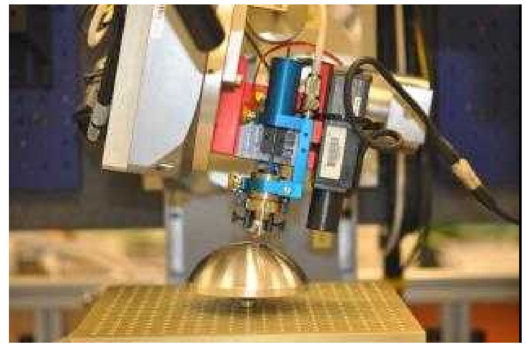
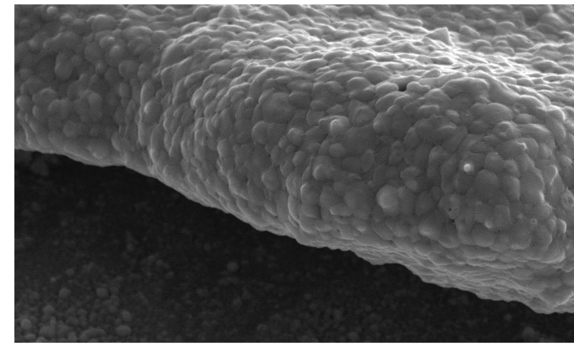
Exceptional service in the national interest

SAND2016-9529C

Sandia National Laboratories





Integration of Multi-materials in Additive Manufacturing

Nelson S. Bell

Pylin Sarobol, A. Cook, T.J. Boyle, Paul G. Clem, D. Keicher, D. Hirschfeld, Aaron C. Hall, M. Chandross, Bryan Kaehr

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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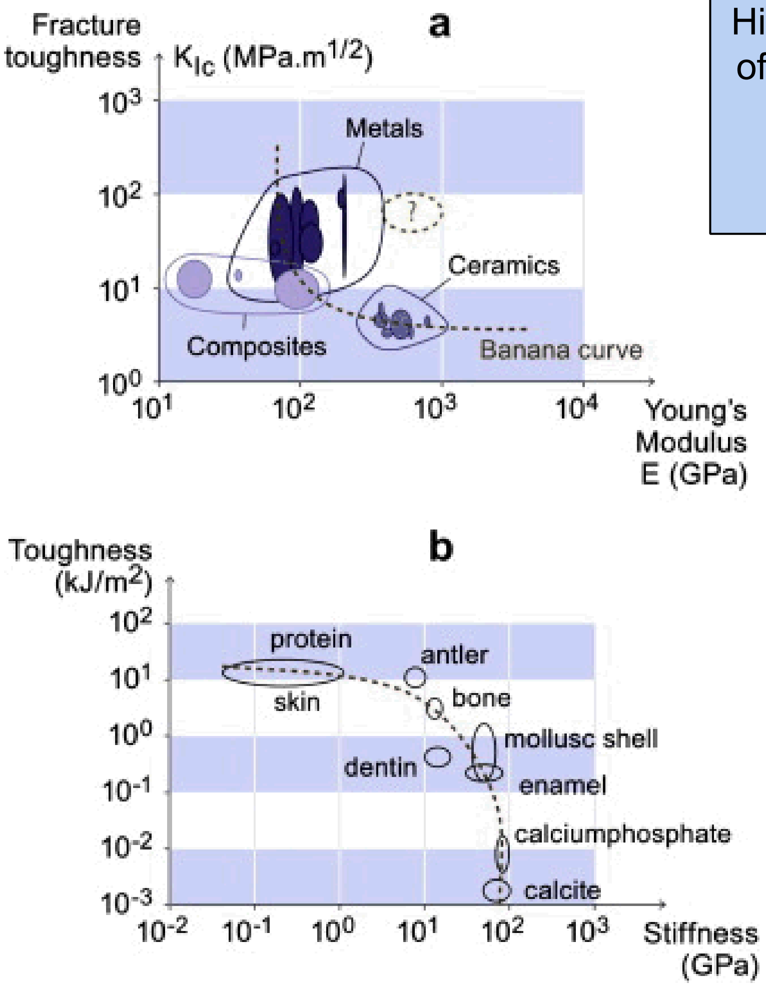
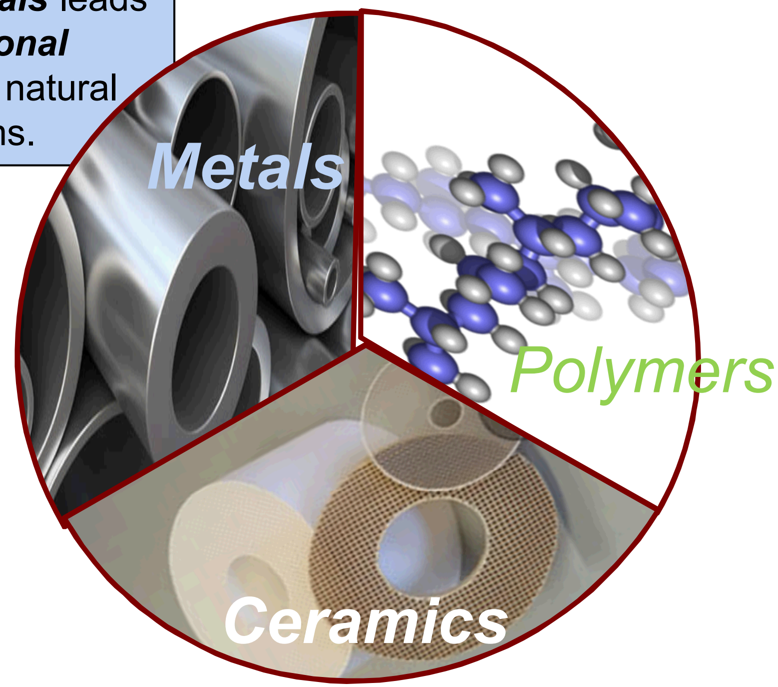
Additive Manufacturing Successes stem from Composition, Microstructure, and Interfaces



H. D. Espinosa, J.E. Rim, F. Barthelat, and M.J. Buehler, *Prog. Mater. Sci.* (2009) **54** 1059-1100.

Hierarchical arrangement of ***weak materials*** leads to ***exceptional properties*** in natural organisms.



Fundamental Research Question:

How can disparate classes of materials be deposited at low thermal cost?
(i.e. without employing vastly differing temperature regimes.)

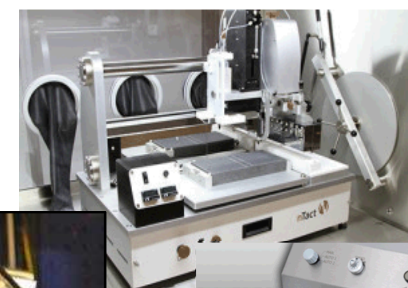
The Advanced Materials Laboratory Performs Research in Novel Advanced Manufacturing at SNL

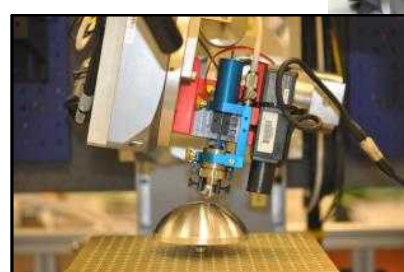
Advanced Materials Laboratory (AML) – a Sandia-leased facility on the campus of the University of New Mexico

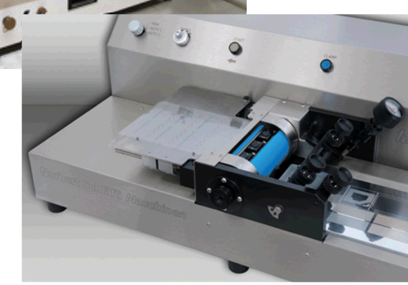
Original Vision: Foster substantive collaborative/partnering relationships in material science with UNM

Digital Printing and Coating Laboratory

- N-Tact precision slot die coater (1-10 micron patch coatings over wide range of viscosity)
- RG gravure printer – 20 micron feature size
- NSM gravure printer with multilayer registration capability – 1-20 micron
- Direct write machines
- Ink characterization: Rheometers, goniometers, DWS, zetasizers, etc.
- Film characterization: multispectral ellipsometer, SAW,
- Two-photon Lithography tool (100 nm)







Sandia Additive Manufacturing Technical Development & Commercialization

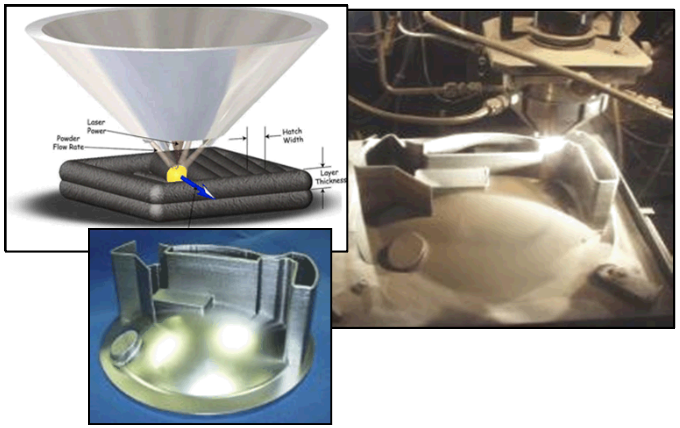
<u>*30+ yrs of Pioneering Process/Materials R&D*</u>

FastCast *

Development housing

Laser Engineered Net Shaping LENS® *

Stainless housing

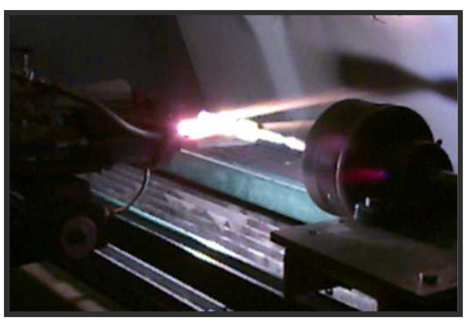


RoboCasting *

Ceramic Parts

Spray Forming

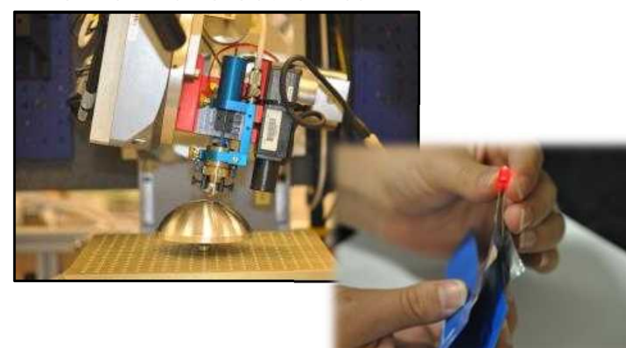
Rocket nozzle



Energetic Materials

Direct Write

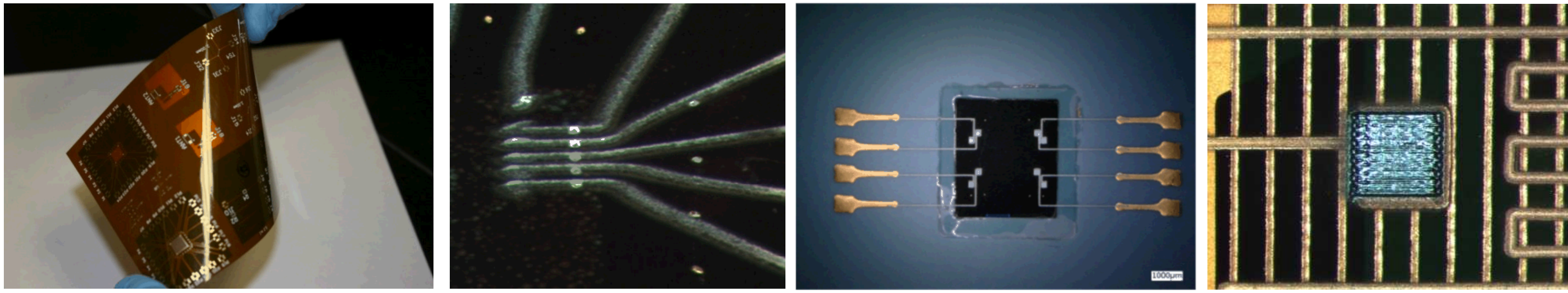
Conformal electronics



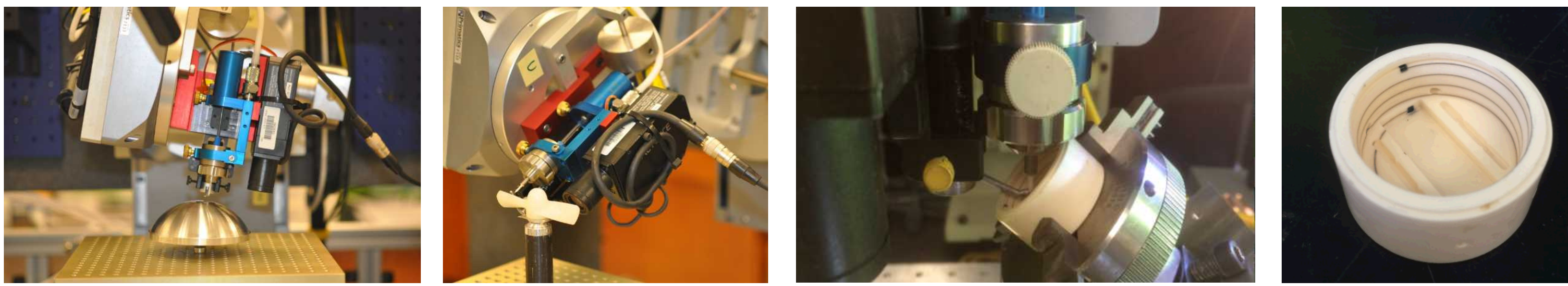
Printed battery

* Licensed/Commercialized Sandia AM technologies

Applications for Additively Manufactured Printed Electronics



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

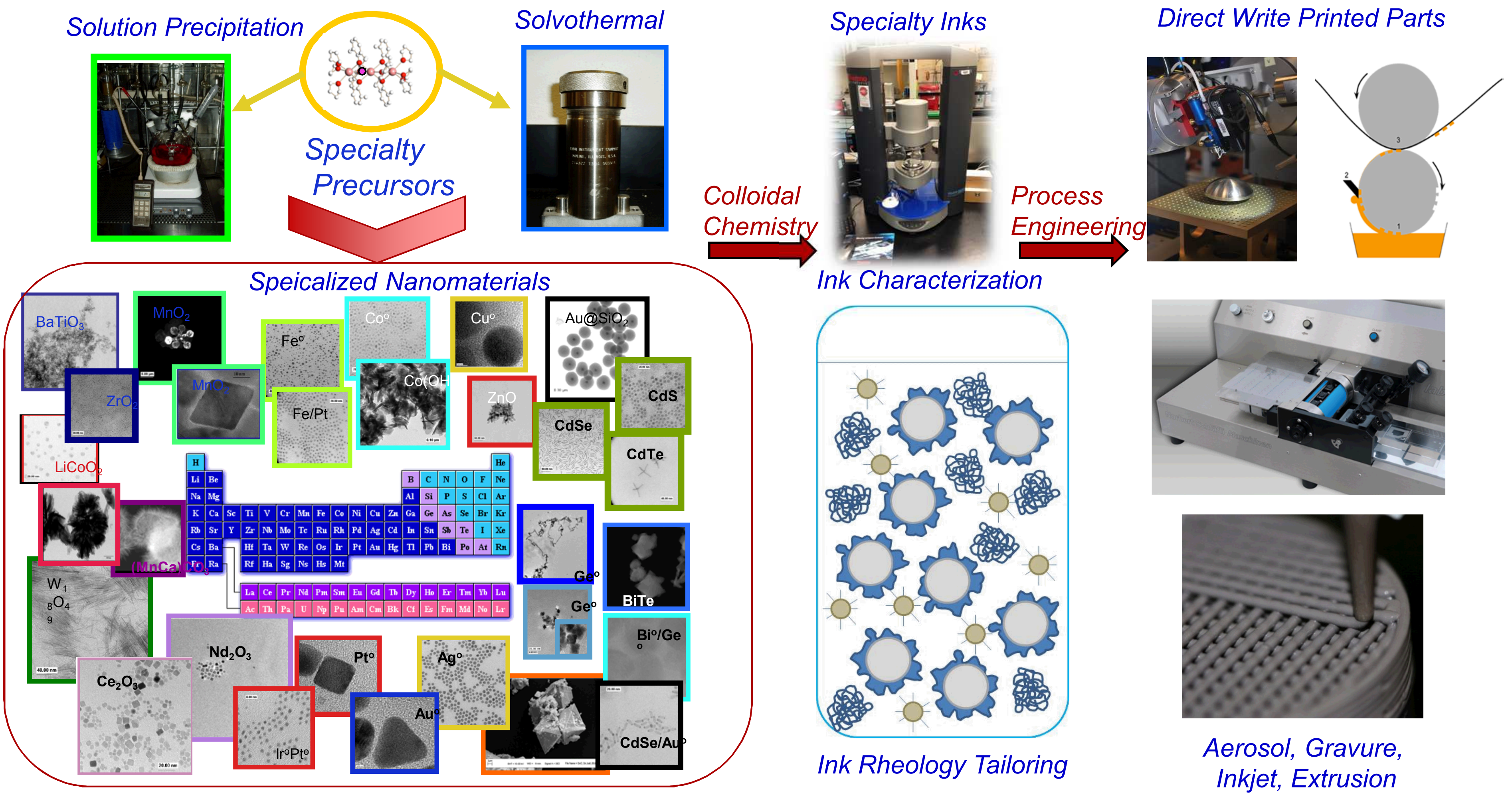


3, 5, and 6 axis conformal printing for non-planar material deposition and device fabrication

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

Device Development Integrates Chemical Synthesis and Processing for AM



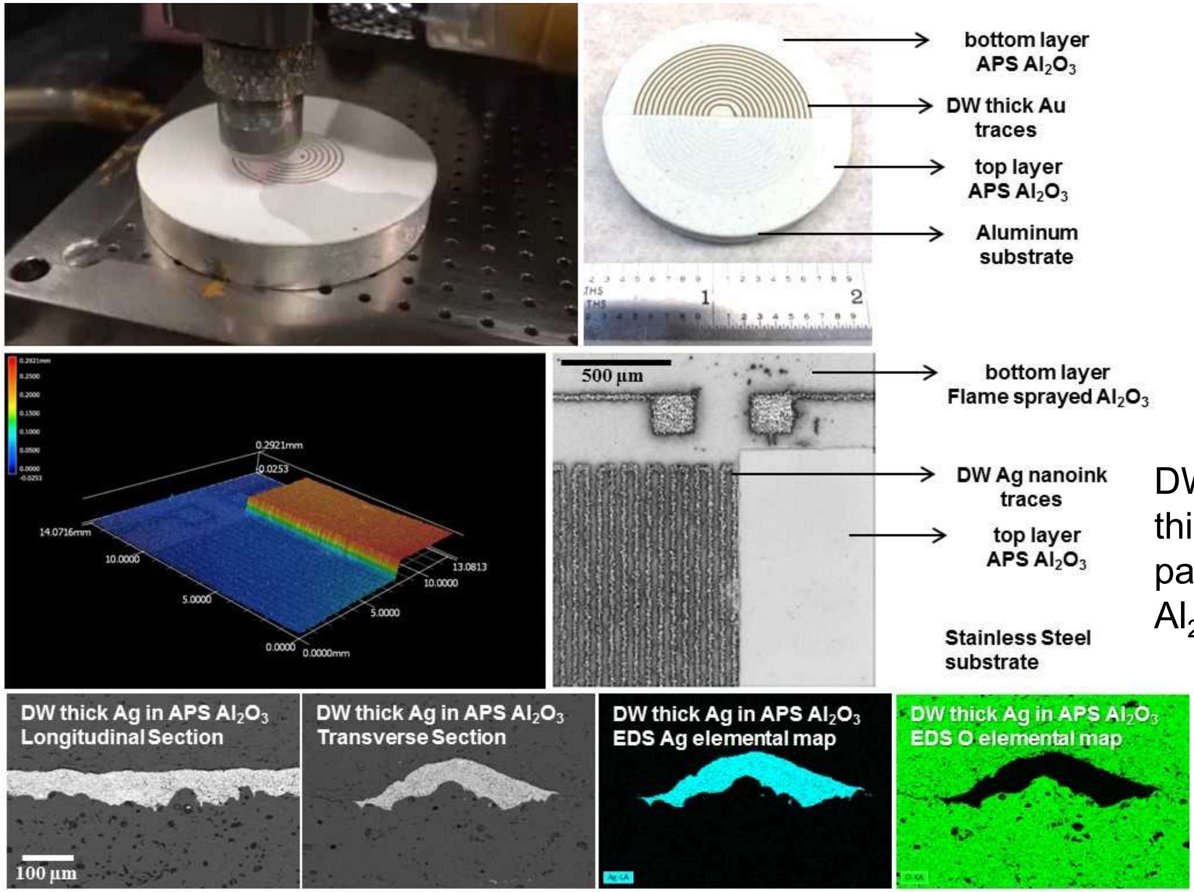
From specialized, tailored nano-materials to process-able inks requires chemical synthesis, colloidal chemistry, rheology/characterization, process engineering

Integration of Multiple AM Processes Leads to Successful Integration of Material Classes

Direct write (DW) extrusion casting of thick-film Au ink onto an air plasma-sprayed (APS) Al_2O_3 coating over an aluminum substrate.

Profilometer topography of the Al_2O_3 APS top coat encapsulating the DW-printed Au trace

APS Al_2O_3 top coat of the DW Au pattern



DW-deposited thick-film Ag ink pattern and APS Al_2O_3 overcoating

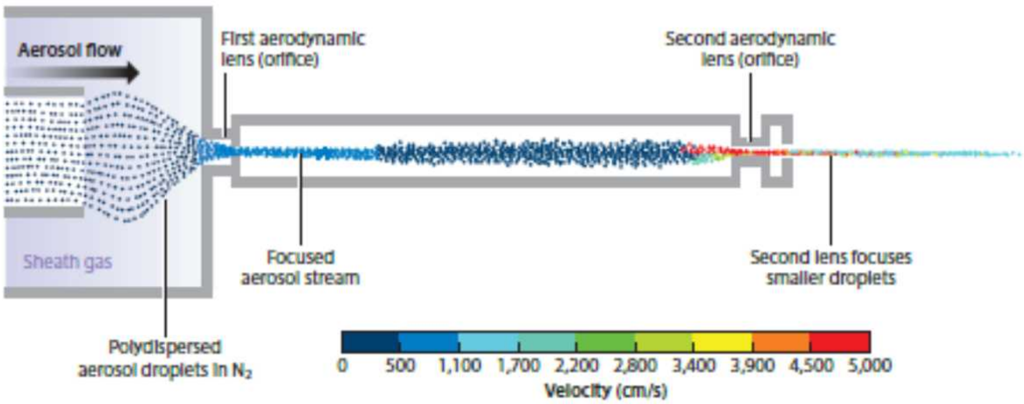
Transverse sectioning and elemental mapping

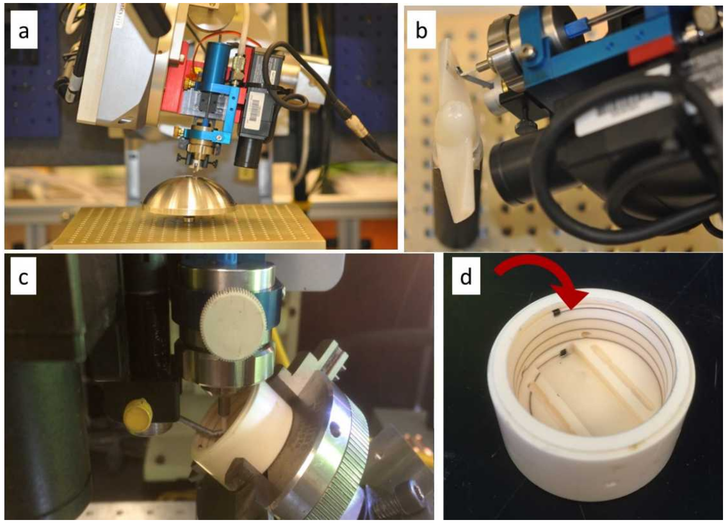
Pylin Sarobol, et al. “Additive Manufacturing of Hybrid Circuits,” *Annu. Rev. Mater. Res.* 2016. 46:12.1–12.22

AML has lead a strong effort in Direct Write (DW) for Multi-Material Processing

- 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

Innovation in theory and modeling improves resolution by droplet collimation in aerosol jet based printing technology.

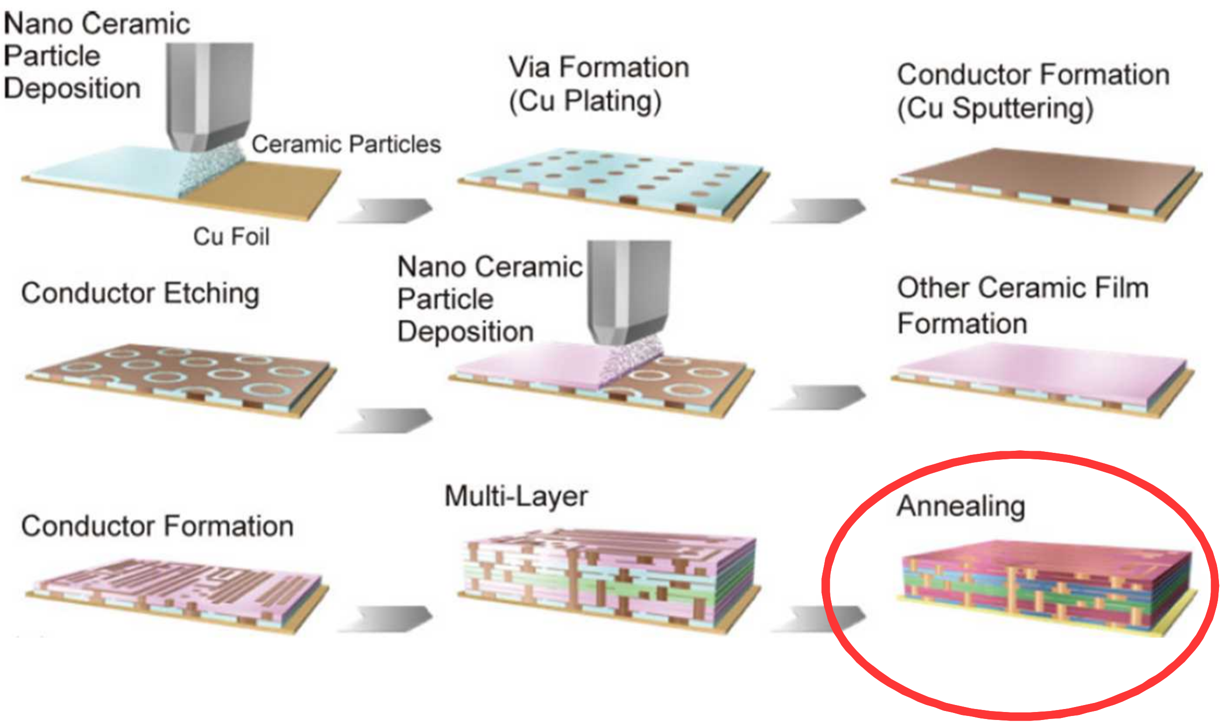




Six-axis robotic platform for contactless electronics printing applications at Sandia National Laboratories.

AM Approaches for Electronic Devices

Schematics of multilayered electronic device fabrication by aerosol deposition to deposit ceramic films, photolithography for patterning and dry chemical (HF/HNO_3) etching, and electroplating/sputtering to deposit internal conductors.



Thermal Processing requires compatible material systems. Polymers and ceramics *generally not* compatible.

Imanaka Y, Amada H, Kumasaka F, Takahashi N, Yamasaki T, et al.. Nanoparticulated dense and stress-free ceramic thick film for material integration. 2013 *Adv. Eng. Mater.* 15:1129–35..

High Performance Materials must use non-traditional approaches to Densification

Sandia National Laboratories

Thermal Energy is traditional for sintering processes

Atomic Diffusion/Transport Mechanism

- Lattice diffusion from grain boundary – atom from grain boundary diffuses through lattice
- Grain boundary diffusion – atoms diffuse along grain boundary
- Plastic deformation – dislocation motion causes flow of matter

Rapid Thermal Processes:
Use localized heating or rapid rates to avoid substrate damage or create unique microstructures.

Novel Processing based on Pressure or Interfacial property manipulation are avenues for novel densification at low temperature.

Nanosize Particles (Curvature)
- Surface Melting

Interfacial Property Control
- Hydrothermal Film Growth

Applied Electric Field Sintering

Plastic Deformation Processing
- High Pressure Consolidation
- Hydrothermal Pressing

Densification of NanoMetals is Enabled by Surface Property Control

Sandia National Laboratories

- Coinage metals (Au, Ag, Cu, Ni, Zn) are critical materials for electrical connection, antenna design, and meta material optical arrays.
- Low Temperature conversion relates to the reactivity of "clean" nanoparticles, and nanoparticle inks incorporating these chemistries prove successful in optimizing many properties.

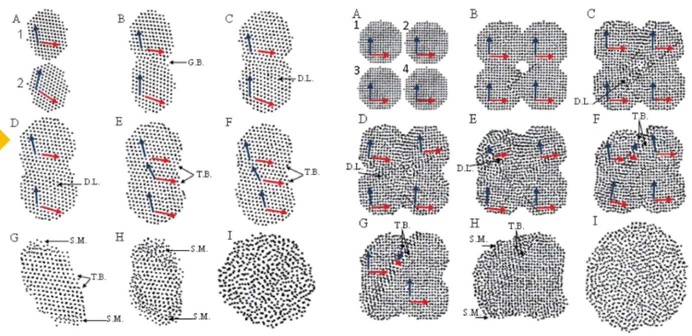
Nanoscale particle size lowers melting temperature

$$T_m(d) = T_{m,0}\left(1 - \frac{\beta}{d}\right)$$

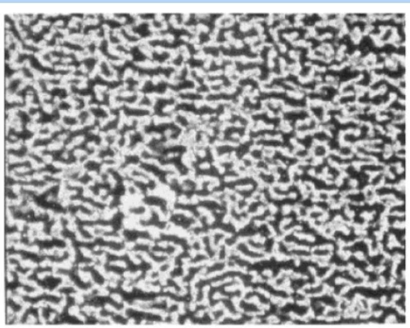
β is a material constant and d is the particle size, and $T_{m,0}$ is the bulk melting point of the material.

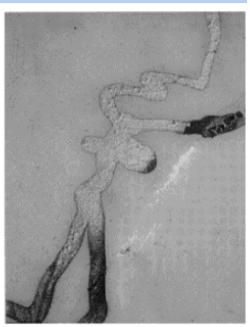
Sintering is spontaneous for clean surfaces.

Alarifi et al. *Mat. Trans.* **54** (2013) 884.



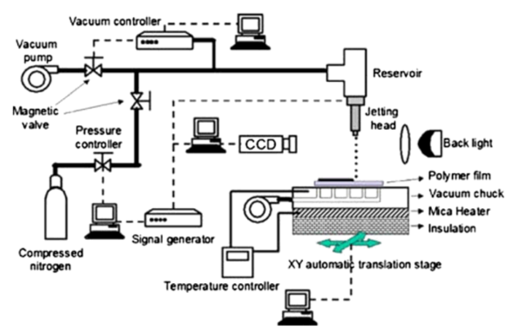
Laser treatment allows for patterning of nanoparticles into conductive films.



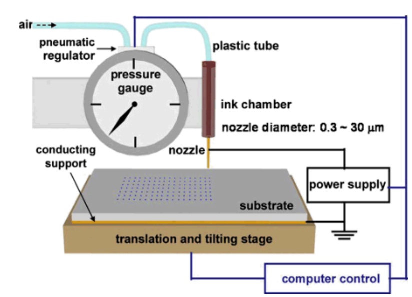


J.E. Martin et al. *J. Phys Chem B* (2003)**107** 430.

Metal Nanoparticle Inks are common to Direct Write Manufacturing



H.J. Gysling, *Curr. Op. Coll. Interf. Sci.* (2014) 155.



eHD Jet Printing

Barton et al. *Mechatronics* **20** (2010) 611.

Routes to Ceramic Densification

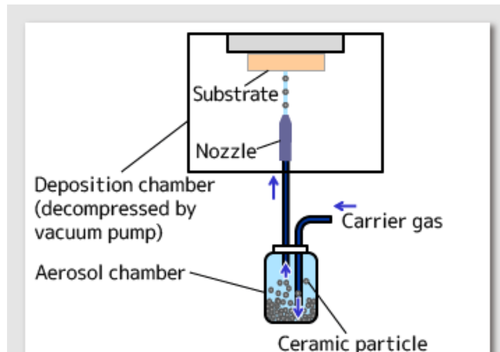
Cements/Geopolymers

- room temperature reaction

Z. Li et al. *JACerS* (2002) 305

Aerosol Deposition

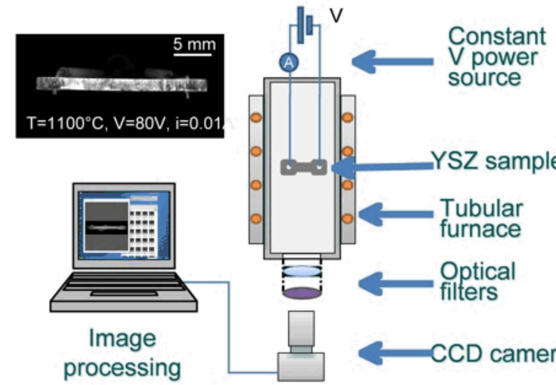
- method for room temp ceramic film deposition



www.hitachi.com

Electrical Flash Sintering

- sintering in seconds under heat and dc electric field



Ceramic Tech Today, Oct 13th, 2010

Rapid Thermal Processing

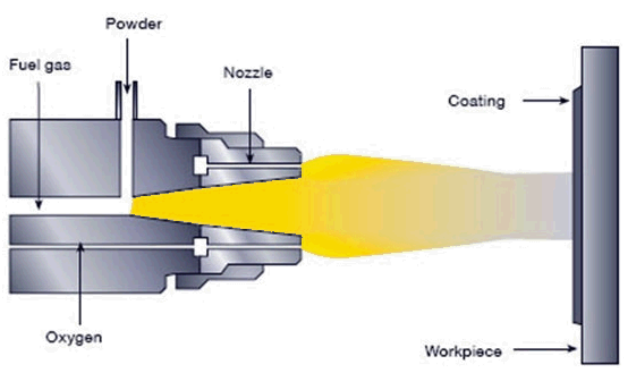
- lamp thermal process for wafer anneals.

RTP/RTA system RLA 1200

https://www.crystec.com/kllrtpe.htm

Flame Spray of Ceramics

- used for ceramic films on metals



dcleng.com.au

Hydrothermal Hot Pressing

- use of pressure and low T for densification

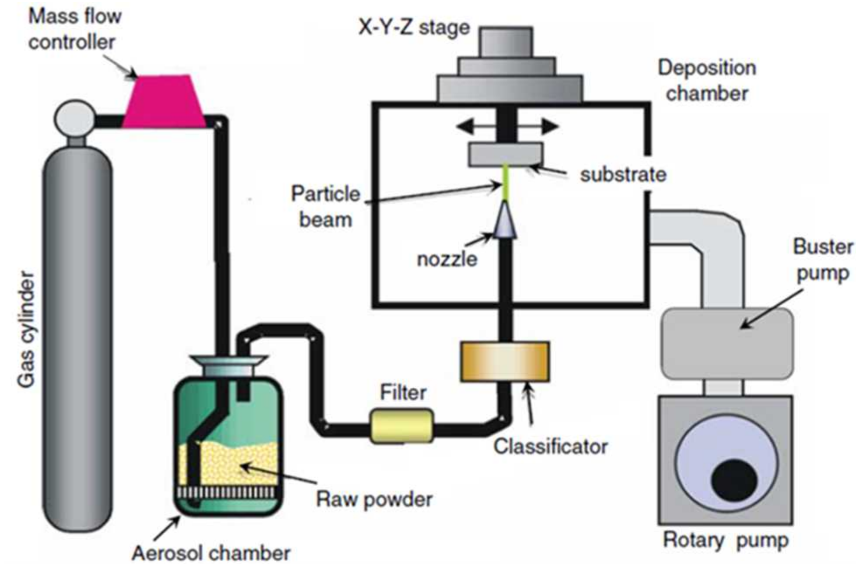
US Patent 8709960 B2 - Riman

Layer Slurry Deposition & Laser Sintering

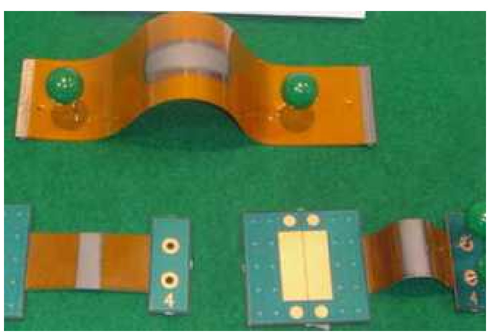
- Complex microstructure, additive manufacturing approach

Aerosol Deposition

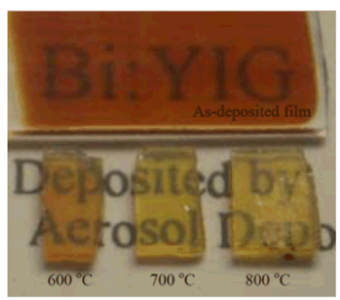
- Aerosol Deposition (AD) - A room temperature (RT) process enables deposition of engineering and electronic ceramics for integration on *plastic, metallic, and glass* substrates.
- Sub-micron ceramic particles accelerated to high velocity by pressurized gas, impact, deform, and consolidate at RT in vacuum, at high rates (10-30μm/min) [Akedo JTTEE5, 2007].

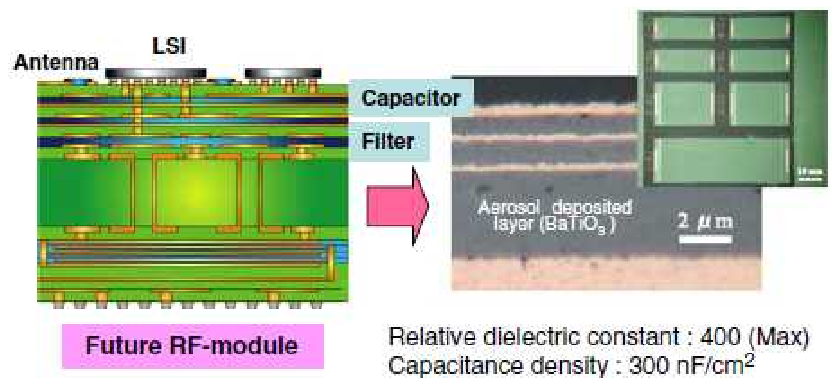


Schematics of AD system from J. Akedo. *JTST.,* 2008:17:181



AD Flexible electronics from J. Akedo. *JTST.,* 2007:17:181

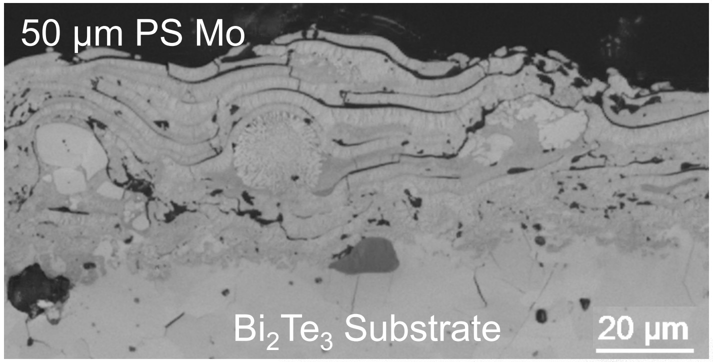


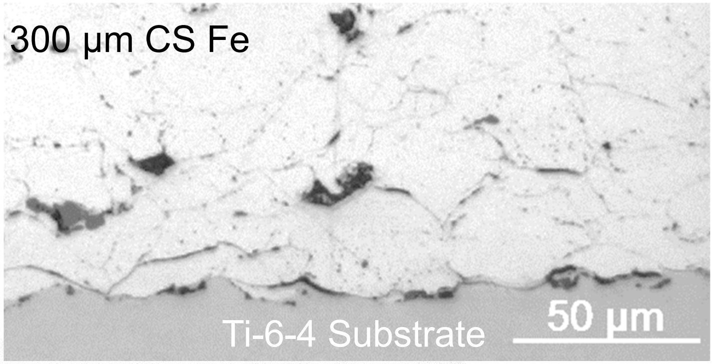


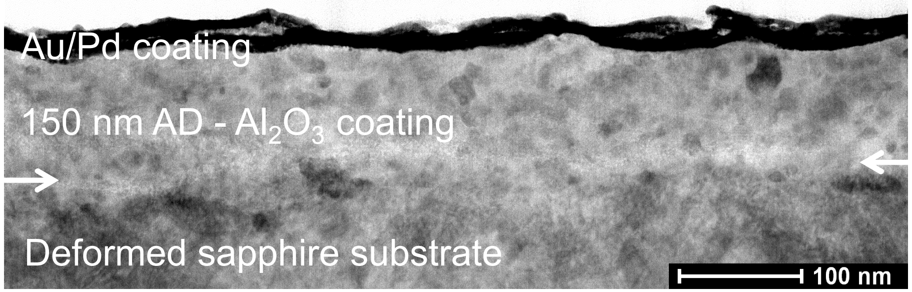
Example of applications enabled by AD. AD magnetic YIG - Y. Imakana 2006. AD Flexible electronics and RF module - J. Akedo. *JTTEE5.,* 2007

Process – Microstructures – Properties

Processes	Energy Input	Feedstock		Environment	Metals	Ceramics	Composite	Thickness
Plasma Spray - PS	Thermal	melted	10-100 µm	atmosphere	√	√	√	100µm - 1mm
Cold Spray - CS	Kinetic	solid-state	10-50 µm	atmosphere	√		√	200µm - 1cm
Aerosol Deposition - AD	Kinetic	solid-state	< 1 µm	vacuum	√	√	√	100nm - 100µm





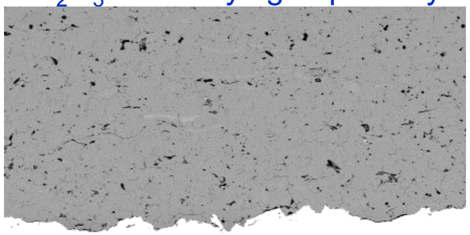


- Sprayed coatings often contains defects, pores, splat boundaries, oxides inclusions, etc.
- Properties can be very different from those of wrought/bulk materials.
- Oxide coatings can be non-stoichiometric.
- Mechanical adhesion to substrate.
- Manage residual stress.

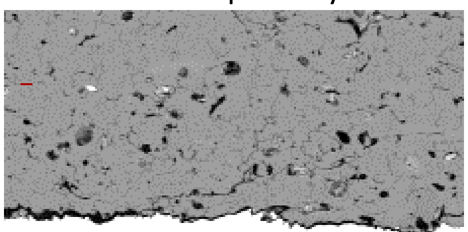
Process – Microstructures – Properties

- Power, gas type/pressure, standoff, feed rate, etc.
  - Particle temperature and velocity
    - Graded materials / density
  - **PROCESS OPTIMIZATION**

Plasma sprayed ceramic
Al_2O_3 with varying % porosity

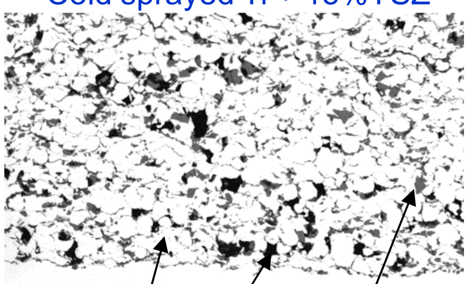


~0.2% porosity



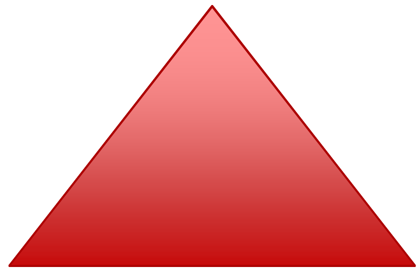
~2.0% porosity

Materials integration - Composite
Cold sprayed Ti + 15%YSZ

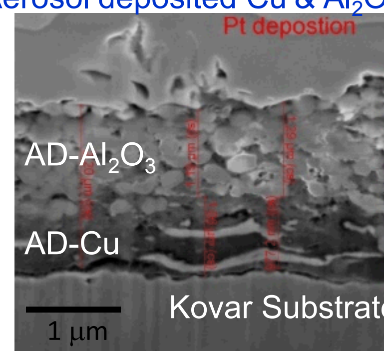


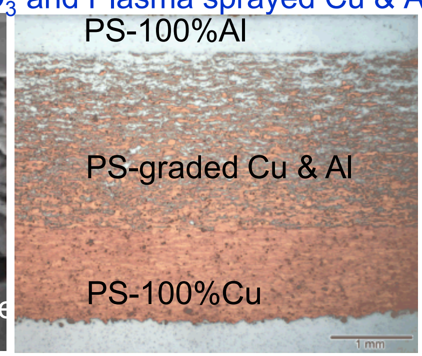
100 µm Ti Porosity YSZ

- Establish Process

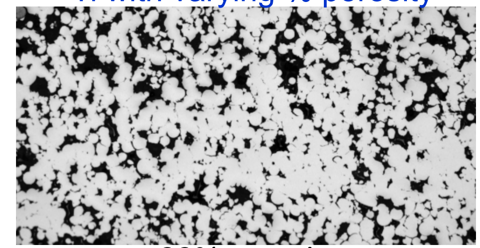


Graded Materials:
Aerosol deposited Cu & Al_2O_3 and Plasma sprayed Cu & Al

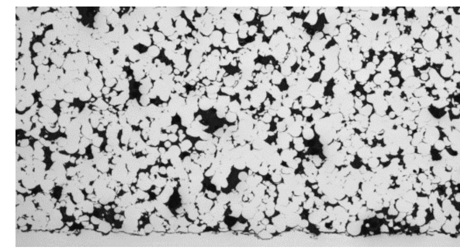




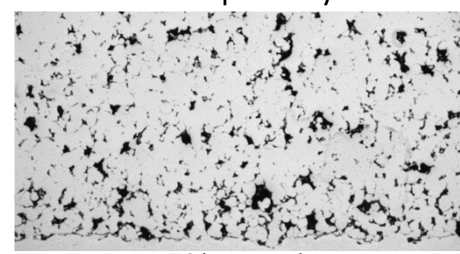
Cold sprayed metal
Ti with varying % porosity



~22% porosity



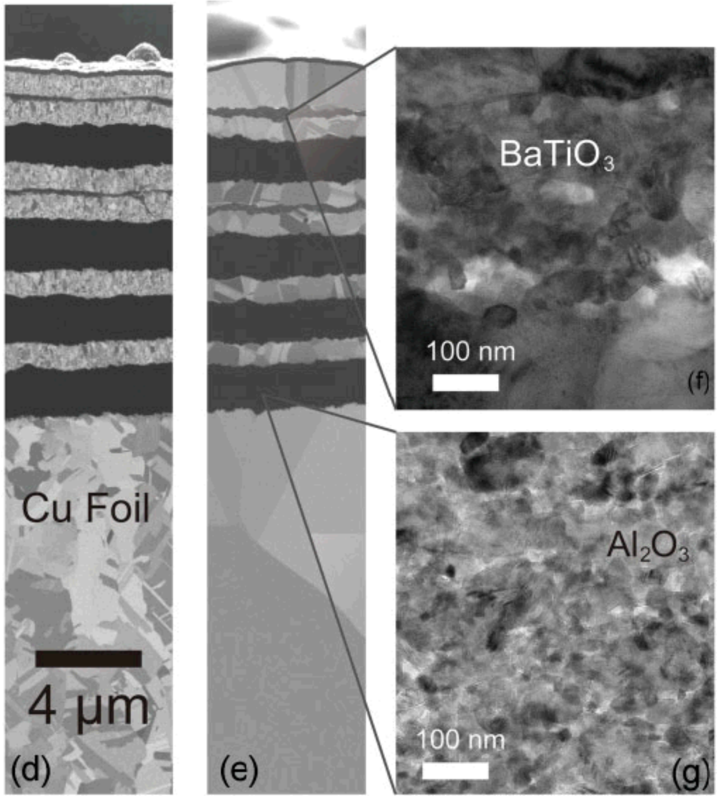
~17% porosity



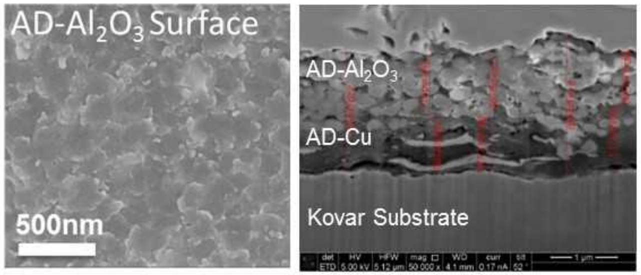
100 µm ~7% porosity

Multiple Ceramic Systems can be layered to form device structures

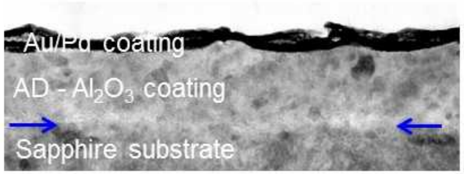
- SNL focuses on the *fundamental mechanisms* behind submicron ceramic particle *deformation*, particle/substrate and particle/particle *bonding* in consolidated films.



$BaTiO_3/Al_2O_3/Cu$ multi-layered structure produced by AD and electroplating from Y. Imanaka *et al. Adv Engr Mater.*, 2013:15:1129

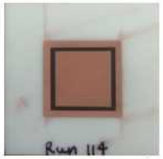


Aerosol Deposition is significant because it allows materials integration.
- Process = 20°C.
- Al_2O_3 T_m = 2100°C.
- Kovar T_m = 1450°C.
- Cu T_m = 1085°C.

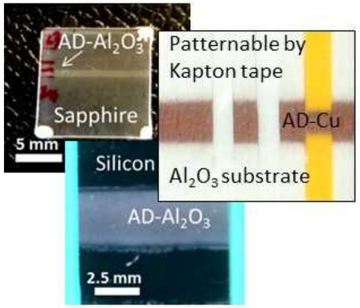


150 nm nanocrystalline AD – Al_2O_3

12 μm AD – Ni interconnects



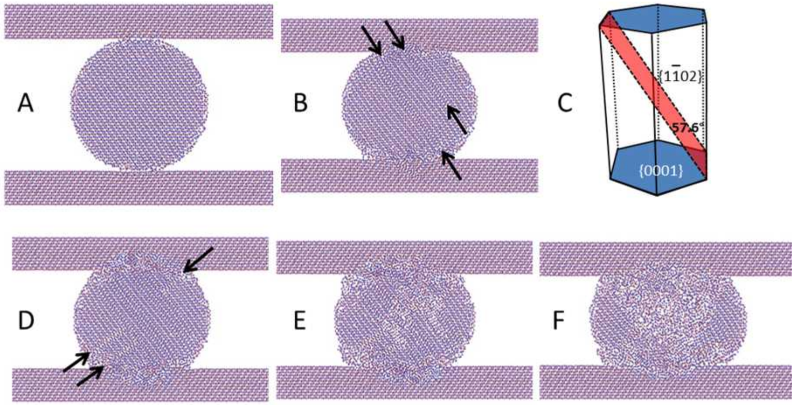
AD – $BaTiO_3$ and Cu towards capacitors

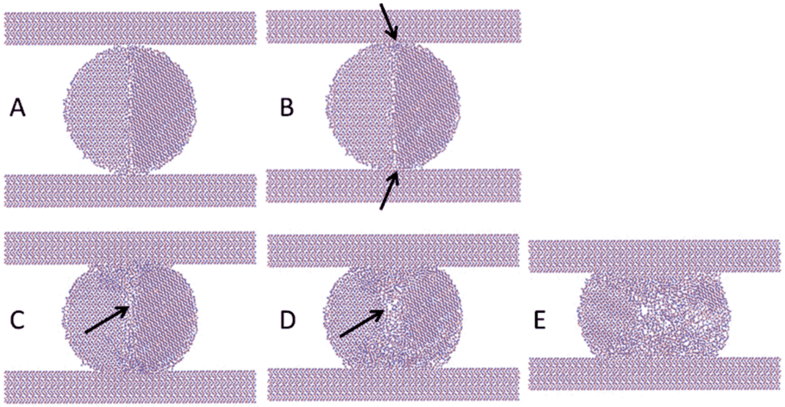


- Patternable coating using Kapton tape.
- Extremely dense, nanocrystalline metallic, ceramics, or composite films on various substrates.
- Future applications – miniaturized hybrid circuits, actuators, sensing, capacitors, shielding, etc.

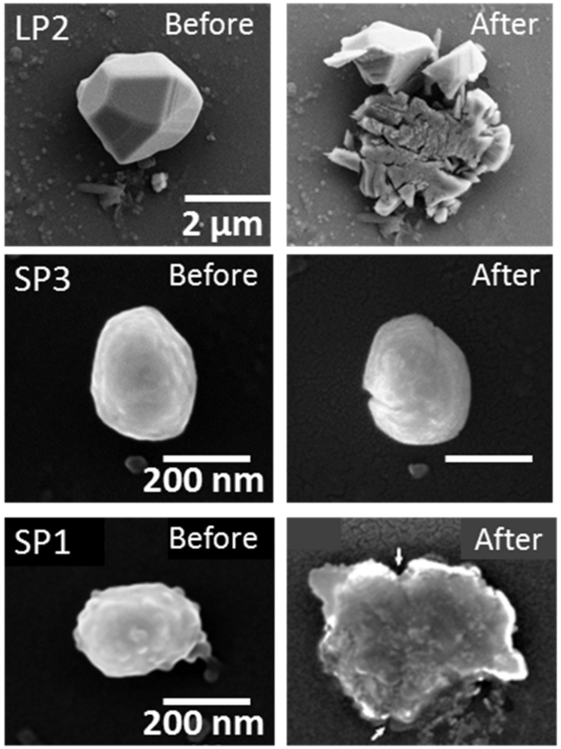
Fundamental Mechanisms in Ceramic Particle Kinetic Deformation

Simulation of Single Crystal or Bicrystal Deformation Mechanics

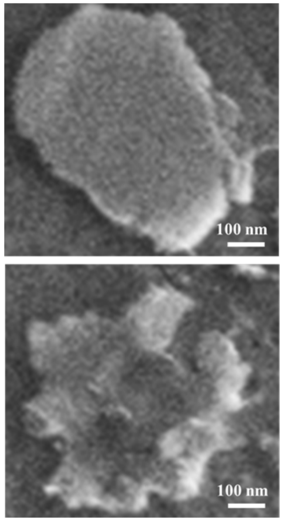




Experimental Verification of Deformation under Pressure



Al_2O_3 single splat particles in AD Sarobol et al. SAND2016-2870

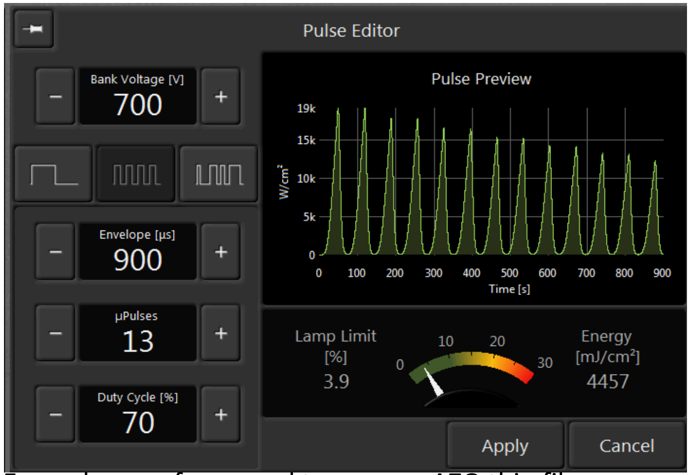


- Submicron particles with mobile dislocations deform to produce coherent films.

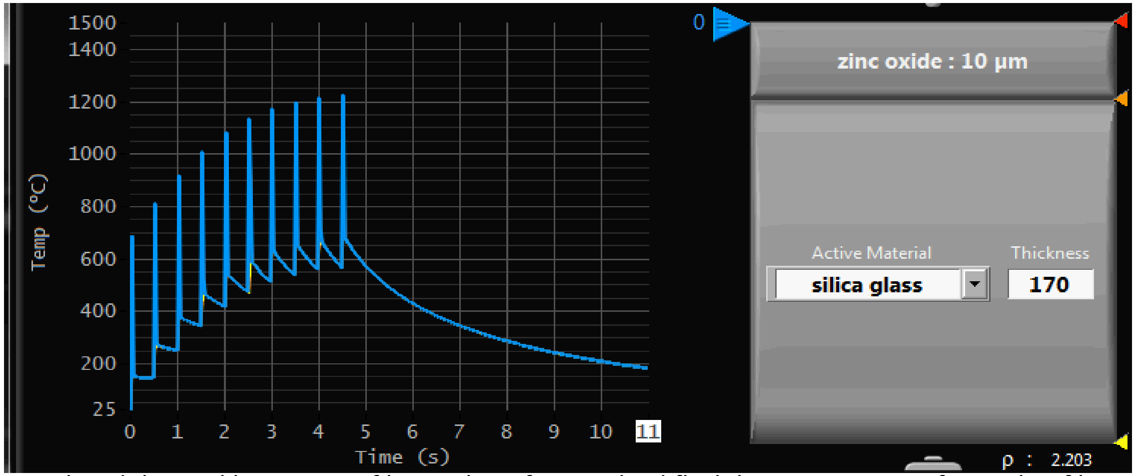
Sarobol, P. et al. "Room Temperature Deformation Mechanisms of Alumina Particles Observed from In Situ Micro-compression and Atomistic Simulations," J. Thermal Spray Tech. (2016) **25** 82-93.

Rapid High Temperature Sintering via Pulsed Flash Lamp Processing (Photonic Sintering)

- 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

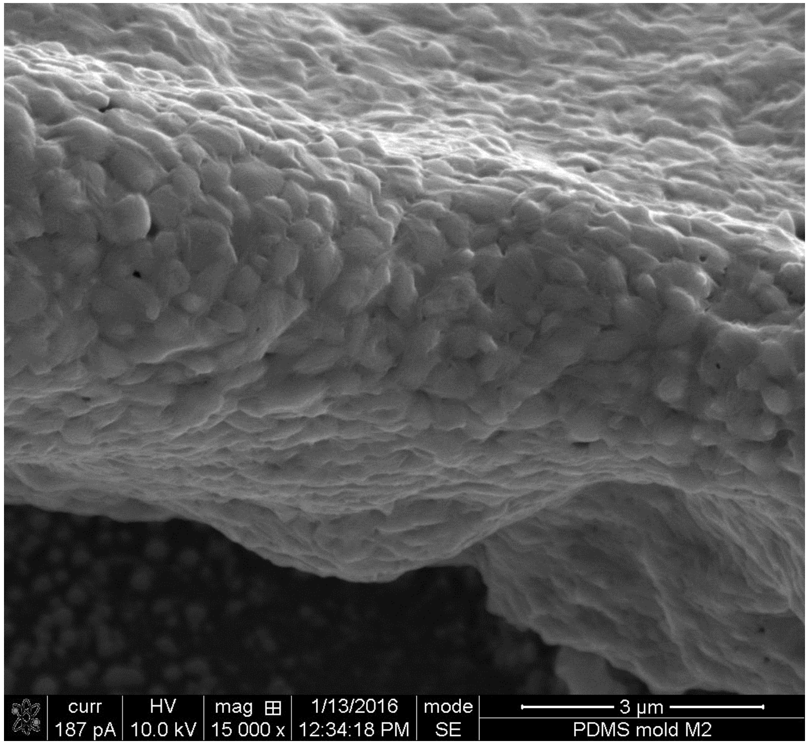


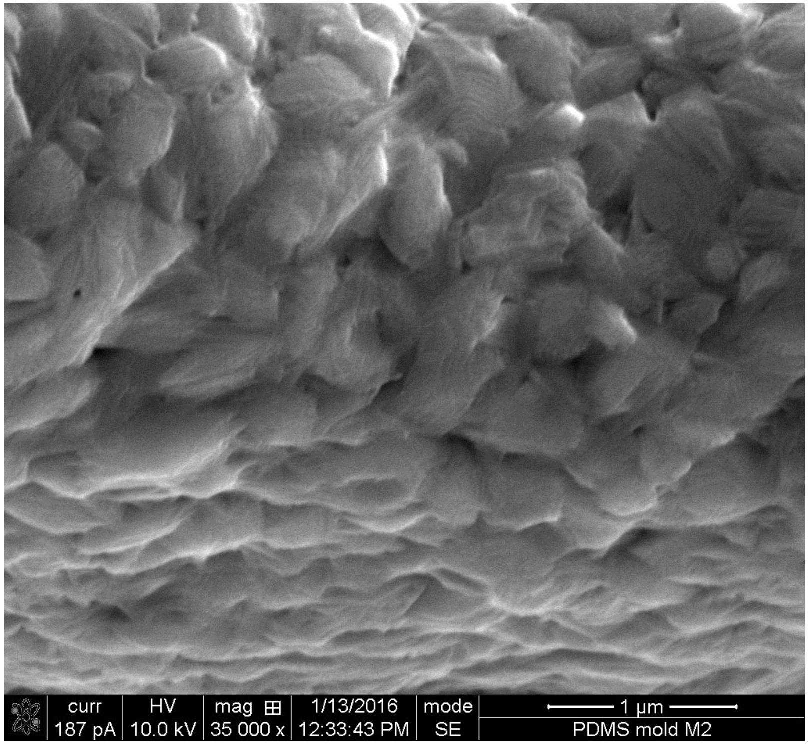
Simulated thermal heating profile resulting from pulsed flash lam processing of AZO thin films

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

Surface Structure of Photonically Sintered AZO Films



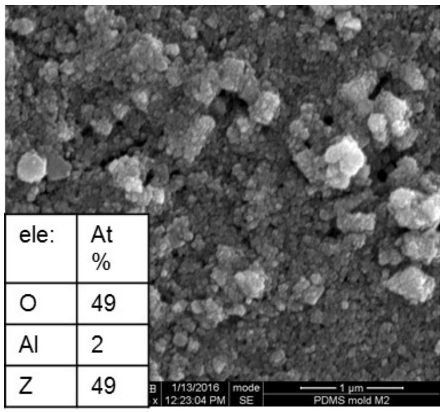


- Surface topologies are fibrous or terraced between initial “grains”, and grain size is larger than the initial material.

Solution Deposited AZO thick film: Photonic Sintering Results

- Photonic Curing densifies ceramic AZO
- Stoichiometry affected by environment and thermal profile

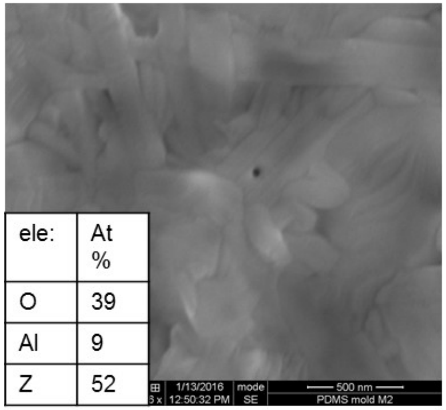
Initial Colloidal Film



ele:	At %
O	49
Al	2
Z	49

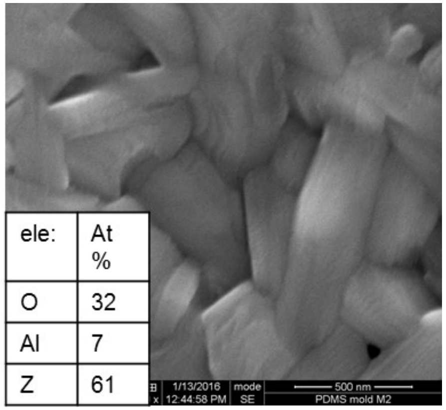
Inset is EDS determined composition

Processed in Air

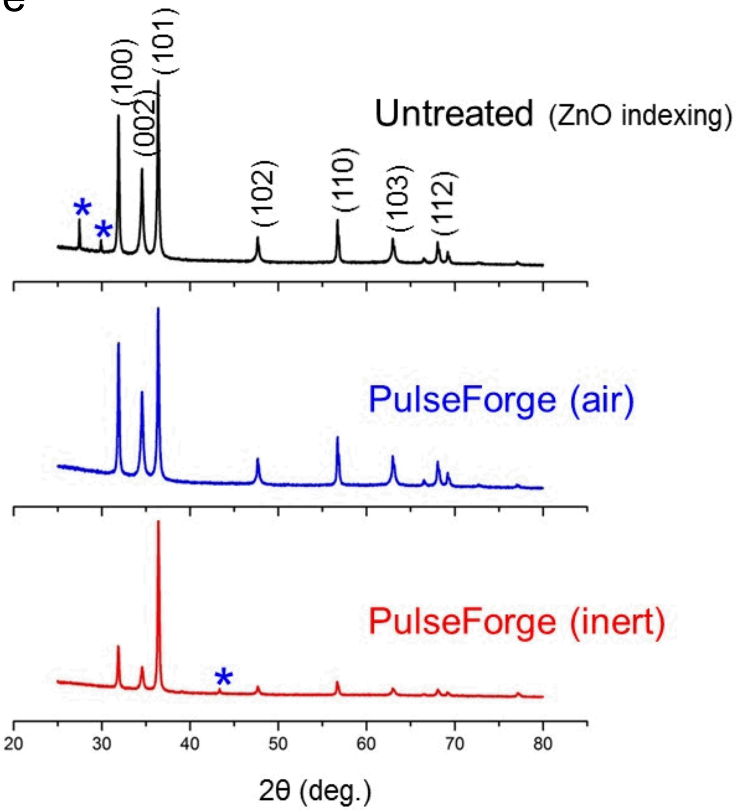


ele:	At %
O	39
Al	9
Z	52

Processed in N_2



ele:	At %
O	32
Al	7
Z	61



*Asterisks indicate loss/gain of from processing conditions

Future Efforts

- The processing conditions to integrate multiple material classes and their thermal regimes for densification is a primary challenge in fabricating novel devices with AM.
- Nanomaterial Development enables the formation of acceptable materials via their surface properties and internal structural defects.
- Aerosol Deposition techniques are useful in the initial and post-fired conditions for creating conformal electronics
- Novel processing in patterning aerosol deposition and in photonic curing are avenues for new achievements.

9/18/2015

Photos placed in horizontal position with even amount of white space between photos and header

Photos placed in horizontal position
with even amount of white space
between photos and header

Line-of-sight process. Use thermal (melting/solidification of feedstock) or kinetic (solid-state deposition – deformation of feedstock) energy.

Traditionally used for making passive coatings. Research now moving towards making active (functional) coatings.

Many knobs to turn. Need to perform process optimization to achieve the process-microstructure-properties relationship. Then use it to make desired coatings.

Included details of 3 processes—plasma spray, cold spray, and aerosol deposition. Please, prioritize the aerosol deposition as it is new/exciting with lots of potential.

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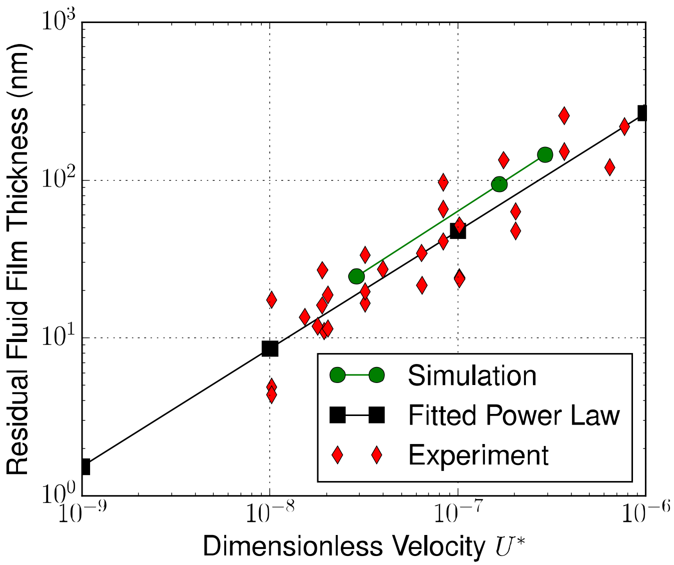
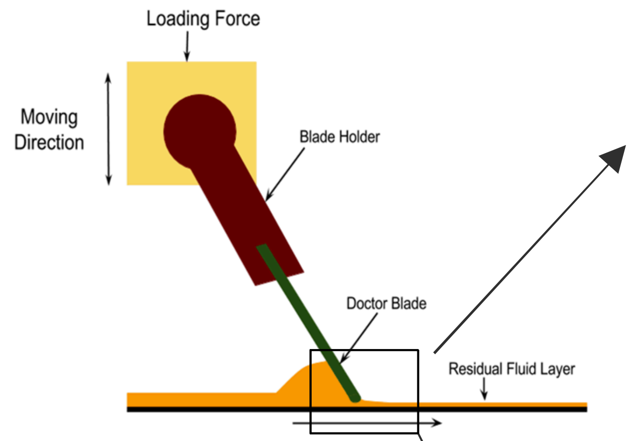
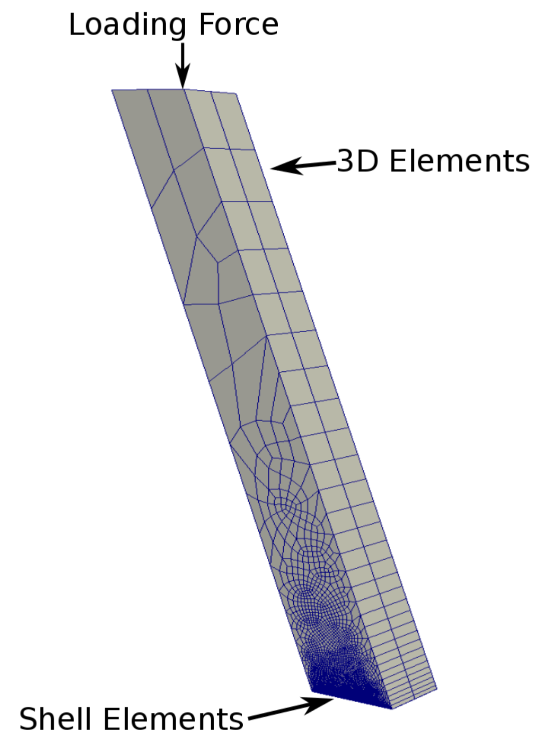
Computational model of doctoring in gravure printing

Thrust: P-2C Reliable Processes for High-Speed Printing





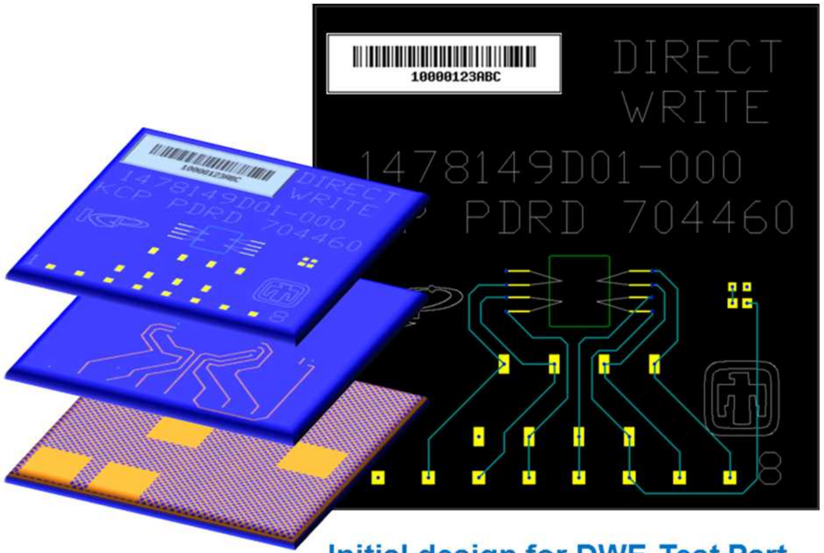
Model predicts residual film thickness over speed and load– arguably the most important factor affecting resolution limits



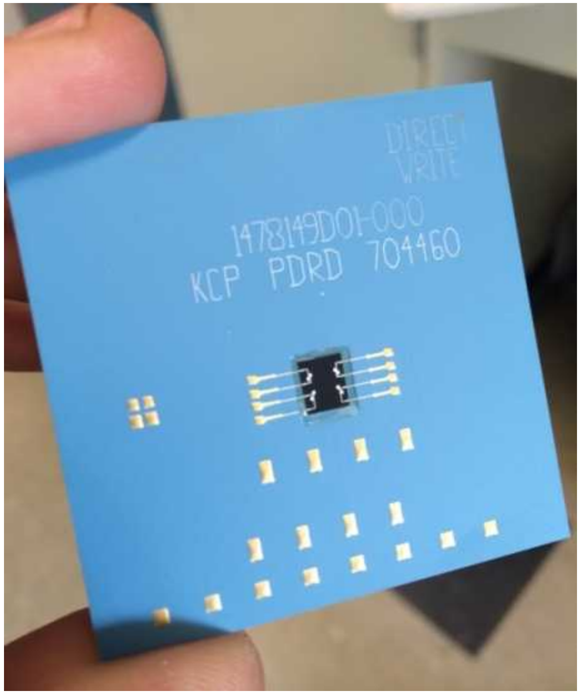
Coupled Ink lubrication model

Hariprasad et al. 2016, J. Applied Physics, DOI: 10.1063/1.4945030

Low temperature co-fired ceramic (LTCC/MCM direct write electronics (DWE) demonstration part.
(a) Schematic desing of layer patterns and vias. (b) Direct write Ag and Au traces on green tape LTCC. Fired LTCC with Ag aerosol jet text and wire bonds. The chip was fixed in place with dispensed, UV-curable adhesive.

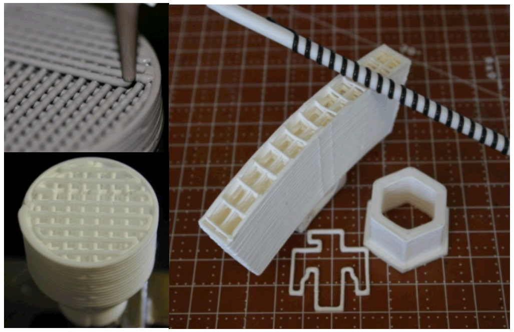


Initial design for DWE Test Part
Commercial Thick film Au paste in/on commercial LTCC tape
Ag ink for graphics & wire bonds

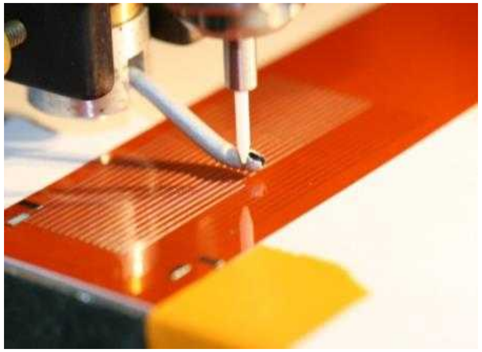


Overview

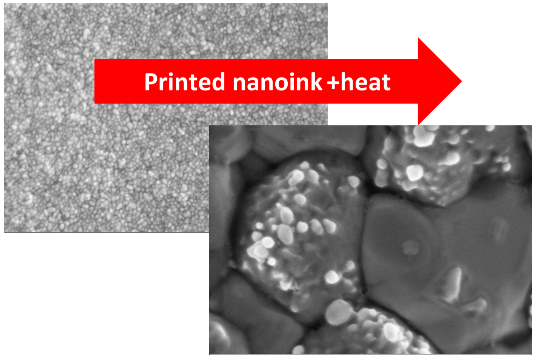
- Additive Manufacturing
- Processing Needs
- Al-Doped ZnO Synthesis
- Pulse Forge Technology
- Photonic Consolidation of AZO Nanopowders
- Summary



Extrusion casting (Robocasting)

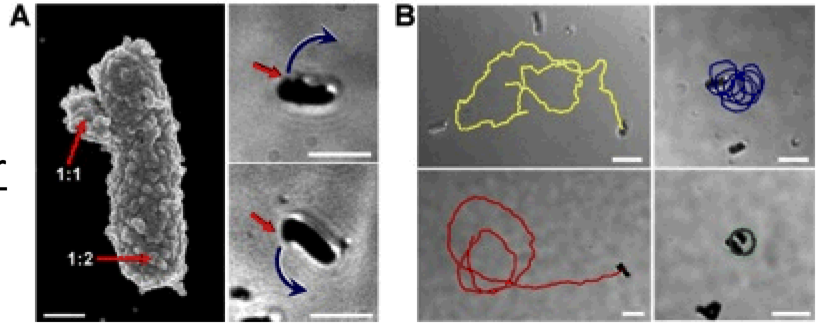


Aerosol jet printing to 10 µm



Nano-particle Ag inks for conductive pathways

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

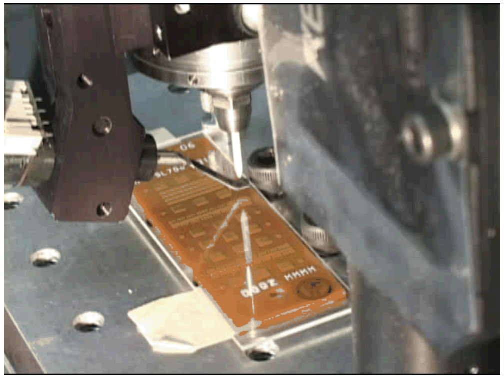


Synthetic Chemistry

- Novel inorganic precursor
- Catalysts
- Sol-gel
- Solvothermal
- Solution precipitation

Ceramic/glass processing

- science of sintering
- composite materials
- unique fabrication
- novel characterization



Nano-scale materials

- Nanoparticle synthesis (0D,1D,2D)
- Surface functionalization/nanoinks
- characterization

Bio-, Nano-materials capability

- BSL-2 Laboratory
- Surface functionalization

Characterization

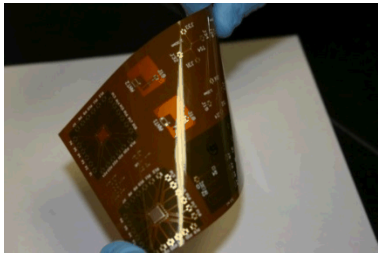
- Diffractometry: SAXS, XRD, XPS
- Thermal (TGA, DSC)
- Spectroscopy (mass, FTIR, ICP)
- Multispectral ellipsometer

Materials processing

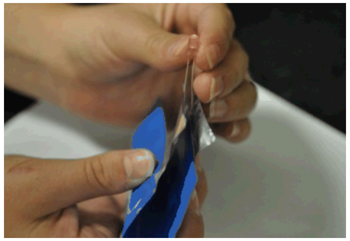
- Self- and directed-assembly
- Films (slot, dip, spin coat)
- Fibers (electrospinning)
- Bulk materials (sintering)
- Multiphoton lithography
- Direct/aerosol write, inkjet
- Gravure/flexo printing

Material Properties must meet the Functional Performance Needs of the Device

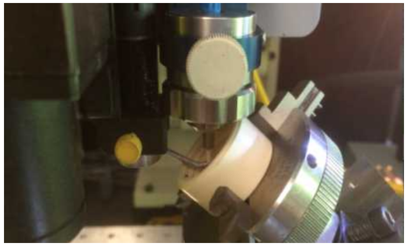
- Device integration: Electrical interconnection via coinage metals (Au, Ag, Cu, Ni, Zn)
- Power components: Nanoparticle solar cells, acoustic power resonators, battery chemistries (Li ion, Li polymer,
- Structural materials: polymers, metals, ceramics with controlled porosity, definition, ion transport, chemical stability (anticorrosives), ceramic cements, composites
- Adsorbants for trace component analysis
- Sensor materials (ZnO, SnO_2, nanoporous C)



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



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



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

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.