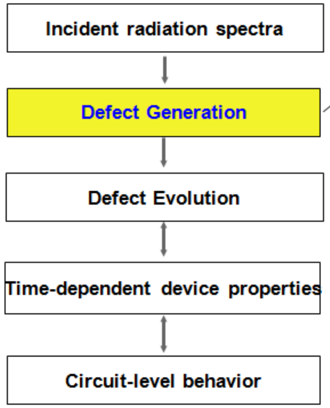
Molecular Dynamics Applications

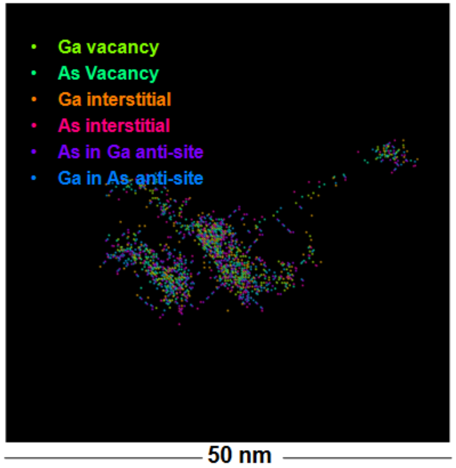
SAND2011-7965P

- Atomistic detail of key processes
- Gases, liquids, polymers, metals, ceramics
- Positions, velocities, forces of every atoms
- Massively parallel simulations to match experimental conditions

- Device models require predictions of the number and type of defects produced by the incident radiation.
- **MD** provides **calibration/validation** for binary collision approximation (BCA) calculations of defect generation

Phenomena required in the model circuit performance



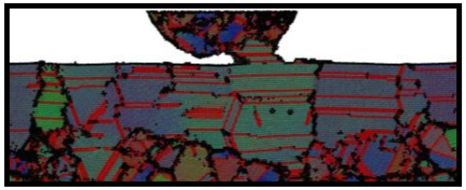


QASPR
QUALIFICATION ALTERNATIVES TO SPR

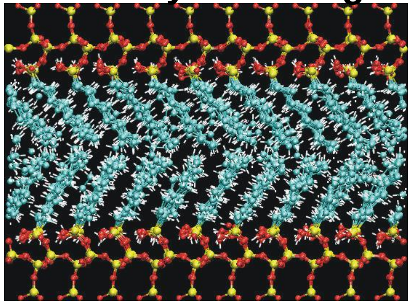
Molecular Dynamics provides key input for qualification of GaAs electronic devices

Molecular Simulation of Friction on a Variety of Materials

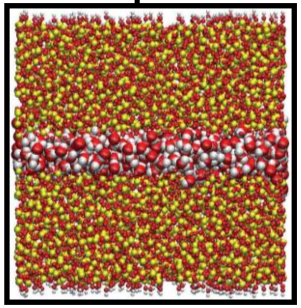
bare metals



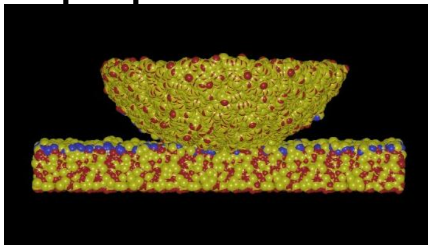
monolayer coatings



liquids



vapor phase lubricants

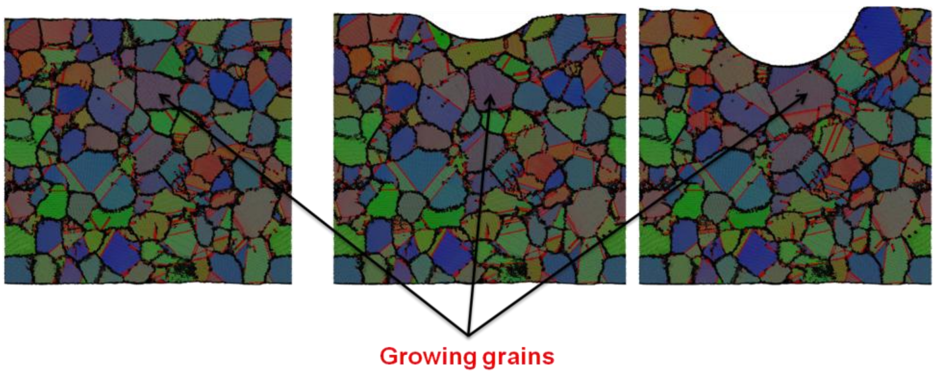


Simulations reveal failure mechanisms of MEMS coatings, and origins of friction reduction in metallic composites

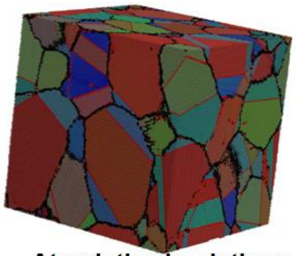
Sandia National Laboratories

Molecular Dynamics of Mesoscale Systems

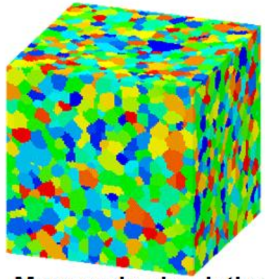
Direct observation of room-T, stress-driven growth



- **Indentation of a nanocrystalline Ni slab at room temperature**
- **Consistent with experimental observations**
- **Atomistic details provides an opportunity to ferret out the mechanism**



Atomistic simulations



Mesoscale simulations

New Insight!

Grain Boundary Roughening

↓

Mobile & Immobile Boundaries

↓

Grain Growth Stagnation

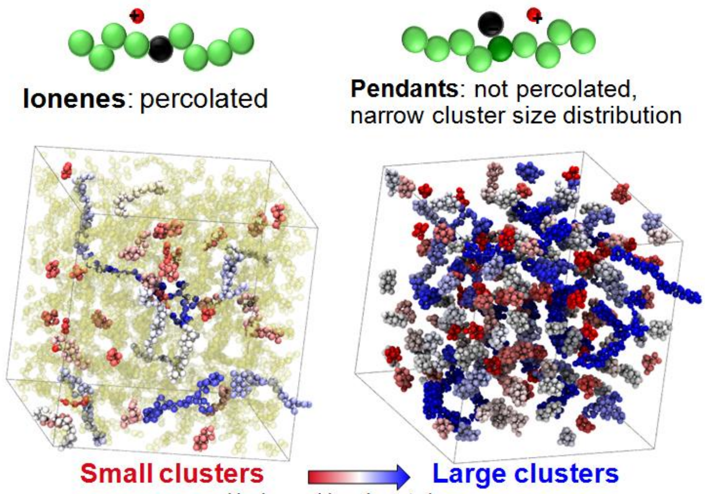
E.A. Holm, S.M. Foiles, "How Grain Growth Stops: A Mechanism for Grain-Growth Stagnation in Pure Materials", Science 328, 1138 (2010)

Combination of Mesoscale and Atomistic Approaches yields New Insight into Grain Growth

Ionomers/Polymers

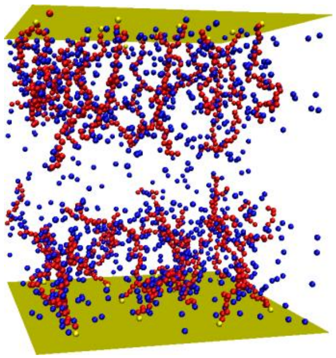
Ionic Aggregates in Ionomers

- Coarse-grained MD simulations
- Polymer architecture matters!
- Aggregate morphology will affect conductivity



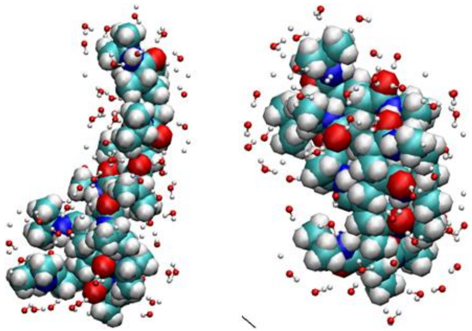
Uncharged beads not shown
Percolated structure is transparent yellow

Theory of Nanolubrication using Polymer Brushes



Two interacting polyelectrolyte brushes. Polymer is in red and counterions are in blue. The grafting surfaces are in yellow.

Adaptive and Reconfigurable Nanocomposites: Simulations of Responsive Self-assembling Molecules

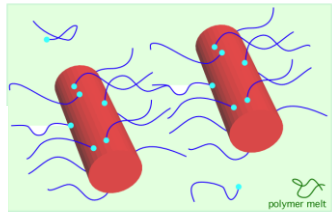


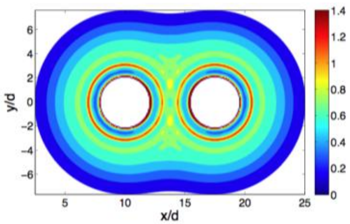
Single PNIPAM polymer images at temperatures above and below the LCST between hydrophilic and hydrophobic states.

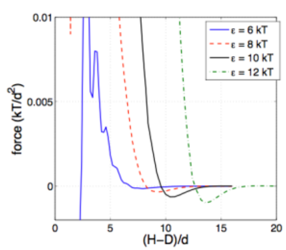
Classical DFT of Complex Fluids

Fluids-DFT

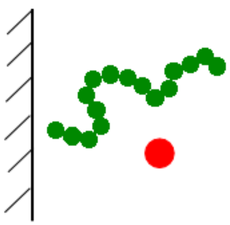
nanorods in polymer melt

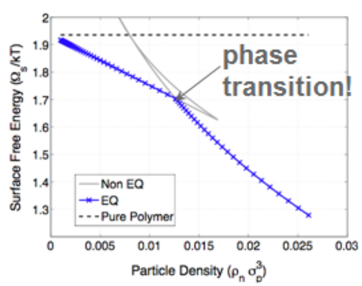






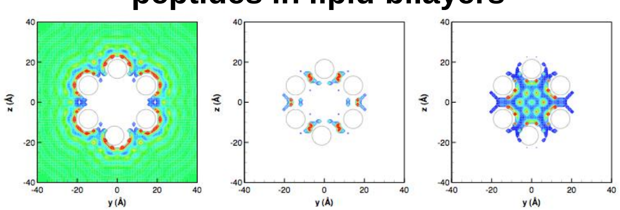
polymer nanocomposites

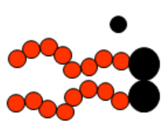


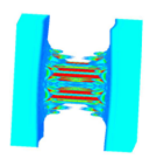


- Forces between particles
- Phase behavior
- Solvation free energies
- Complex geometries
- Electrostatics
- Compare to simulation

peptides in lipid bilayers

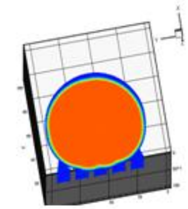


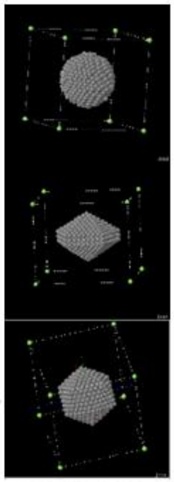


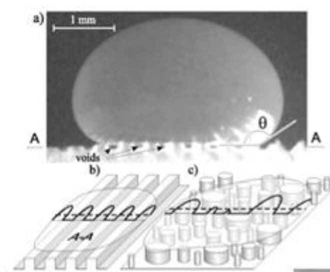


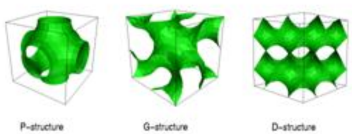
Molecular theory and modeling of Interfacial phenomena, self-assembly and nanostructures

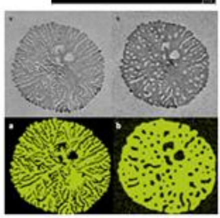
- Classical density Functional Theory of (charged) interfaces
- Ionic materials
- Stochastic phenomena in dense fluids
- Dendritic metallic nanostructures
- Droplets, wetting and capillarity
- Superhydrophobic surfaces
- Self-assembly of floating particles

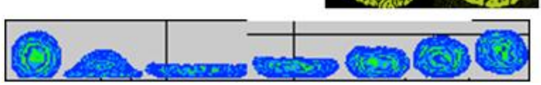












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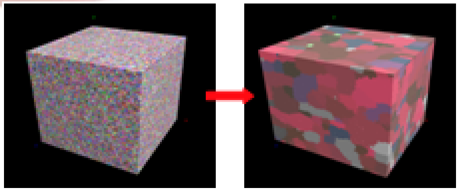
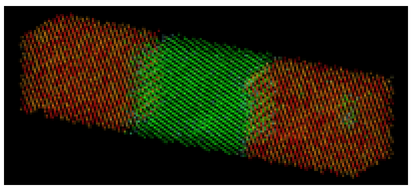
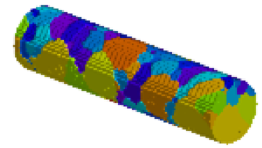
Grain Scale Research



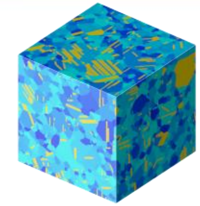
material point method



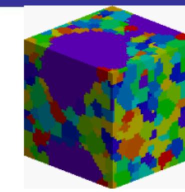
synthetic driving force MD



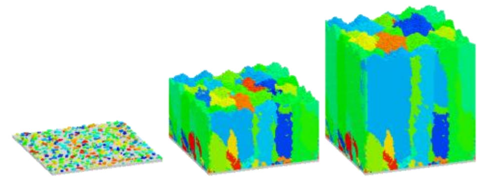
recrystallization



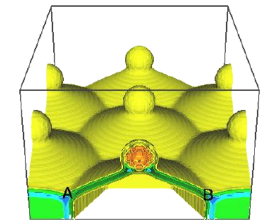
twinning



Abnormal grain growth



film growth



particle pinning

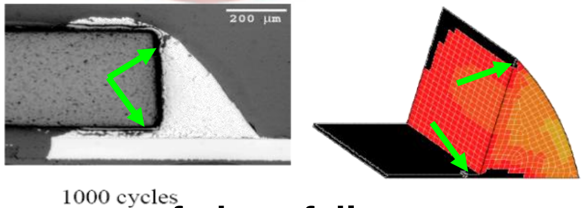
Probing material behavior using novel computational algorithms and method

- Novel methods: *synthetic driving force, kinetic MC, random grid, meshless, …*
- Predictive physics: *structure, properties, processing, performance, …*
- Bridging length and time scales: *atomistic, mesoscale, continuum, …*
- High performance: *small systems/high throughput, large systems/highly parallel, …*

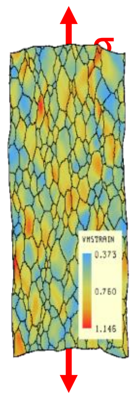
Modeling microstructural evolution and response in complex polycrystals

- Many phenomena: *recrystallization, grain growth, coarsening, wetting, diffusion, fracture, …*
- Many materials: *metals, ceramics, nanocrystals, polyphase, composite, …*
- Many factors: *particles, pores, solutes, twins, surfaces, defects, …*
- Many methods: *Monte Carlo, front tracking, cellular automata, genetic, …*

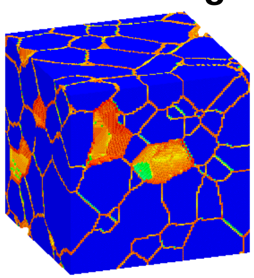
Simulations of Weld Aging



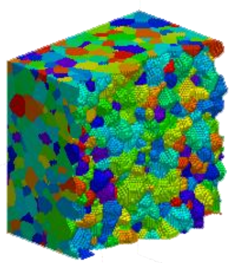
fatigue failure



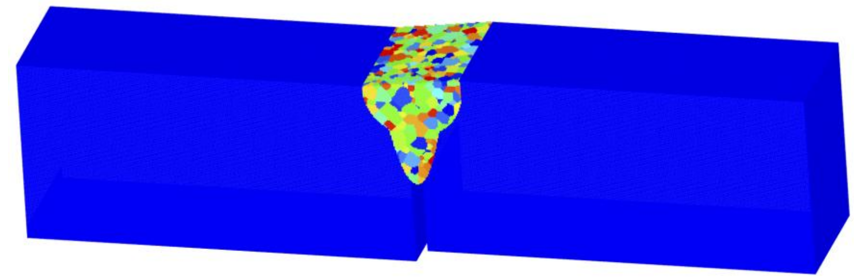
microscale plasticity



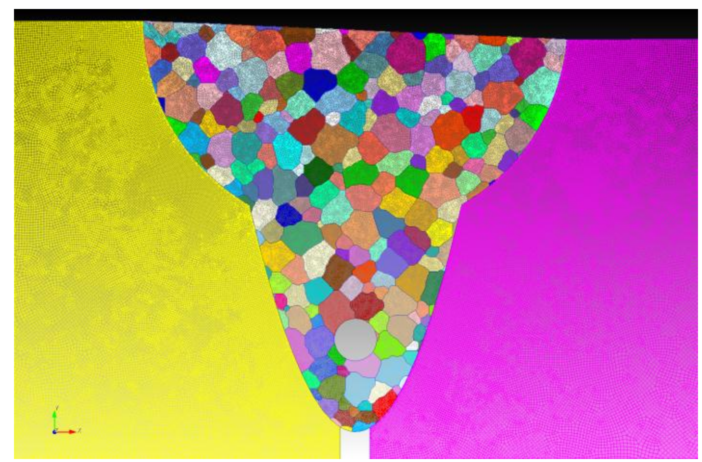
solute diffusion and pore migration



brittle fracture



Microstructure in a 3-D Weld



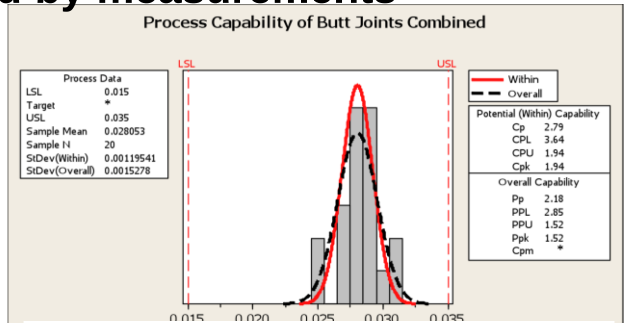
Microstructure and Pore in a 2.5-D Weld

Goal: Optimize materials properties over the lifetime of the system

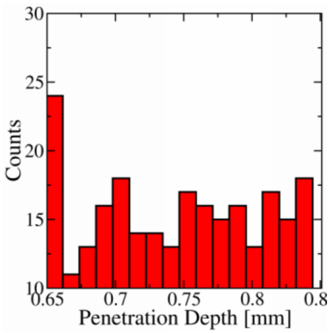
- **Processing:** ***shaping and forming, annealing, solidification, joining, …***
- **Service:** ***mechanical, electrical, and magnetic properties, hermeticity, …***
- **Aging and reliability:** ***substructure evolution, lifetime prediction, …***
- **Failure:** ***ductile and brittle fracture, fatigue cracking, breakdown, corrosion, …***

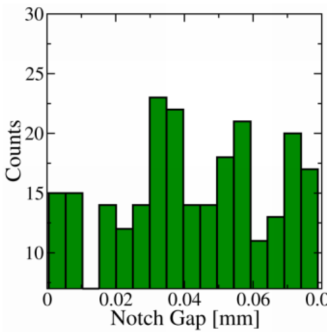
Simulations of 304L Weld Variability

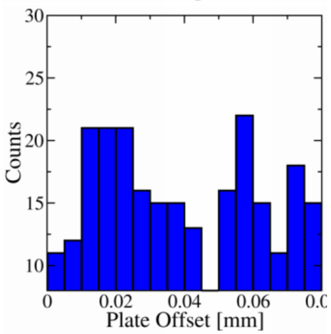
- **250 simulations performed on randomized geometries**
- **Geometrical variables informed by measurements**

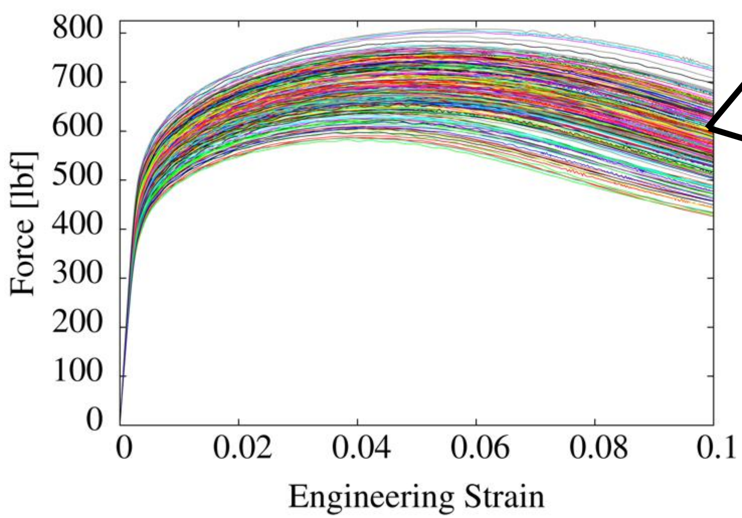


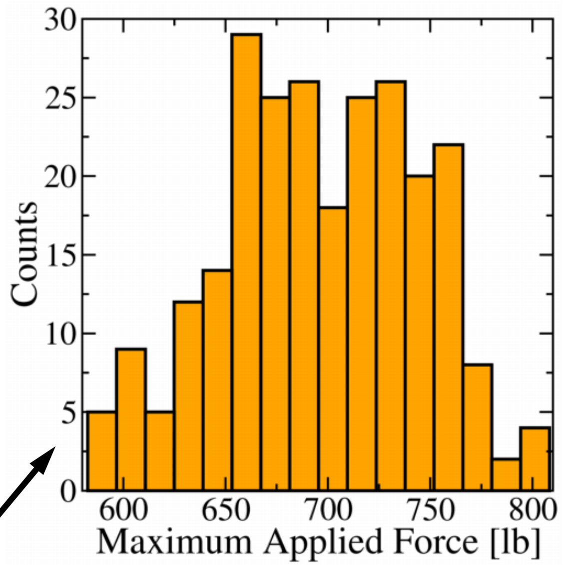
Typical penetration variance for production laser welds (*courtesy J. Samayoa, Kansas City Plant*)

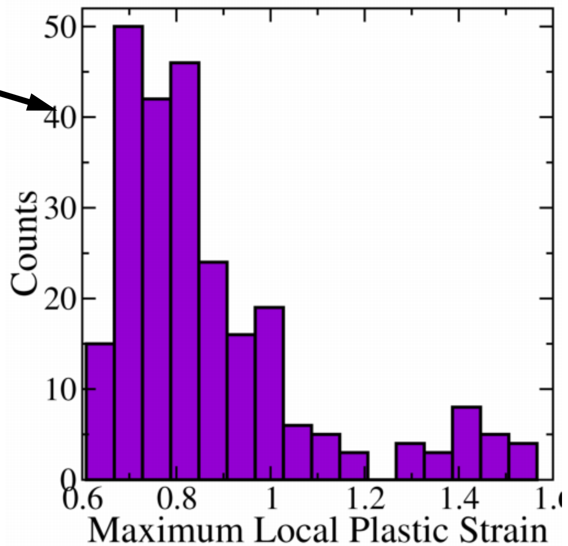












- **The method provides a means for quantification of property *variability***

Sandia National Laboratories

Ceramic Processing and Inorganic Materials Department at the AML

The Advanced Materials Laboratory, a part of Sandia National Labs since August, 1992

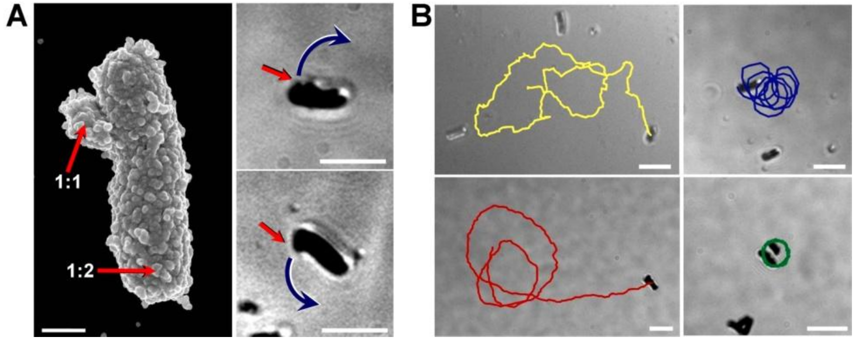
Developing materials science and engineering technology in the National Interest

The Ceramic Processing and Inorganic Materials Department is located at the Advanced Materials Laboratory (AML) – a Sandia-leased facility on the campus of the University of New Mexico

Strategic Advantages:

- **Access to students**
- **Greater opportunity for collaborations with UNM faculty**
- **Access to campus resources – equipment, library, computer resources**
- **Funding sources not readily available to Sandia (NSF)**
- **Joint purchase of novel instrumentation**

The AML has a wide range of capabilities important to Sandia's mission

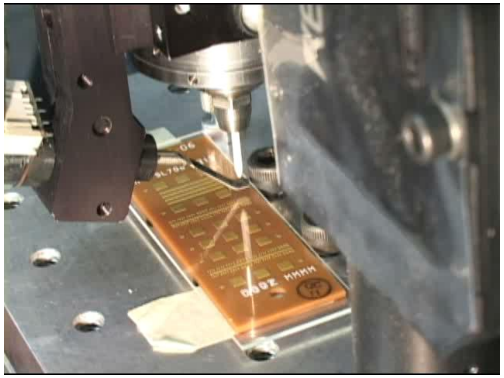


Synthetic Chemistry

nano particles
catalysts
films
bulk materials
surface functionalization

Ceramic processing

science of sintering
composite materials
unique fabrication
novel characterization



Nano-scale materials

synthesis
characterization
self-assembly
direct write

Bio-, Nano-materials capability

BSL-2 Laboratory
Multiphoton Lithography

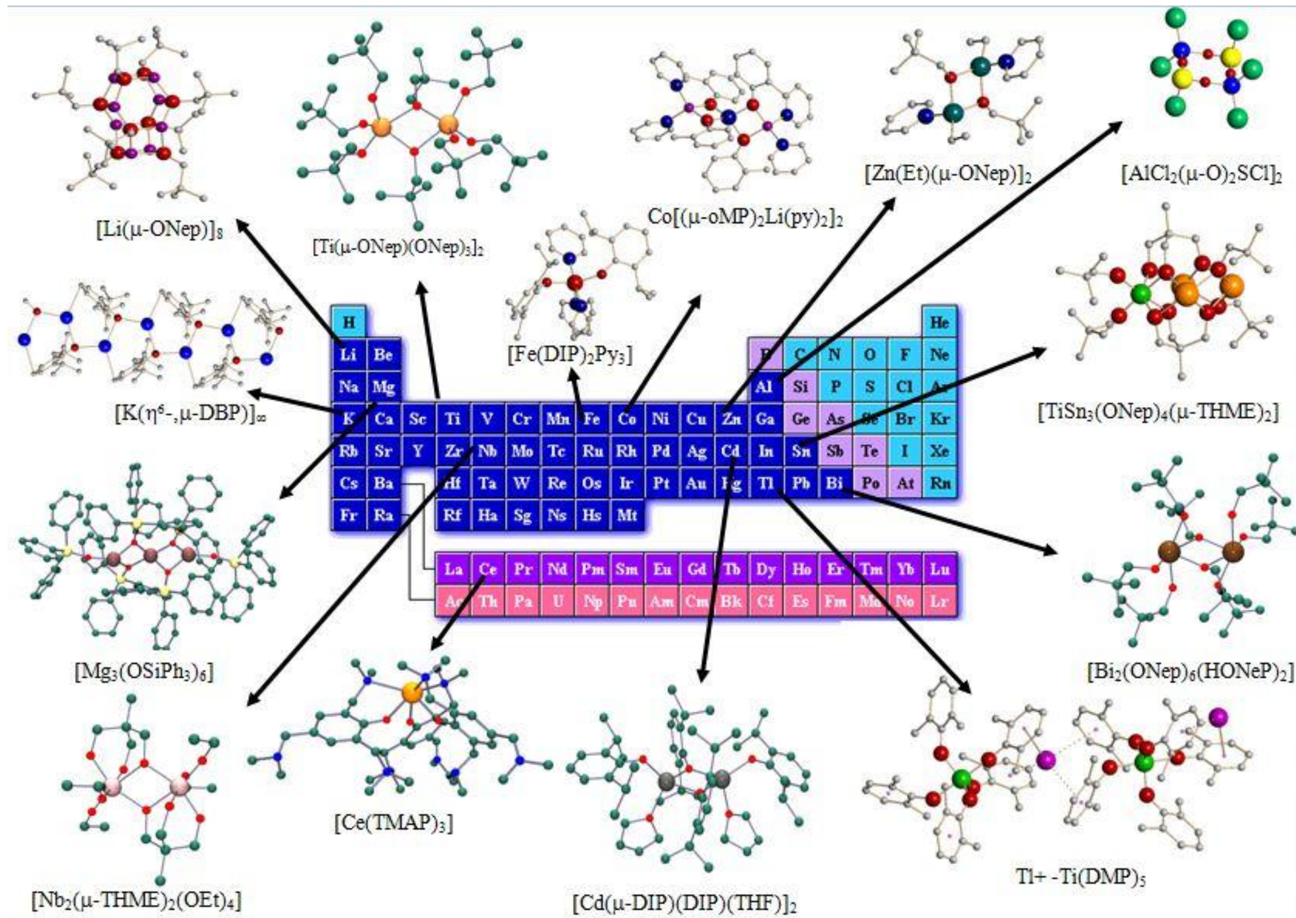
Characterization capabilities

x-ray diffraction, single XL
IR, EA, TA, Bio-AFM, etc.
optical microscopy, confocal

Chemical Synthesis underpins our capabilities to support Sandia's mission

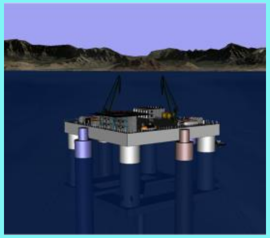
Design and synthesis of custom chemical precursors enables us to make novel materials and unique forms (nano scale particles, thin films, etc.) of a wide variety of materials

Our researchers have made over 1000 chemical precursors that were previously unreported in the technical literature

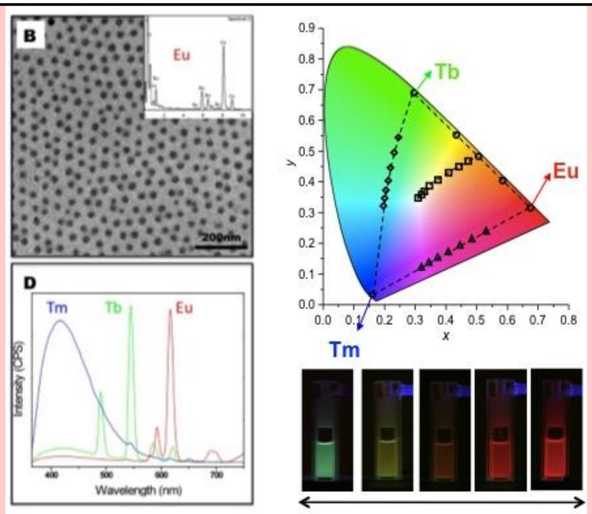


We believe this capability enhances our control of composition, particle size, morphology, and ultimately, the properties of the materials we synthesize

Our ability to make a wide range of materials and morphologies allows a wide range of application

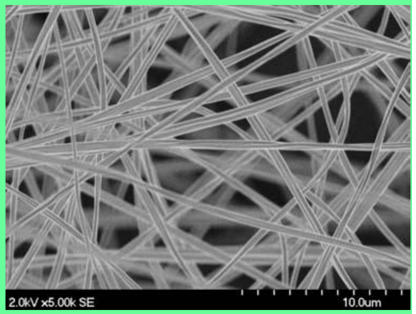


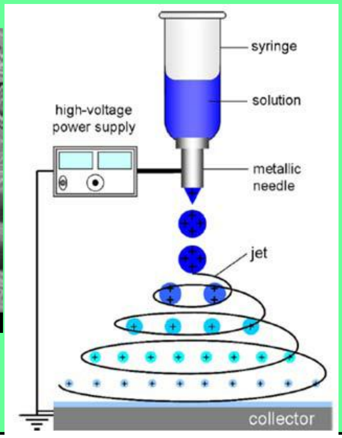
Corrosion resistant, anti biofouling coatings for Marine Hydrokinetic applications



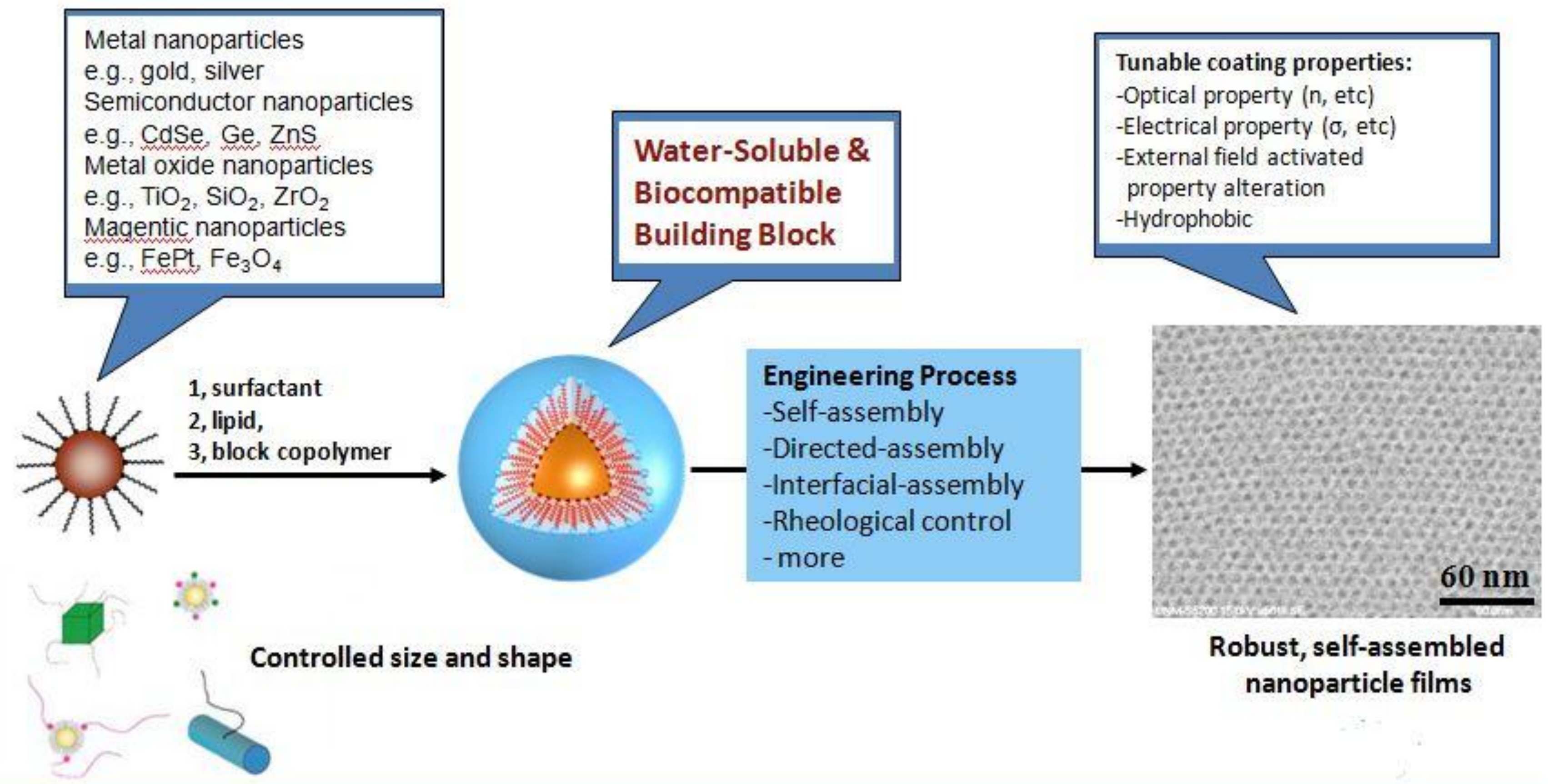
Polymer nanoparticles with controlled additions of rare earth elements allow tunable emitted color

Electrospun fibers and fiber mats for battery electrodes



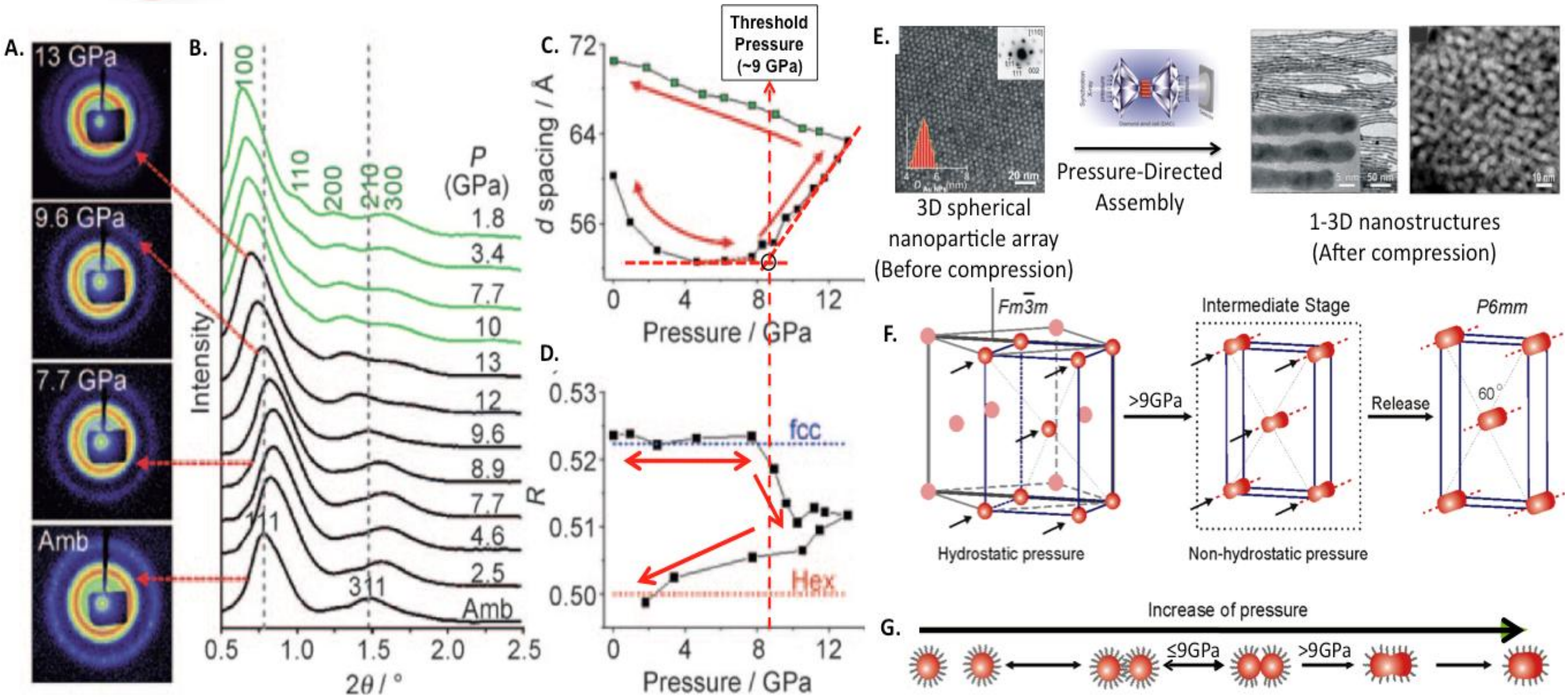


We are developing novel self-assembly strategies for unique applications



Water soluble, biocompatible surface functionalization leads to unique structures and an ability to investigate the bio-, nano- interface

Pressure directed assembly reveals new classes of functional nanostructures



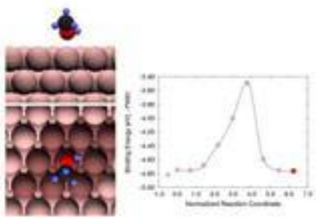
Films of unordered nanoparticles, subjected to high pressure, form new phases and, in some materials, nano-scale wire-like bundles

Our catalysis work builds on our strategic investment in synthetic chemistry

Synthetic Chemistry *and* Catalysis

Transportation Fuels from CO_2
(with Manos Mavrikakis, Christos Maravelias, Wisconsin – ChemEng)

Reduce CO_2 to MeOH with H_2, & Process Modeling for Overall System

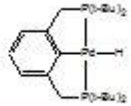


Sandia

Direct Oxidation of Olefins Using Molecular O_2
(with Karen Goldberg, U-Washington)

Mid-Late Transition Metals
Pincer Ligands on Rh, Pd, Pt, etc.

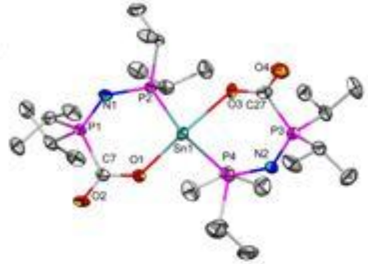
DOE-BES



CO_2 "Catch and Release"
(with Bill Geiger, Rory Waterman – Vermont)

Use Main Group-CO_2 Adducts to Aid in Conversion to Useful Fuels, Particularly Using Electrochemistry

Sandia



Sandia

Self-Assembly of PV Chips
Chemical SA Principles Applied to PV Chips

ACS-PRF

Olefin Polymerization/Catalysis
$6\pi e$ P-N, P-C Cationic Ligands to Replace Cp
Novel Weakly-Coordinating Anions

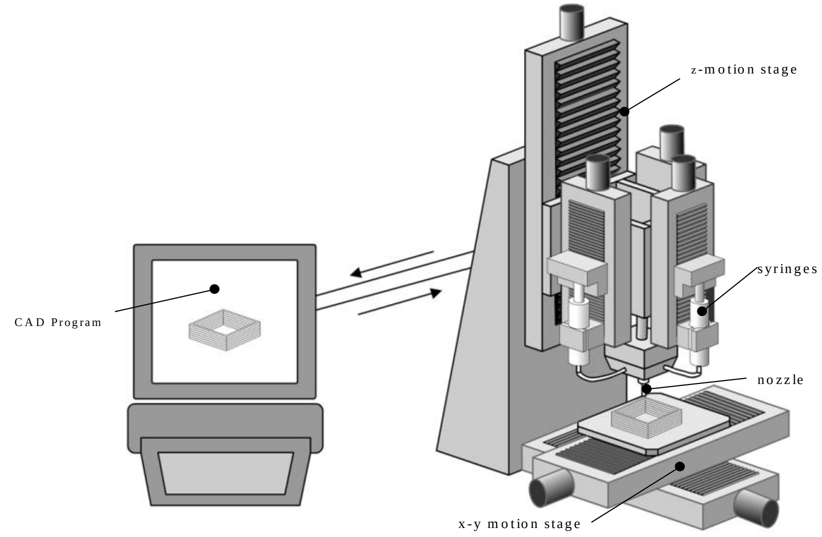
NSF

Lanthanide/Main Group - CO_2 (CX_2) Chemistry
Main Group Synthesis to Generate Useful Chemicals from CO_2 and Other Small Molecules

Computational Help: *Rick Muller (Sandia), Hua Guo (UNM), Jonas Oxgaard/Bill Goddard (Caltech)*

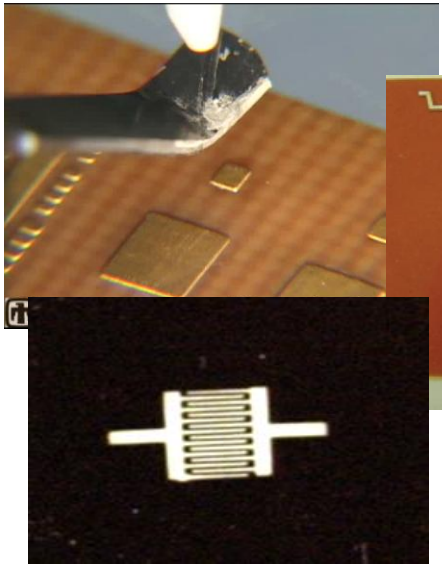
Sandia National Laboratories

Our "Direct Write" capability is unique within the DOE complex

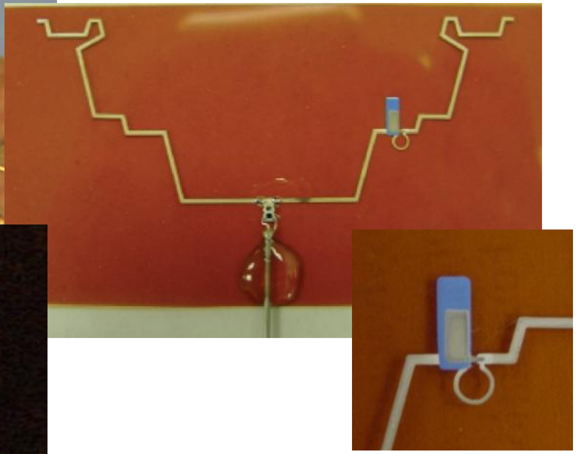


Computer controlled robotic deposition of custom and COTS ceramic slurries and metal "inks" allow fabrication of ceramic parts that could not be obtained through conventional ceramic processing.

Conductive lines and electrical components can be printed on almost any substrate with room temperature "curing." Features on the order of 20µm can be "printed" with only 4X bulk resistivity.

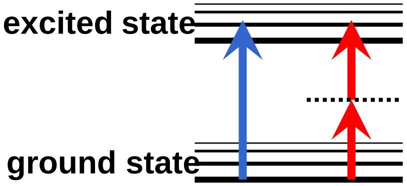


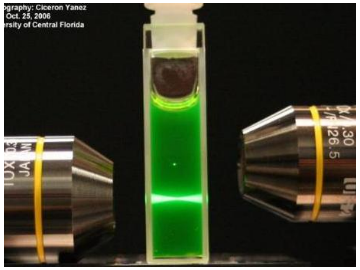
Dual Band GPS Antenna on Capton

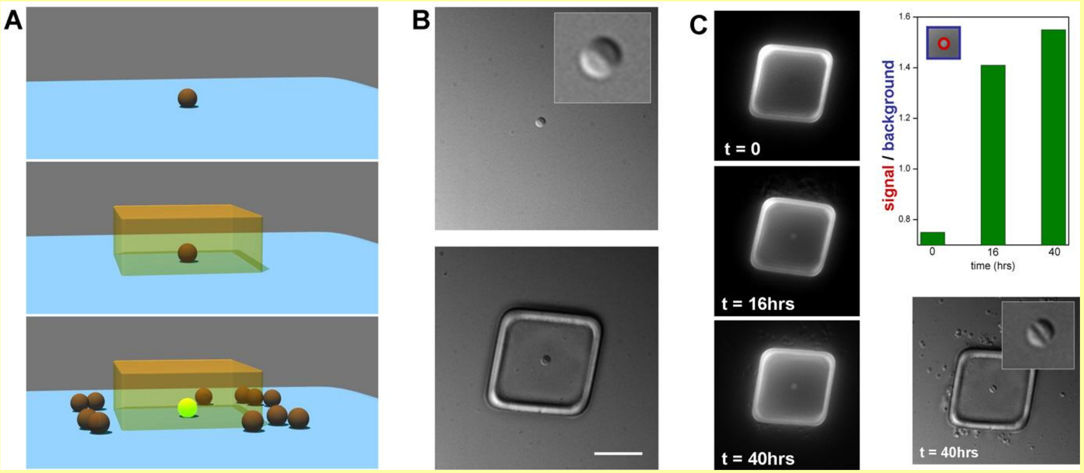


Multiphoton Lithography (MPL) is our new biocompatible 3D fabrication technique

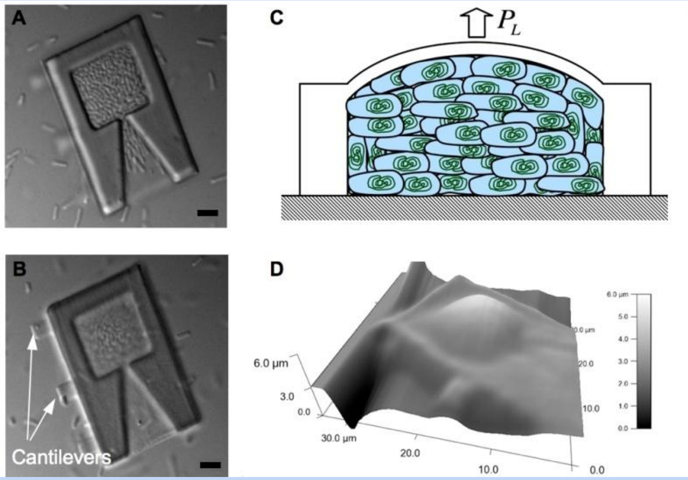
Pulsed laser light is focused into a solution of a photosensitive reagent solution (e.g., photoresist) to initiate photochemical reactions using two or more photons. This nonlinear excitation is restricted to regions of high photon density (e.g., proximal to the focal volume of a focused laser beam) which enables photochemical reactions, such as photopolymerization, to be confined to highly resolved 3D volumes on the order of ~ 1fl.







In situ confinement enables 'self-signaling' of individual cells via intercellular chemical signals



Trapped bacterial cells grow and exert pressure on the chamber ceiling which can be modeled, revealing pressures similar to that reported for tumors.

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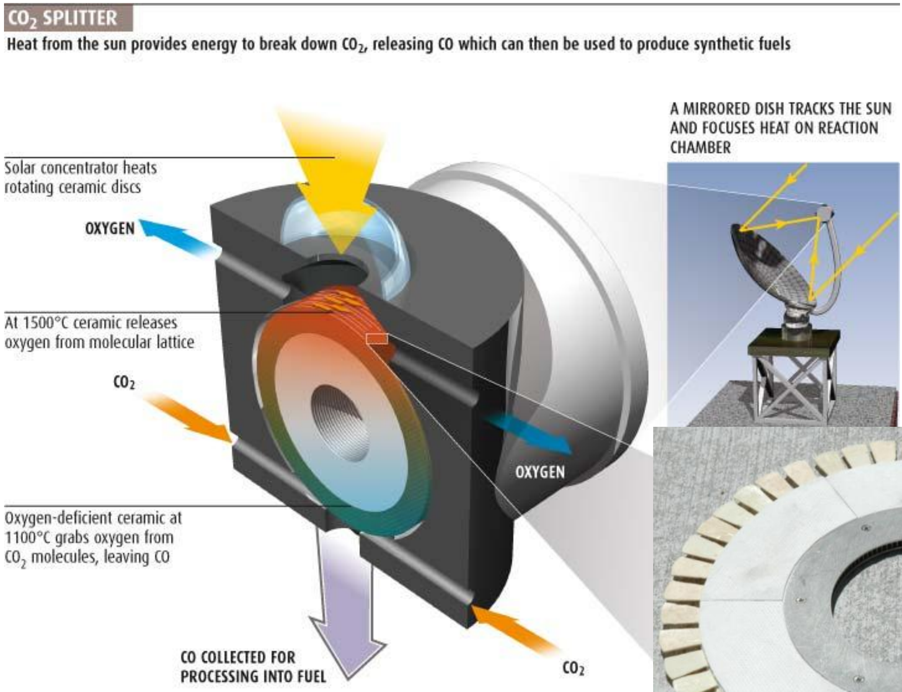
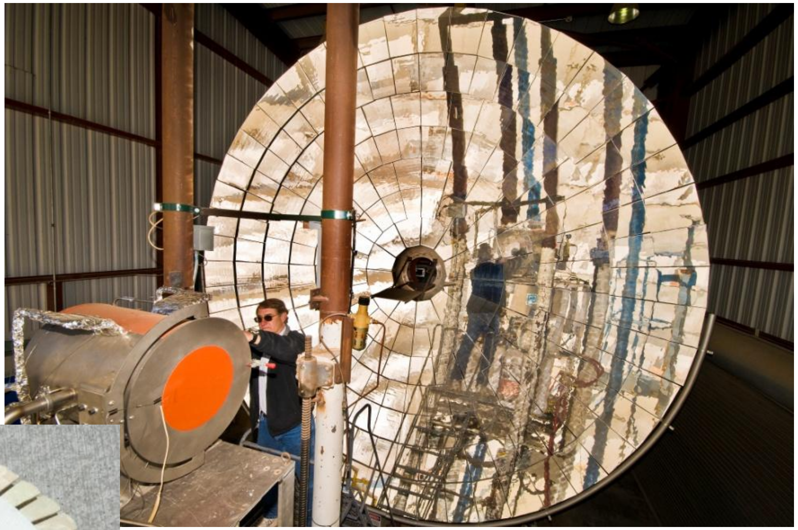
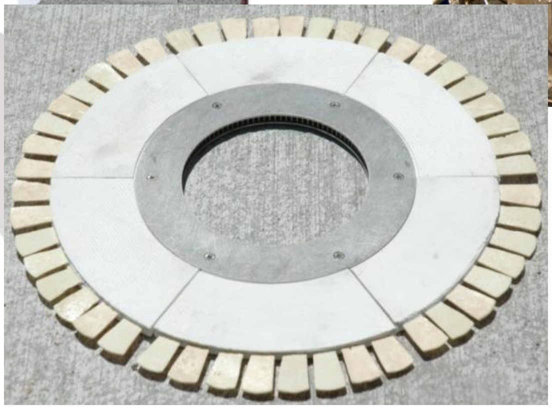
The "Sunshine to Petrol" (S2P) Grand Challenge brings together a variety of Sandia capabilities

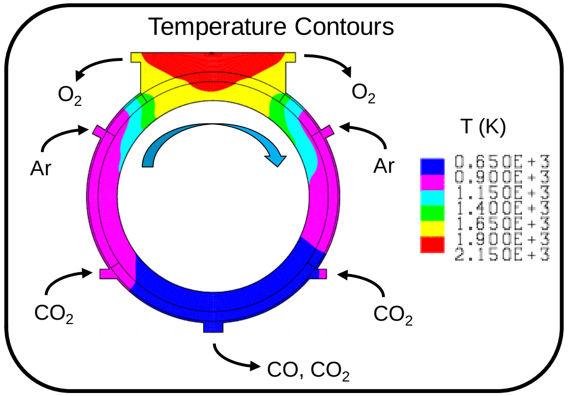
Basic Premise: *Sunlight + CO_2 + $H_2O \rightarrow$ Fuel + O_2*







Catalytic ceramic fins are the key to the necessary reactions



By collaborating with several universities and industry partners, we have assembled the capability to move this concept from the lab-scale to a commercial-scale demonstration.

Sandia National Laboratories

Advanced Electronic Ceramic Materials

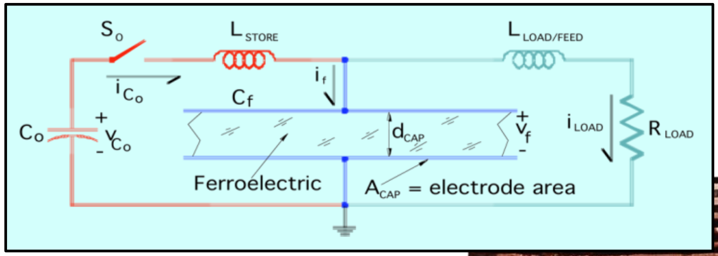
- Develop advanced ferroelectric and other electronic oxide ceramic materials

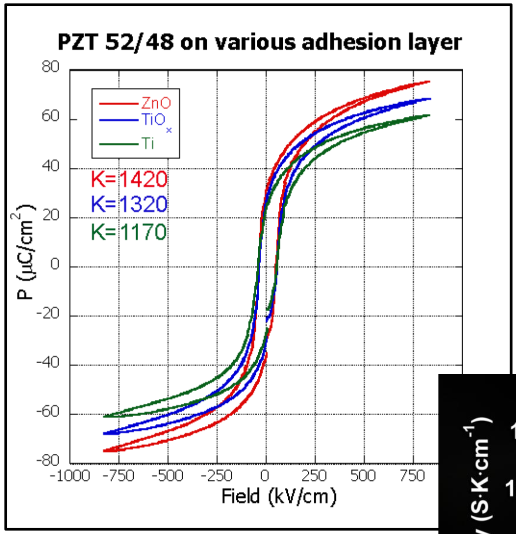
- Advanced processing from thin film to bulk device structures – high energy density capacitors to thermoelectrics to ionic conductors

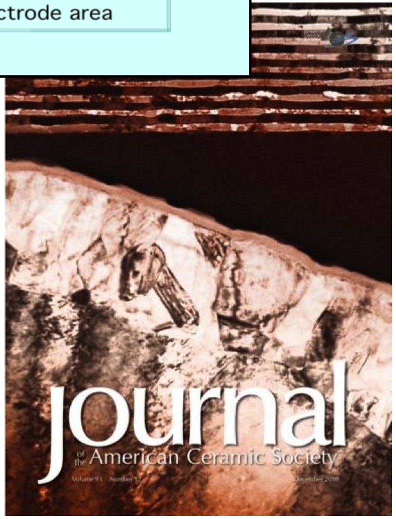
- Integration of oxides with electrode and other non-oxide materials

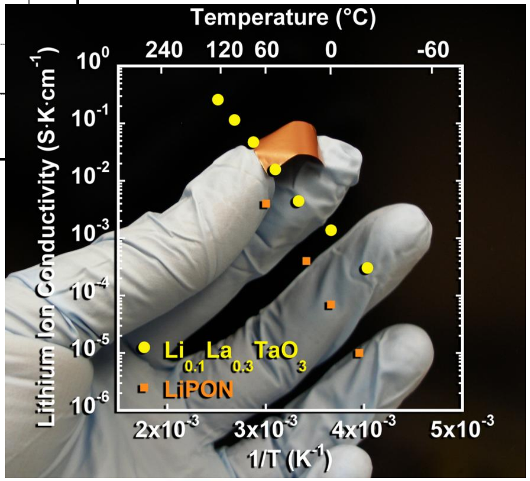
- Material and device characterization

- Electronic materials evaluation for a variety of internal and external customers







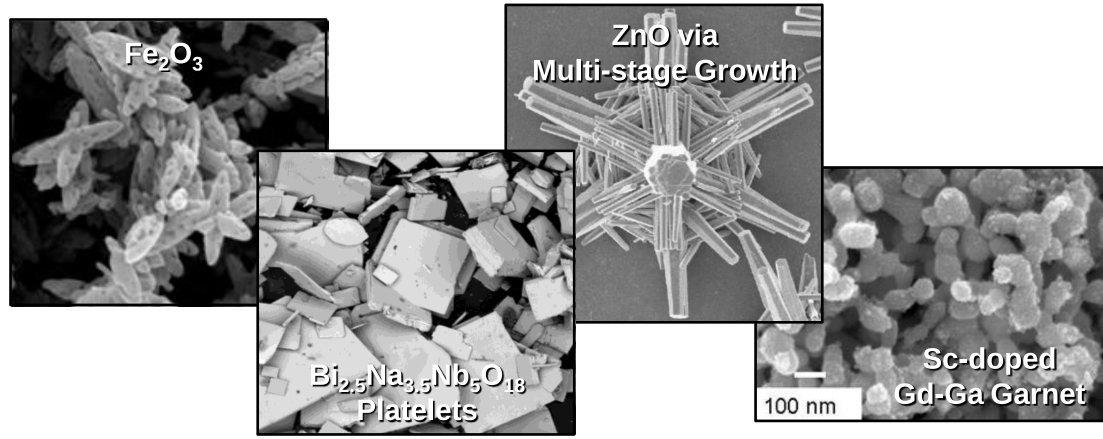


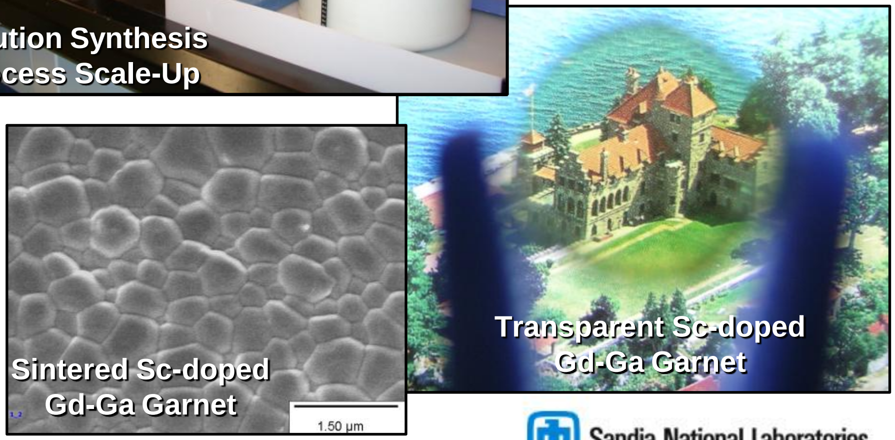
Ceramic Material Synthesis & Processing

- Utilize a variety solution synthesis approaches to produce a wide-range of controlled size, morphology ceramic powders and nanofibers

- Demonstrated capability to scale solution-based powder synthesis processes to multi-kilogram quantities

- Develop science-based processing approaches to produce a wide range of products from nanoparticle inks and suspensions to high density ceramics with controlled microstructures and properties





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Nanomaterials Assembly for Function

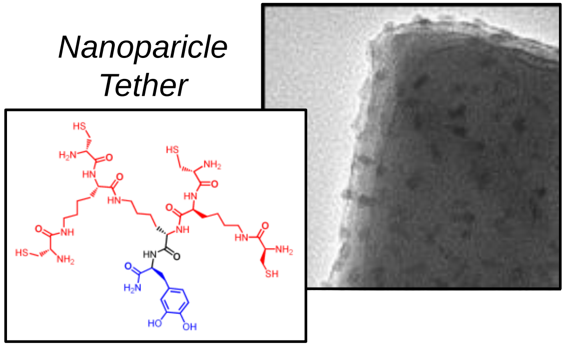
- Apply a variety of molecules and chemistries to functionalize surfaces for nano-architecture rearrangement due to external stimuli

- Biomimetic assembly and tailoring of molecular function though use of designer peptide synthesis and motor proteins

- Develop and assemble nanostructured materials for energy storage (batteries, ultracapacitors), energy conversion (next generation photovoltaics), and reversible CO_2 sequestration

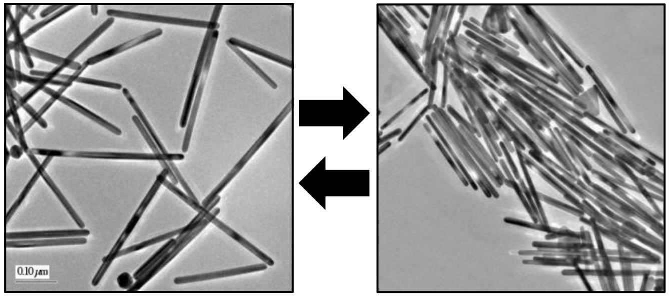
Designer peptide synthesis used to tailor molecular function.

Nanoparicle Tether



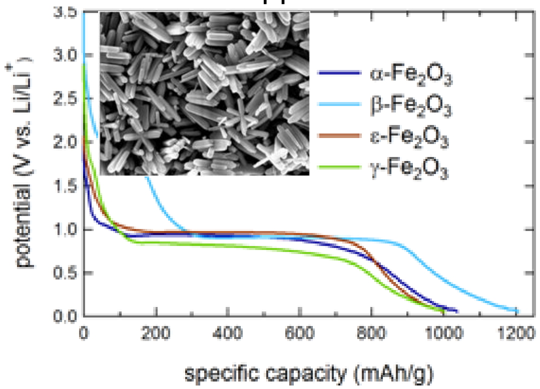
Self-assembled monolayers to mediate interactions + assembled architectures.

CTAB (cationic) POPC (zwitterionic lipid)

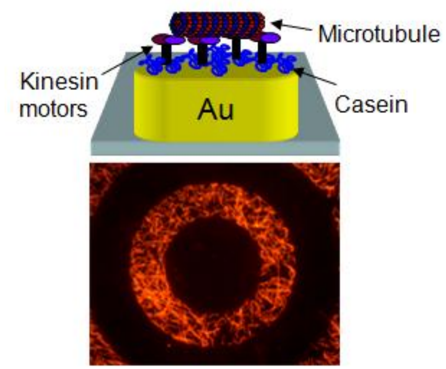


(ACS Nano, 3, 971 (09))

Synthesis & assembly of iron oxide polymorphs for battery cathode applications.



Selective integration of protein microtubules into lithographic defined architectures.

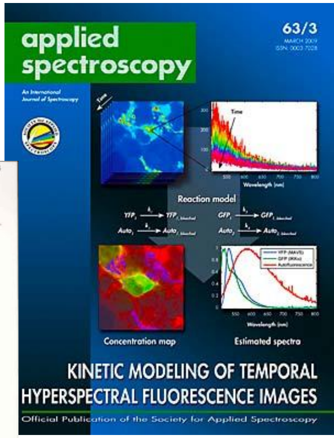


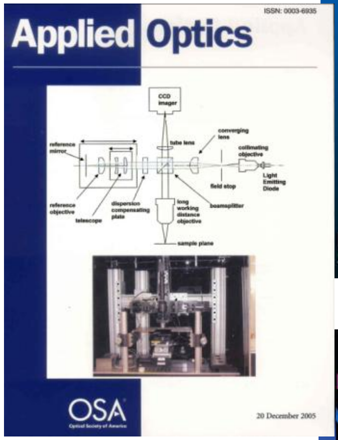
Optical Instrumentation Development & Nano/Micro-structure Simulation and Characterization

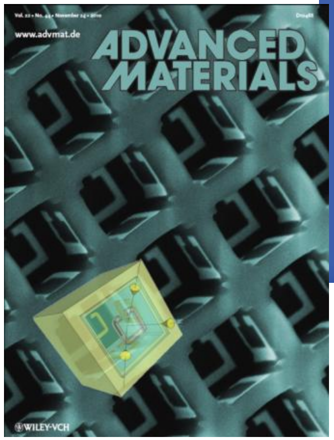
- Optical instrument development → addressing specialized requirements
  - Optical design (ray tracing), optomechanical design, fabrication and construction
  - Hyperspectral Confocal Microscope (R&D100 Award 2009)
  - Long working distance interference microscope (commercialized)
  - Polychromator: IR MEMs programmable diffraction grating
  - Hyperspectral microarray scanner

- Characterization of nano/microstructured materials
  - VIS & FTIR spectroscopy
  - Brillouin spectroscopy --- phonon band structures
  - Femtosecond spectroscopy
  - Light scattering spectroscopy

- Electromagnetic simulation and theory of nano/microstructured materials → metamaterials, plasmonics, diffractive optics
  - Optical properties (absorption, reflection, thermal emission, etc)
  - Finite Difference Time Domain (FDTD), Rigorous Coupled Wave (RCWA), Method of Moments (MOM), Optical Multilayers







Sandia's NMR Spectroscopy Facility

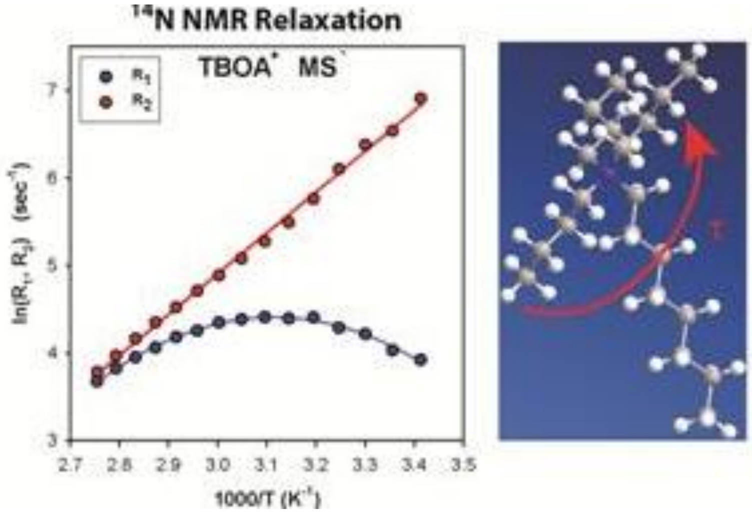
- Maintain both high resolution solution and solid state capabilities for the characterization of chemical structure, reaction kinetics, morphology and dynamic properties

- Continue to develop and implement new and novel multi-dimensional and multi-frequency NMR capabilities

- Maintain an active research component linking computational simulations and NMR experimental results

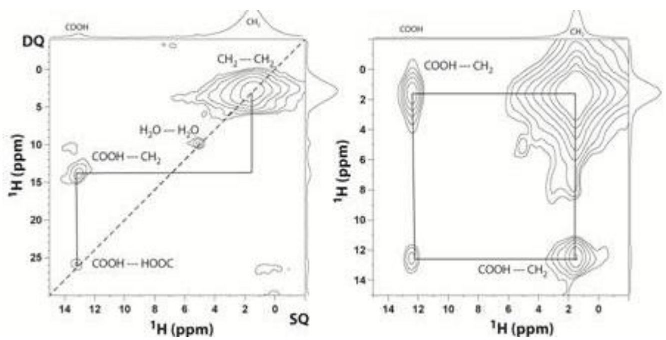
- Recent additions: 1) high field gradient probes for measurement of diffusion constants of molecules in solutions and membranes and 2) ultra-high speed MAS NMR capabilities allowing improved resolution for ^{1}H containing materials

Dynamics in Ionic Liquids



^{14}N NMR relaxation experiments for the direct determination of molecular correlation times.

Structure and Dynamics in Ionomers



2D ^{1}H MAS NMR correlation experiments in P(E-AA) ionomers: a) DQ BaBa and b) NOESY.

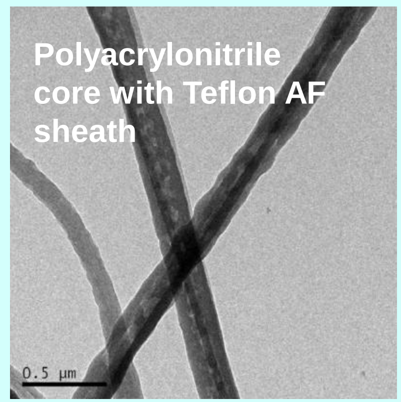
(see: http://www.sandia.gov/materials/science/nmr_lab/)

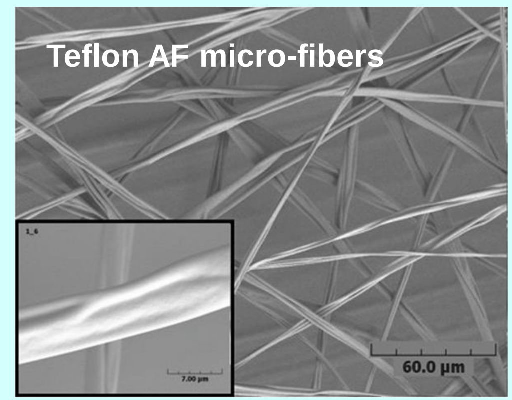
We successfully developed a technique to electrospin fibers of nonpolar teflon AF to produce superhydrophobic membranes

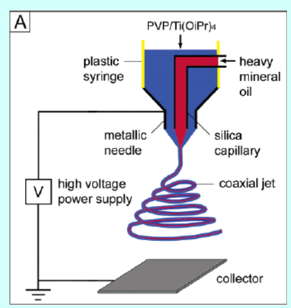
Electrospinning is a method to form nanosized fiber morphologies of organic polymers or inorganic materials via sol-gel chemistry, leading to the production of unique membranes and/or support materials.

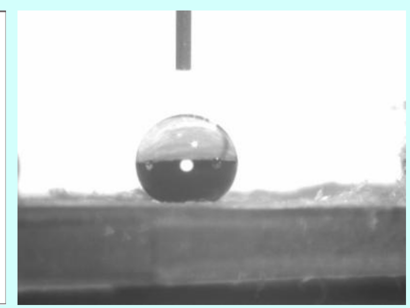
Electrospinning requires a polar dielectric nature in the solvent and polymer to respond to an applied electric field. Non polar materials require co-spinning with a responsive material in order to successfully develop fiber morphologies. We made morphologies of Teflon AF fibers by two approaches:

- co-electrospinning to form nanosized fiber dimensions
- solvent dielectric constant manipulation to achieve ribbon like micron sized fibers.









Water contact angle of 151.1 ± 2.64 measured over nanofibers.

"Electrospun Teflon AF fibers for superhydrophobic membranes," J. Mater. Res., Vol. 25, No. 8, (2010) 1595-1600.

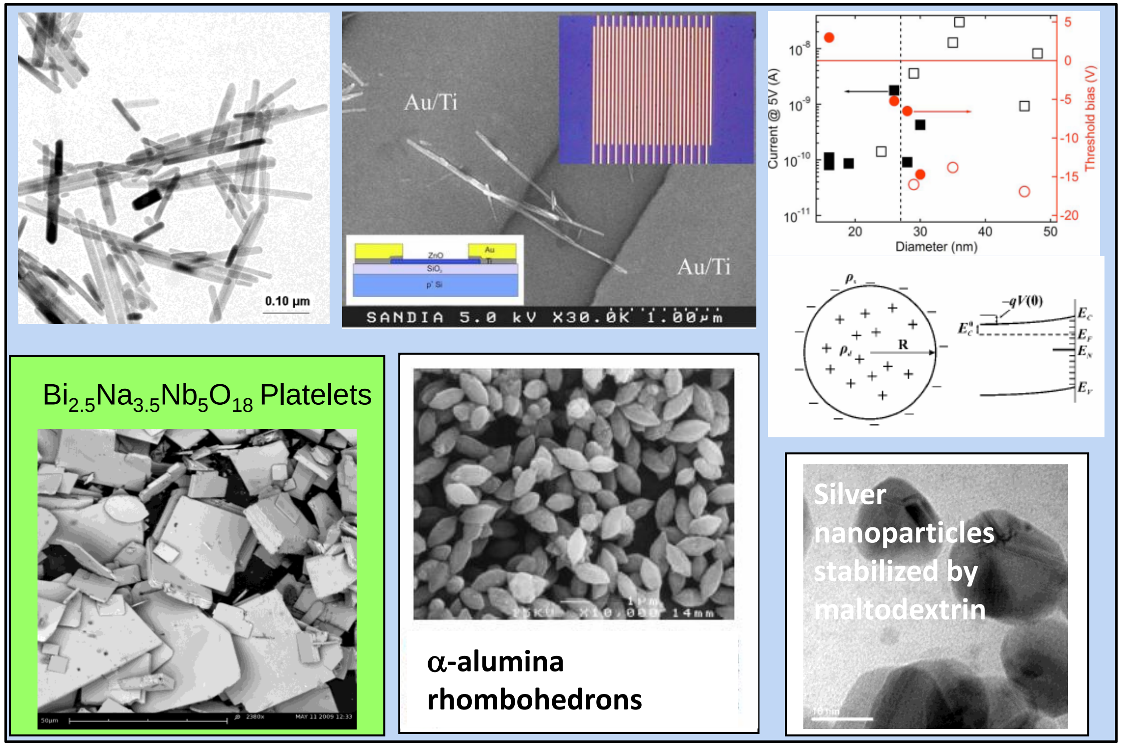
Sandia National Laboratories

Solution precipitation with particle shape control allows for fundamental materials characterization of nanomaterial properties or control of texturing in electronic ceramics.

The control of component properties can be greatly impacted by crystal orientation, leading to a need to easily fabricate nanomaterial seed or templating particles using solution growth techniques.

Our chemical expertise in solution processing fabricates desired particle morphologies for testing of electrical properties of nanowires, or other systems requiring templated grain growth

- ZnO nanowires were formed using hydrothermal or solvothermal synthesis routes, and individual wires were tested for the effect of width vs. electric conduction.
- Molten salt techniques are used to generate template platelet particles of large size (> 10 micron).
- Additional metals and ceramics formed by similar routes



Frank Jones, François Léonard, A. Alec Talin, and Nelson S. Bell, J. Appl. Phys. **102**, 014305 2007.

Sandia National Laboratories

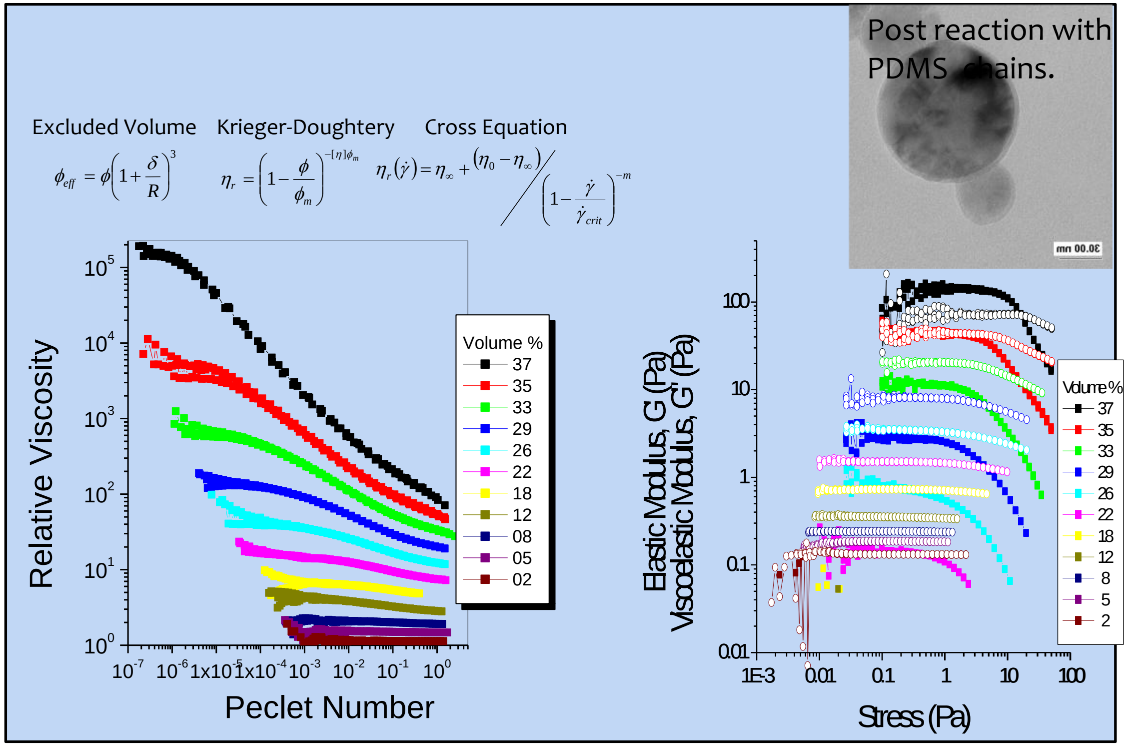
Colloidal dispersion is critical to effective development of ceramic processing routes, component fabrication, and understanding of filled particle systems

Operations at Sandia often encounter a need to control dispersion of discrete particles in either fluid or polymeric matrices. To succeed and optimize, this work requires a detailed understanding of the science and practice of particle dispersion.

We performed a fundamental experimental study coupled with interfacial modeling of the ability of nanopowders to achieve high solid content loading with flow properties involving:

- Surface modification of TiO_2 nanopowders
- Dispersion within compatible fluid
- Rheological testing of flow and structural properties

These studies impact Sandia's work in filled epoxy nanodispersions and filled elastomer composites .



Nelson S. Bell, Amalie L. Frischknecht, and Martin PiechGrafted Low Molecular Weight Polymers as Steric Stabilizers of Commercial Titania Nanoparticles in Polydimethylsiloxane Fluids," J. Dispersion Sci. Tech, Vol. 32 [1] (2011) 1-13.

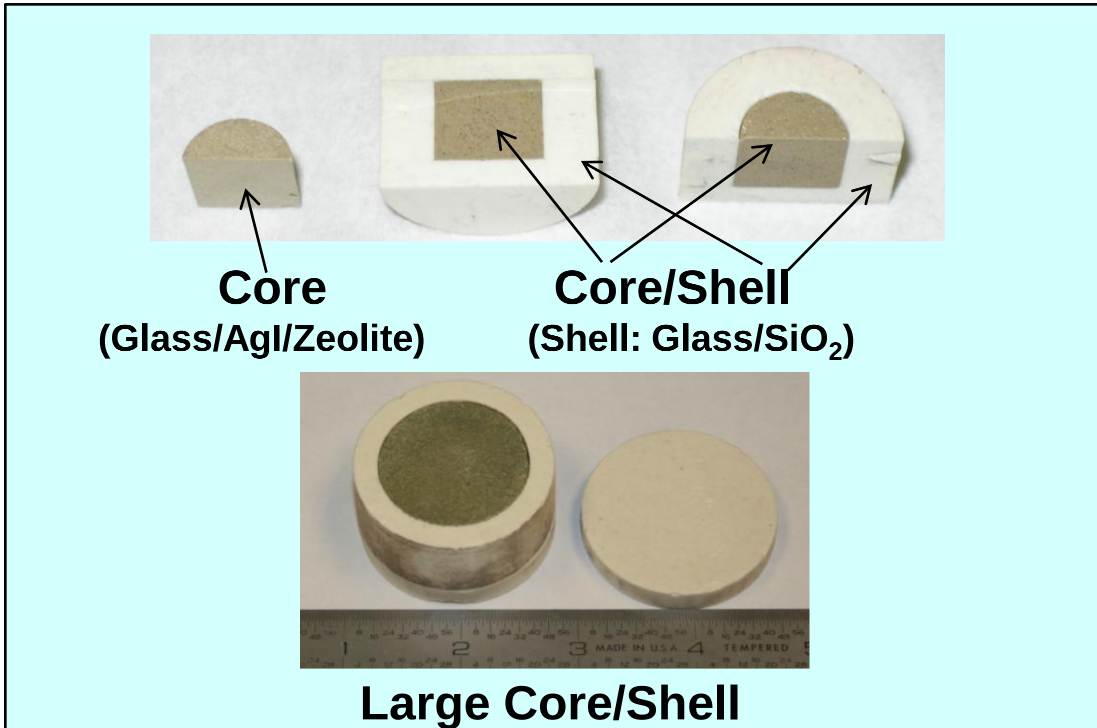
We have developed a new ^{129}I waste form by encapsulation in a low sintering glass and then forming a core/shell structure.

^{129}I from used nuclear power plant fuel must be safely stored for millions of years due to its long half-life (~17 million years) and its toxicity to human and other life.

Utilizing our ceramic processing expertise:

- ceramic fabrication
- constrained sintering
- composite processing,

we have developed a waste form for ^{129}I that consists of a core containing the ^{129}I encapsulated with a durable glass that is surrounded by a shell of glass that is surrounded by a shell of the same glass mixed with silica to match the CTE of the core. The shell protects the core from the environment. The structure is densified by sintering at a low temperature where AgI is stable.



*accepted for pub. J. Am. Ceram. Soc.

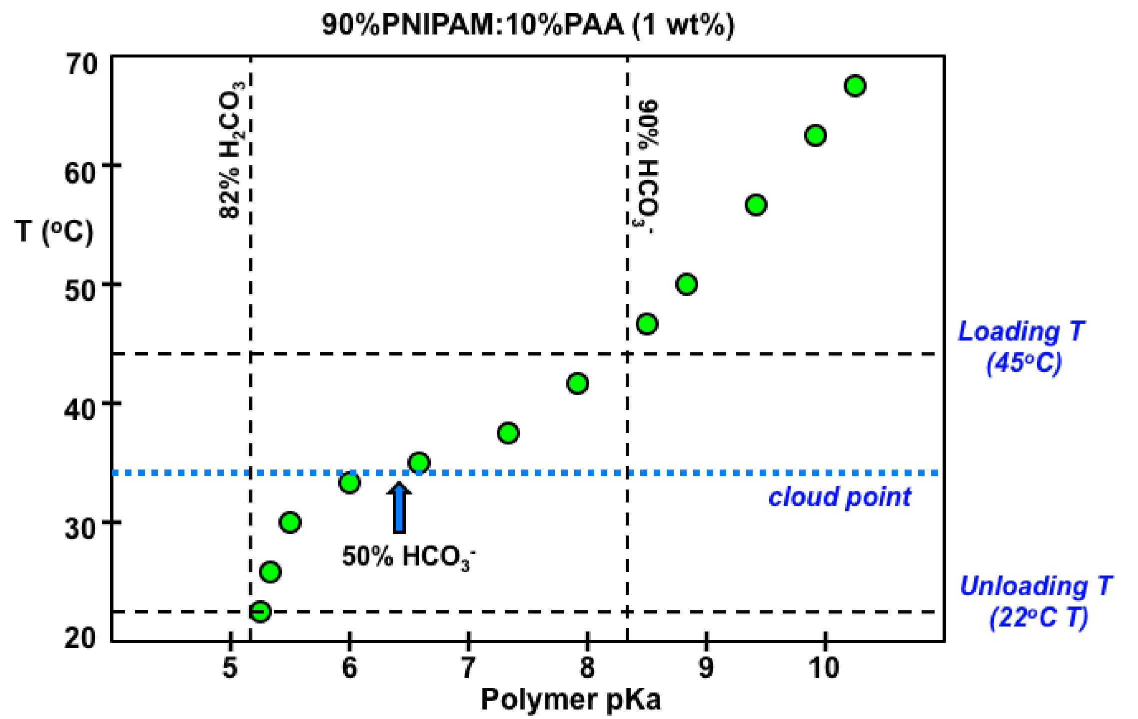
We have developed a polymer-based programmable pH buffer for use in the reversible sequestration of CO_2

The Department of Energy has a stated goal of reversible capturing 1 billion metric tons of CO_2 per year from the air to mitigate Global Warming. We are developing nanomaterials to "program" water to achieve this goal.

Results: Relatively insoluble CO_2 gas becomes highly soluble if converted into anionic bicarbonates in mildly basic solutions.

We have created a polymer that can be programmed with temperature to reversibly switch between acidic and basic states to promote the unloading and loading of CO_2 from water, respectively, using this mechanism.

Our first polymer composition exhibits sufficiently large shifts in acidity (related to pKa values shown at right) to promote both loading and unloading processes.



*submitted to Advanced Functional Materials

We have recently developed a lithium ion solid electrolyte that is 35X more conductive than state-of-the-art

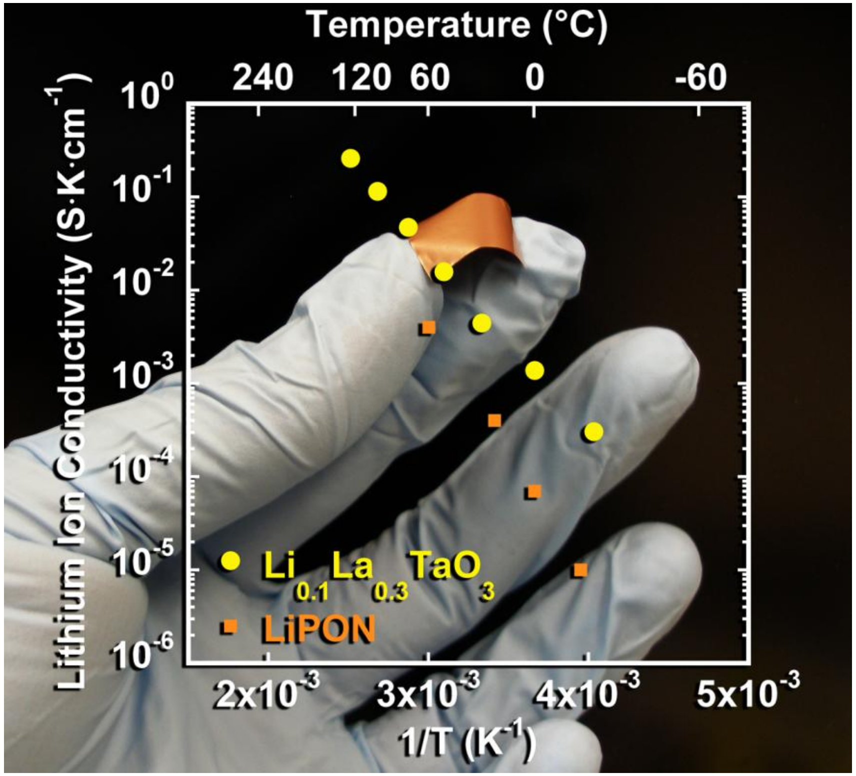
Higher ionic conductivity solid electrolytes are needed to realize higher power solid-state batteries

Lithium lanthanum tantalate thin films have been integrated with copper foil substrates

- RF sputtering and CSD
- Controlled atmosphere processing
- Phase-pure films

Room temperature lithium ion conductivity 35X greater than COTS electrolytes.

Very low form factor (18 µm total thickenss) appropriate for flexible electronics.



Temperature dependent ionic conductivity and photograph of film on foil

Sandia National Laboratories

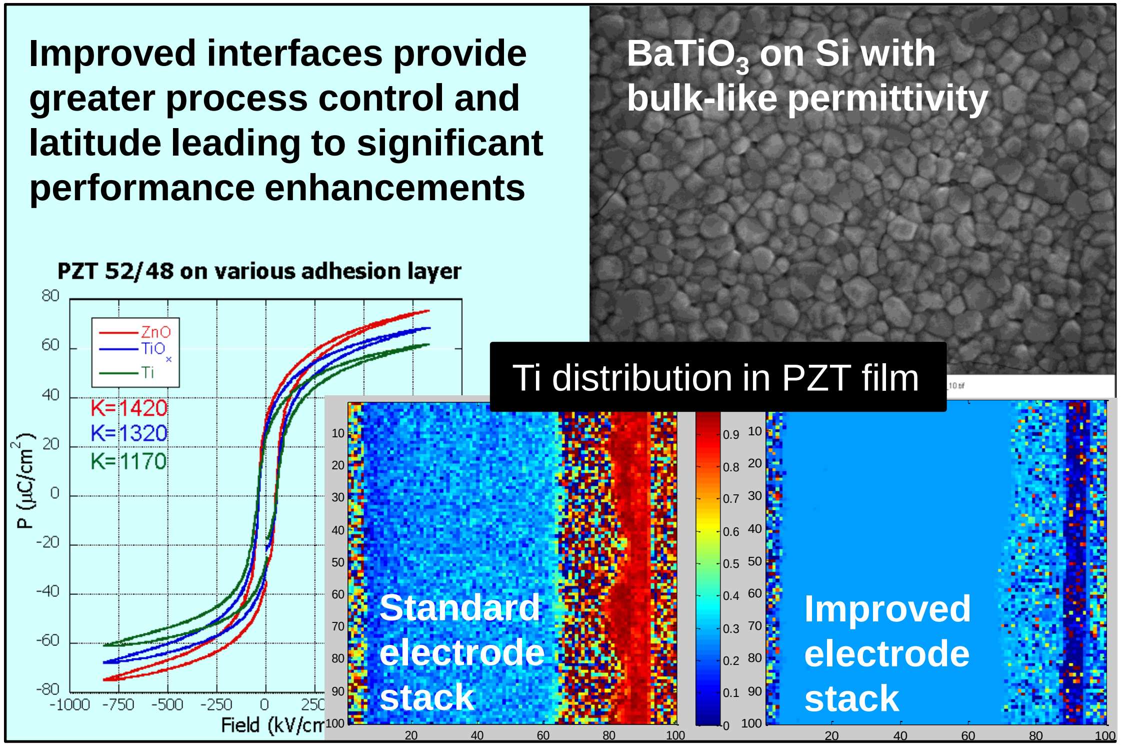
We have recently developed an electrode technology that greatly enhances dielectric and ferroelectric film properties

Despite more than 20 years of study on ferroelectric thin film synthesis, a key weak link in electrode technology remains. Traditionally platinum coated silicon wafers are used with a Ti or TiO_x adhesion layer. We have shown that this embodiment imparts strong chemical inhomogeneity in ferroelectric films.

The effect of adhesion layer on ferroelectric PZT film properties was assessed using Ti, TiO_x, and ZnO.

- Buffer layers and electrodes deposited via RF sputtering
- PZT deposited via CSD
- Polarization-Field and Permittivity-Field measured
- STEM-EDS and PCA for chemical distributions

ZnO-buffered films display virtually no chemical gradient and improved electronic response. This is the first known observation of chemical homogeneity in solution deposited PZT from a single solution.



In preparation for submission to *Advanced Functional Materials* (TA Number 11780)

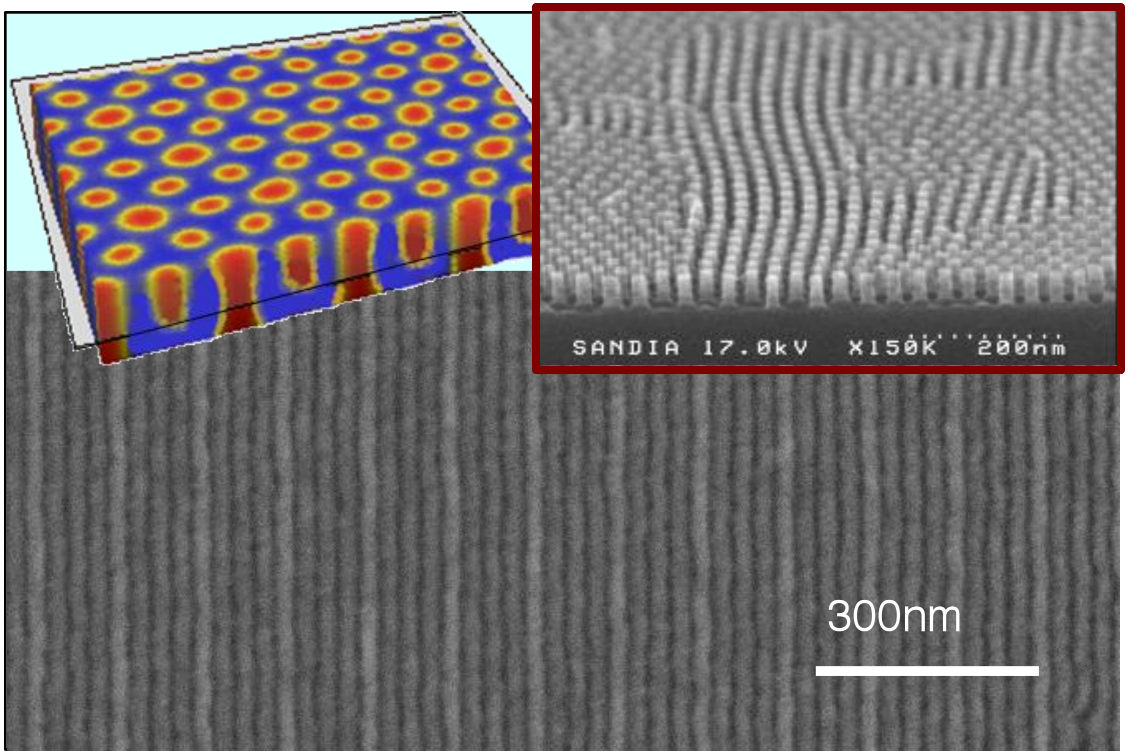
Sandia National Laboratories

Directed assembly of block copolymers by simple, inexpensive interference lithography; transfer to nanoimprint lithography

The ITRS has stated that no proven optical lithography technique is available below the 22nm node. Developing a feasible approach for 22nm and beyond is critical for SNL-specific applications as well as the IC industry as a whole.

Combining top-down interference lithography (IL) with bottom-up self assembly techniques, we have:

- directed self-assembly of block copolymer masks with 4x feature density multiplication (22nm-pitch features from 88nm-pitch IL pattern)
- quantified quality of ~20nm-scale patterns and features over >100um^2
- transferred BCP-defined features to nano-imprint master for repetitive fabrication of nanofeatures free from optical diffraction limitations
- simulated stability and dynamics of directed self-assembly processes



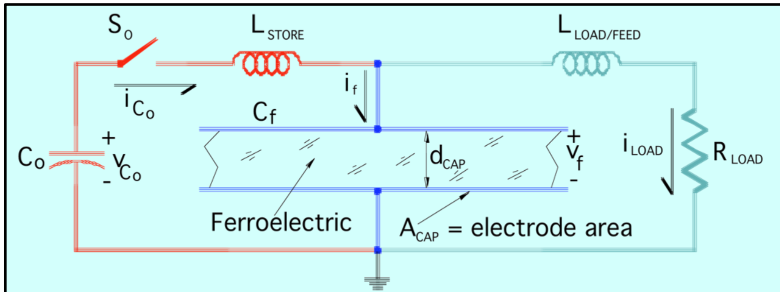
Multiple publications in JVST-B (2010)

We have demonstrated the use of a high-power ferroelectric opening switch (FEOS)

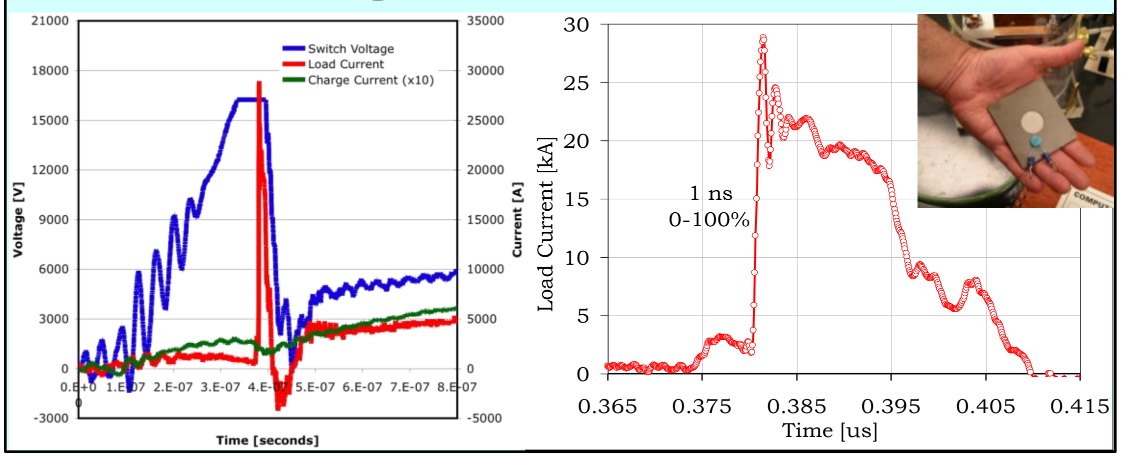
Development of a reliable, reusable, fast high voltage opening switch would revolutionize pulsed power by enabling the use of inductive energy storage (leading to enormous improvements in efficiency, reduced size and complexity, faster rise times, and many secondary enhancements).

Utilizing our science-based understanding of ferroelectric materials, we developed a ferroelectric opening switch that takes advantage of the dramatic change in permittivity during ferroelectric switching to redirect inductively-stored current to a load to provide:

- >10kA with ~1ns rise time
- voltage AND current gain
- solid state reusable high voltage switch



Revolutionary inductive energy storage requires fast and reliable high voltage opening switches



TA Number 11626

Sandia National Laboratories

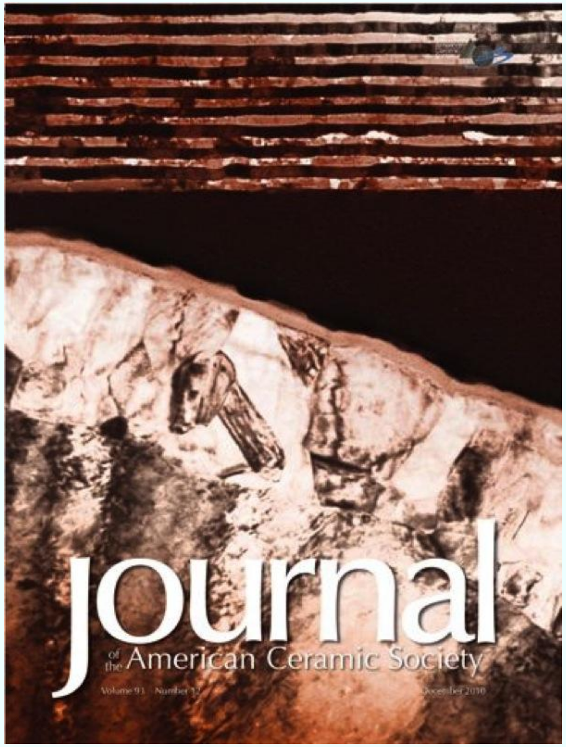
Our work on ferroelectric thin films was recently recognized with an invited feature article and cover art in the J. Am. Ceram. Soc.

Our fabrication and processing routes using inexpensive and reliable chemical solution deposition of ferroelectric thin films on technologically-relevant substrates for functional device structures is recognized as leading the world.

With proper processing, solution-derived ferroelectric thin films can be:

- feasibly fabricated from 10–1000nm thickness
- high-performance, inexpensive, reliable, and IC process-compatible
- viable integrated alternatives to discrete MLCC technologies
- used for energy storage, energy harvesting, actuation, sensing, information storage, etc.

World-recognized leaders in the chemical solution-derived fabrication of functional thin film ferroelectrics on technologically-relevant substrates including ultrathin films, multilayer thin films, and high-performance films on base metal foils.



G.L. Brennecka, J.F. Ihlefeld, J-P. Maria, B.A. Tuttle, and P.G. Clem, J. Am. Ceram. Soc., 94[12] 3935-54 (2010).

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