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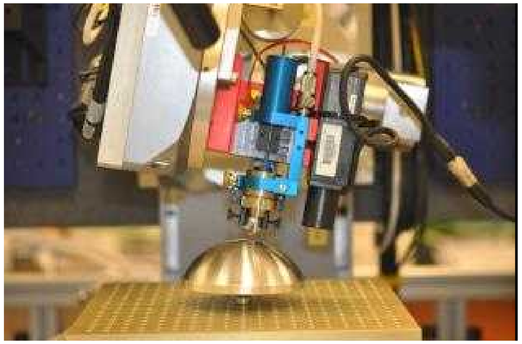

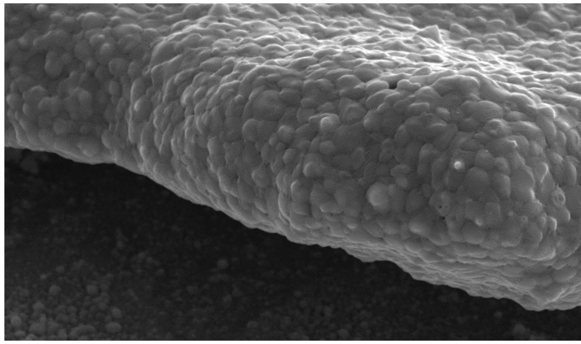

Additive Manufacturing of Aerosol Deposited AZO Conductive Patterns

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Albuquerque, NM

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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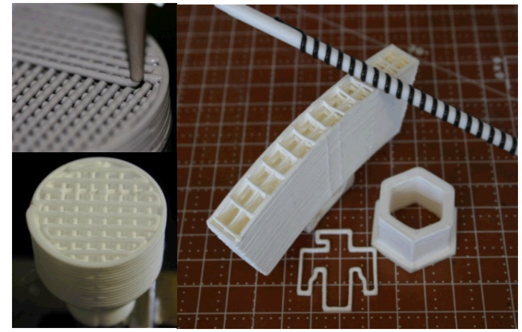
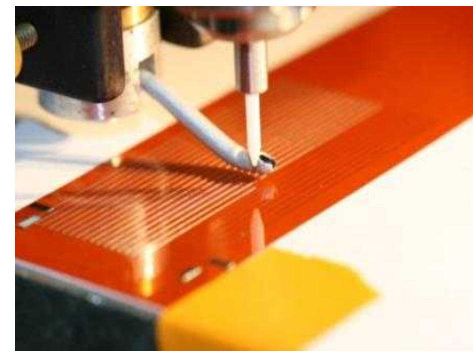
Overview

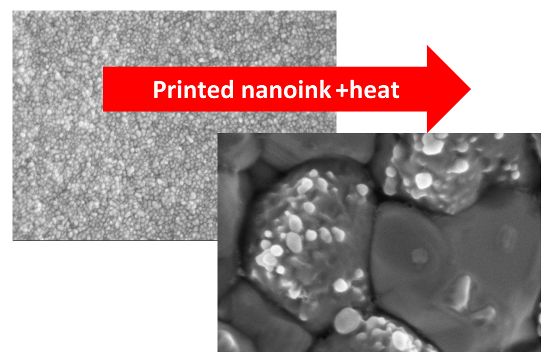
- Additive Manufacturing
- Processing Needs
- Al-Doped ZnO Synthesis
- Pulse Forge Technology
- Photonic Consolidation of AZO Nanopowders
- Summary



Extrusion casting (Robocasting)



Aerosol jet printing to 10 µm



Nano-particle Ag inks for conductive pathways

Sandia Additive Manufacturing Technical Development & Commercialization

Sandia National Laboratories

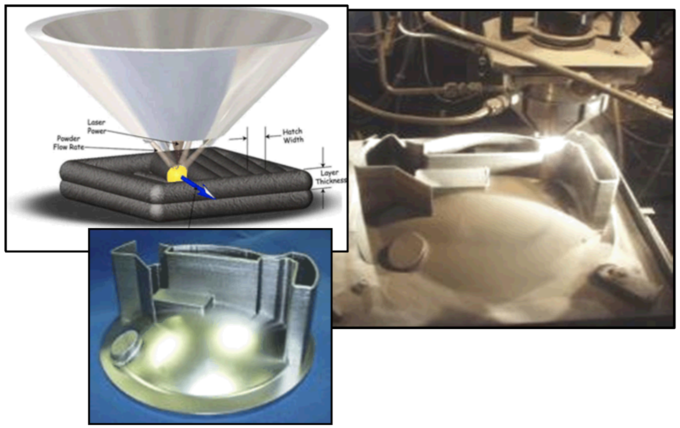
30+ yrs of Pioneering Process/Materials R&D

FastCast *

Development housing

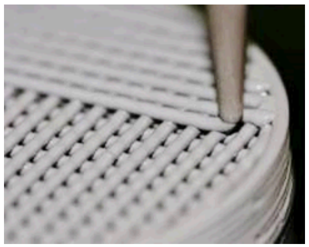
Laser Engineered Net Shaping LENS® *

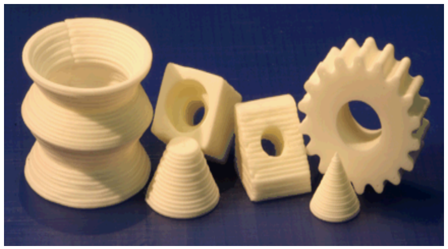
Stainless housing



RoboCasting *

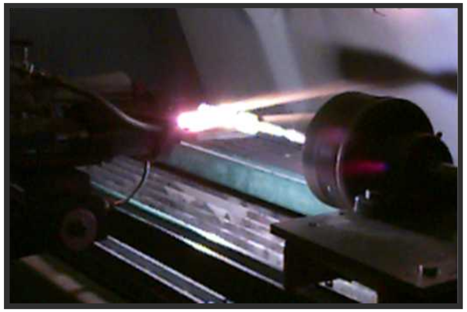
Ceramic Parts



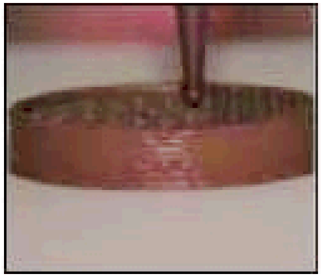


Spray Forming

Rocket nozzle

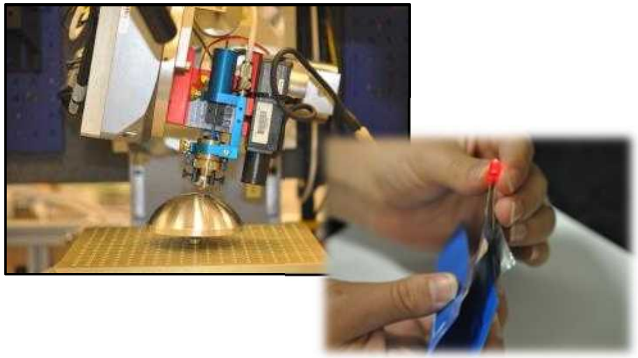


Energetic Materials



Direct Write

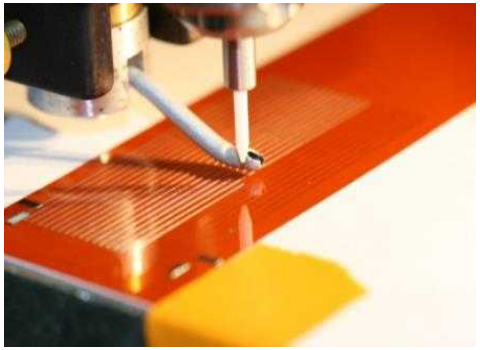
Conformal electronics

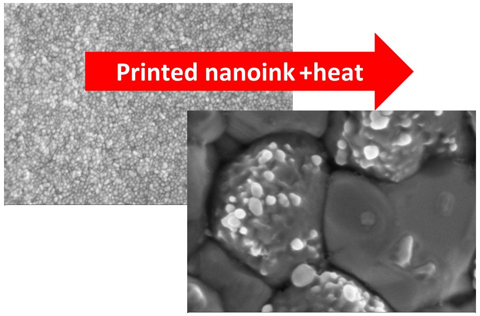


Printed battery

Direct Write, A Versatile, Multi-Material Process

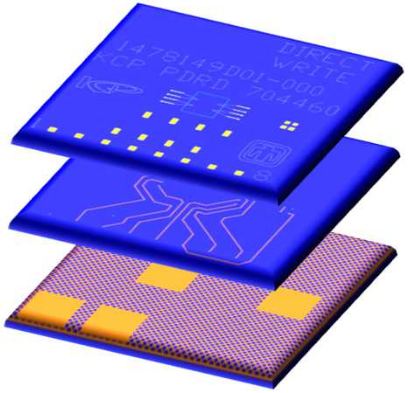
- Useful for 3D printing of polymers, metals, and ceramics
- Compatible with an extremely wide range of materials (1-1,000,000+ cPs
- Provides an ideal platform for materials development and evaluation
- Allows for component fabrication using novel research materials not supported by the commercial 3D printing industry

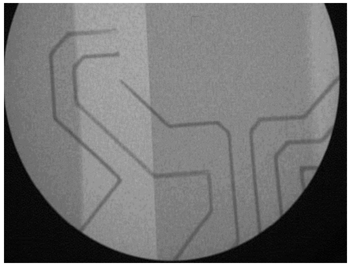

Aerosol jet printing to 10 µm



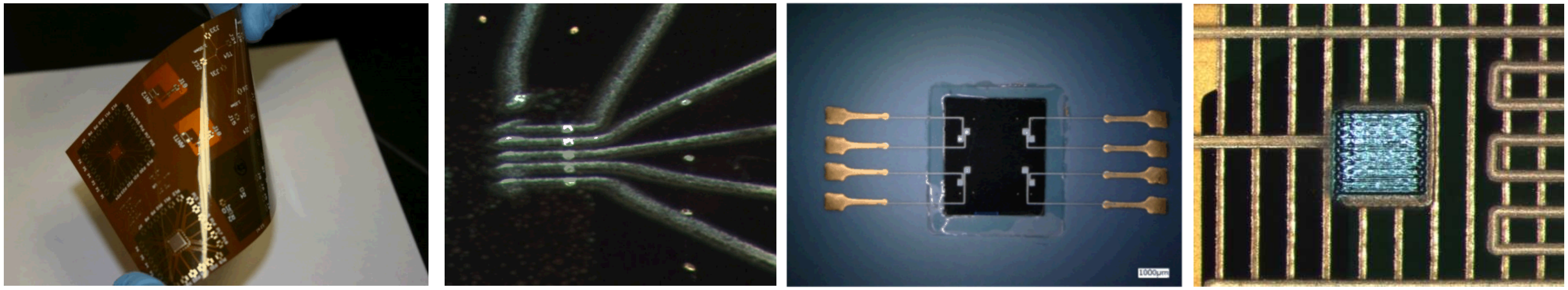
Nano-particle Ag inks for conductive pathways


DW circuit fabrication

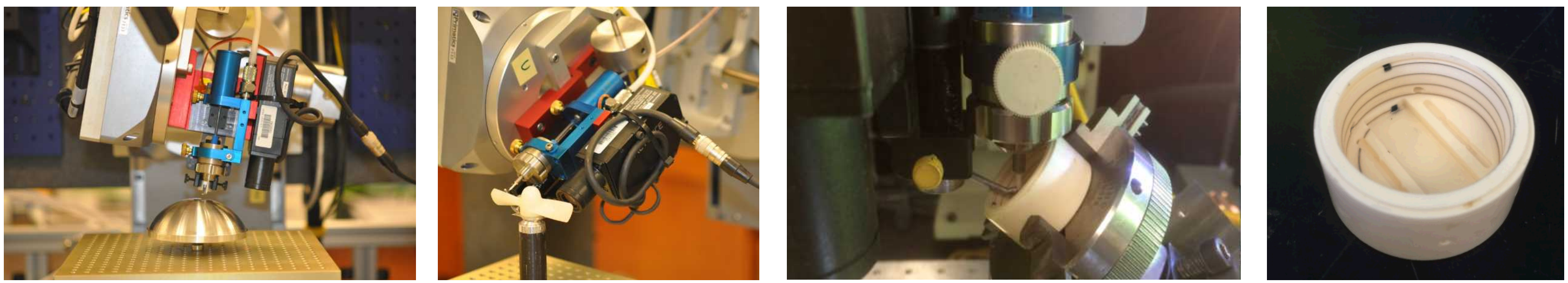

Multi-level circuit


X-ray of 4 layer composite system, 200 µm conductors

Applications for Additively Manufactured Printed Electronics



Flexible electronics, printed wire bond replacement, multi-level circuit fabrication



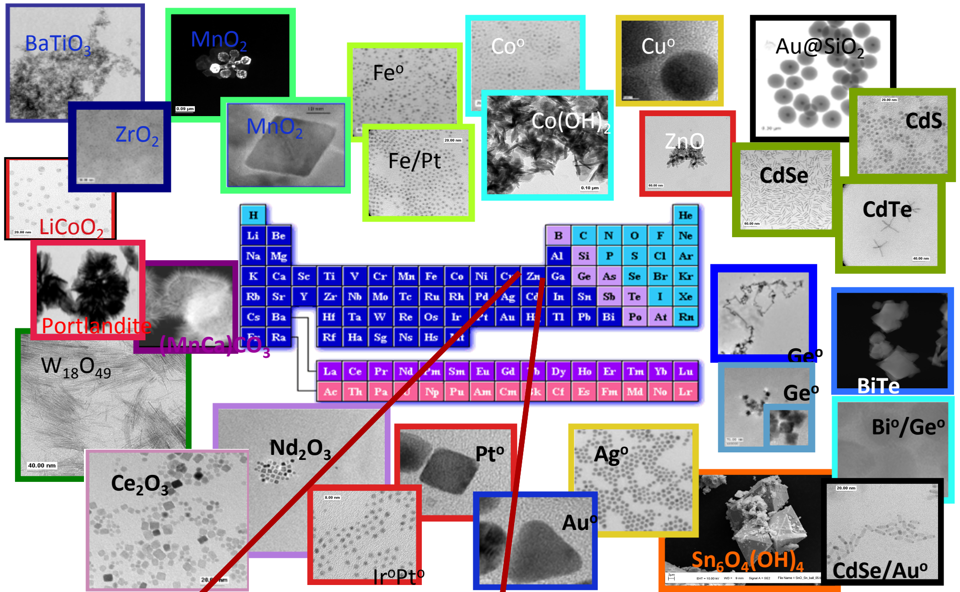
3, 5, and 6 axis conformal printing for non-planar material deposition and device fabrication

Printed power system components including ferrite based transformers and $LiFePO_4$ flexible batteries

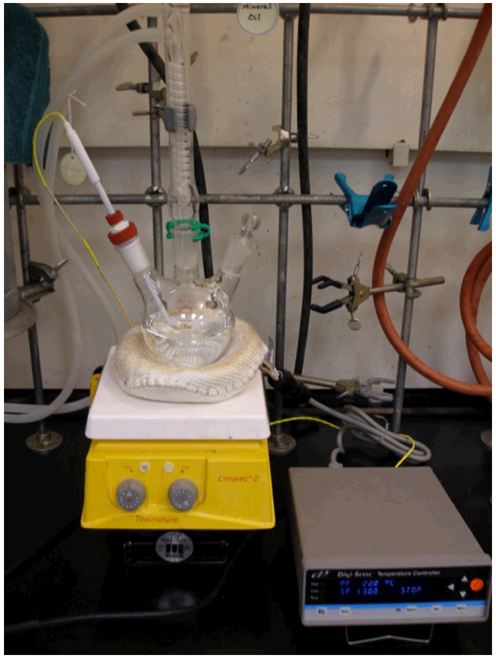
Materials and processing limitations have historically restricted curing of electronic materials and components to low temperatures

Chemical Solution Synthesis

Sandia National Laboratories



Courtesy Dr. Timothy Boyle, SNL

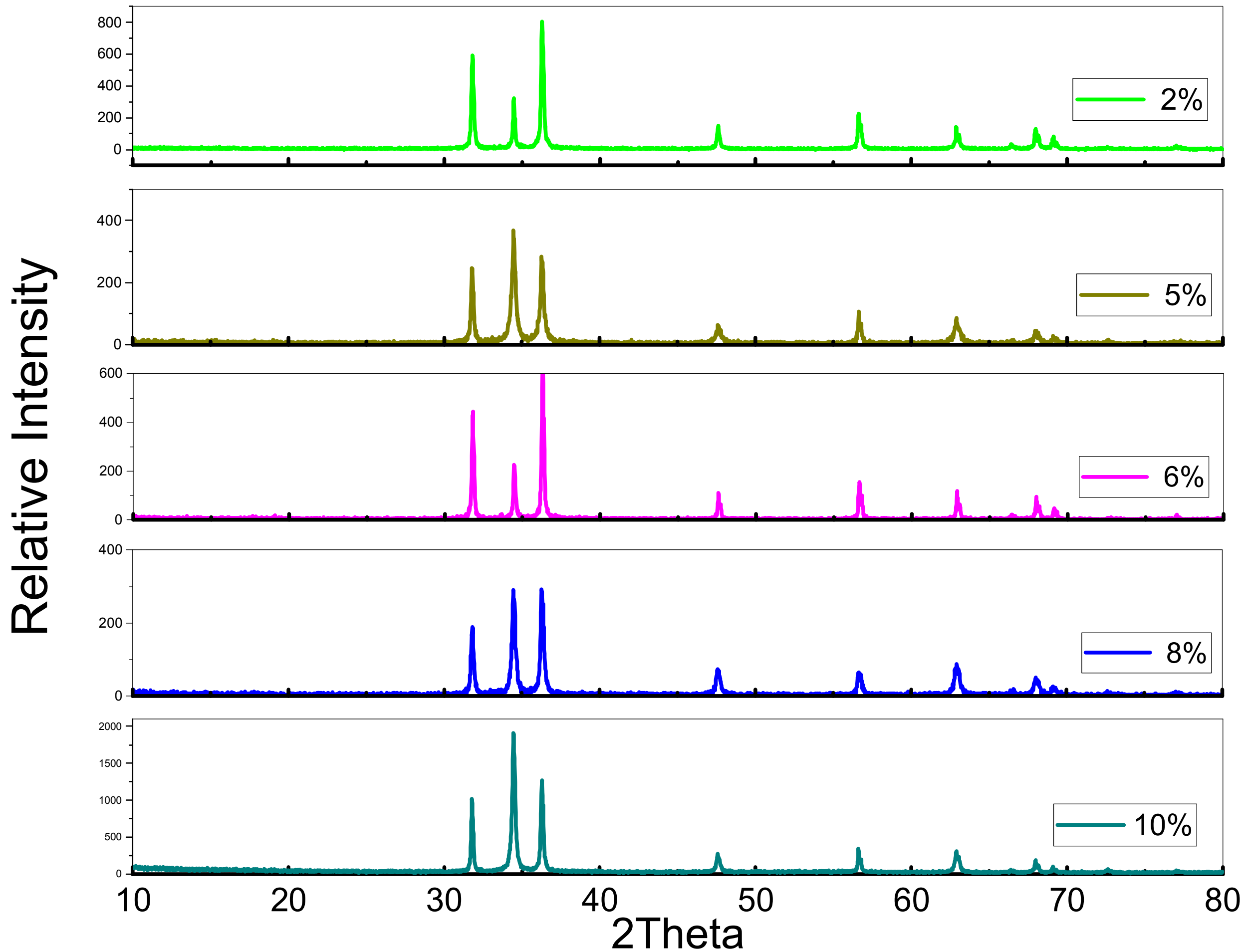


AZO
Has been identified and is interesting because…

- AZO is a common conductive oxide
- Model system for fundamental study of rapid photonic sintering
- Incorporation of dopants changes the defect concentration
- Material stability issues of the dopant in photonic sintering can be tested.

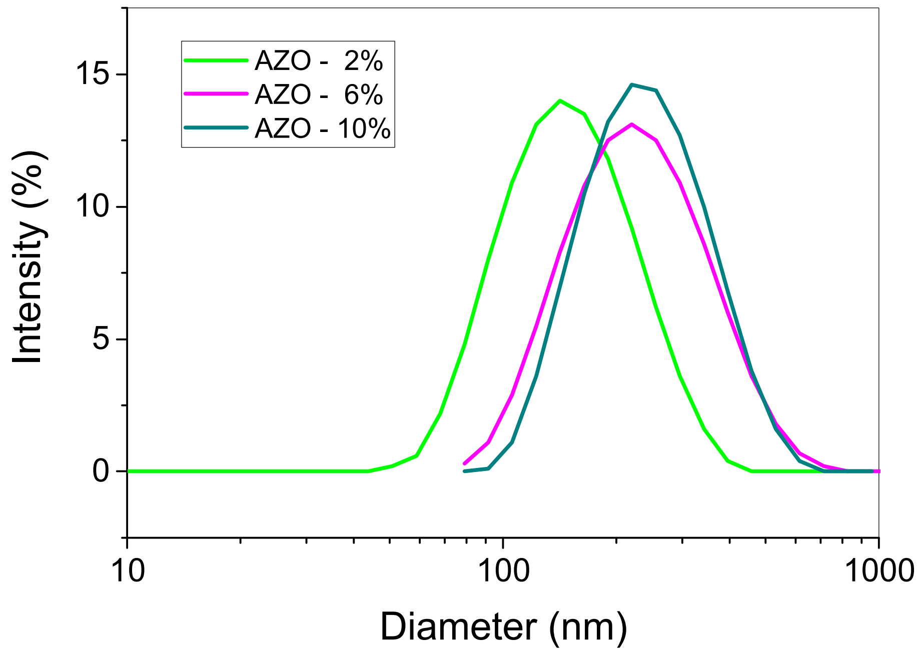
Al doping up to 10% is phase pure

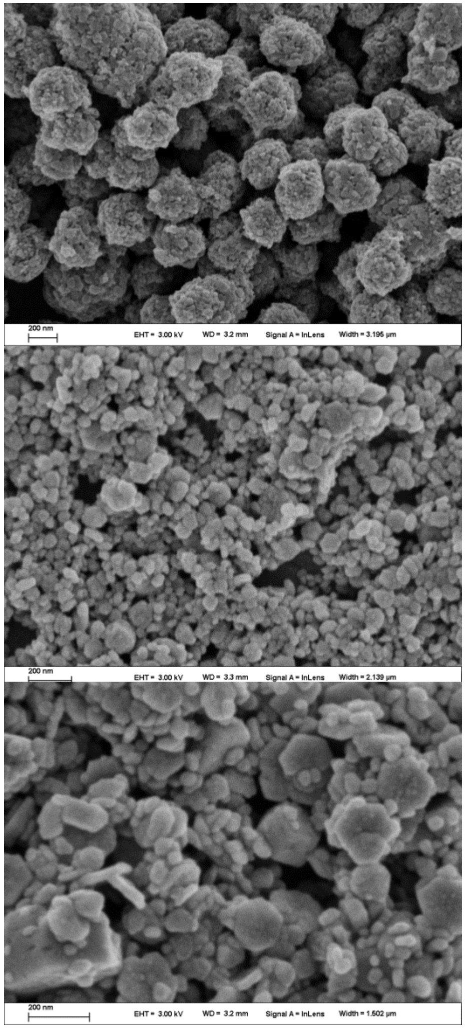
- Reaction of zinc acetate, aluminum nitrate, and potassium hydroxide solution in 1,4 butanediol at 130 C.
- Suitable for ambient atmosphere processing.
- All Al doping levels match ZnO (wurtzite) structure.



Glycothermal Method Allows for Facile AZO Nanoparticle Synthesis

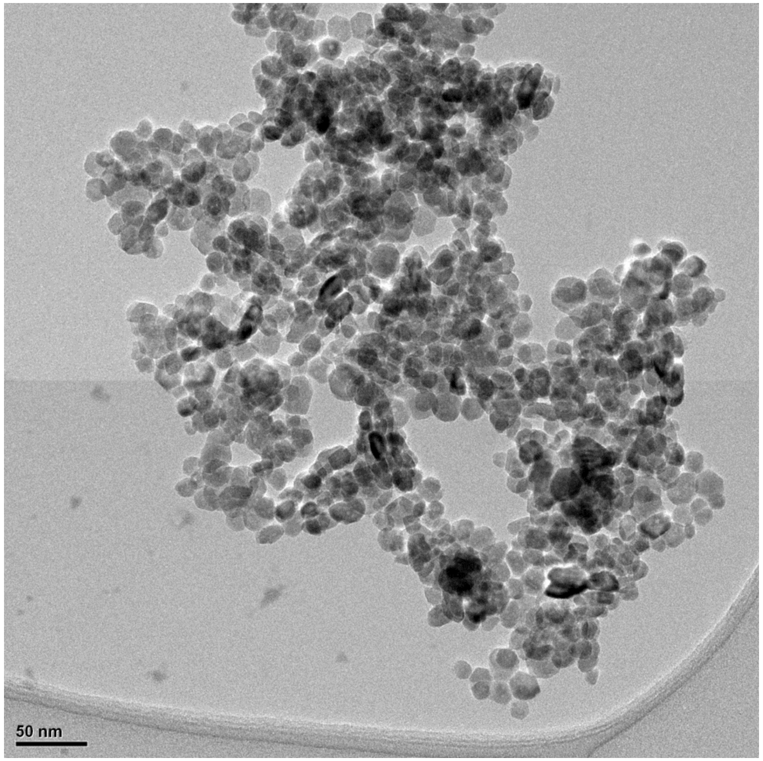
- Suspensions are processed in acetone to recover and concentrate materials.
- Size distributions reflect agglomeration, with increasing Al dopant giving larger particle sizes.
- Morphology changes from equi-axed to platelet with rising Al content.



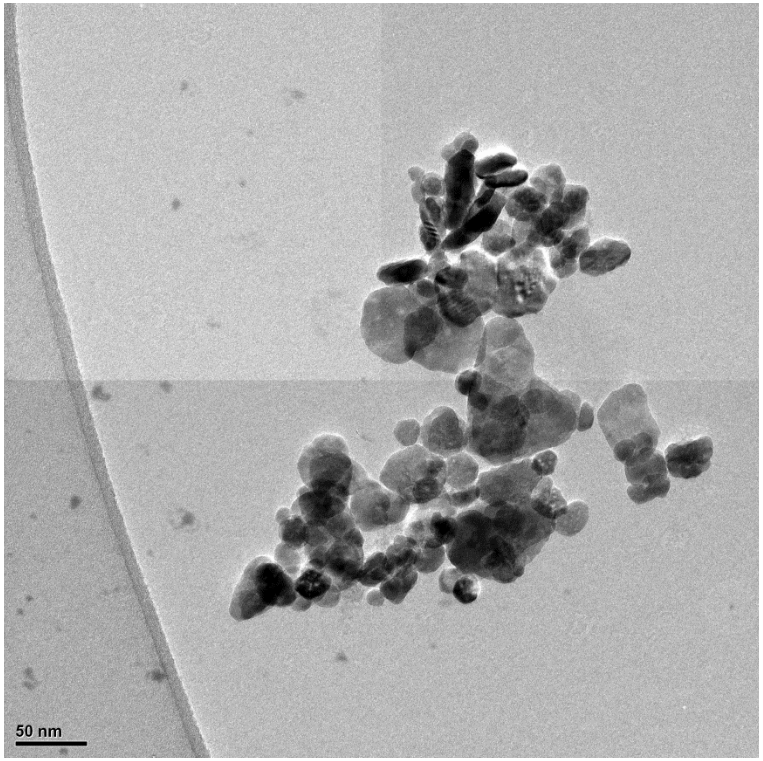


TEM Analysis shows crystallite sizes are nanometric, and platelets are favored with increasing Al doping

2 % Al doped ZnO



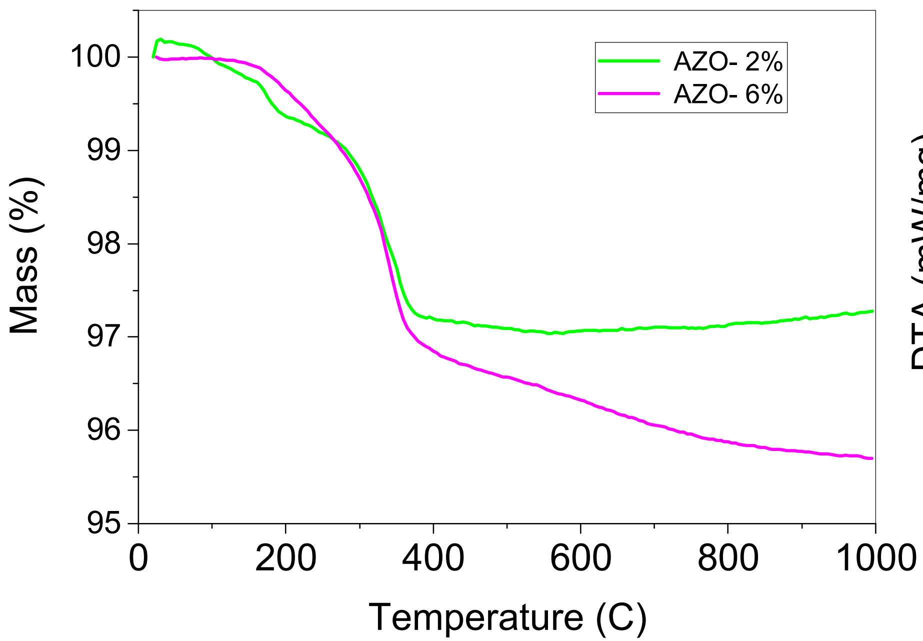
6 % Al Al doped ZnO



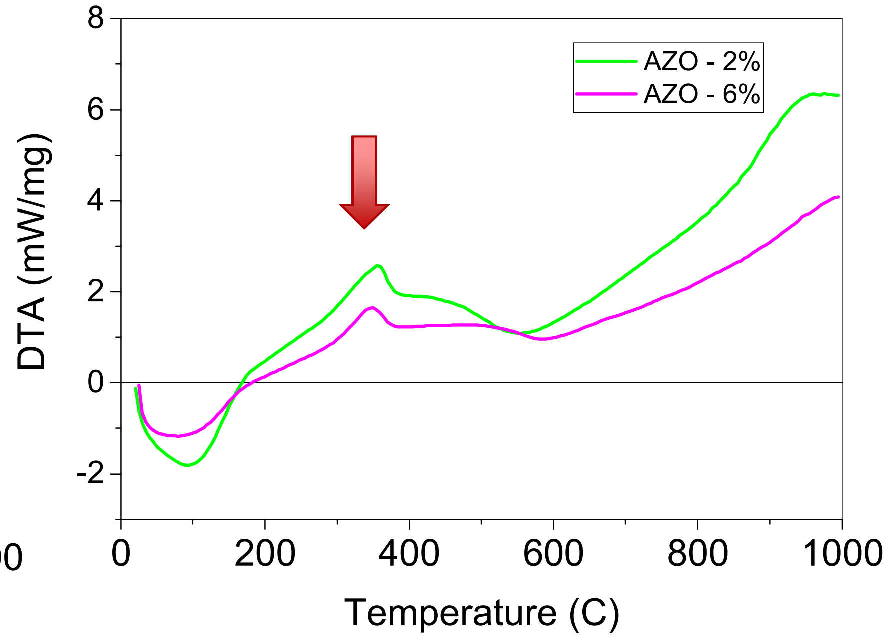
Thermal Stability of AZO powders

- TGA/DTA conducted in air, to 1000 ˚C at 10 ˚C/min.
- Mass loss in these systems is largely complete at 365 ˚C, although 6% Al has a continuing drop in mass.
- Thermal energetics show a weak peak at 351 ˚ C (AZO-2) and 341 ˚ C (AZO-6) indicating some material reaction.

TGA Analysis



DTA Analysis

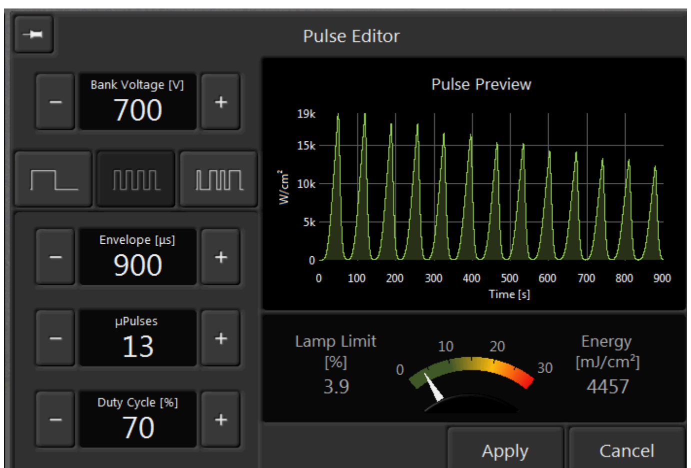


Optical Band Gap Determination

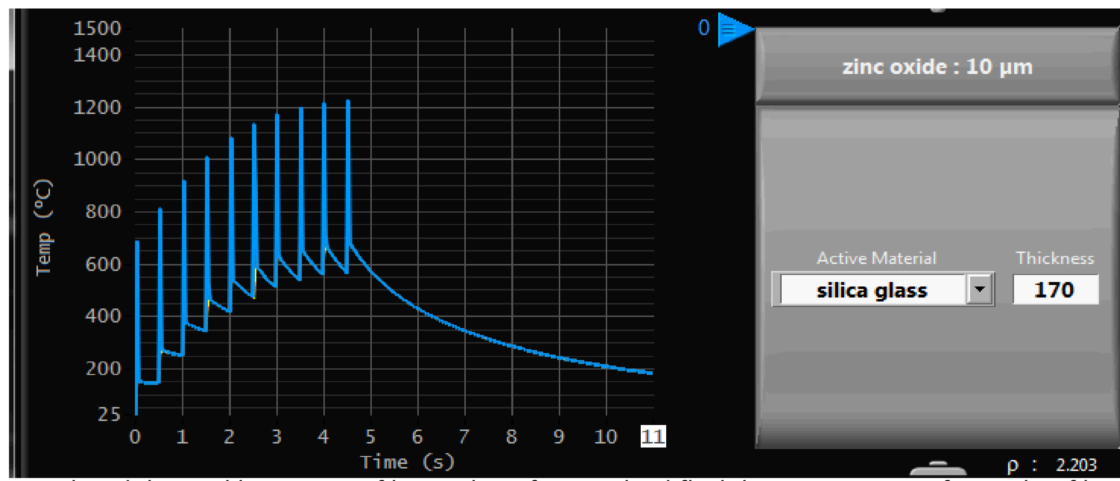
- AZO materials shift ZnO bandgap based on Al doping.
- Optical properties will affect adsorption of light in photonic curing/sintering.

Rapid High Temperature Sintering via Pulsed Flash Lamp Processing

- Pulse Forge (Novacentrix) utilizes photonic curing by a pulsed flash lamp.
- Transient heating enables reaction on low temperature substrates like paper and polymers.
- Thermal pulses allow for much higher temperatures in 1 millisecond timeframes.



Example waveform used to process AZO thin films



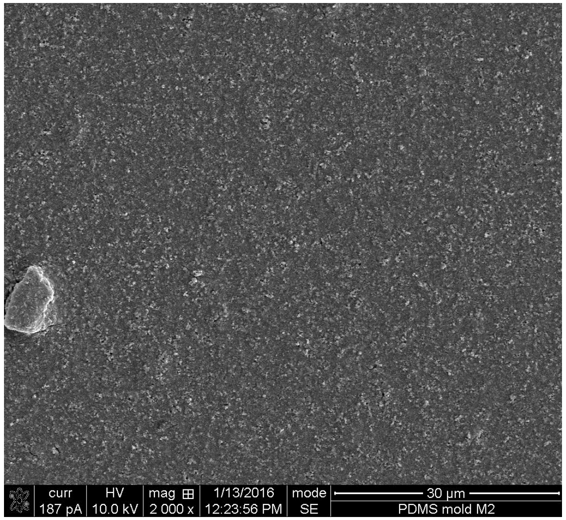
Simulated thermal heating profile resulting from pulsed flash lam processing of AZO thin films

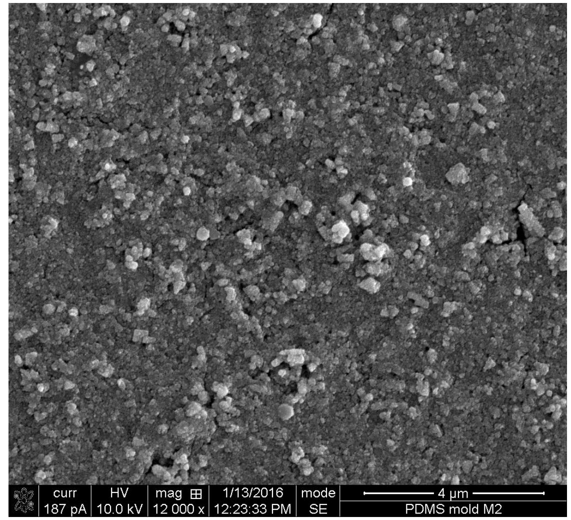
Material Name	Thermal Conductivity (W/mK)	Mass Density (g/cm3)	Specific Heat (J/kg)	Melt Temp (deg. C)	Heat Fusion (kJ/mol)	Boil Temp (deg. C)	Heat Vapor (kJ/mol)	Mol Weight (g/mol)	Attenuation (1/cm)
zinc oxide	15	5.606	523	1975	348	2360	4000	81.408	0.5

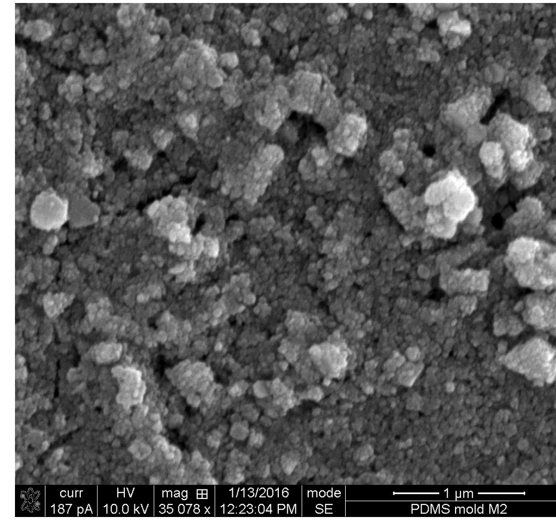
Material properties used in the Novacentirx proprietary modeling software for estimation of thermal heating profiles

Solution deposited AZO thick film

Top surface

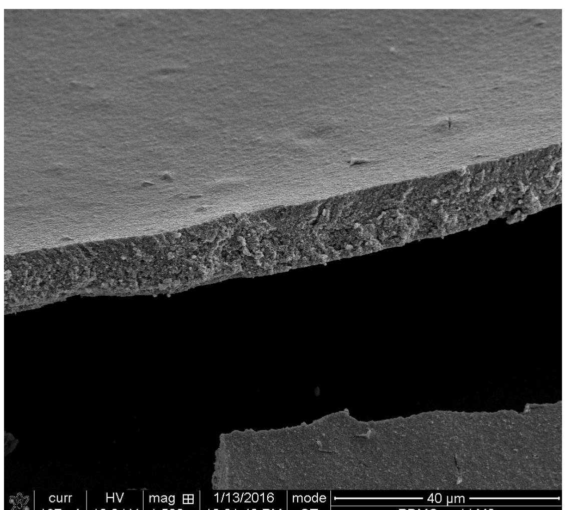


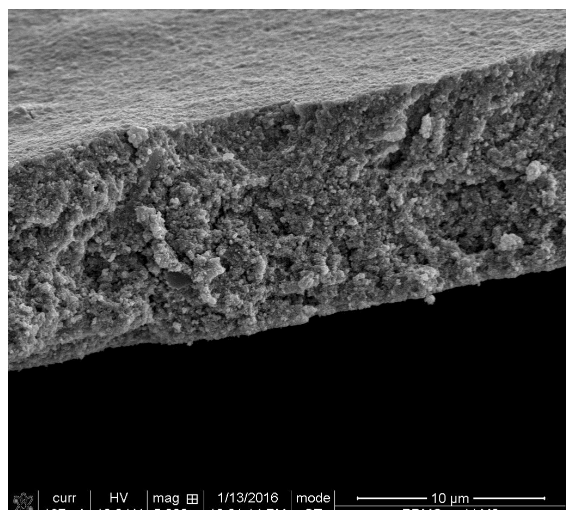


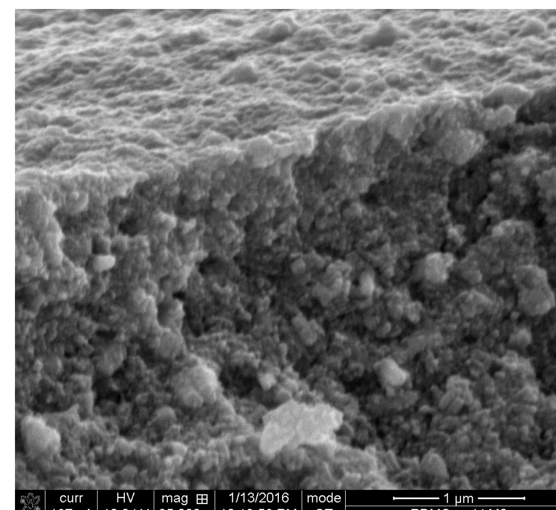


Increasing magnification →

Cross-section





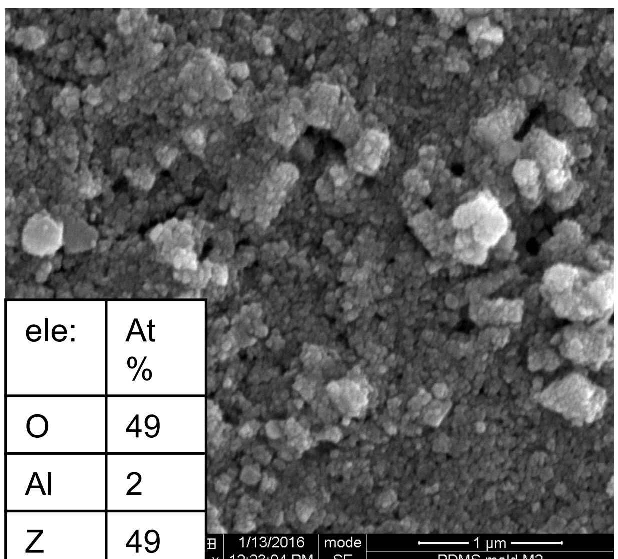


Solution Deposited AZO thick film: Photonic Curing (PulseForge)

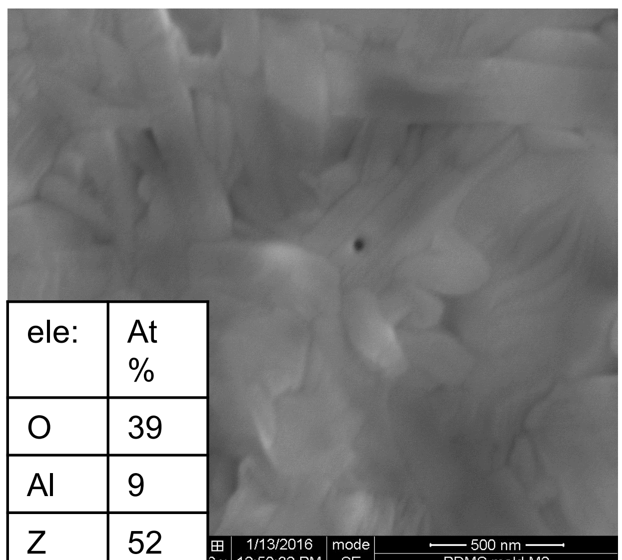
Pulse trains and resultant thermal model

Processed in air

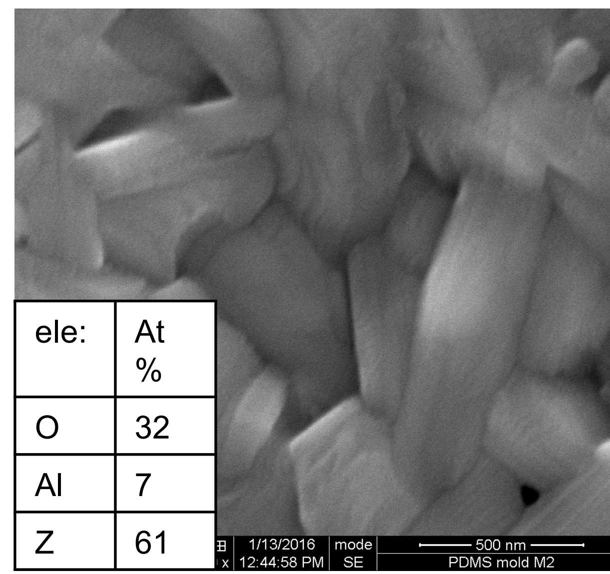
Processed in inert (N_2)



ele:	At %
O	49
Al	2
Z	49



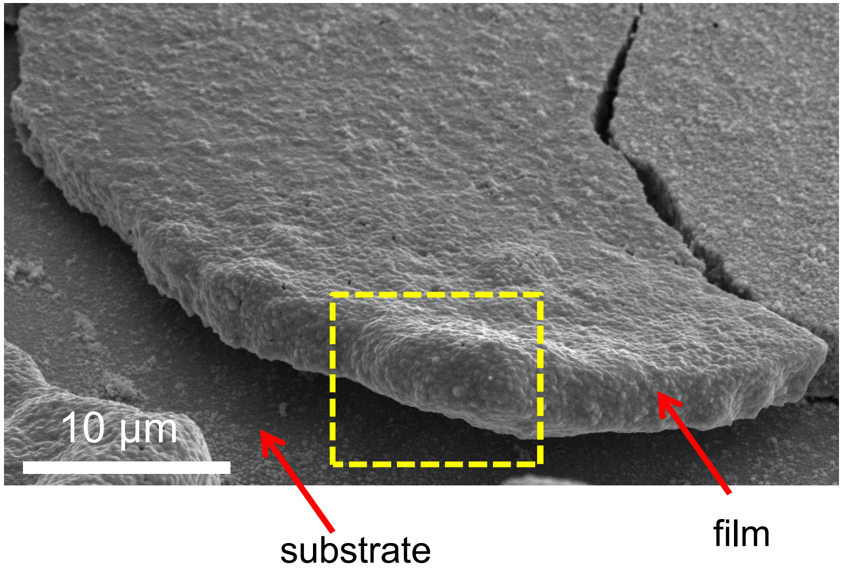
ele:	At %
O	39
Al	9
Z	52

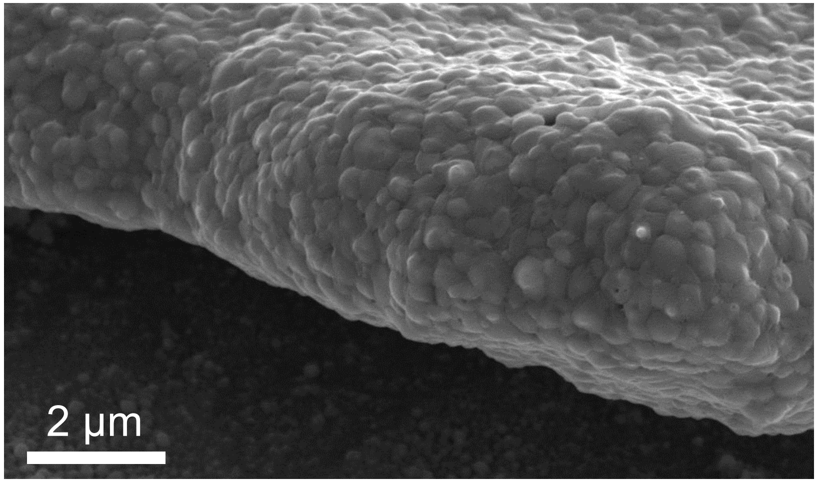


ele:	At %
O	32
Al	7
Z	61

Inset is EDS determined composition

Cross-section of AZO film sintered in air

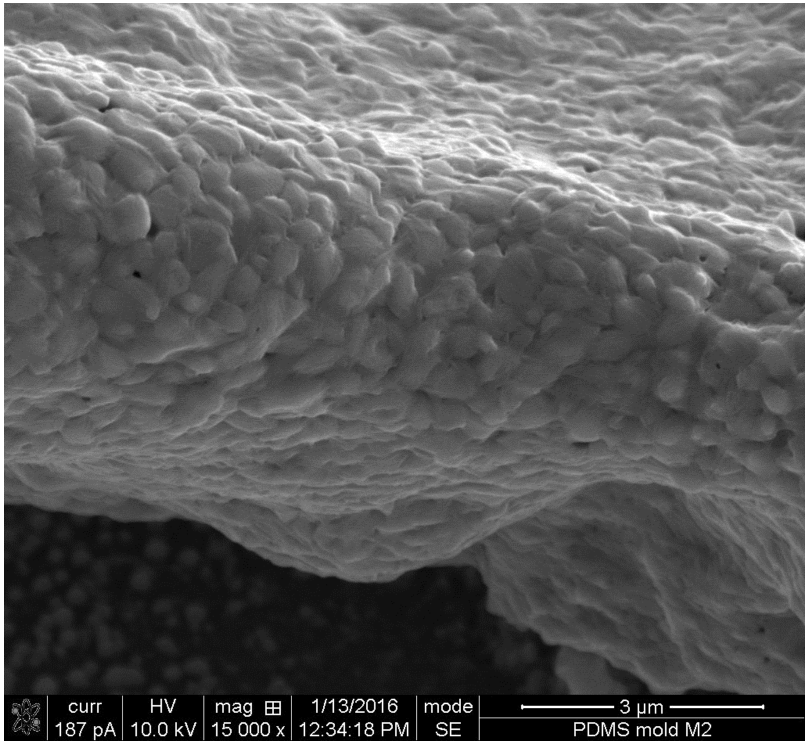


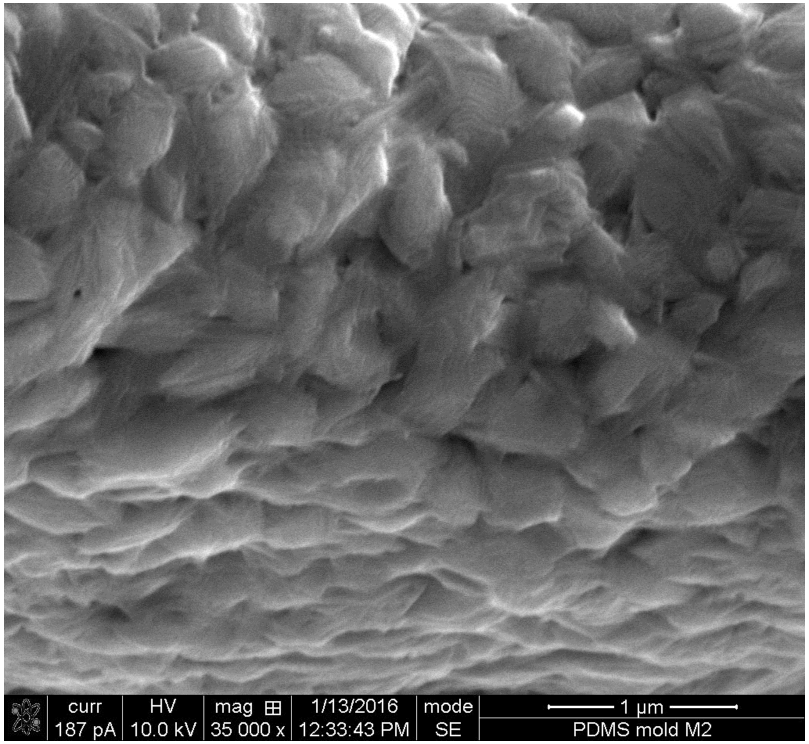


Consolidation thickness ~ 5 µm

- Sample contains 6% Al.
- Dense films are formed on glass substrates via the Pulse Forge instrument.
- Reaction depths are homogeneous for 5 micron thicknesses.

Surface Structure of Photonically Sintered Films

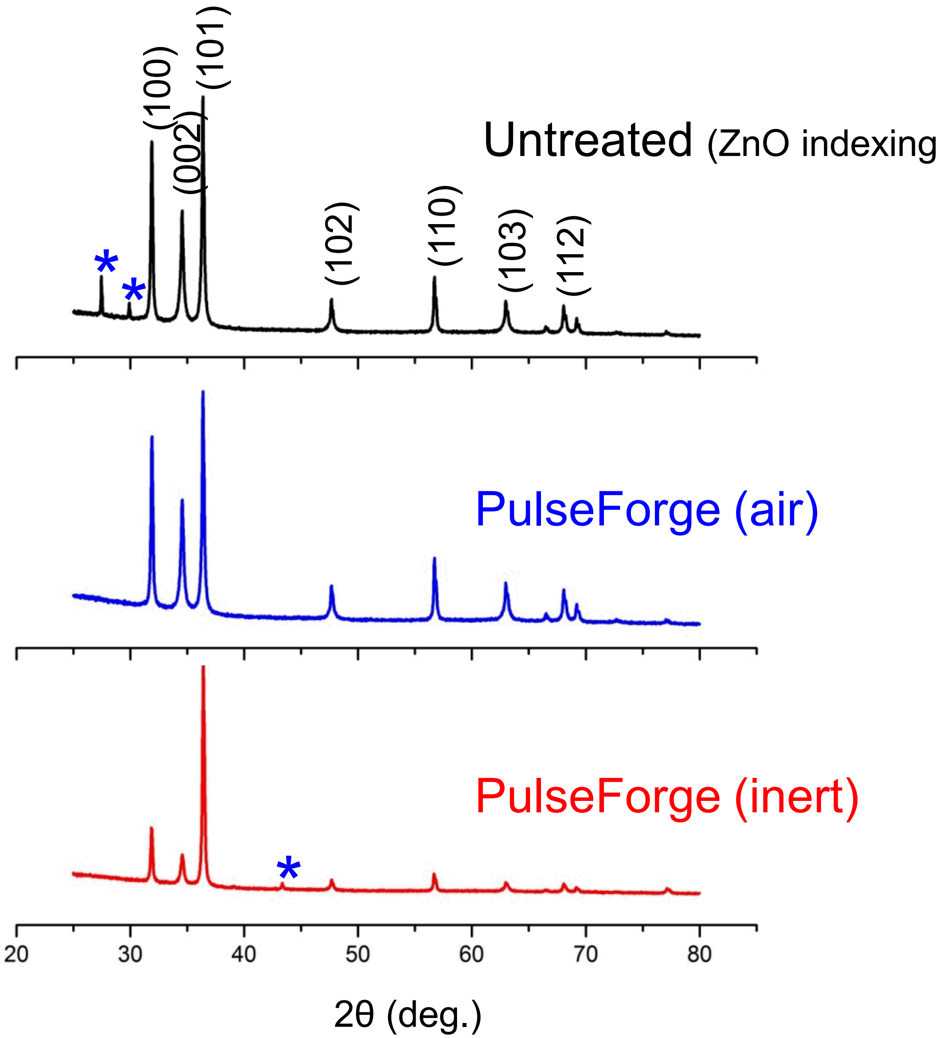




- Surface topologies are fibrous or terraced between initial “grains”, and grain size is larger than the initial material.
- Thermal processes are activated by the Pulse Forge technique.

XRD Characterization of Processed Films

- Concerns lie in maintaining the crystallinity of the prepared materials.
- Potentially, Al could phase separate, or Zn metal could be developed in a reducing environment.
- We see good crystallinity in air, but increased orientation (101) for processing in N_2.
- Processing may indicate reduction of an Al-ox phase and in inert possibly reduction of ZnO'



*Asterisks indicate loss/gain of from processing conditions

Summary and Future Studies

- Photonic curing of nanoparticle AZO inks is viable for thin film processing on polymeric substrates. This demonstrates viability for multi-material integration in roll-to-roll processing.
- Process variables including power, nanoparticle properties and environment are relevant to optimization of properties for integrated films.
- Additional materials must be tested to explore the thermal conditions and viable integration of ceramics.
- Issues of phase stability and electronic properties will be explored for future discussion.