from the surface of graphene without damaging graphene itself – enabling the elusive ability to etch undesirable C (e.g., residues) from desirable sp^2 C (graphene). See two-year publication list at end of document.

Future Plans

The mechanism causing the secondary nucleation in single-crystal graphene is still uncertain. New hypotheses and research investigations will be pursued. Moving forward, there is a large opportunity to connect defect metrology and CVD synthesis studies to discover how and why defects form during hBN CVD and tune defect concentrations. Looking ahead, our hypothesis is that the incidence of PAH clustering will exponentially decrease as the molecular weight of the PAH is increased – due to larger diffusion barrier. By suppressing clustering, we expect to obtain (a) more monodisperse GNRs and (b) better control their density.

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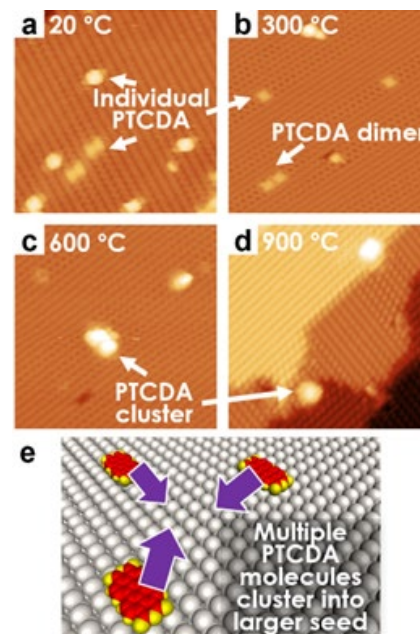


Figure 3. *In situ* STM of PTCDA on Ge(001). (a) PTCDA molecules are individualized up to 300 °C. (b-d) From 300-900 °C PTCDAs diffuse & cluster to form larger graphene-like seeds. (e) Schematic.

Publications

Publications with publication dates over the last 24 months supported by this project:

1. R. M. Jacobberger, Z. Miao, K.-M. Yu, Y. H. Lam, Z. Li, Y. He, J. Wang, K. A. Su, Y. Pathaare, V. Saraswat, D. A. Rhodes, M. G. Lagally, M. S. Altman, and M. S. Arnold, *Overcoming Secondary Nucleation of Misoriented Domains during Wafer-Scale Epitaxy of Single-Crystal Graphene on Ge(110)* ACS Nano **19** 21046 (2025).
2. K. A. Su, S. Li, W.-C. Wen, Y. Yamamoto, M. S. Arnold, *Chemical vapor deposition of hexagonal boron nitride on germanium from borazine*. RSC Advances **14**, 25378 (2024).
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A Unified Model for Epitaxy of Metastable Crystal Polytypes at the Nanoscale

Rachel S. Goldman and Liang Qi, University of Michigan; Judith C. Yang, University of Pittsburgh and Brookhaven National Laboratory

Keywords: crystal, epitaxy, polytype, nanoscale, nitride

Research Scope

It has been hypothesized that metastable NW polytype selection is governed by surface/interface energies, surface diffusivities, and/or droplet angles that determine ABC vs. AB stacking of atomic planes, resulting in zincblende (ZB) or wurtzite (WZ) polytypes. For ZB-polytype-preferring materials, such as III-As and III-P, ZB vs. WZ polytype selection has been described by empirical “contact angle” models, enabling the design and fabrication of NW polytype superlattices. However, for GaN, a WZ-polytype preferring material, the “contact angle” models for NW polytype selection predict ZB polytype formation, across contact angles, even though WZ GaN NWs are most frequently reported in the literature.

The purpose of this work is to develop the fundamental materials science to controllably synthesize NWs with meta-stable polytypes, stable polytypes, or some combination of both, through coordinated synthesis, in situ atomic-scale characterization, and multi-scale simulations. We utilize multi-scale simulations to construct a physics-based atomistic model for nanoscale epitaxy of metastable crystal polytypes and iteratively verify its nucleation and growth components via experiments in chemical environments using both molecular-beam epitaxy (MBE) and environmental TEM (E-TEM). Although GaN is selected as a model system, these results will be widely applicable to systems that have multiple metastable polytypes. The new knowledge generated will significantly broaden our capabilities to produce nanowires of complex materials composed of multiple polytypes, with properties of interest for various functional devices.

Recent Progress

Determined the influence of excess silicon on the polytype selection of GaN nanowires We investigated the origins of polytype selection in GaN nanowires (NWs) during metal-mediated molecular-beam epitaxy (MBE). Using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), we observed [111]-oriented zinc blende (ZB) NWs and [0001]-oriented wurtzite (WZ) NWs, with Si_xN_y at the interface with the Si (001) substrate. Quantitative energy dispersive X-ray spectroscopy (EDS) showed significantly higher Si concentrations in ZB NWs compared to WZ NWs. Density functional theory (DFT) calculations indicated that incorporating Si at the Ga sublattice stabilizes the ZB polytype. These findings suggest that high Ga beam equivalent pressure during pre-deposition leads to the dissolution of excess Si into Ga droplets, stabilizing ZB GaN during the subsequent NW growth. Additionally, calculations predict that substituting Group IVA elements for Ga and Group VIA elements for N also stabilizes the ZB polytype. This understanding of ZB polytype stabilizers will facilitate the development of polytype heterostructures in WZ-preferring compounds.

Self-catalyzed growth of III-N nanowires: role of the solid-melt interface To understand the atomic-scale mechanisms underlying dopant-induced polytype selection, we combined molecular dynamics simulations with machine-learning interatomic potentials to model GaN nucleation and growth during the droplet epitaxy. These simulations show that local atomistic structures of the liquid Ga droplet play a pivotal role in modulating N adatom adsorption and migration at the solid–liquid interface. Free energy sampling reveals interface polarity-dependent energetics of N adatoms, with adsorption and migration profiles varying sharply across different interface configurations. Bridging atomistic energetics to mesoscale growth, Kinetic Monte Carlo (KMC) simulations suggest that nanowire growth is governed by diffusion-limited kinetics from the Ga liquid bulk to the solid–liquid interface, rather than by interfacial reaction kinetics. This interpretation is consistent with the experimentally observed low-defect solid–liquid interfaces.

Developed MBE-TEM block for deposition on TEM grids/chips

To facilitate MBE of gallium and indium droplet arrays on TEM grids/chips, we designed and fabricated a specialized MBE-TEM block. The MBE-TEM block is made of 0.03” thickness molybdenum with 3” in diameter. A molybdenum mask covers the grids and chips, exposing only the film windows. This design ensures that material deposition occurs exclusively on the film windows, protecting other areas from unwanted deposition. For TEM chips, this is particularly crucial to prevent any deposition on the electrodes, thereby avoiding electrical shorts. TEM grids/chips and the mask are held in place by two molybdenum clamps.

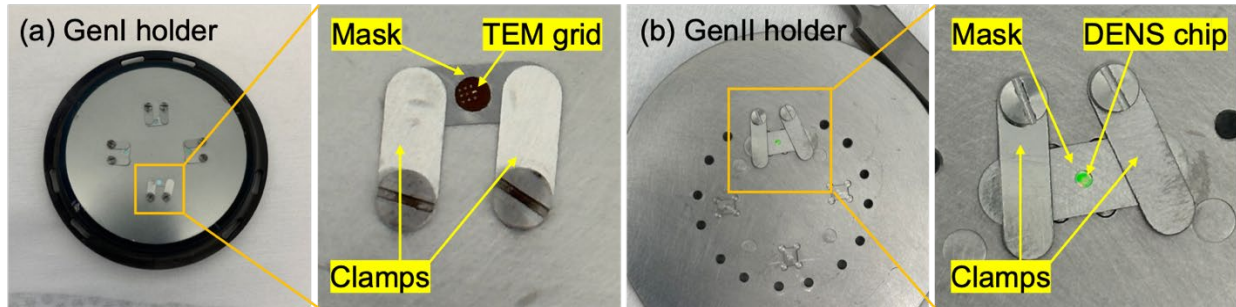


Fig. 1: (a) MBE-TEM block for Si (001) and SiN TEM grids. (b) MBE-TEM block for DENS wildfire TEM chip. A molybdenum mask covers the grids/chips, exposing only the film windows.

Visualizing nucleation and growth of GaN during droplet epitaxy We use E-TEM to investigate the competition between Ga droplet evaporation/coarsening and GaN growth during droplet epitaxy. For this purpose, arrays of Ga droplets, with and without pre-nucleated GaN seeds, were prepared by molecular-beam epitaxy and inserted into the E-TEM. The dynamics of the Ga and Ga/GaN arrays are then visualized during NH_3 exposure at 460 °C. Real-time low-magnification TEM imaging reveals reduced Ga desorption for the partially nucleated Ga/GaN arrays (**Figs. 2 (a), (b)**), with in-situ high-resolution (HR) TEM imaging (**Fig. 2(c)**) revealing GaN growth. We hypothesize that the Ga/GaN interface promotes ammonia dissociation, enhancing the local concentration of active nitrogen and facilitating GaN crystallization.

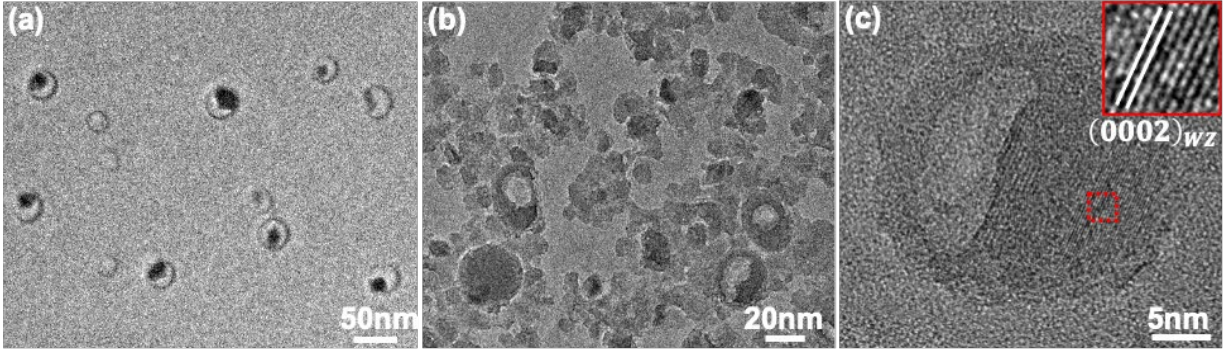
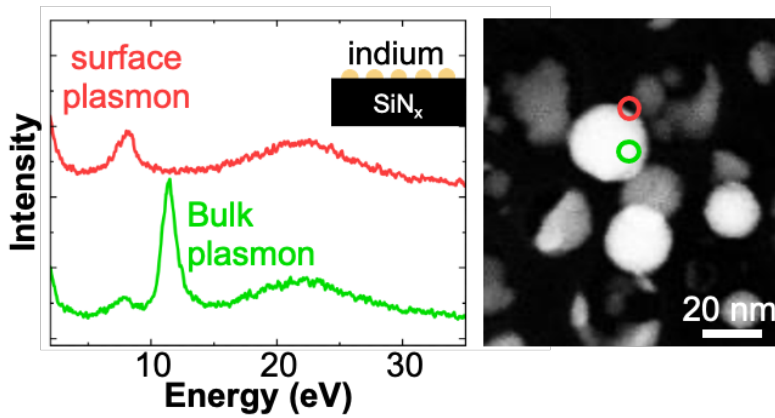


Fig. 2: Comparison of NH_3 -exposed ($\sim 10^{-2}$ Torr) arrays of (a) Ga droplets and (b) partially-nucleated GaN ("Ga/GaN"), with (c) HRTEM image revealing GaN growth from Ga/GaN.

Quantified the plasmonic properties of indium nanoparticle arrays on silicon We examined the influence of indium nanoparticle (NP) arrays on deep-ultraviolet (UV) plasmon resonances. For photon energies < 5.7 eV, analysis of ellipsometric spectra reveals an increase in silicon reflectance induced by indium NP arrays. For various energies in the range 5.7 to 7.0 eV, a decrease in reflectance is induced by the NP arrays. Similar trends in reflectance are predicted by finite-difference time-domain (FDTD) simulations using NP size distributions from atomic-force micrographs as input. In the energy range of 7.4 to 9.2 eV, the FDTD simulations reveal reflectance minima, characteristic of localized surface plasmon resonances (LSPR). Electron-energy loss spectroscopy (EELS) collected



from individual indium NPs reveals LSPR at ≈ 8 eV, supporting the promise of indium NP arrays for deep-UV plasmonics.

Fig. 3: EELS spectra and annular-dark field images revealing the indium surface plasmon (~ 8.0 eV) and the bulk plasmon (~ 11.5 eV) at the NP edge and bulk, respectively.

Visualizing In_2O_3 nanoparticle dynamics during reductive gas exposure The as-prepared indium NP arrays typically consist of a metallic indium core encapsulated by an In_2O_3 shell, which needs to be removed within the E-TEM in order to initiate InN growth. Therefore, we investigated the dynamics of fully oxidized In_2O_3 NP arrays. Within the E-TEM, we ramped the structures to 300°C within 3 min under various reducing environments (H_2 , CO , and NH_3). Under CO and H_2 atmospheres, in-situ HRTEM images illustrate the shrinkage of In_2O_3 , presumably due to the removal of lattice oxygen, followed by the desorption of the reduced metallic indium species. In contrast, exposure to NH_3 induces size and shape fluctuations of the In_2O_3 NPs.

Visualizing nucleation of InN during droplet epitaxy To visualize nucleation of InN in the E-TEM, In/In₂O₃ core/shell structures were ramped in vacuum to 650 °C in 4 s. Following the introduction of 100 mTorr NH₃, indium evaporation and In₂O₃ dissociation were observed under the 300 kV beam. A series of low-magnification TEM images were collected following beam exposure. Although dissociation of In₂O₃ and desorption of indium were observed directly under the beam, in an area ~ 500 nm away from the beam, faceted structures are apparent. HRTEM and FFTs suggest that these faceted structures are WZ InN. Building upon our recent visualization of indium droplet nitridation with low resolution TEM, we plan to image the formation of InN nucleation sites by ammonia using HRTEM. As InN nucleation sites form and grow, we will use HRTEM to elucidate their polytype and formation mechanisms.

Future Plans Our Future plans include the following:

- We are currently finalizing the following manuscripts (all intellectually led by the BES Project):
 1. “The role of the solid-melt interface on accelerating kinetics during the self-catalyzed growth of III-N semiconductors”
 2. “Atomic-scale visualization of vapor–liquid–solid interfacial reactions: GaN growth at the Ga/GaN interface”
 3. “Visualizing In₂O₃ nanoparticle dynamics during reductive gas exposure”
 4. “Visualization nucleation and growth of InN during droplet epitaxy”
- We are currently testing a commercial Aura plasma source on the ex-situ reactor at CFN and plan to integrate it into the ETEM system for in-situ plasma-assisted experiments.
- We are performing atomistic simulations using machine learning interatomic potentials and DFT to identify alloying elements that can modify diffusion and growth kinetics at the Ga/GaN interface.
- We are developing kinetic Monte Carlo simulations to model diffusion and polytype transitions in GaN, guided by ML-based calculations of surface and interfacial energetics.
- We are optimizing nitridation of In and Ga droplet arrays in E-TEM between 300–900 °C under varying gas types and pressures.
- We are developing real-time, high-speed in-situ TEM capabilities to directly capture dopant-modulated nucleation and polytype transitions using ETEM. Machine learning (ML)-driven analysis enables quantitative interpretation of dynamic processes, overcoming challenges posed by manual labeling and low signal-to-noise ratios. ML is rapidly advancing TEM data interpretation, providing insights previously inaccessible through conventional methods.
- We will utilize a newly installed monochromated, aberration-corrected NION microscope with a secondary electron detector for ex-situ atomic-scale characterization of nanocrystals before and after growth, complementing in-situ ETEM studies. It offers < 1 Å spatial and < 5 meV spectral resolution, enabling direct surface imaging at the atomic level.

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10. A. Liu, Z. Xi, M. Li, D. Zakharov, F. Camino, J.C. Yang, L. Qi, R.S. Goldman, "*In situ investigation of Ga droplet nitridation using environmental transmission electron microscopy*", Advances in In-Situ (S)TEM Workshop, (Ann Arbor, MI), June 19, 2024.
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Platforms for imaging and controlling crystal growth in situ from vapors and fluxes

Daniel P. Shoemaker – University of Illinois

Keywords: Crystal growth, flux growth, semiconductors, vapor transport, in situ synthesis

Research Scope

This project will create platforms for active control of crystal growth, embodied in systems that manipulate liquid fluxes and vapors via temperature ramps and gradients while recording in-situ tomographic or optical movies of the process. The methods and understanding developed by this project will enable the growth of high-quality single crystals with millimeter sizes with a high rate of success for a diverse array of systems. Because flux and vapor transport methods of crystal growth are, in theory, thermodynamically reversible, they can be driven backward in growth by reversing the thermal profile. This ability to “rewind” synthesis will provide control over the material phase and its specific crystal size, shape, and orientation. From a practical point of view, the work involves selecting suitable systems with proper time scales and crystal quality to demonstrate that the growth processes are indeed reversible. Next, platforms for in situ crystal growth will be built with visible light, X-rays, and neutrons. Finally, the control methods should be developed to actively “drive” the growth. The outcomes will be novel materials in physical forms and qualities that have been previously unavailable, greatly accelerated processes for obtaining materials with complex functionality, and a suite of control and optimization programs that are extendable to other techniques that will benefit from reaction monitoring, artificial-intelligence- aided growth, and rapid prototyping of novel materials syntheses.

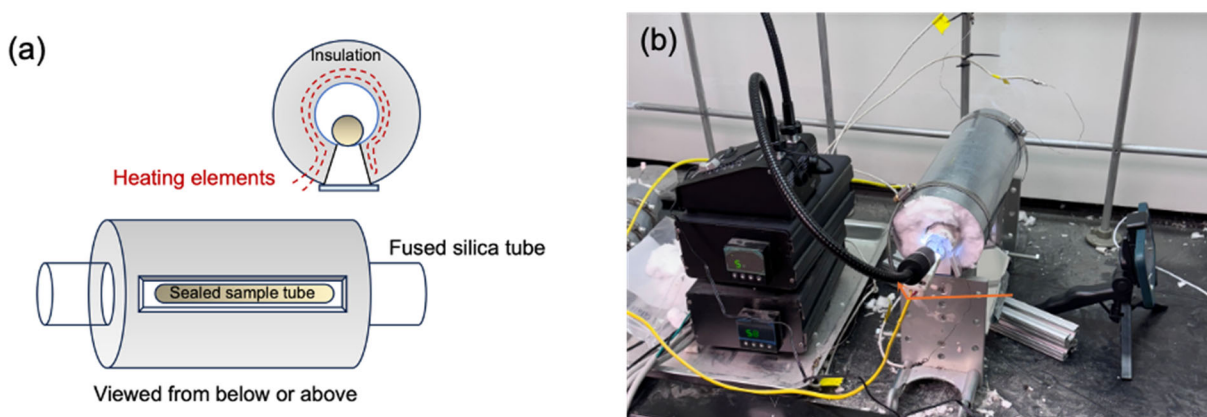


Figure 1: Panel (a) shows a schematic of our two-zone chemical vapor transport (CVT) crystal growth furnace with a viewing window. The constructed furnace is shown in (b), with imaging via a mirror below, with imaging path shown in orange.

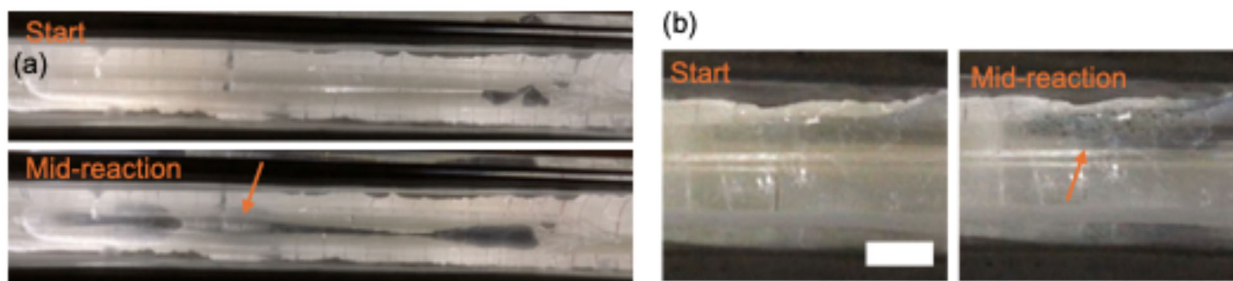


Figure 2: (a) A representative in-situ view of a CVT growth of Bi_2Te_3 , before and mid-reaction. Field of view is 15 cm. A single crystal is arrowed. In (b), a separate growth gives a collection of Bi_2Te_3 crystals (scale bar is 1 cm).

Recent Progress

Chemical vapor transport: We constructed a “see through” 2-zone chemical vapor transport furnace, confirmed that our first version easily reaches 600°C . The furnace is constructed with kanthal heating elements and a double-wall quartz reactor. Backlighting is accomplished using a gooseneck LED light. To prevent loss of heat via convection, the crystals are imaged from below using a mirror. The furnace is shown in Figure 1. We evaluated several imaging systems and found the best solution is a dedicated DSLR camera, which permits resolution of about 100 microns at 30 cm imaging distance and a 20 cm field of view.

Our first model vapor crystal growth is Bi_2Te_3 , which shares the plate-like morphology and reflective surfaces of our narrow-gap semiconductor target materials (charge-density-wave chalcogenides). This growth was performed at $560/600^\circ\text{C}$ gradient. In attachment Figure 2(a), a growth gives a one single crystalline nucleus. In Figure 2(b), a “cloud” of transported crystals is visible during the reaction. These images were taken with an older imaging system with about 400 micron resolution.

Solution precipitation: We have identified CsCuCl_3 as an aqueous crystal growth candidate, which forms from a transparent green liquid to form black prismatic rugby-ball-shaped

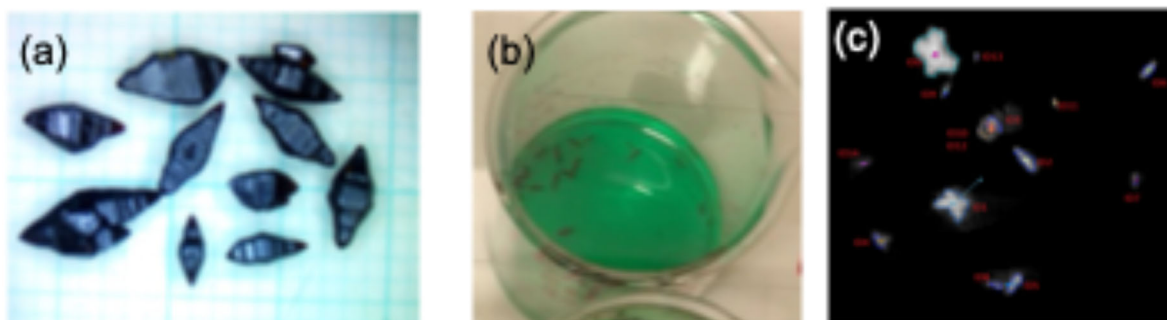


Figure 3: (a) Typical crystals of CsCuCl_3 on a mm grid, grow from green aqueous solutions in (b). Tracking the growth in (b) is accomplished by particle finding shown in (c). The recorded crystallization movie creates a collection of area evolution curves for each particle, shown in Figure 4.

crystals. Typical crystals are shown in Figure 3(a,b). Our optical tracking is based on the package TrackMate. This algorithm recognizes individual crystals, tracks their sizes, and the current count versus time. A typical analyzed frame of a CsCuCl_3 crystal growth is shown in Figure 3(c). For a full growth, particle size is tracked individually, giving a plot of time evolution shown in Figure 4. The earliest particles grow quickly, while subsequently nucleated crystals grow more slowly. Surprisingly, the overall growth rate (total crystal area) continues to increase, so the reaction clearly proceeds by increased nucleation, meaning it maintains a high level of supersaturation. A time lag between the first and second crystal nucleus makes it clear that there is time available to engineer and optimize the growth.

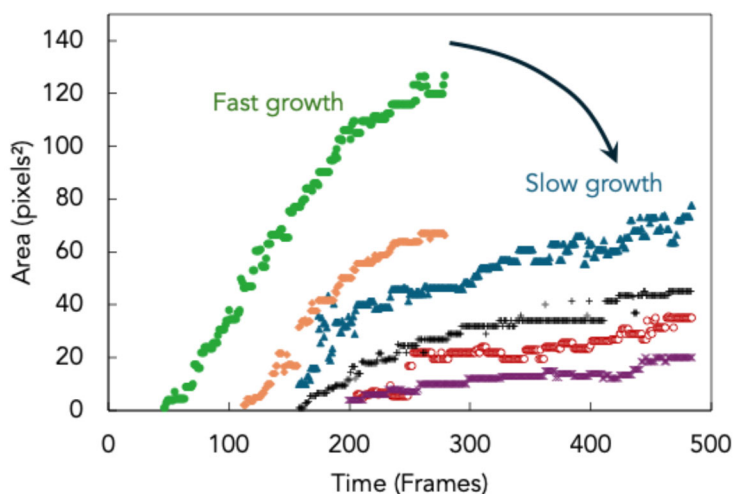


Figure 4: Tracked particle sizes for CsCuCl_3 during crystallization show that early growth is fast, while increased nucleation leads subsequent particles to grow slowly. We aim to accelerate growth of the early crystals and avoid subsequent nucleation.

Future Plans

Our imaging systems for solution and vapor transport are mature, and our future goal is to develop more automated software and actively control crystal growth. We must investigate the behavior of Bi_2Te_3 and judge its thermodynamic reversibility. The model systems we investigated here will be investigated via X-ray tomography using a Zeiss Versa 630 system equipped with diffraction contrast tomography.

A proposal was accepted to the VENUS beamline at the Spallation Neutron Source, Oak Ridge National Laboratory. We will conduct neutron tomography of a flux-grown sample of WTe_2 in tellurium flux. This is the first cycle of user experiments on VENUS, so we will assess the ability of the instrument to accommodate varying chemistries and in situ experiments in the future.

Publications

Publications are forthcoming for this project.

Design of Cementitious Chemistries for Enhanced Geothermal Systems

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Interdisciplinary Science Department, Brookhaven National Laboratory

Keywords: Enhanced geothermal systems, cementitious materials, non-equilibrium dynamics, strain, *in situ* characterization

Research Scope

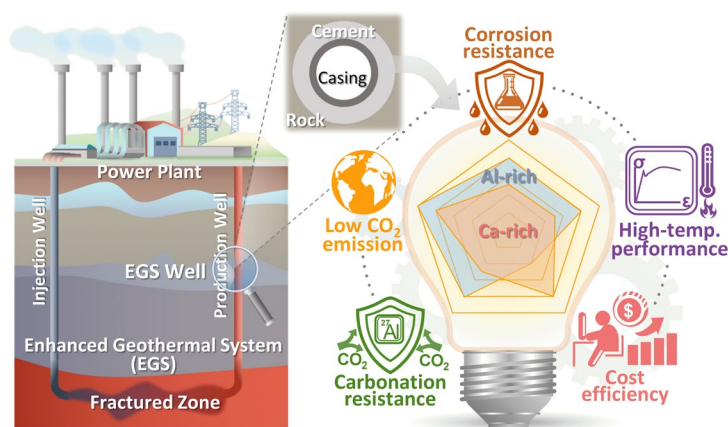


Figure 1. Enhanced geothermal system with radar chart showing performance trade-offs in the design and discovery of advanced cementitious chemistries.

Enhanced Geothermal Systems (EGS) represent one of the most promising frontiers for sustainable baseload energy, but they expose well construction materials to some of the most extreme known subsurface conditions – subcritical and supercritical environments ($> 374\text{ }^{\circ}\text{C}$, $> 22\text{ MPa}$), highly corrosive brines, and prolonged thermal cycling. These aggressive environments rapidly degrade traditional cement systems and metal pipes (casing) that they protect, leading to loss of structural integrity and well failure. The EGS wells impose a unique set of constraints on wellbore materials, which are intrinsically different in nature, such as metal, cement, and formation rocks, yet must perform as an integrated system under extreme conditions (**Figure 1**). Meeting these demands requires a shift in materials design from traditional Portland systems to tunable, non-equilibrium chemistries capable of dynamic adaptation under geothermal stimuli. To address these challenges, the Center for Coupled Chemo-Mechanics of Cementitious Composites for EGS (C4M) investigates phase evolution and material resilience from a physicochemical perspective, focusing on metastable-to-stable transformations, bonding mechanisms, and the structural development of hydrous aluminosilicates and carbonates. We identify and elucidate the control mechanisms governing these phase transitions to enable the design of materials with targeted microstructural and functional properties. Our approach integrates *in situ* synchrotron tools, atomistic modeling, and performance-guided synthesis to uncover transformation pathways under coupled thermal, chemical, and mechanical driving forces.

Recent Progress

Our recent efforts focus on elucidating how thermally induced metastable-to-stable phase transformations in aluminous and carbonate cementitious systems can be leveraged to design durable composites from economical mineral sources for EGS applications. We bridge atomic-level structure change and macroscale mechanics through coupled synthesis, characterization, and modeling workflows. By combining *in-operando* synchrotron XRD, TEM, DFT calculation, and targeted chemistry, we establish composition–structure–property relationships that enable predictive control of cement chemomechanics.

Alkali-activated aluminous systems. We synthesized a boehmite-based composite material (BBCM) via alkali activation of gibbsite, enabling tunable control of the competition between solid-state and

dissolution–precipitation reaction pathways to achieve optimized mechanical properties. Structural characterization and thermodynamic modeling collectively reveal the formation of metastable intermediates, which arise from non-equilibrium reaction routes. Their relative stabilization depends on alkali concentration and reaction history, showing that selective

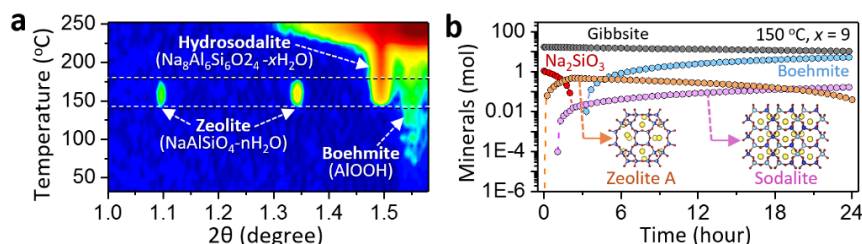


Figure 2. (a) Observed metastable phases during the solidification of the BBCM. (b) Geochemical modeling of the corresponding phase evolution.

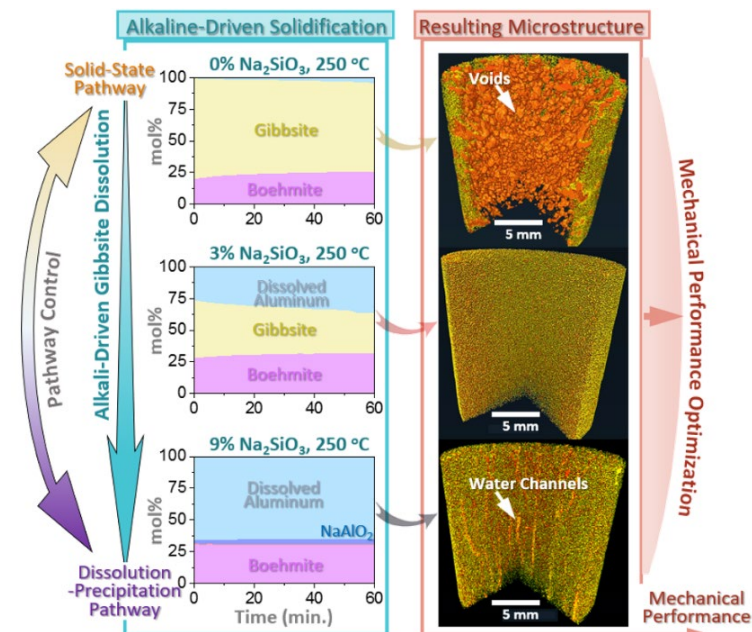


Figure 3. Controlling alkali-driven dissolution kinetics to tune microstructure and mechanical performance in BBCM.

ordering and suppresses defect formation. This mechanistic insight provides a direct route for tuning mechanical properties via controlled dissolution kinetics.

promotion or suppression of these intermediates can encode designated mechanical outcomes (**Figure 2**).

To elucidate how alkali-promoted Al^{3+} dissolution governs the crystallization dynamics of boehmite, and how this, in turn, determines the resulting microstructural morphology, we employed *in situ* synchrotron XRD and tomographic imaging to track the materials' solidification process (**Figure 3**). The results reveal that mechanical performance can be enhanced by selecting the reaction gibbsite-to-boehmite transformation pathway, which promotes structural

Strain release via layer twisting in cementitious oxides. In boehmite-based cementitious materials, strain relaxation during thermally induced phase evolution plays a critical role in

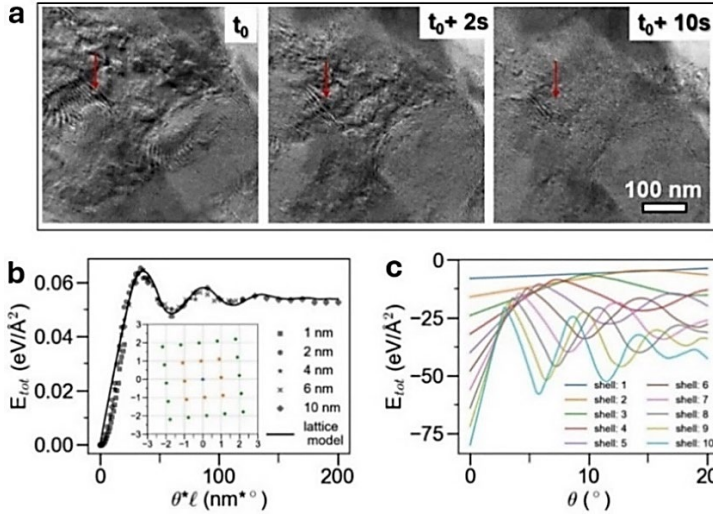


Figure 5. (a) *In situ* TEM captures real-time moiré pattern evolution during thermal transformation, indicating nanoscale strain release via interlayer twisting. (b) Interfacial energy varies with twist angle and domain size, revealing preferred metastable configurations. (c) Energy contributions from different atomic shells show that outer layers dominate the twisting response due to larger atomic displacement.

microstructural stabilization and hardening. Strain is released through discrete interfacial twisting modes, including rapid moiré propagation, localized angular fluctuations, and grain-boundary trapping. Neural-network force field simulations trained on DFT data reveal a twist-angle-dependent energy landscape with damped oscillatory behavior and metastable minima near 6° and 11°, originating from interference-like modulation of interfacial hydrogen bonds (**Figure 5**). The interfacial energy scales universally with the product of twist angle and patch size, indicating coherent long-range coupling within the hydrogen-bond network. This mechanism, fundamentally distinct from van der Waals systems, establishes hydrogen-mediated layer twisting as a strain-dissipation mode intrinsic to non-van der Waals oxides.

Carbonate-based composites and mud-to-cement conversion. We explored carbonate-based cement systems derived from calcium carbonate, olivine, and sodium metasilicate (SMS),

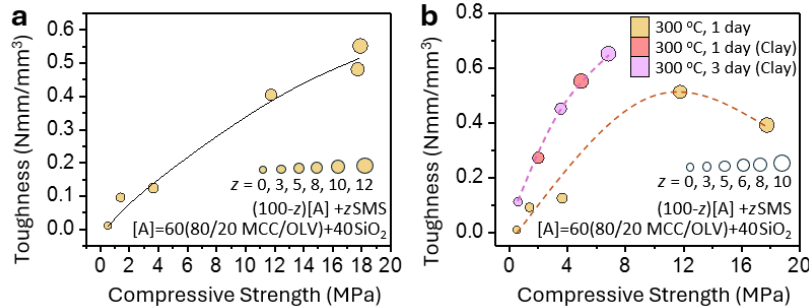


Figure 4. Progressive SMS activation (a) and clay incorporation with varied curing durations (b) reveal a tunable strength–toughness behavior.

and mechanical response. The measured compressive strength and fracture toughness exhibit a nonlinear correlation, reflecting the interplay between phase assemblage and load-bearing capacity during curing (**Figure 4**). These findings demonstrate a compositionally driven route for converting silicate-rich drill muds into high-temperature cements.

focusing on carbonate transition into stable carbonated minerals under geothermal conditions. By adjusting precursor ratios and incorporating clay additives, we tuned the extent of mineral dissolution and secondary phase formation, which in turn controlled microstructural development

Future Plans

Despite recent progress in formulating alkali-activated, aluminum-rich cement systems for geothermal wells, a fundamental gap remains in understanding the governing mechanisms of phase formation and transformation during synthesis and thermal exposure. These systems often evolve through metastable intermediates, whose formation is highly sensitive to processing history, water activity, and local structural disorder—factors that remain poorly constrained. We aim to address this challenge by establishing a mechanistic understanding of how nucleation, diffusion, and dehydration-driven phase evolution dictate the microstructure and performance of these materials. Key efforts will include: (i) Uncovering the kinetic and thermodynamic pathways that control transformations from hydrated precursors to stable phases; (ii) Identifying the role of defects, interfaces, and strain in directing phase selection and growth; (ii) Constructing quantitative structure–processing–property relationships to guide material design under non-equilibrium conditions. This work will bridge fundamental synthesis science with application-relevant performance metrics and aligns with BES priorities in metastability, phase transitions, and mesoscale structure evolution. By coupling *in-situ* characterization with controlled processing strategies, we will lay the foundation for predictive synthesis of durable, cost-effective cementitious materials for extreme geothermal conditions and related high-temperature corrosive environments.

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Polymorph-Dependent Synthesizability Prediction of High-Entropy Materials

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Keywords: synthesizability prediction, high-entropy materials, high-throughput first principles calculation, entropy effects

Research Scope

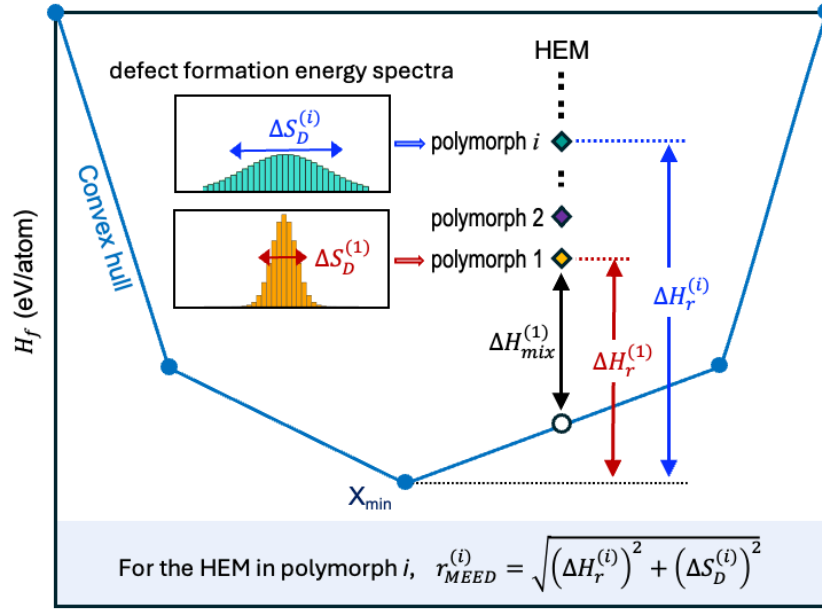
As the exploration of conventional binary and ternary material systems approaches its combinatorial limit, high-entropy materials (HEMs) have emerged as a promising frontier for discovering novel functional materials.^[1,2] Despite two decades of progress, the development of predictive principles and reliable composition–structure–synthesis relationships for HEMs has remained slow and limited. A key limitation of current screening and understanding methods is that they are often constrained to a single hypothetical polymorph or entirely overlook the critical role of polymorphic variability in determining material stability and synthesizability.

To address this gap, this research advances a mixed enthalpy–entropy descriptor (MEED) framework capable of predicting the relative synthesizability of HEMs across both compositional and polymorphic spaces. We initially focus on prototype two-dimensional high-entropy transition metal chalcogenides (2D-HETMCs) in three technologically relevant polymorphs: 2H, 1T, and 1T'. The project aims to uncover underlying physical principles and systematic trends governing the synthesizability of 2D-HETMCs as a function of both composition and polymorph. These predictions will be benchmarked against available experimental synthesis outcomes, providing guidance for the rational design of next-generation high-entropy materials with targeted functional properties.

Recent Progress

Insights into the synthesizability criteria of HEMs: A central challenge in HEM research is the absence of a consistent, predictive criterion for synthesizability. Practical synthesizability varies by synthesis method and is governed by growth conditions that are often far from thermal equilibrium—conditions difficult to capture using first-principles calculations.^[3] To address this, we proposed a focus on high-temperature synthesizability near thermal equilibrium as a tractable and meaningful proxy. Based on the thermodynamic relation $G = H - TS$, HEMs generally become stable only at sufficiently high temperatures due to the entropic contribution. As temperature decreases, this entropy benefit wanes, destabilizing the HEM. We define synthesis in three stages: (i) heating well-mixed precursors, (ii) forming the HEM phase at high temperature, and (iii) retaining the phase during cooling. Successful phase formation in stage (ii) is a prerequisite for

overall synthesizability, even though stages (i) and (iii) vary across synthesis methods. This framework provides a physically grounded foundation for predicting HEM formation.



Physical Principles of Mixed Enthalpy-Entropy Descriptor for predicting HEM synthesizability. The underlying physics of ΔH_r is that the HEM and its competing phases compete for growth at high temperatures, with their formation probabilities following the Boltzmann distribution—lower formation enthalpy corresponds to a higher formation probability. The central principle behind ΔS_D is that the entropy-forming ability, or degree of chemical disorder, is correlated with the distribution of substitutional point-defect formation energies: the more uniform the distribution, the smaller the ΔS_D , and thus the higher the entropy-forming ability. The polymorph dependence of synthesizability is reflected in both ΔH_r and ΔS_D .

Advanced the Mixed Enthalpy-Entropy Descriptor (MEED) with Polymorph Sensitivity: Our originally proposed MEED has been successfully applied to identify experimentally known high-entropy metal carbides and high entropy 2D metal sulfides.^[4] However, this MEED has also been limited to a fixed polymorph structure as well. By MEED, both parameters are integrated into a dimensionless auxiliary descriptor, defined as $r_{MEED} = \sqrt{\left(\frac{\Delta H_r}{\Delta H_r^o}\right)^2 + \left(\frac{\Delta S_D}{\Delta S_D^o}\right)^2}$, where ΔH_r^o and ΔS_D^o are the MEED values for the solid solution composed of all elements within the considered chemical space in a given polymorph. In r_{MEED} , the ΔH_r and ΔS_D for different polymorphs are scaled to a common baseline using ΔH_r^o and ΔS_D^o . As a result, while r_{MEED} effectively differentiates relative synthesizability within a given polymorph, it is polymorph independent. To capture both polymorphic and compositional dependence of synthesizability, we propose utilizing MEED as a 2D vector alongside its unscaled norm parameter, given by $r_{MEED}^N = \sqrt{(\Delta H_r)^2 + (\Delta S_D)^2}$. As illustrated in the above figure, both ΔH_r and ΔS_D exhibit clear polymorph dependence, making r_{MEED}^N an indicative measure of synthesizability variations across different polymorphs.

Through mining of thousands of element combinations, our improved MEED uncovers the unusual entropy-driven trends in synthesizability that go beyond traditional empirical rules and purely enthalpy-based understanding. Among the top candidates identified by MEED, 18 new 2D-HETMCs are successfully synthesized in this study, with additional 8 validated experimentally in prior reports. These 2D-HETMCs exhibit exceptional lithium adsorption and mechanical properties that markedly deviate from linear mixing rule, underscoring their promise for flexible lithium-ion battery technologies.

Future Plans

- (i) Incorporate strain and lattice distortion into synthesizability predictions: Lattice strain and local distortions arising from atomic size mismatches can strongly influence the phase stability of HEMs. We will further refine the MEED framework to account for these effects by explicitly incorporating alloying-induced stress and lattice distortions.
- (ii) Apply the improved MEED to representative classes of high-entropy oxides and metallic alloys: The initial focus will be on rocksalt high-entropy oxides (HEOs) composed of 12 cations: Mg, Ca, Al, V, Ti, Cr, Mn, Fe, Co, Ni, Cu, and Zn. Experimentally reported HEOs in this system will be systematically benchmarked against the new MEED predictions. Following this, the MEED will be extended to other structural families, including perovskite and spinel. Considerable effort will be devoted to identifying the physical principles and synthesizability trends across both polymorphs and chemical compositions of these new HEMs.

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Integration of in situ Monitoring and Artificial Intelligence in the Synthesis of Uranium Alloys and Compounds to inform Performance Following Melt Fabrication Processes

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High temperature stability is a hallmark property of many materials required for technological advancements in the energy sector, from steam turbine blades to oil/gas tooling to nuclear reactor materials. However, the material design and discovery process can be painstaking, requiring enormous time and effort to develop and test novel systems. The objective of this project is to develop and test a methodology to rapidly provide high quality, performance indicating data during the fabrication of uranium-based alloys and compounds. These data will be leveraged in the development of an artificial intelligence (AI) algorithm aimed to reduce time-to- and cost-of-discovery for high temperature materials. In turn, this matures a capability with the potential to predict performance for a broad set of materials and fabrication methods, including melt-pool based technologies like welding and additive manufacturing. Thermal and optical imaging as well as pyrometry facilitate in situ monitoring of the melting, solidification and rapid/quenched cooling of melt-synthesized compounds with temporal and spatial accuracy to the 10's of microns (approximately the thickness of a human hair). The principal investigator hypothesizes that by correlating the temperature, visual spectrum, and thermal (infrared) image data collected during part fabrication, several key performance-predicting phenomena will be identified. In essence, the research effort would employ fundamental materials science and AI to understand, predict, and ultimately control the synthesis and fabrication of novel material systems focusing on Uranium alloys as a test case to enable transformation of advanced manufacturing processes.

Electrodeposition and Mechanistic Study of the Growth of Copper Nanoparticles

PI: Michelle L. Personick, University of Virginia

Keywords: electrodeposition, nanomaterials, metals, surface structure, shape control

Research Scope

This project responds to a critical need for fundamental principles for materials design to replace platinum group elements (PGE) in energy applications by addressing the gap in understanding of how to precisely control the surface structure of nanoscale materials composed of non-PGE such as nickel (Ni), copper (Cu), cobalt (Co) and iron (Fe). This goal will be achieved using an integrated electrochemical approach to metal nanoparticle synthesis pioneered by our research group, in which real-time, *in situ*, electrochemical measurements bridge colloidal and electrochemical materials synthesis to elucidate the fundamental chemical principles that direct metal nanoparticle growth.¹ The work is organized around the following specific aims:

Aim 1: Direct the development of electrochemical and colloidal syntheses for non-PGE nanoparticles with well-defined shapes by applying detailed mechanistic insight from *in situ* electrochemical measurements. **Aim 2:** Push boundaries in the shape control of non-PGE nanoparticles by harnessing the unique tunability of electrochemical synthesis. **Aim 3:** Enable the epitaxial deposition of PGE onto non-PGE nanoparticle cores by using halide free surfactants, control of solubility, and manipulation of diffusion in colloidal growth.

Recent Progress

In the current period, efforts have been made to advance Aim 1 by establishing an approach for the *in-situ* measurement of the mixed solution potential (open-circuit potential, OCP) of colloidal nanoparticle synthesis reactions for non-platinum group metals, enabling us to obtain a real-time measurement of the chemical environment in which these nanoparticles grow and guiding development of novel colloidal and electrodeposition-based syntheses. The previously reported electroanalytical method developed by the PI's research group—established for room temperature reactions of palladium (Pd) nanoparticles¹—proved to not be amenable for studying colloidal Cu nanoparticle syntheses due to the increased temperatures required for the synthesis of nanoparticles of non-PGE. The elevated temperature resulted in contamination of the growth solution by the reference electrodes as well as a sensitivity to the specific glassware used, leading to a loss of shape selectivity and/or failure of the nanoparticle synthesis all together. These problems were resolved by switching from a reference electrode that contained a leachable electrolyte (such as Ag/AgCl electrodes) to a reversible hydrogen electrode paired with monitoring of the solution pH over time. In addition, we switched to smaller electrodes so that the OCP measurement could be conducted directly in the glass scintillation vials normally used for the colloidal synthesis reaction instead of in specialized electrochemistry glassware. Together, this enabled the measurement of the OCP of multiple syntheses of cubic copper nanoparticles in

different chemical reaction environments, which will now be used to develop electrodeposition approaches for shaped Cu nanoparticles with novel morphologies via direct translation of reaction conditions from colloidal synthesis. The use of oxidation-reduction potential (ORP) probes, as a cost-effective and accessible

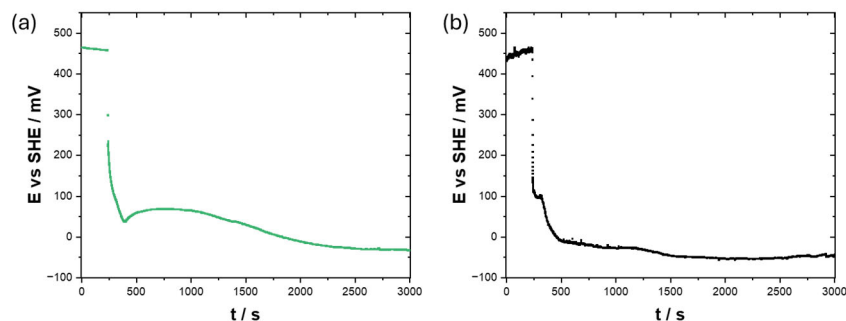


Figure 1. *In situ*, time-resolved open-circuit potential measurements of a synthesis of cubic copper nanoparticles measured with (a) an oxidation-reduction potential probe and (b) a reversible hydrogen electrode, showing the correspondence between the measurements.

method of measuring the solution potential, was also investigated and established as a viable method (Figure 1, *manuscript in preparation*).

To advance Aim 2, we took advantage of the added reaction tunability available using electrodeposition to independently control the nucleation and growth conditions of Cu nanoparticle synthesis, resulting in the production of Cu nanoparticles with unique shapes using a conventional three-electrode cell setup. Cu particles were electrodeposited onto a glassy carbon electrode (GCE) from a copper precursor solution, while an Ag/AgCl electrode and a platinum (Pt) wire served as the reference and counter electrodes, respectively. The electrodeposition was performed at a temperature of 30°C under an argon atmosphere. We separated the nucleation and growth phases of the synthesis by employing two distinct but consecutive electrochemical techniques: chronoamperometry and square wave potentials. Chronoamperometry was used to create nucleation sites (or seeds) by applying more reducing potentials, as the nucleation step requires a higher energy input. The square wave potential method was then employed to control nanoparticle growth by modulating the rate of metal ion reduction through adjustment of the upper potential (E_u), which enables the growing nanoparticles to be oxidized, and the lower potential (E_l), which governs the rate of metal ion reduction and, consequently, nanoparticle growth. The frequency of oscillation between these two potentials is also crucial in influencing nanoparticle growth. We also introduced alcohols such as ethanol and isopropanol during growth to promote the formation of additional facets on the growing nanoparticles. As a result of this strategy, we successfully electrodeposited Cu nanocubes, truncated nanocubes, and cuboctahedra.

To more finely control the growth process, we introduced an additional growth step aimed at creating higher energy facets during growth onto the nuclei or seeds generated in the nucleation step. The schematic representation of this process is detailed in Figure 2a. The electrolyte was initially purged with argon, followed by a nucleation step, where chronoamperometry was performed at a negative potential to create Cu nuclei on the GCE. After this step, shape-controlling additives such as alcohols or halide ions were introduced to the electrolyte, which was then continuously purged with argon for an additional 5 min before proceeding to the growth phases. The first growth step involves carefully controlled electrodeposition to develop facets on the

nuclei. This is followed by a second growth step in which additional deposition occurs to generate highly faceted Cu nanostructures. The first growth step is typically a shorter step that involves very few pulses. In contrast, the second growth step has a greater number of pulses to electrodeposit Cu onto the faceted seeds under kinetic conditions. Both growth steps are performed using the square wave potential method. By tuning E_L and E_U values for both growth steps and

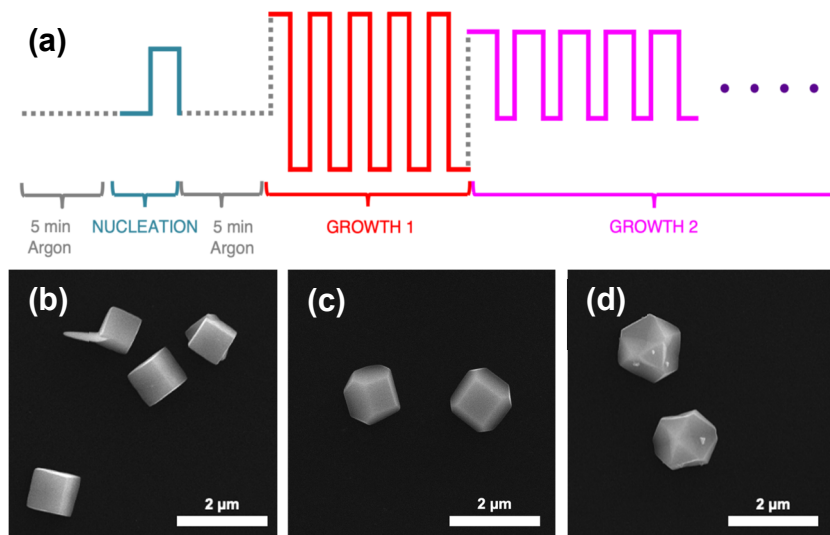


Figure 2. (a) Schematic representation of the electrodeposition of Cu nanoparticles. (b-d) Scanning electron microscopy (SEM) images of electrodeposited Cu (b) cubes, (c) cuboctahedra, and (d) concave cuboctahedra synthesized with the optimized multi-step deposition.

introducing various concentrations of halide additives to the growth solution, we successfully generated Cu cubes, cuboctahedra and concave cuboctahedra (Figure 2b-d).

Concurrently, the parallel 96-well plate-based approach to electrochemical synthetic development detailed in the last program review² was expanded to Cu electrodeposition. We determined that the Ag/AgO quasi-reference counter electrodes (QRCEs) previously used for the parallel electrodeposition of Pd nanoparticles were degrading at the more reducing potentials needed for Cu electrodeposition. Switching the QRCEs to a more robust Pt-based QRCEs allowed for the successful deposition of shaped Cu nanoparticles from simple aqueous growth solutions consisting solely of dissolved Cu precursors. To increase the available potential range in which electrodeposition of metallic Cu was viable, an argon sparging system was constructed, allowing for air-free experimental conditions to be run. Multiple electrodeposition conditions were tested for these simple growth solutions, resulting in the predominant formation of cubic nanoparticles in environmental conditions and cuboctahedra-shaped nanoparticles in air-free conditions.

While the Ag/AgO QRCE was determined to be a non-viable electrode for the formation of Cu nanoparticles, we observed that at the electrochemical conditions tested, porous Ag nanoparticles were produced when chloride was present in the deposition solution. It was established that a multi-step mechanism utilizing leached Ag^+ ions from the QRCE as the Ag source with an intermediate formation of AgCl cubes was responsible for the formation of these porous cubes (*manuscript in preparation*). It was further established that through an adjustment of the growth solution pH the predominant shape of the porous nanoparticles could be influenced, forming concave cubes, as well as tripodal and rhombohedral shapes (Figure 3a-d). Additionally, we determined that Cu could be incorporated into the porous Ag particles by increasing the Cu concentration of the growth solution, leading to the formation of Ag/Cu porous particles. The

Ag/Cu ratio was shown to be controllable by adjusting the concentration of Cu in the growth solution (Figure 3e-g).

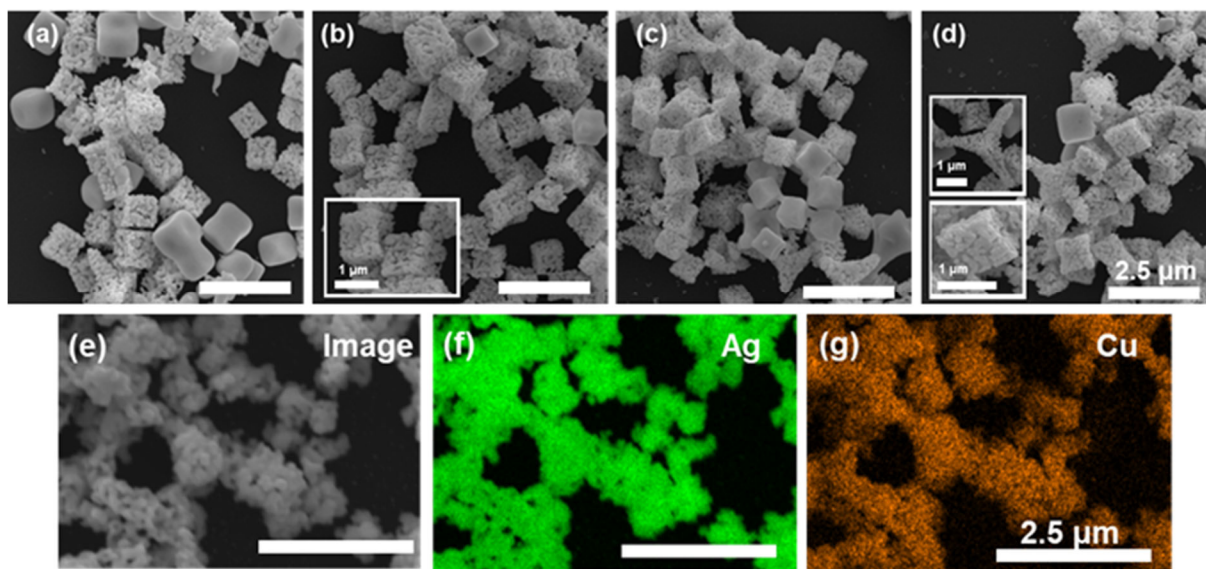


Figure 3. (a-d) SEM images of the shape evolution of porous Ag cubes with increasing pH of the growth solution. Insets show magnified porous particles of different shapes prevalent at different pH values. (e-f) Energy dispersive x-ray spectroscopy (EDS) elemental maps of the Ag/Cu porous cubes. Scale bars: 2.5 μm ; inset scale bars: 1 μm .

Future Plans

Now that a method has been developed and validated for time-resolved OCP measurements of syntheses of non-PGE nanoparticles, this measurement approach will be expanded to Ni, Co, and Fe. The *in situ*, real-time, chemical information obtained using these measurements for the limited number of existing shape-controlled syntheses for nanoparticles of these materials will be used to develop electrodeposition and colloidal synthesis methods that expand the scope of accessible shapes for these compositions. Future work on the multistep electrodeposition method and the parallel electrodeposition approach to synthesis discovery for non-PGE nanoparticles will continue to focus on the generation of high-index facets that are not accessible via colloidal approaches, as well as using the separation of growth stages to develop methods for tuning the crystalline defect structure of the nanoparticles. We are also planning to explore the use of shape-directing additives, which are more traditionally employed in colloidal synthesis of shaped nanoparticles, in electrodeposition systems under mild conditions. The study of the formation of the porous Ag cubes will be advanced by investigating if this approach is generalizable for the synthesis of other Ag/M (M=transition metal) porous particles.

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How transparent is graphene? An analytical model and experimental tests of remote epitaxy

Jason Kawasaki, University of Wisconsin – Madison

Keywords: remote epitaxy, Heusler alloy, photoemission, magnetism, superconductivity

Research Scope

In remote epitaxy, a single crystalline film is thought to grow on a graphene-covered substrate via remote interactions that permeate through graphene, as if the graphene is transparent. This concept has enabled the synthesis and exfoliation of single crystalline membranes for application in flexible electronics and discovery of new properties via extreme strain, and has enabled the synthesis of lattice mismatched heterostructures with reduced dislocation densities. However, the fundamental mechanisms of remote remain unclear since there are many competing growth mechanisms [1].

Here I will discuss progress towards understanding remote epitaxy mechanisms in two directions. First, I will explain a new analytical model for the remote permeated potential through graphene, which includes free carrier screening. Our model, based on a Morse interatomic potential, shows that the remote potential of the substrate is much weaker than previously thought, comparable to the van der Waals potential of graphene itself. Our model suggests that interference between the film and remote substrate potentials must be considered when interpreting experiments on remote epitaxy. Second, I will show an experimental consequence of the interference: remote epitaxial frustration. Using GdAuGe films grown on buffer graphene / SiC (0001), we show competing interactions between the GdAuGe film and the graphene lattice, the SiC lattice, and the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ interfacial reconstruction, cause (1) a rotated superstructure and (2) a disordered interface with thickness two atomic layers. To our knowledge, these observations are the first two signatures of remote epitaxy that cannot be explained by a competing pinhole mechanism.

Recent Progress

Analytical model for remote potential. We propose an analytical model for the remote bonding potential of the substrate ϕ_{remote} that permeates through graphene during remote epitaxy. Our model, based on a Morse interatomic potential, includes attenuation due to (1) the increased separation between film and substrate and (2) free carrier screening from graphene. Compared with previous slab density functional theory calculations [2], which use the electrostatic potential as a proxy for bonding, our analytical model provides a more direct description of bonding, explicitly includes screening (which is often ignored), and is based on simple, interpretable, and well benchmarked parameters. We show that the magnitude of ϕ_{remote} for typical semiconductor and oxide substrates is few meV or smaller, similar to the van der Waals potential of graphene.

This suggests that the potential of graphene, plus the interference between the graphene and remote substrate potentials, must be considered when interpreting experiments on remote epitaxy. We use our model to interpret previous experiments from the remote epitaxy and related literature, highlighting connections to moire epitaxy. True remote effects are often obscured by defect-seeded nucleation, e.g. pinhole epitaxy, that mimics the macroscopic behavior of idealized remote epitaxy. Our model also points to tests, based on tunable screening and spatial extent of the substrate potential, that may increase the strength of the remote potential towards the more idealized picture.

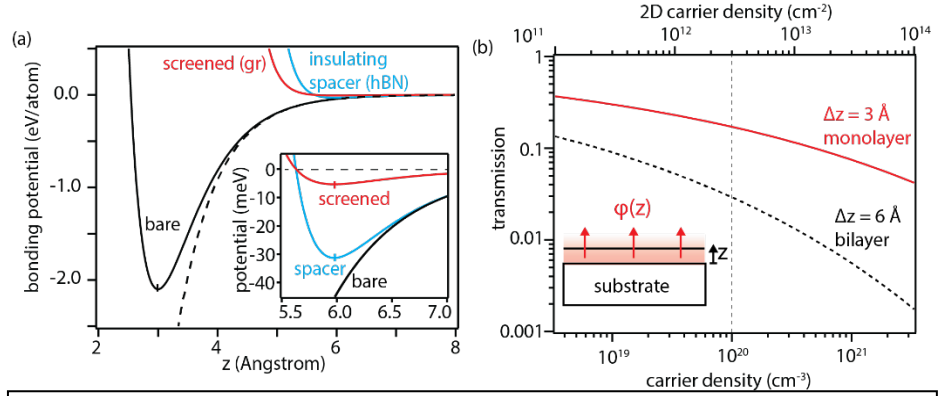


Fig. 1. (a) Morse model for the remote potential of a GaAs substrate through graphene. (b) Screening through monolayer and bilayer graphene in the Thomas Fermi approximation.

Remote frustration. Remote epitaxy holds great promise for synthesizing membranes and low defect density films; however, direct experimental evidence for a remote mechanism is lacking because it is difficult to rule out direct nucleation at pinholes. Our previous experiments demonstrate that pinhole epitaxy also produces exfoliatable epitaxial films with an atomically smooth morphology [1]. In Year 2 we discovered two new signatures of remote epitaxy that cannot be explained by pinholes: (1) a 30 degree rotated epitaxial superstructure and (2) a 2 atomic layer thick disordered region at the GdAuGe/graphene/SiC interface. These fingerprints arise from a competition between direct epitaxy to graphene versus remote epitaxy to the substrate, i.e. remote “frustration.” This observation also breaks the common assumption in the remote epitaxy field that the graphene is lattice transparent.

Fig 2 illustrates the concept of remote frustration based on our slab DFT calculations, where we analyze the contributions to the electrostatic potential from direct interactions with graphene, versus remote interactions from an SiC substrate. Here we compute the electrostatic potential at a distance of 3 Angstrom above the surface for freestanding graphene, epitaxial graphene on SiC, buffer graphene on SiC, and 6H-SiC (0001). We choose this system because the bonding interactions out of plane range from purely van der Waals (freestanding graphene, meV scale) to purely covalent (SiC, approaching eV scale). Our calculations show that for epi graphene on SiC the graphene lattice itself appears (black unit cell, Fig. 2b), in contrast with the commonly assumed “transparent” graphene lattice, plus a long range modulation from the graphene-induced $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ surface reconstruction (red unit cell). Similarly for buffer graphene our calculations reveal an even larger potential modulation from the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$

reconstruction. We quantify the relative strengths at different periodicities by computing the Fourier components of the potential at the Q vectors for graphene Q_{gr} , the reconstruction Q_R , and SiC Q_{SiC} (Fig. 2c). This Fourier analysis avoids background subtraction procedures that often subtract away key features of the potential [2]. Our analysis shows that for epi graphene and buffer graphene there are two (epi) or three (buffer) potentials with magnitude larger than 100 meV. Thus a film that grows on such a surface is expected to experience a competition between these different potentials at different periodicity.

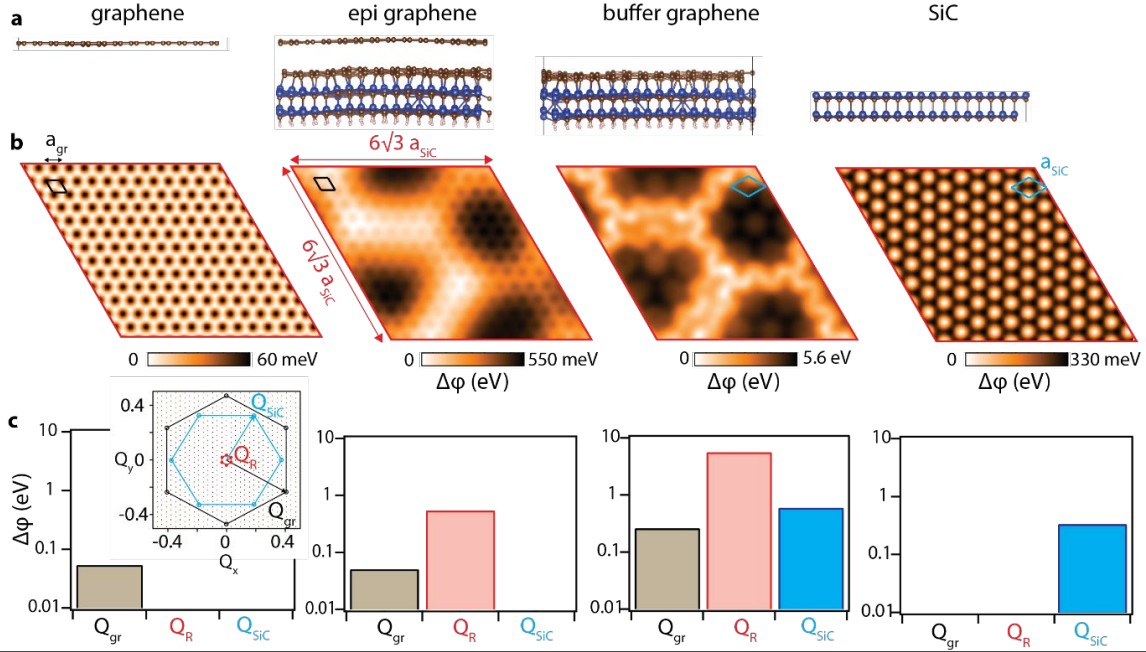


Fig. 2. DFT calculation of potentials above graphene/SiC, illustrating remote frustration. (a) Slab models for graphene, epitaxial graphene on 6H-SiC (0001), buffer graphene on SiC, and SiC (0001). (b) Calculated electrostatic potential at 3 Angstrom above each surface. (c) Fourier components of the electrostatic potential, at the reciprocal lattice vectors for graphene (Q_{gr}), the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstruction (Q_R), and SiC (Q_{SiC}).

Fig. 3 shows the consequences of remote frustration for synthesis of GdAuGe films by molecular beam epitaxy on graphene/SiC. We choose GdAuGe because it has a similar lattice mismatch to graphene (-3.8% for a 30 deg rotated alignment) as to SiC (3.9% to SiC for $2a_{GAG} \sim 3a_{SiC}$), thus providing the ingredients for competition between epitaxy to these two different lattices. We use H-intercalated graphene on SiC as our approximation for freestanding graphene, since the H decouples graphene from the SiC substrate. Our TEM measurements reveal a first signature of remote frustration: for GdAuGe grown on epi graphene and buffer graphene, the first 2 atomic layers are highly disordered, followed by a single-crystalline GdAuGe layer that begins at the third layer. Azimuthal (ϕ) x-ray diffraction scans reveal a second signature: whereas GdAuGe on H-intercalated graphene, epi graphene, and SiC produce the expected hexagon-on-hexagon epitaxial relationship, the GdAuGe grown on buffer graphene is rotated by 30 degrees around the c axis. Together, these observations cannot be explained by pinholes: pinholes in the graphene would produce only the aligned 0 degree orientation. Similarly pinholes cannot explain

the disordered region, since growth on both H-intercalated graphene and on SiC produces films that are crystalline at the interface.

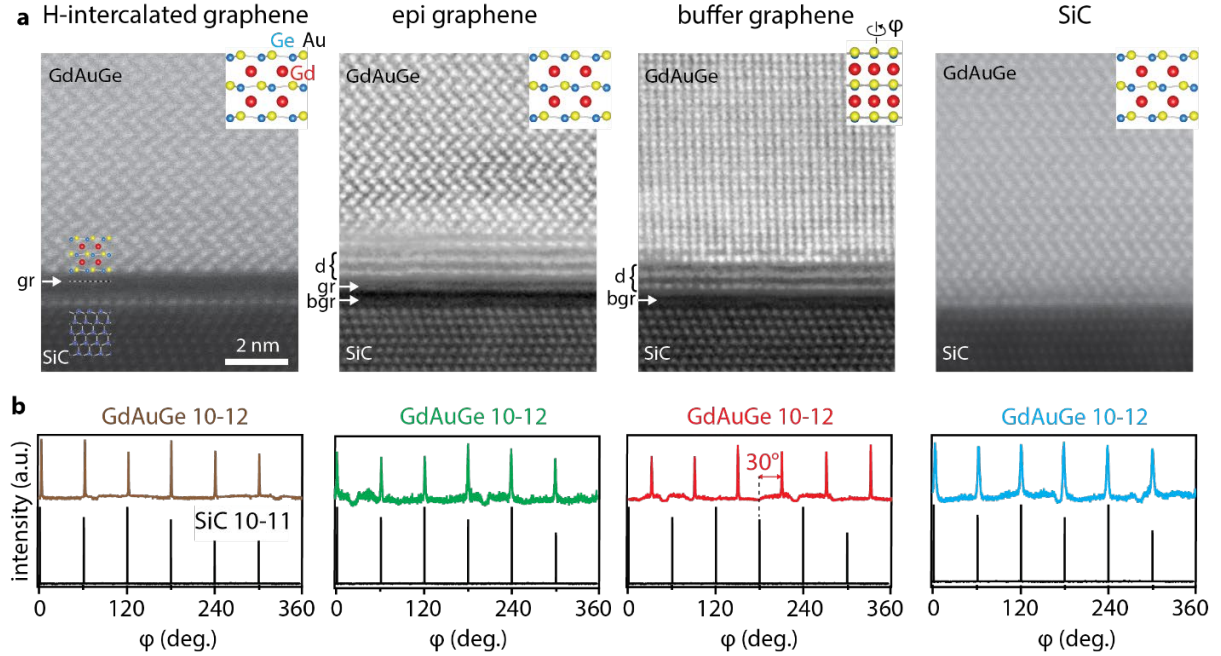


Fig. 3. Remote frustration of GdAuGe on graphene/SiC. (a) Cross sectional TEM, showing a 2 monolayer disordered layer at the graphene interface, for GdAuGe on epi graphene and on buffer graphene. Gd (red), Au (yellow), Ge (blue). (b) X-ray azimuthal scan showing GdAuGe on buffer graphene is rotated in-plane by 30 deg.

Future Plans

Ongoing in-situ XPS measurements are aimed at understanding how long-range ordered single crystalline film forms on top of the disordered layer on buffer and epi graphene, and to better understand why the 30 degree rotation appears only on buffer graphene. Our core level analysis reveals differences in bonding and charge transfer between GdAuGe on buffer graphene, GdAuGe on epi graphene, and bulk like thick films of GdAuGe. Namely, we observe a 0.5 eV binding energy shift of the Au 4f core level for 2 monolayer thick GdAuGe on buffer graphene, compared to 2 monolayer thick graphene on epi graphene, suggesting a difference in charge transfer for. We are comparing these measurements with DFT slab calculations of the charge transfer and low energy bonding configurations and epitaxial orientations.

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Put the list of publications in the recent 2-years SUPPORTED BY BES here. **If more than 10 publications, list only the 10 most relevant.**

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3. S. Manzo, K. Su, M.S. Arnold, and J.K. Kawasaki. *Nucleation selectivity and lateral coalescence of GaAs over graphene on Ge (111)*. ACS Applied Materials and Interfaces. **15** (51), 59905 (2023).
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6. Z. LaDuca, A. Sirohi, Q. Campbell, J. Kawasaki. *How transparent is graphene? Invited perspective to be submitted to 2D Materials July 2025*.

Oscillatory redox behavior in oxides: cyclic surface reconstruction and reactivity modulation

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Keywords: Redox reactions; Surface Restructuring; In-situ Transmission Electron Microscopy

Program Scope

Nearly all metals spontaneously form an oxide layer upon exposure to reactive environments. This oxide skin critically mediates the metal's interaction with its surroundings and underpins a wide range of technological and environmental processes—from corrosion resistance and catalytic activity to the fabrication of gate oxides in electronics. However, much of our current understanding of metal oxidation stems from mesoscale studies, which lack the resolution to capture atomistic mechanisms. This work addresses that gap by conducting an atomic-scale investigation of surface oxidation using advanced in-situ techniques that integrate imaging, diffraction, and spectroscopy under realistic conditions of temperature and pressure. These experiments are closely guided by theoretical modeling—including density functional theory, first-principles thermodynamics, and reactive molecular dynamics—which incorporate environmental effects to reveal how thermodynamic drivers and kinetic barriers together shape oxidation dynamics. The combined experimental and computational approach aims to uncover fundamental principles governing metal-environment interactions. Insights from this study will enable the rational control of gas-surface reactions, with broad implications for corrosion mitigation, heterogeneous catalysis, thin film processing, and semiconductor device engineering.

Recent Progress

In catalytic chemistry, the dynamic interplay between a catalyst's surface structure and its reactivity governs reaction pathways and overall efficiency. A key component of this interaction is the Mars-van Krevelen (MvK) mechanism (1), where lattice oxygen from the catalyst itself actively participates in redox cycles, enabling catalytic oxidation while periodically regenerating the catalyst surface. While the MvK mechanism is central to many oxide-catalyzed reactions (2-5), a fundamental question remains: how do atomic-scale surface reconstructions and subsurface oxygen dynamics synchronize to sustain redox cycles under reaction conditions. Traditional techniques struggle to capture the spatiotemporal complexity of these processes, as they require real-time, atomic-scale imaging of surface reconstructions, subsurface response, and oxygen replenishment under operando conditions.

Using direct in-situ environmental high-resolution transmission electron microscopy (HRTEM) observations along with atomistic modeling, we demonstrate oscillatory redox behavior in CuO under H₂, where cyclic surface reconstruction and reactivity modulation occur via the MvK mechanism (6). We observe self-switching between oxygen-rich (Cu₈O₇) and oxygen-deficient (Cu₈O₂) surface reconstructions, alternately activating and deactivating the surface for H₂O formation. During periods of chemical inactivity, the oxygen-deficient surface undergoes slow re-oxidation via lattice oxygen diffusing from subsurface and bulk reservoirs, restoring the active oxygen-rich surface termination. The inherent disparity in chemical activity among undercoordinated surface ions, along with sluggish subsurface-to-surface oxygen replenishment, drives this oscillatory redox cycle, modulating H₂-induced loss of lattice oxygen at the surface and its delayed replenishment from the subsurface. This creates spatiotemporally separated redox steps at the oxide surface. The phenomena and atomistic insights presented here have significant implications for manipulating the surface reactivity of oxides by tuning the separation of these redox steps.

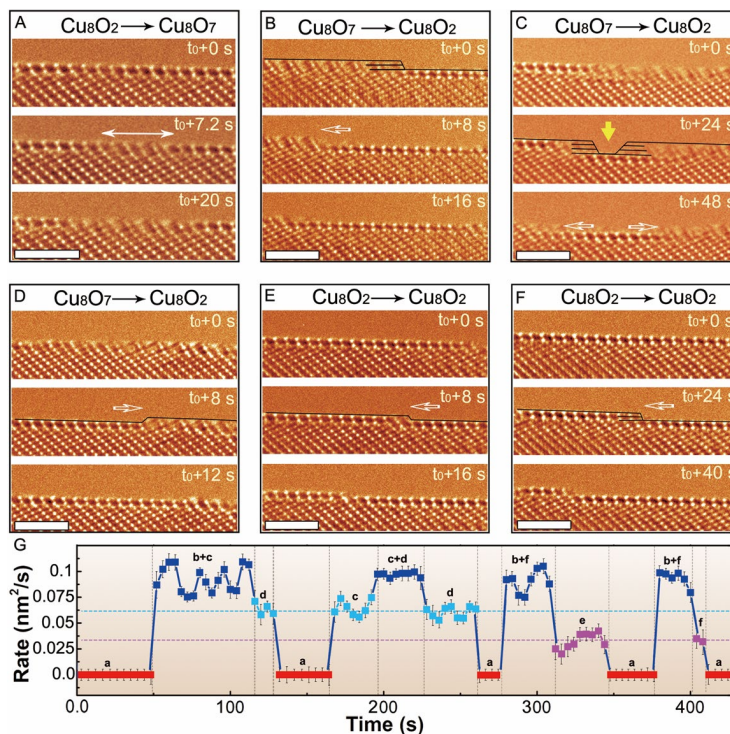


Fig. 1 shows time-lapse HRTEM images capturing the dynamic interconversion between Cu_8O_7 and Cu_8O_2 surface reconstructions under H_2 flow, revealing their contrasting chemical reactivities during oxide reduction. Three types of transformations are observed:

(i) $\text{Cu}_8\text{O}_2 \rightarrow \text{Cu}_8\text{O}_7$ (Fig. 1A): Cu_8O_7 nucleates on Cu_8O_2 via subsurface oxygen diffusion, without surface height change. This re-oxidation reflects Cu_8O_2 's inertness toward H_2 , allowing subsurface oxygen to refill vacancies and restore the more active Cu_8O_7 termination. (ii) $\text{Cu}_8\text{O}_7 \rightarrow \text{Cu}_8\text{O}_2$ (Fig. 1B–D): This occurs via step retraction or surface pitting, with step flow rates up to 0.412 nm/s , indicating high reactivity and oxygen loss. (iii) $\text{Cu}_8\text{O}_2 \rightarrow \text{Cu}_8\text{O}_2$ (Fig. 1E–F): Surface refresh occurs via slow retraction of mono- or bilayer steps, with lower flow rates, due to limited H_2 interaction and oxygen loss. Fig. 1G quantifies surface shrinkage during these transformations. $\text{Cu}_8\text{O}_7 \rightarrow \text{Cu}_8\text{O}_2$ shows fast shrinkage ($0.061 \text{ nm}^2/\text{s}$), $\text{Cu}_8\text{O}_2 \rightarrow \text{Cu}_8\text{O}_2$ shows slower rates ($0.033 \text{ nm}^2/\text{s}$), while $\text{Cu}_8\text{O}_2 \rightarrow \text{Cu}_8\text{O}_7$ exhibits no shrinkage, confirming a net oxygen gain. Cu_8O_2 is more stable, requiring $\sim 7 \text{ s}$ for nucleation of Cu_8O_7 via subsurface oxygen diffusion. Once formed, Cu_8O_7 promotes further oxygen migration but quickly reverts to Cu_8O_2 due to its high reactivity. These dynamics underscore the rate-limiting role of subsurface oxygen mobility.

Fig. 1: In-situ HRTEM visualization of the cyclic interconversions between the Cu_8O_7 and Cu_8O_2 surface

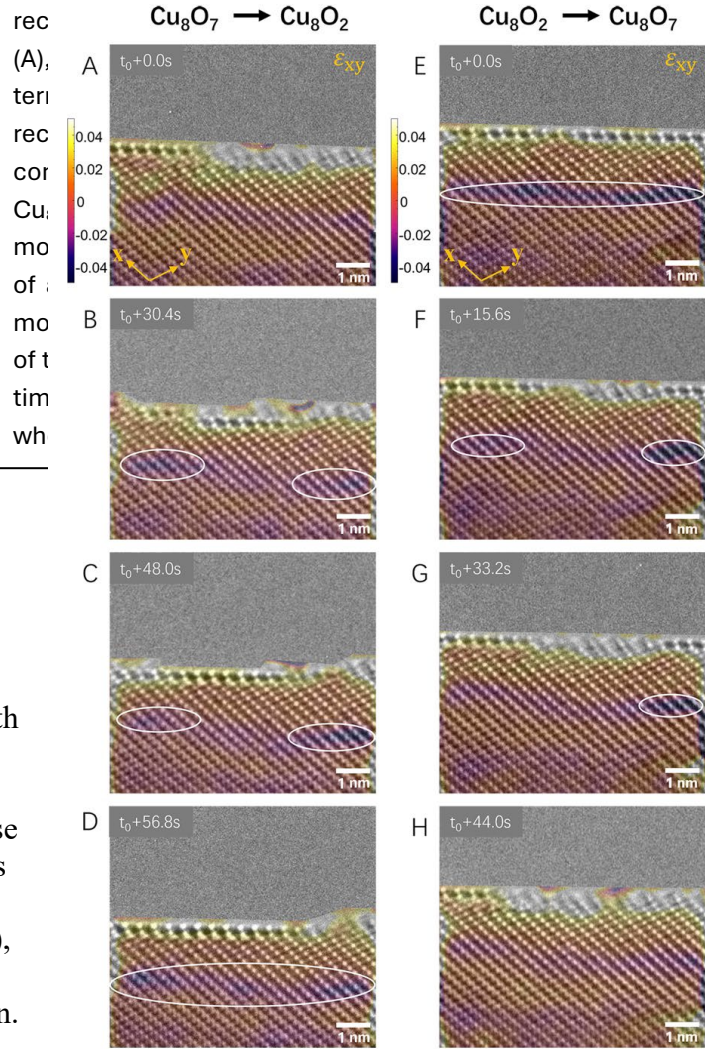


Fig. 2 uses Geometric Phase Analysis (GPA) to visualize strain evolution during interconversion. $\text{Cu}_8\text{O}_7 \rightarrow \text{Cu}_8\text{O}_2$ causes compressive subsurface strain from oxygen vacancy accumulation. Conversely, $\text{Cu}_8\text{O}_2 \rightarrow \text{Cu}_8\text{O}_7$ relieves strain as subsurface oxygen migrates upward. The strain band ($\sim 2 \text{ nm}$ below the surface) forms only beneath Cu_8O_2 , indicating limited oxygen mobility. Structurally, Cu_8O_7 is compact and facilitates faster oxygen diffusion, reducing strain. Cu_8O_2 is open, impeding diffusion and accumulating vacancies and strain. This structural contrast underpins their bistability and distinct surface behaviors.

This study reveals a self-sustaining oscillatory redox mechanism in CuO mediated by MvK dynamics. Combining in-situ measurements and density functional theory (DFT) modeling, we demonstrate that the CuO surfaces cyclically alternate between an oxygen-rich, reactive state and an oxygen-deficient, inactive state, along with sluggish bulk-to-surface oxygen replenishment driving spatiotemporally separated redox steps. These findings provide atomic-scale insights into redox-driven surface transformations in oxides, offering new avenues for controlling catalytic processes by tuning oxygen exchange kinetics. Our results refine the understanding of how surface-bulk interactions shape reactivity, with broad implications for catalysis and materials design. This phenomenon holds considerable significance in understanding various gas-oxide reactions, as it reflects the elemental processes that govern the surface reactivity of oxides more broadly.

Fig. 2: In-situ visualization of subsurface strain evolution during the reversible surface reconstruction of CuO at 300 °C and 0.5 Pa H₂, with GPA maps (overlaid on the HRTEM images) tracking stain dynamics during interconversion of Cu₈O₇ and Cu₈O₂ surface terminations. (A-D) Cu₈O₇→Cu₈O₂ conversion: progressive accumulation of compressive strain (dark blue regions) in the subsurface, highlighted by the expanding white ovals. (E-H) Cu₈O₂→Cu₈O₇ conversion: release of compressive strain, indicated by the

Future Plans

We will continue our integrated effort combining in-situ environmental electron microscopy, ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), and coordinated modeling to address several critical issues in oxidation mechanisms:

(i) Conduct aberration-corrected in-situ environmental TEM to investigate atomistic oxidation pathways in model systems including pure metals (e.g., Ni) and alloys (e.g., Ni–Al and Ni–Cr).

(ii) Perform AP-XPS experiments focused on the oxidation behavior of Ni–Cr and Fe–Cr alloys under competing oxidizing and reducing environments. Gas exposures will include O₂, H₂O, CO₂, and CO₂ + H₂O mixtures to simulate realistic reactive atmospheres.

(iii) Utilize aberration-corrected low-energy electron microscopy (AC-LEEM) to study the oxidation of NiAl(100) and Fe–Cr surfaces. These studies, conducted at the Electron Spectro-Microscopy beamline at NSLS-II, leverage high-brilliance synchrotron X-rays and advanced microfocusing optics to perform real-time, sub-micrometer-resolution XPS during surface oxidation. This spatially resolved chemical-state mapping provides critical insight into atomistic oxidation processes.

(iv) Carry out density functional theory (DFT) and ab initio thermodynamics modeling to support and interpret the in-situ and operando experiments, providing a predictive framework for understanding oxidation under realistic conditions.

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Harnessing Recycled Aluminum for Enhanced Alloy Performance: Primary Intermetallic Phase Control through Rapid Solidification

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Keywords: Recycled aluminum alloys, Fe-rich intermetallic compounds, Cooling rate, Casting

Research Scope

Recycling aluminum (Al) significantly reduces carbon emissions and cost, as it saves up to 95% of the energy required to produce new Al from raw minerals. Despite these environmental and economic benefits, the use of recycled Al in structural applications is limited, primarily due to high levels of iron (Fe) impurities. Excess Fe in Al alloys leads to the formation of large, brittle Fe-rich intermetallic compounds (FeRICs) during casting, which severely impair mechanical properties like fatigue resistance, ductility, and toughness. While adding alloying elements and increasing cooling rates can mitigate the negative effects of excess Fe, the complex interplay between alloy composition and cooling rates on FeRIC formation remains poorly understood.

This research aims to develop a comprehensive understanding and predictive capability for controlling FeRICs in recycled Al alloys. As such, we will combine innovative real-time high-temperature Raman microscopy, *in situ* high-temperature confocal scanning laser microscopy, and state-of-the-art phase-field modeling to investigate the mechanism governing the formation and growth of FeRICs at a microscopic level. Insights from our integrated studies will help identify optimal alloy compositions and process conditions for large-scale casting using recycled high-Fe containing Al alloys based on industrial demands. Additionally, our efforts will enable the design of novel Al alloys strengthened by controlled primary intermetallic compounds for high pressure die casting, additive manufacturing, and other rapid solidification processes.

Recent Progress

Experimentally, we have successfully cast binary Al-2.66wt%Fe alloys and performed wedge mold casting trials with fiber optic sensor embedded inside the mold cavity. This wedge geometry yields a systematic gradient in cooling rates, directly translating to varied microstructural development across the sample, as shown in **Fig. 1**. Our in-house developed fiber optic sensors [1-5], based on Rayleigh scattering, are embedded in the center of the wedge mold to track

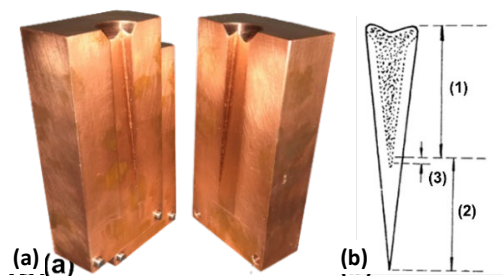


Fig. 1. (a) Copper wedge mold. The two halves join to make a 3" × 3" × 6" block. (b) Schematic of a cast wedge-shaped sample of an alloy.

temperature changes and collect cooling curves at multiple locations simultaneously. These sensors offer ultrahigh spatial resolution (temperature measurements every 0.5 mm) and high temporal resolution (update rate of 8 ms). Notably, Fig. 2 shows the setup of the fiber sensor and recorded cooling curves on commercial Al alloy 2024 (Al-4.5wt%Cu). The measured freezing temperatures are around 660 °C, and difference cooling rates on different locations are clearly demonstrated. We have also conducted casting trial on Al-2.66wt%Fe alloy. The experimental data is under analysis.

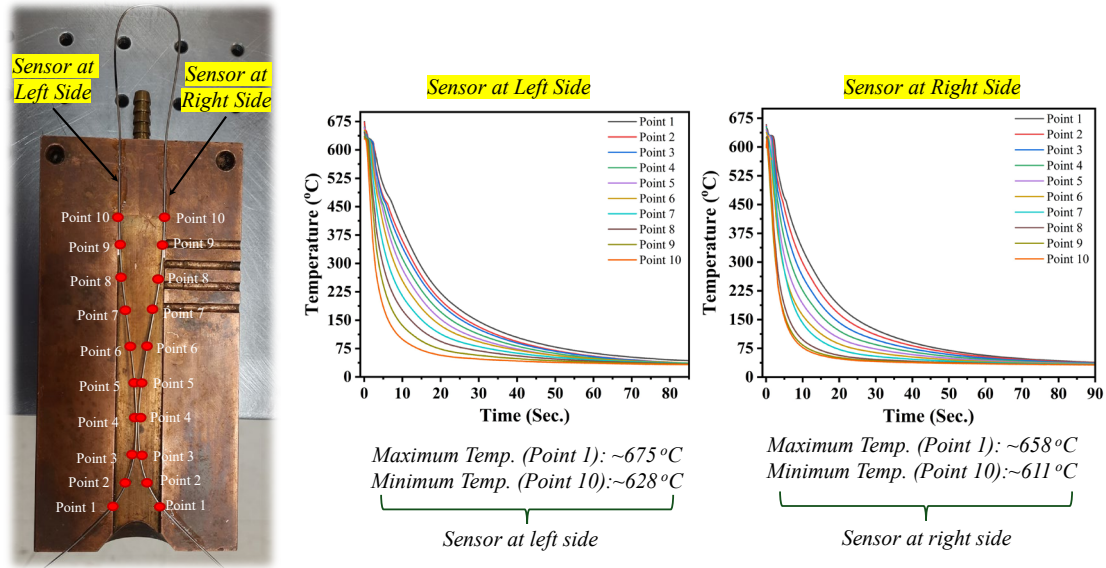


Fig. 2. Wedge mold casting of AA2024 with fiber sensor setup and measured cooling curves on both sides of the mold cavity.

On the modeling side, ORNL has developed a refined Al-Fe thermodynamic database that offers improved description of the FeRICs. The multiphase field model of FeRIC is underway. We are performing literature reviews to collect the parameters for the model.

Future Plans

We will complete the analysis of the wedge-cast Al-2.66wt%Fe samples, extracting site-specific cooling rates and degrees of undercooling. These will be mapped against microstructural features (phase fraction, distribution, and morphology) obtained through advanced microscopy and image segmentation workflows. Building on initial findings, we will extend casting and fiber-sensing studies to Al-3wt%Fe and ternary Al-Si-Fe systems to systematically probe the influence of increased Fe and introduced Si on phase selection. In parallel, in situ diagnostics, such as high-speed Raman spectroscopy for nucleation and confocal scanning laser microscopy for real-time growth, will be implemented under selected conditions. On the modeling side, we will deploy the improved Al-Fe thermodynamic database to develop and validate phase selection models for FeRICs in Al-Fe and Al-Si-Fe systems. Lastly, a multiphase field model will be developed to simulate the kinetics of the growth of FeRICs.

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Investigation and Prediction of Structural Ordering in Nitrides Through Machine Learning and Tunable Energetics

Robert Makin, Western Michigan University

Brelon May, Idaho National Laboratory

Keywords: disorder, nitrides, MBE, machine learning

Research Scope

Disorder in crystalline materials appears in many forms ranging in both length scale and dimensionality. This disorder can be either detrimental or beneficial, depending on the material, defect, and application. Processing-disorder-performance relationships are well-studied at some length scales but others, such as 0D anti-site disorder, are less emphasized and less understood. Achieving high quality, atomically-precise materials through the control of antisite disorder at manufacturing scale would enable unprecedented functionality across a range of applications and would have high technological and economic impact. However, to achieve this, a comprehensive understanding of the complex relationship between the synthesis environment and resulting structural ordering is needed. Our work combines enhanced tunability and control of adatom energetics during synthesis with machine learning (ML) techniques to understand and predict disorder in the wafer-scale synthesis of high-quality, single crystalline nitrides.

Disorder-controlled synthesis of these nitrides requires overcoming the high formation energy associated with the low order structures of these materials. Due to its inherent non-equilibrium conditions, plasma-assisted molecular beam epitaxy (PAMBE) provides a powerful platform with unique potential to overcome this barrier. The energy range accessible with PAMBE is often sufficient for growing high-quality ordered material. However, conventional elemental sources have limitations on the magnitude and control of the energy that they can impart to the constituent atomic species. We are addressing this energy deficiency issue through the development and testing of corona discharge effusion and plasma sources. We are coupling these sources with the quantitative study of the evolution of anti-site disorder during synthesis by measuring the Bragg-Williams order parameter (S) *in-situ* via reflection high-energy electron diffraction (RHEED). This will allow for real-time measurement of the effects of the energy of incoming atoms, and various other synthesis conditions, on the formation of disorder in materials.

The corona discharge sources provide needed degrees of freedom for the synthesis of disordered materials, but they also add more variables to the already high-dimensional, non-linear PAMBE growth space. Machine learning presents a method for the determination of complex relationships between synthesis conditions and disorder while simultaneously providing a path toward predictive control of disorder in advanced materials. We are creating robust training datasets comprised of PAMBE synthesis parameters, quantifying the resulting energetics of the atomic species produced by various sources when possible, and the corresponding measured degree of disorder in samples. We are developing both classical and deep learning ML models to provide predictive PAMBE synthesis and source operations. We are creating generative adversarial networks (GANs) to generate key outputs, such as RHEED images based on synthesis parameters, to investigate if such models provide increased accuracy compared to the other ML models. We are developing an understanding regarding the synthesis of atomic-level anti-site structural disorder in known and new high-quality monocrystalline nitride thin films by applying ML interpretation methods to predictions from developed models, combining this with atomically

precise thin film synthesis information, and determining methods for quantifying and controlling source energetics.

Recent Progress

We have begun a calibration process between two PAMBE chambers to enable development of chamber agnostic ML models from new and historic data for both machines. A graduate student from Western Michigan University (WMU) has been fully onboarded and trained to perform unsupervised MBE synthesis experiments at Idaho National Laboratory (INL). We are currently using the synthesis of NbN and GaN to calibrate the substrate heaters, electron beam sources, effusion cells and nitrogen plasma sources between the two chambers. We are using benchmark films grown in each chamber along with *in-situ* and *ex-situ* structural characterization and compositional measurements of the films to develop calibration factors between the chambers. These samples are also serving as the initial mapping the 0D anion-cation disorder-synthesis parameter space for NbN and ZrN. We are systematically sweeping the space of synthesis parameters and measuring S *in-situ* using RHEED (Fig 1a) and *ex-situ* using x-ray diffraction (XRD) (Fig. 1b). While our goal is to create ML models that can predict synthesis parameters for high-quality monocrystalline 0D disordered samples, we have included synthesis parameters that produce low-quality films, such as ones that are polycrystalline or amorphous, in our mapping of the 0D disorder-synthesis parameter space. Having this variety of samples will help our ML models to fully capture the complex relationship between synthesis parameters and 0D disordered samples and more accurately predict and aid our understanding of synthesizing high quality monocrystalline disordered samples. Additionally with these initial sets of films, we are investigating the impact of synthesis parameters on the time evolution of S during synthesis for NbN (Fig. 1c). and ZrN.

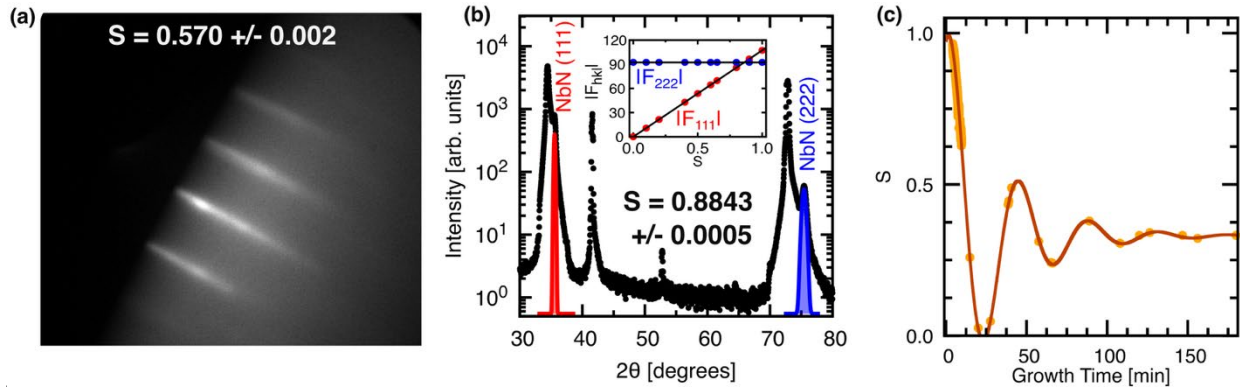


Figure 1. (a) RHEED pattern from NbN film showing the calculate S from RHEED. (b) θ -2 θ XRD plot for NbN showing the integrated area under the fitted fundamental (blue) and superlattice (red) peaks used to calculate S. (c) Time evolution of S during PAMBE synthesis, as measured from RHEED, in a NbN sample.

We have made refinements to the design of our corona discharge supersonic free-jet (CD-SFJ) plasma source to enable both improved performance and less complex fabrication process for the glass tube and connections between the vacuum-side and air-side of the source. We have completed fabrication of the gas and electrical connections through the ultra-high vacuum flange and are nearing completion of the glass tube, support structures, and accelerating plate. We are

also nearing completion for characterizing the radio-frequency nitrogen plasma sources on both chambers. We have collected over 2,000 optical spectra over a wide range of operating parameters for plasma sources and have analyzed them to characterize the distribution of species of nitrogen in the plasma.

Using our robust plasma source dataset from WMU, we are developing ML models for the nitrogen plasma sources to aid in controlling the nitrogen energetics through the prediction of the distribution of nitrogen species in the plasma at given operating parameters. For this task, we are training both multi-output regression models as well as generative models (Fig 2a) and are investigating model performance using objective scores based on predicted distribution of nitrogen species for a given set of operating parameters. For both the generative and regression models, we are employing conformal prediction to provide confidence intervals for the predictions from the models. Additionally, we are implementing SHAP values [1] (Fig. 2b) and LIME [2] to interpret the outputs from the models and gain a deeper understanding of the relationship the models learn between the plasma source operating parameters and the nitrogen species distributions predicted by the model. Similar data has been collected using the plasma source at INL, and comparisons made between the two different sources under a range of various operating conditions. As expected, due to both cells being N-plasma there is substantial overlap in behavior, however there are also some unexpected similarities and trends related to temporal aspects and ratios of molecular to atomic species. We are progressing in the development of a GAN model for predicting RHEED images and x-ray diffraction plots for NbN based on the synthesis parameters.

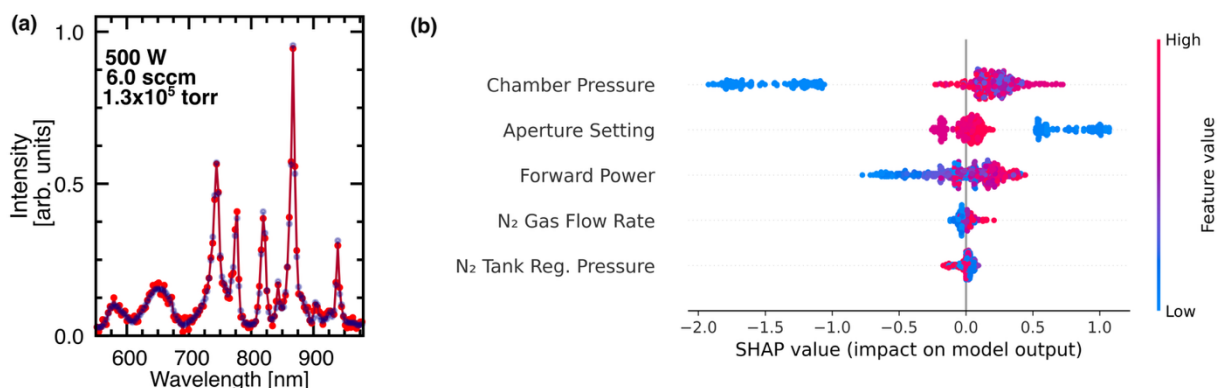


Figure 2. (a) Measured spectra from a nitrogen plasma source (blue) and spectra for a nitrogen plasma source generated by a GAN (red) for a given set of plasma operating parameters (inset). (b) A bee-swarm plot of the SHAP values for a regression deep learning model for predicting the distribution of nitrogen species in the plasma based on the source operating parameters. The color of the points corresponds to the value of the feature from the maximum (red) to the minimum (blue) and the position of the point along the x-axis corresponds to the SHAP value of that feature for the given data point.

Future Plans

In the next twelve months, we will continue our mapping of the NbN and ZrN disorder-synthesis parameter space. We will also perform calibrations between the two chambers using TaN to provide more calibration points for the e-beam sources and MnN and GaN to add effusion cells with different source material to further strengthen the non-electron beam calibration factors for the two chambers. Real time quantification of source stability and

energetics will be continued at INL using spectral analysis of the N-plasma and relating spatially resolved black-body measurements of the e-beam sources to sweep parameters and material quality. Current investigations have focused on (111) growths on GaN and (100) growths on MgO, and will be expanded to explore the impact of growth direction on disorder. For the rock salt structured materials, specific consideration will be given to the differences between the polar [111] and non-polar [100] directions.

We will also investigate the impact of source energetics and synthesis parameters on the time-evolution of S during synthesis using RHEED. After concluding our mapping of the selected binary nitrides, we will begin expanding our study of 0D disorder to investigate cation-cation disorder-synthesis parameter space in the ternary nitrides, such as Mn_3GaN and NbTaN_3 .

We will begin testing of our CD-SFJ plasma source and begin construction of the corona discharge effusion cell at WMU. We will explore the energetics of the corona discharge sources and conventional PAMBE sources using a quadrupole mass spectrometer and a combined electrostatic analyzer (ESA) and Wein velocity filter. The optical emission spectrum, ion energy distributions and ion velocities distributions (via ExB spectra obtained from the combined ESA and Wein velocity filter) will provide information regarding the energy and charge states of atomic species in the source beam and quadrupole mass spectrum will provide quantitative details regarding the mass within the source beam. We will investigate these spectra and beam characteristics over a range of operating parameters to collect data regarding the dependence of source energetics on various operating parameters, such as flow rate and voltages. The RF plasmas sources, standard effusion cells, e-beam sources CD-SFJ plasma sources and corona discharge effusion cells will be analyzed in this manner.

We will continue to develop our ML models for both prediction and control of source energetics and the models for predictive control of atomic-level anti-site structural disorder in known and new monocrystalline nitride thin films. For the GAN models, we will use the generated RHEED images qualitatively to assess properties such as crystallinity and surface quality and possibly to extract additional information, such as S. We will experimentally verify such model predictions. We will also explore using the GANs to create more intuitive relationships for operating conditions of equipment to achieve desired outputs. We will aim to extend the models trained for the binary nitride systems to ternary nitrides materials, through transfer learning techniques such as fine tuning, providing a method for predictive synthesis of monocrystalline nitrides.

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2. A. S. Messecar, C. A. Mensah, K. D. Vallejo, S. M. Durbin, B. J. May, and R. A. Makin. *Forecasting Active Species in Radio Frequency Nitrogen Plasma with Quantum and Conventional Supervised Learning*, Physics of Plasma, **(in submission)**.

END OF ABSTRACT BOOK