

Thermal Spray Research at Sandia

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Acknowledgement

Support of TSRL Staff & Students

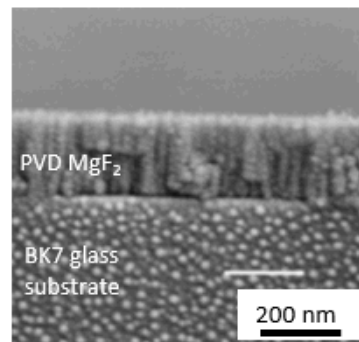
- Jesse Adamczyk, NM Tech now Grad Student Colorado School of Mines
- Pylin Sarobol, former staff now with Lance
- Awesome Techs
 - Tom Holmes
 - Andrew Miller
 - Carlos Silva
 - Joe Padilla
 - Mike Clearwater
 - Andy Mayer
 - Dave Beatty

General Coating Comparisons

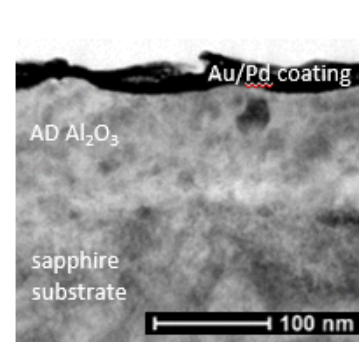
Film Characteristics of Various Processes

Film Parameters	Physical Vapor Deposition [1]	Aerosol Deposition	Thermal Spray
Max Film Thickness	5 μm	100 μm	1 mm
Grain Size	10-100 nm	10-100 nm	10-100 μm
Density	Low	Near Theoretical	Low

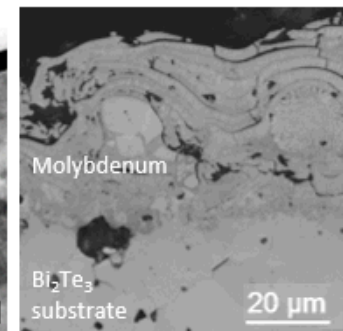
Microstructures of
PVD, AD, and TS
coatings



Physical Vapor
deposited
columnar MgF_2 [2]



Aerosol deposited
 Al_2O_3 on Sapphire
substrate



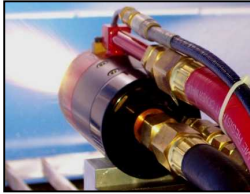
Thermal sprayed Mo
On Bi_2Te_3 Substrate

Thermal Spray at Sandia

- Thermal Spray Technologies
 - Plasma Spray, CAPS (VPS, VLPPS)
 - TWA
 - Cold Spray
 - HVOF
 - Powder Flame Spray
 - Aerosol Deposition
- Process Diagnostics
- Highlight Recent Work in Aerosol Deposition

TSRL operates at least one version of every major spray process

**Atmospheric
Plasma Spray**

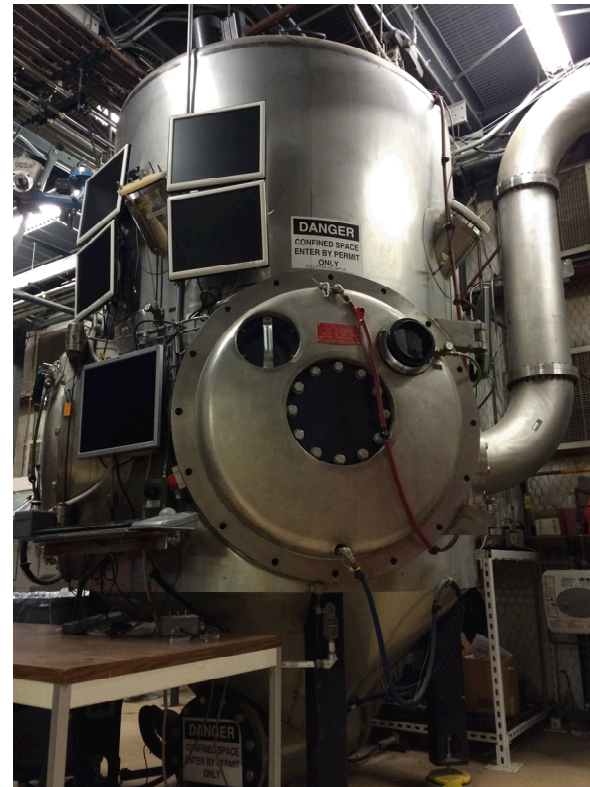
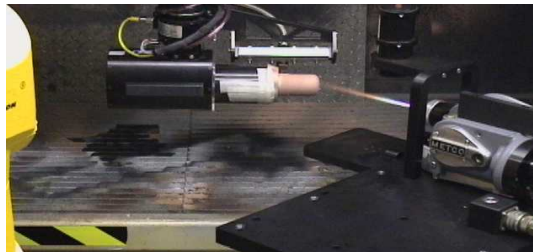


**CAPS: Vacuum,
low pressure,
and very
low pressure
plasma spray**

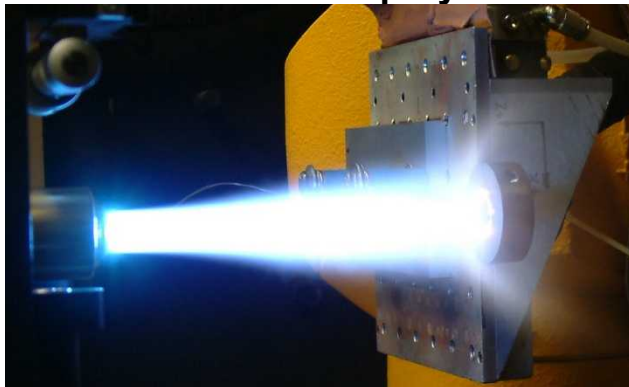


Twin Wire Arc Spray

**Aerosol
Spray
Deposition**

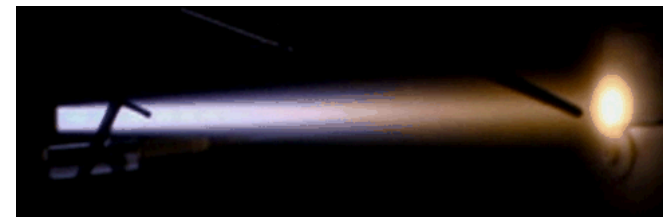


**Cold
Spray**



Powder Flame Spray

Wire Flame Spray



HVOF

TSRL



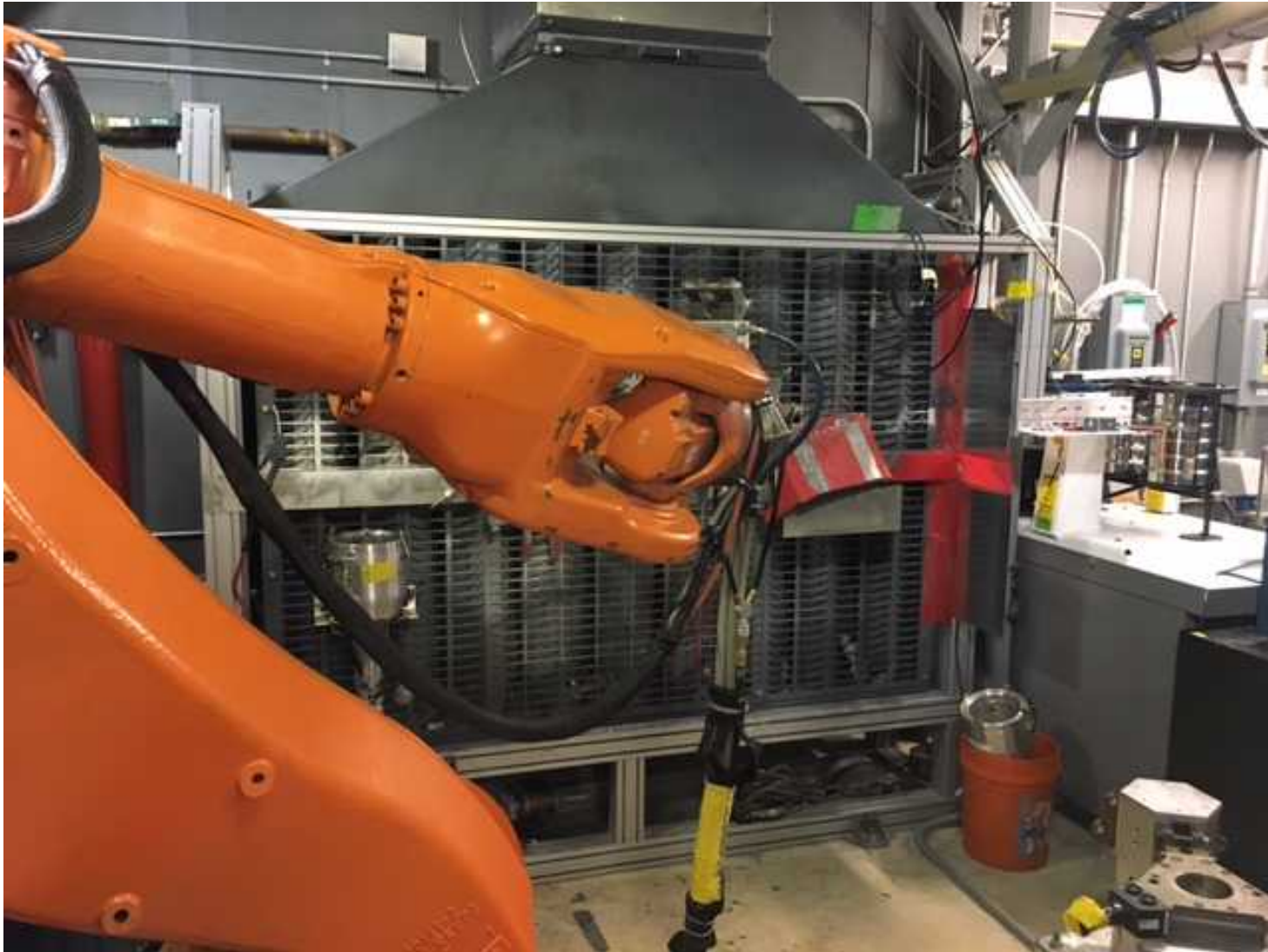
TSRL



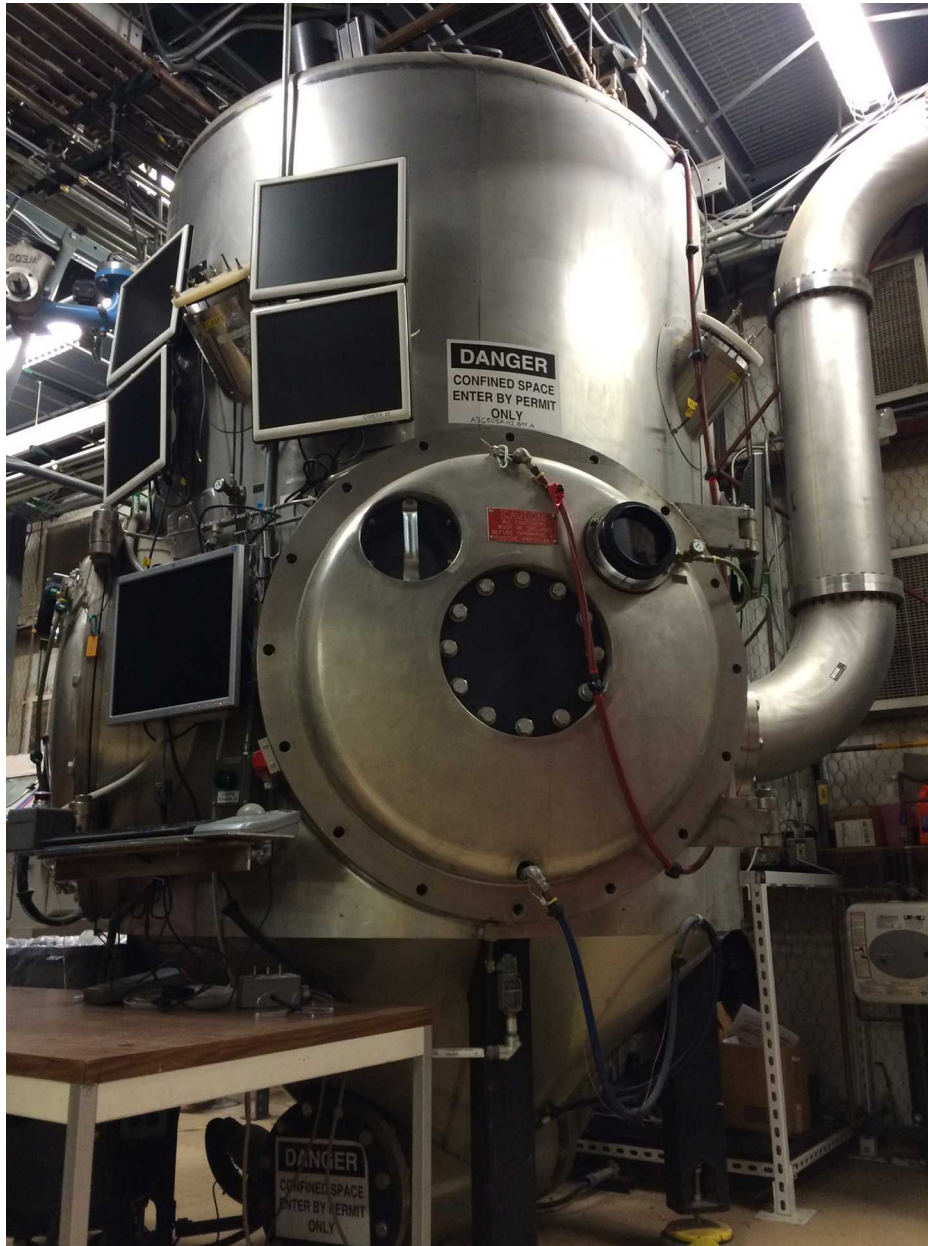
Booth 1



Booth 1



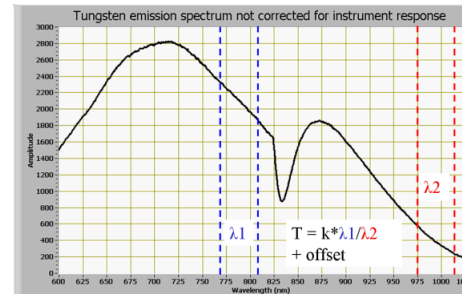
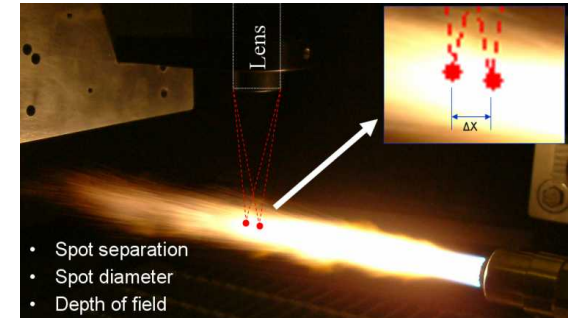
CAPS



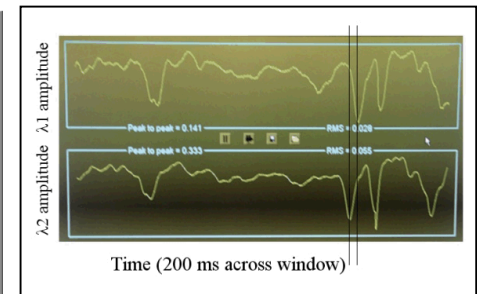
What makes the TSRL unique?

- **Focus on Process Diagnostics for Thermal Spray**
 - DPV-2000, Accura G3
 - Control Vision
 - Spectroscopy
 - Xenon-Flash Thermal Diffusivity
 - Beckman Coulter Particle Size Analysis
 - In-Situ Coating Property (ICP)
 - Laser Doppler Velocimetry
- **Materials Science Expertise and Analysis Capability**
- **Strong Ties to Materials & Process Modeling at SNL**
- **LPPS® Thin Film & Cold Spray**
- **Experience supporting spray processes across entire technical and manufacturing readiness levels**

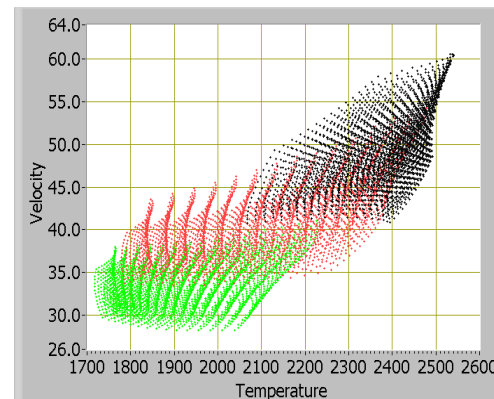
Sensor based particle diagnostics measure particle temperature (T_p) and velocity (V_p).



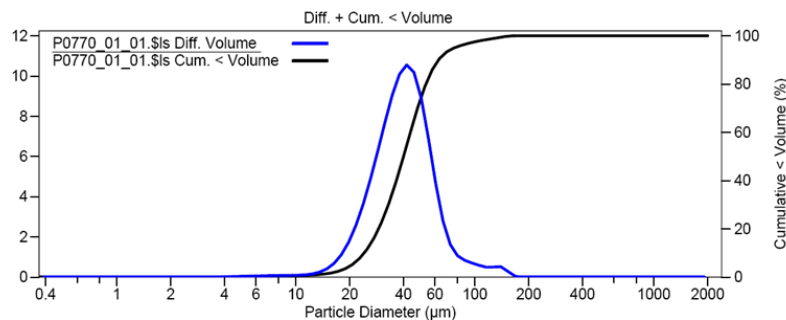
$$T_p \propto \lambda_1 / \lambda_2$$



$$V_p = \Delta x / \Delta t$$



Wire tip imaging

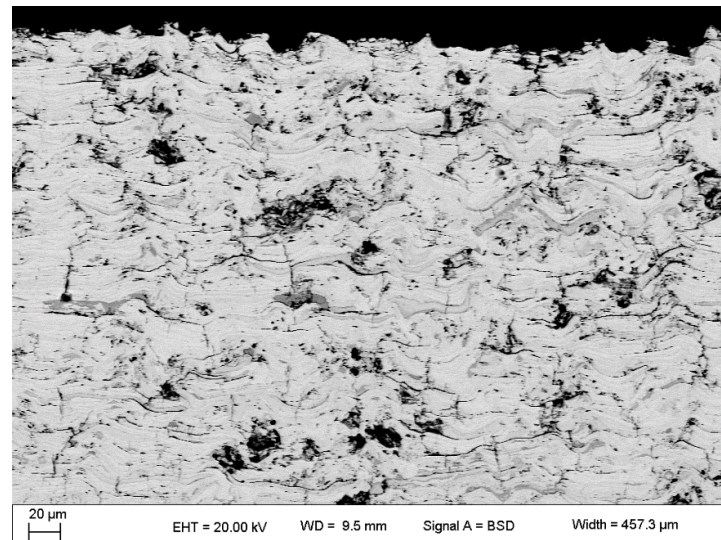
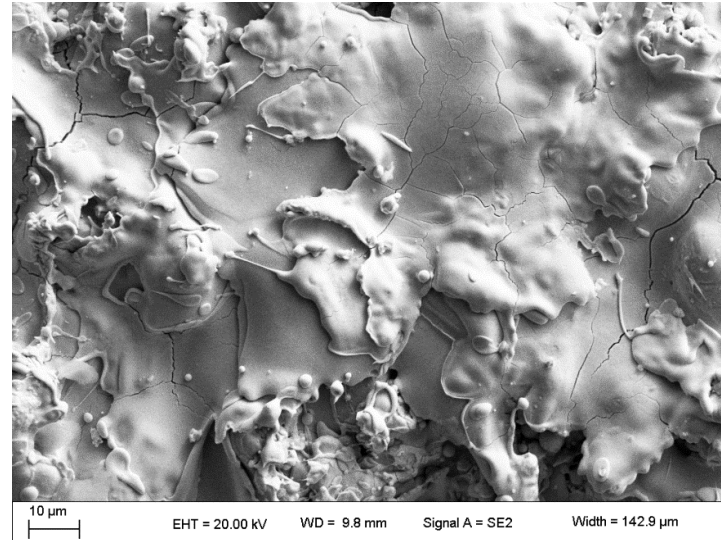
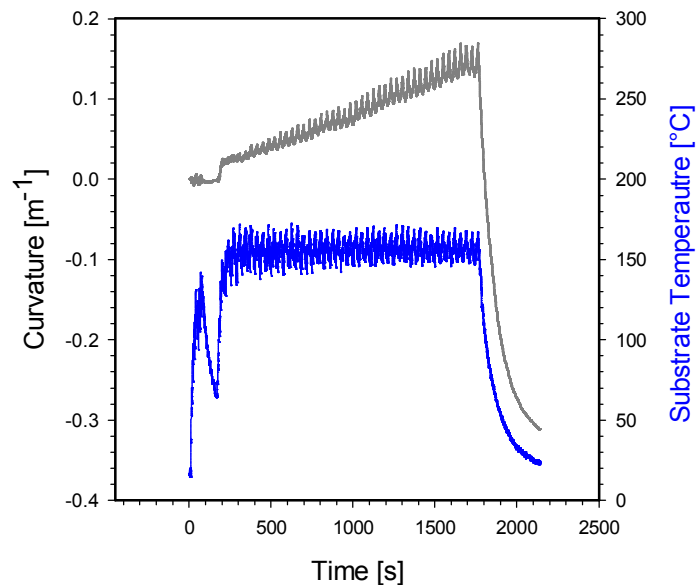


11 Powder particle size distribution

Incorporation of spray diagnostics for process optimization



Coating diagnostics tools for coating stress, modulus

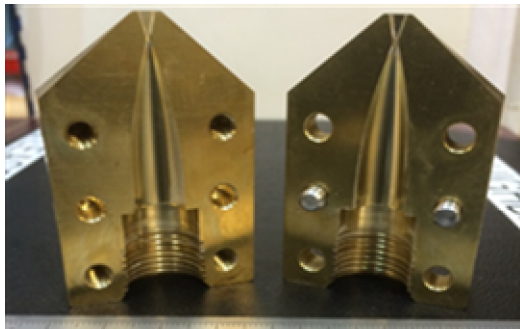


BaTiO₃ , Cu, and Residual Stresses

AEROSOL DEPOSITION RESEARCH

Aerosol Deposition (AD)

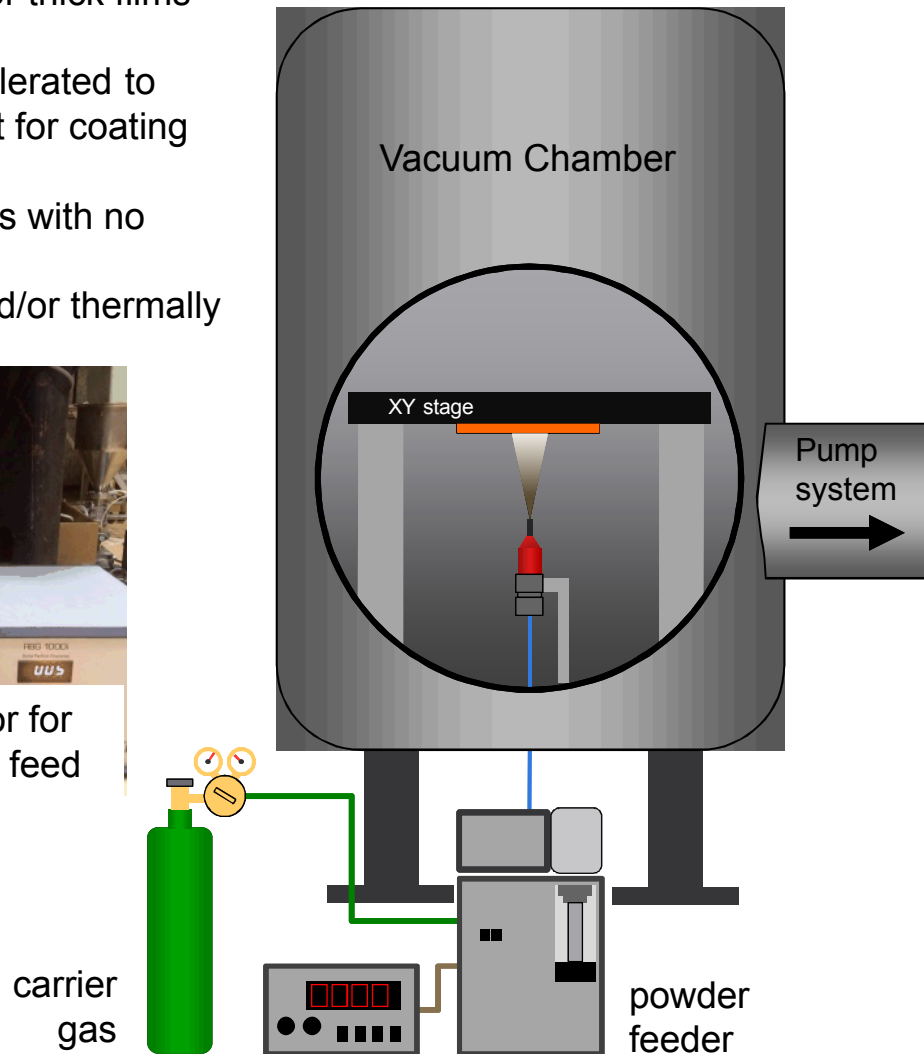
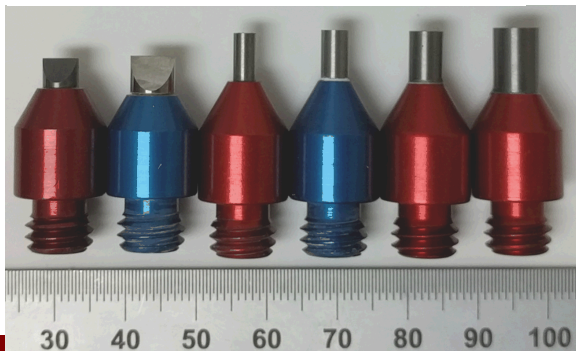
- Room temperature, solid state deposition process for thick films ($>1\mu\text{m}$)
- Relies on aerosolized fine powder (sub-micron) accelerated to high speeds ($>300\text{m/s}$) within a vacuum environment for coating consolidation
- Capable of depositing ceramics, carbides, and metals with no feedstock melting or substrate heating
- Enabling integrations of high melting temperature and/or thermally sensitive materials



Nozzles for achieving supersonic particle flow

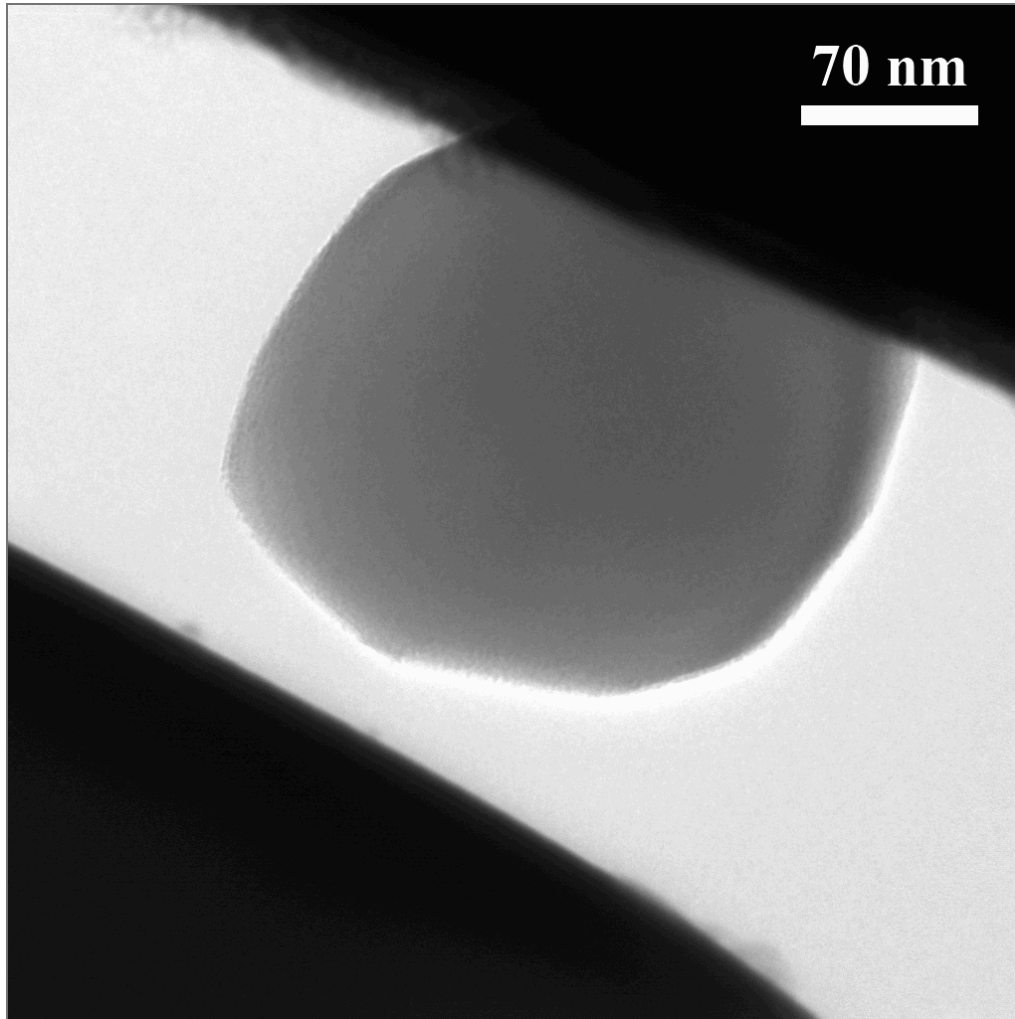


Aerosol Generator for controlled powder feed



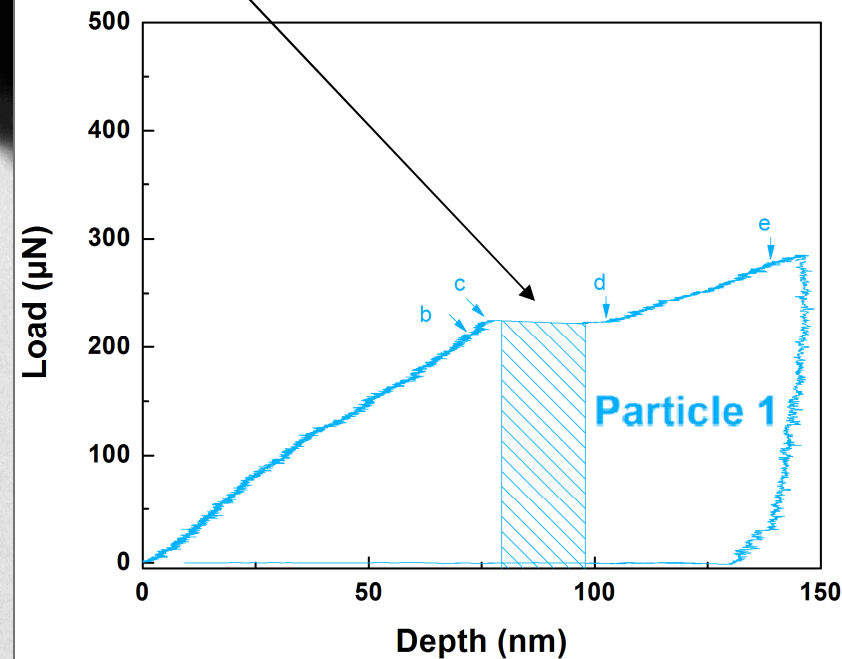
In Situ TEM Compression Results

Diameter $\sim 0.24 \mu\text{m}$, Open loop, Strain rate $\sim 0.009 \text{ s}^{-1}$



Observed dislocation nucleation & movement. Dislocation plasticity preceded fracture.

Large displacement gain at a constant load ("burst") corresponds to particle fracture.



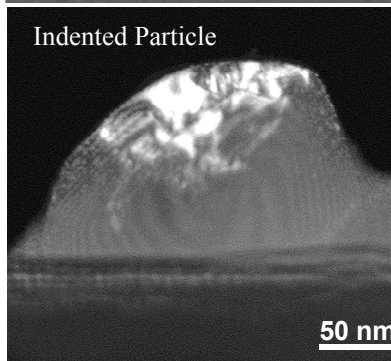
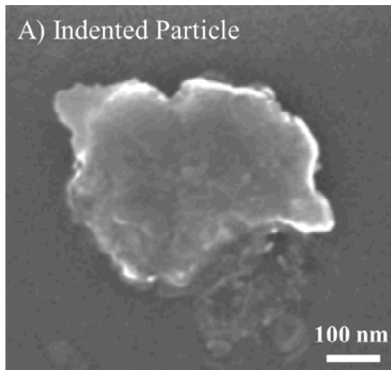
Mechanisms Underlying AD



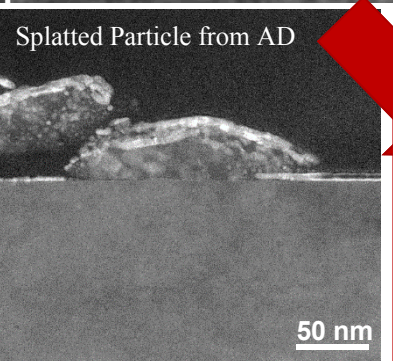
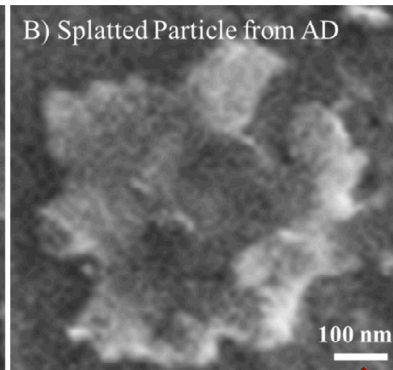
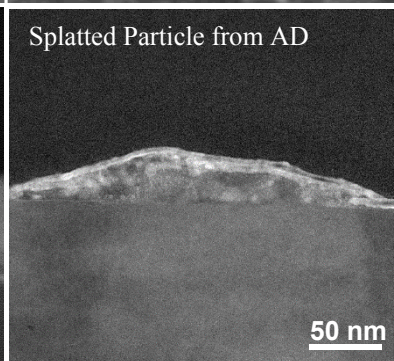
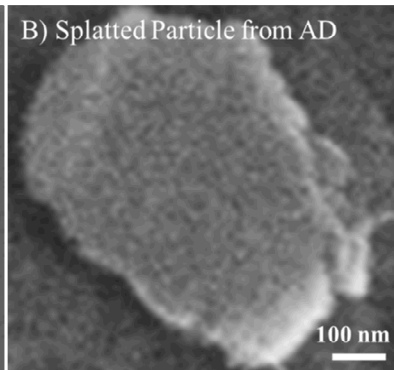
Sandia
National
Laboratories



INDENTATION



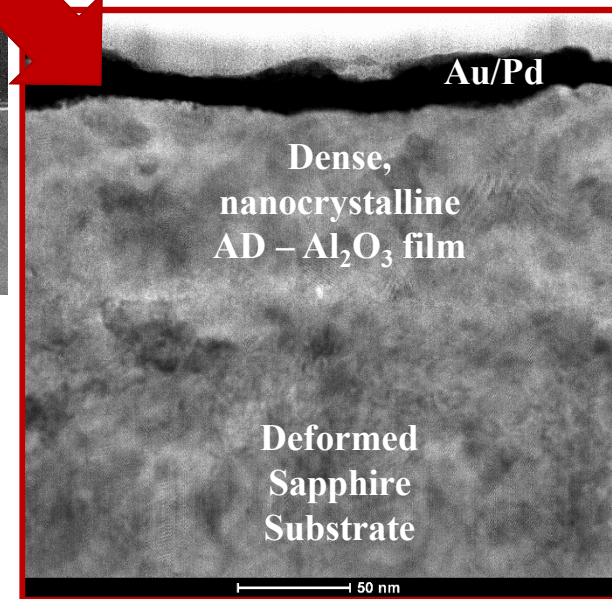
SINGLE-PARTICLES DEPOSITION



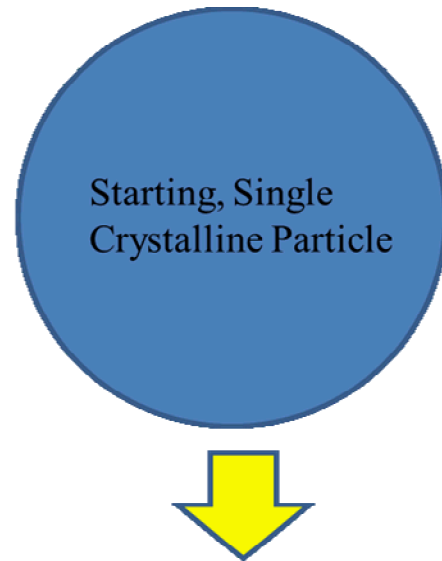
- Kinetic energy → Absorbed strain energy
- Dislocation plasticity
- Fracture without fragmentation
- Tamping from subsequent impacting particles → building up dense coating

In both quasi-static and high strain-rate loadings, $0.3 \mu\text{m}$ Al_2O_3 feedstock particles underwent plastic deformation. Characteristics include:

- dislocation nucleation and slip
- shape change
- fracture into nanocrystals (15-30 nm)
- polycrystalline with mosaicity



RT Deformation & Bonding Mechanisms

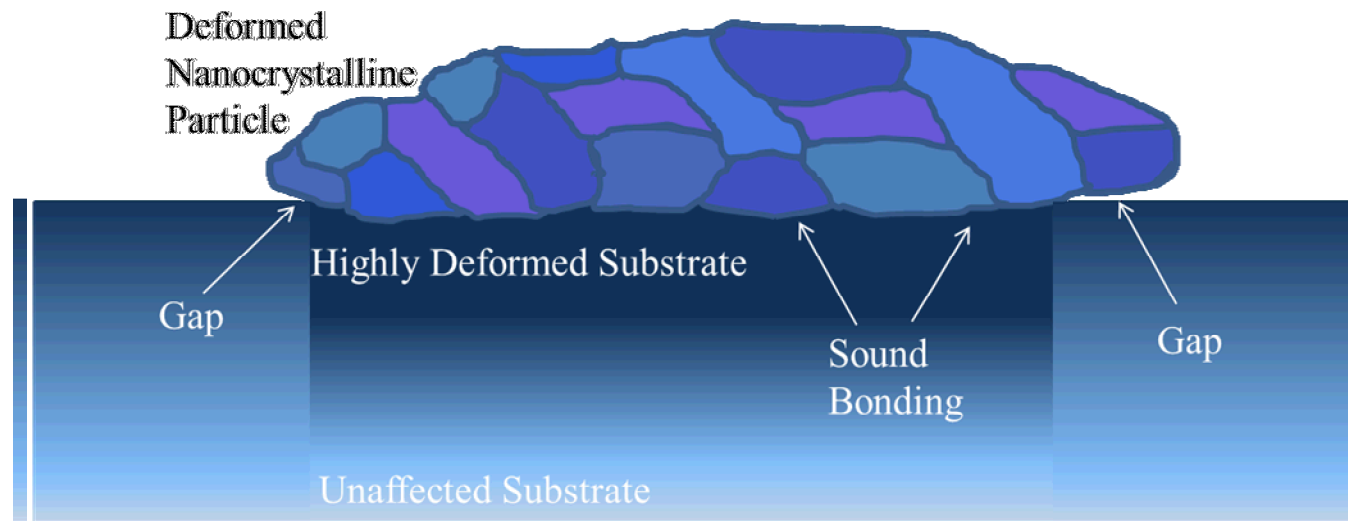


Unaffected Substrate

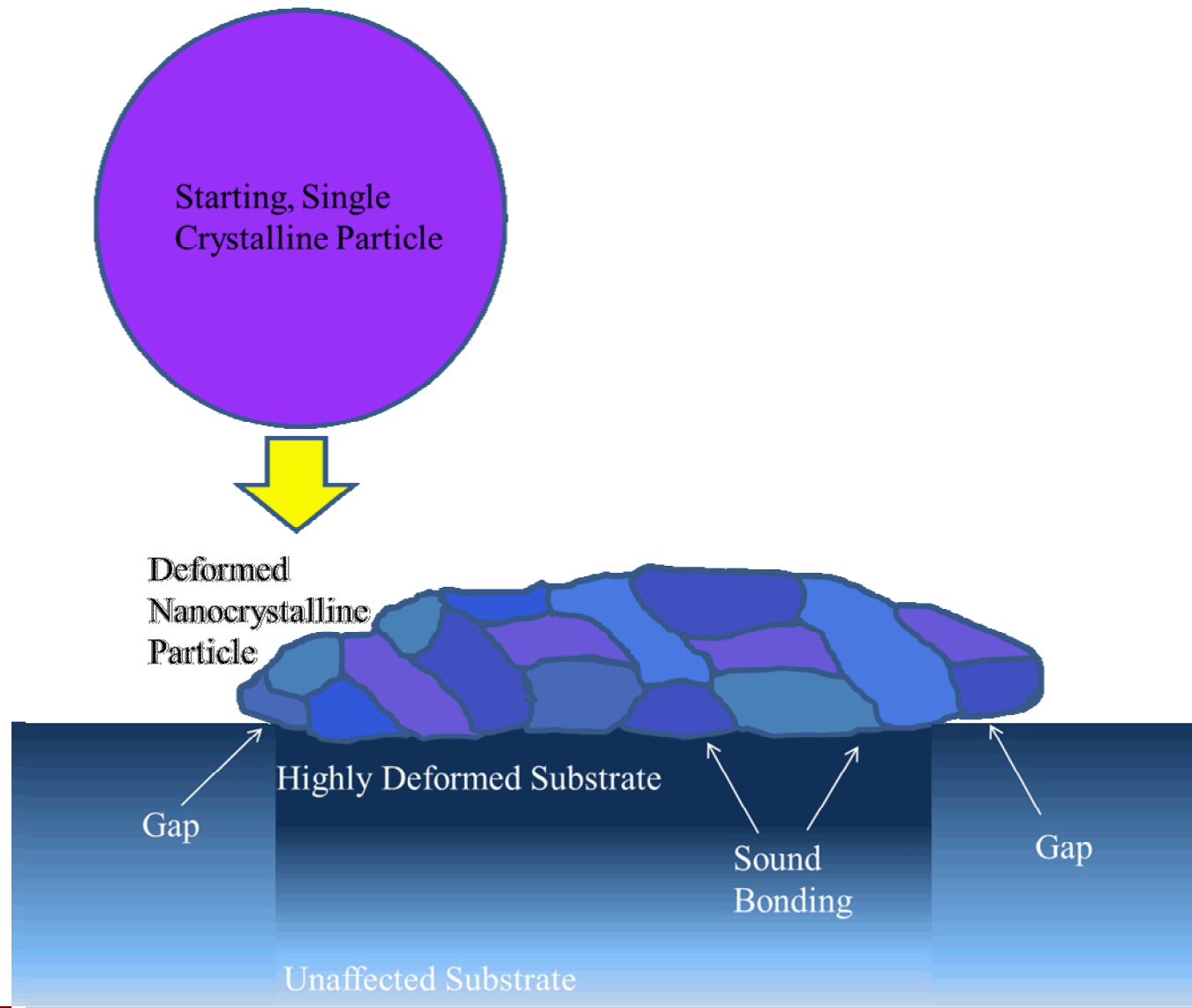
RT Deformation & Bonding Mechanisms Sandia National Laboratories

Kinetic Energy converted to absorbed strain energy, providing

- Dislocation plasticity to deform particle
- Fracture - nanocrystalline formation in particle
- Chemi-mechanical bond between alumina particle-sapphire substrate



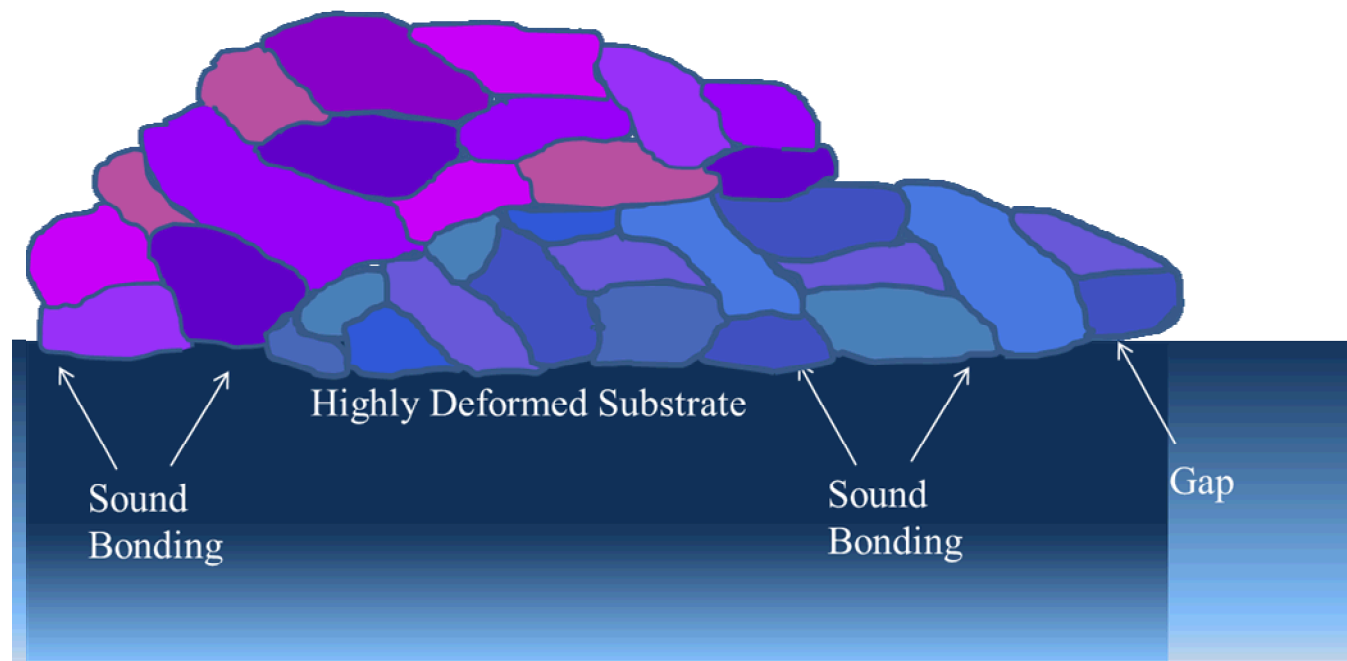
RT Deformation & Bonding Mechanisms



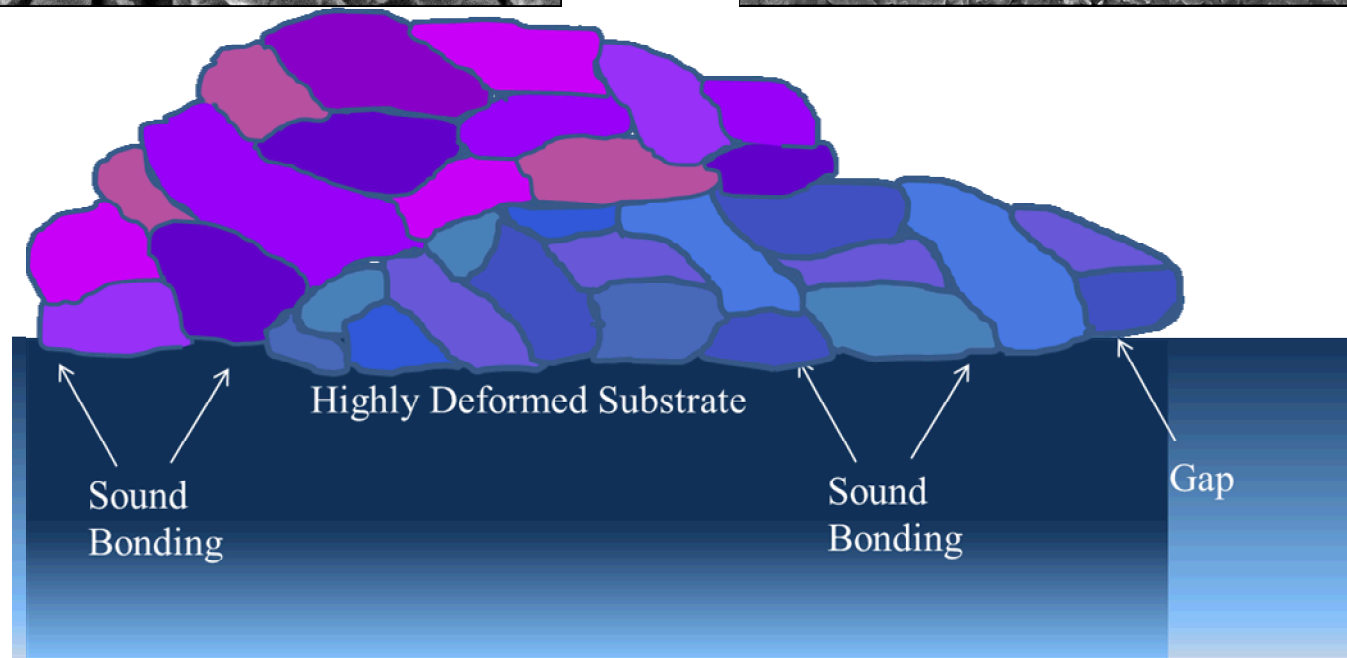
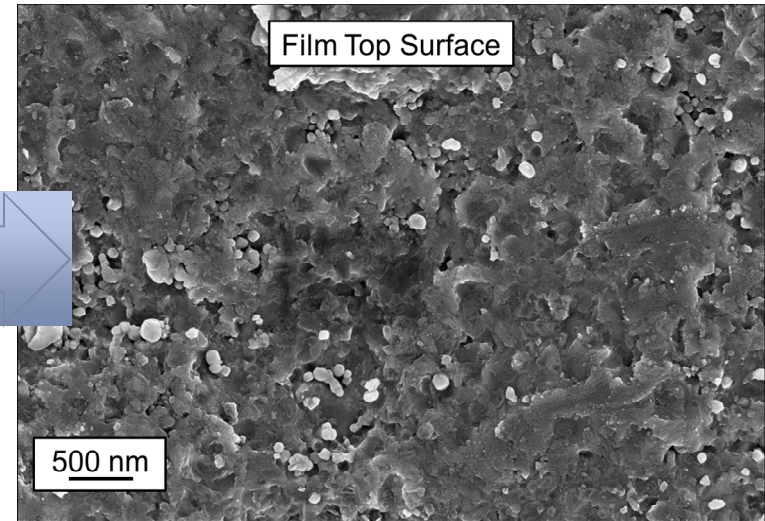
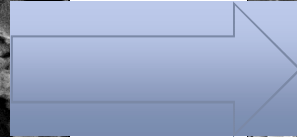
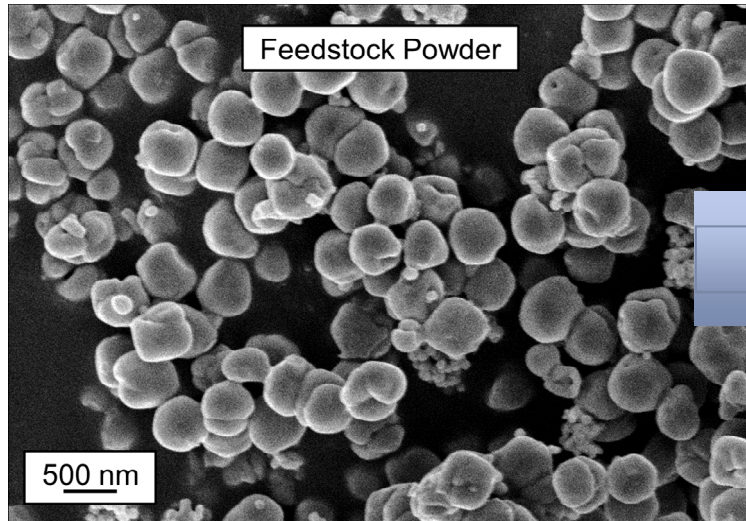
RT Deformation & Bonding Mechanisms Sandia National Laboratories

Subsequent impacting particle imparts sufficient energy to

- Further deform splatted particle
- Provide further bond formation between splatted particle-substrate from “tamping effect”
- Compaction and densification of deposited coating from “tamping effect”



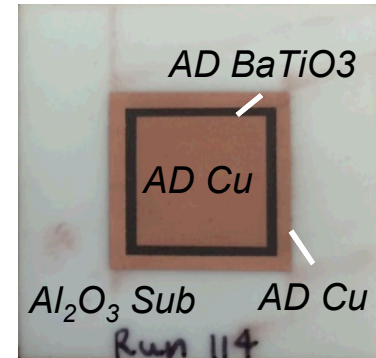
RT Deformation & Bonding Mechanisms



Residual Stress in AD films

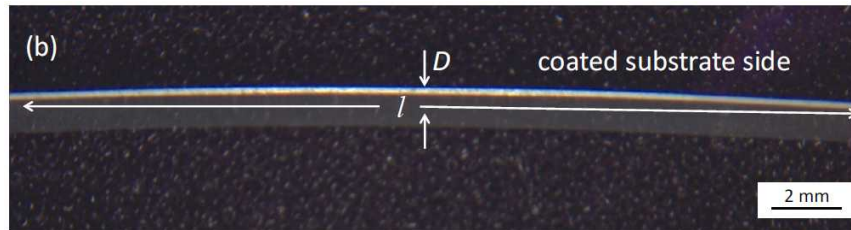
- Motivation for study

- Multi-layer integration, device building utilizing AD films
- Understand process parameter influence on stress, coating formation dynamics, and resultant properties
- Additional method for accessing repeatability of process

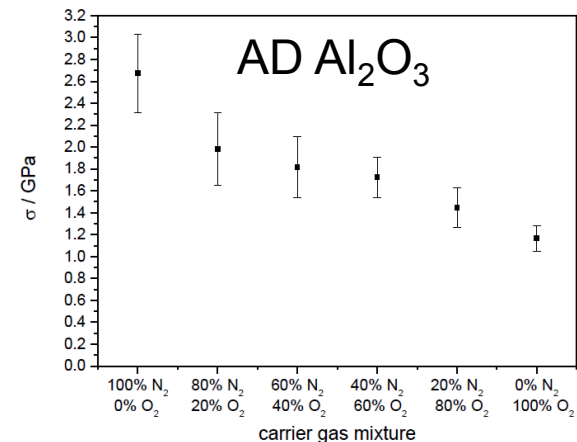


- Common measurement techniques for thin/thick films

- X-Ray diffraction (Ψ^2 method)
- Neutron diffraction
- Substrate Curvature – Stoney Formula

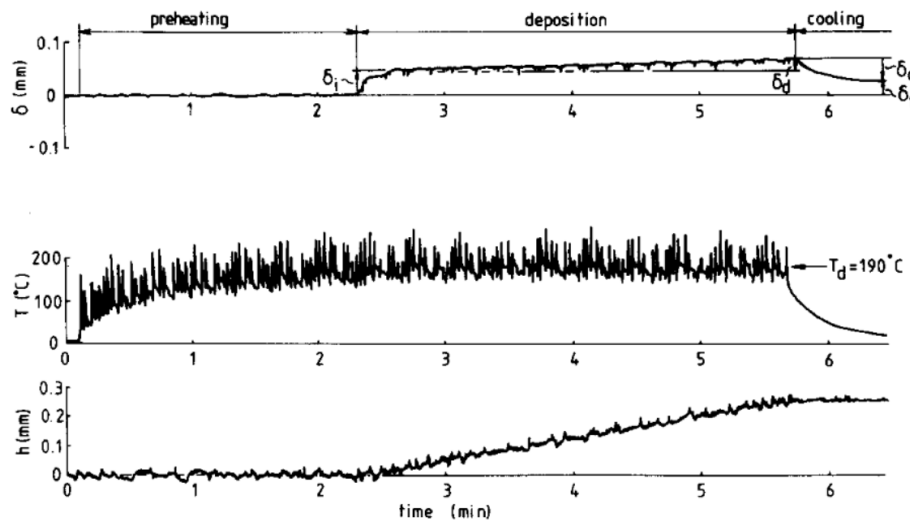


Schubert, Michael, Jörg Exner, and Ralf Moos. "Influence of carrier gas composition on the stress of Al₂O₃ coatings prepared by the aerosol deposition method." *Materials* 7.8 (2014): 5633-5642.

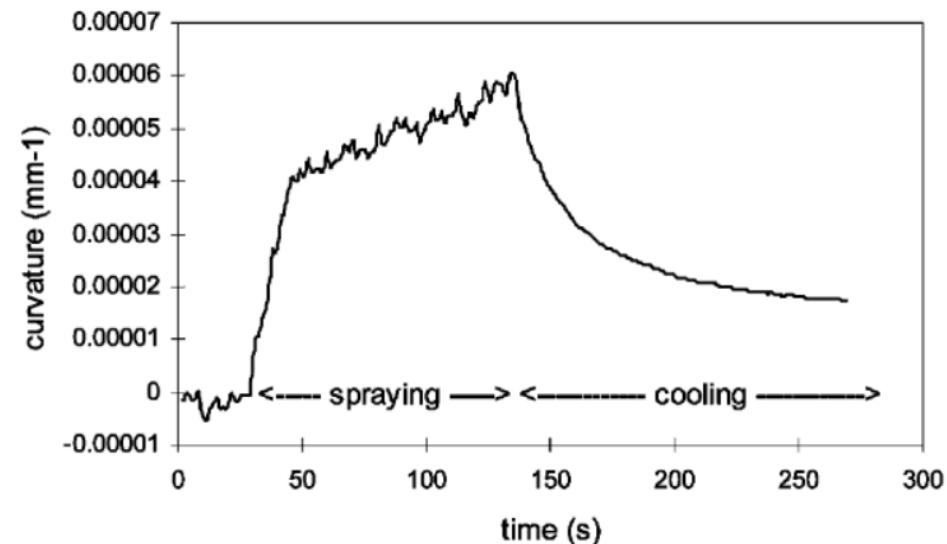


In-situ Curvature Measurements in Thermal Spray

- Allows observation of coating dynamics in real time
- Discrete measurements of stress during deposition and cooling
- Available as commercial tool



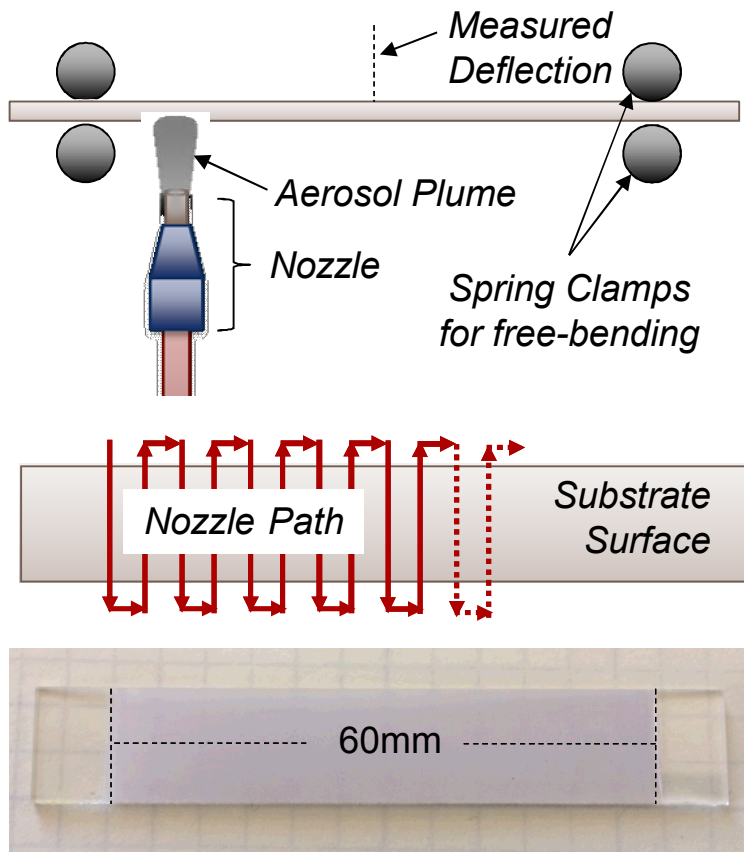
Kuroda, S., T. Fukushima, and S. Kitahara. "Simultaneous measurement of coating thickness and deposition stress during thermal spraying." *Thin solid films* 164 (1988): 157-163.



Matejicek, J., et al. "In situ measurement of residual stresses and elastic moduli in thermal sprayed coatings: Part 2: processing effects on properties of Mo coatings." *Acta Materialia* 51.3 (2003): 873-885.

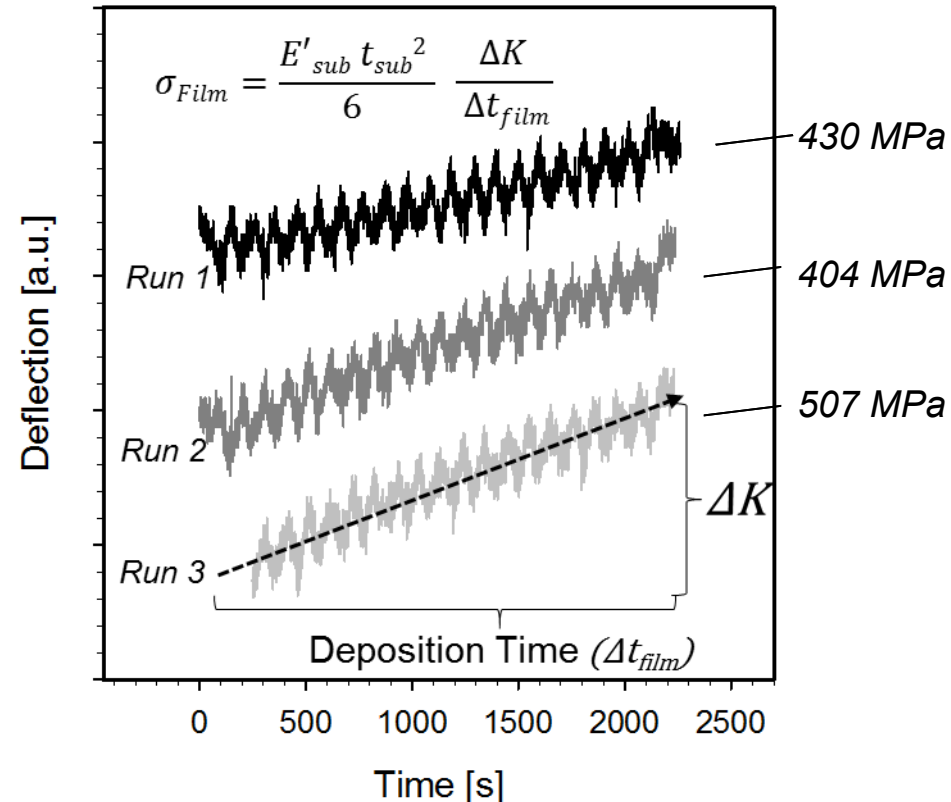
In-situ deflection monitoring of AD films

Experiment Schematic



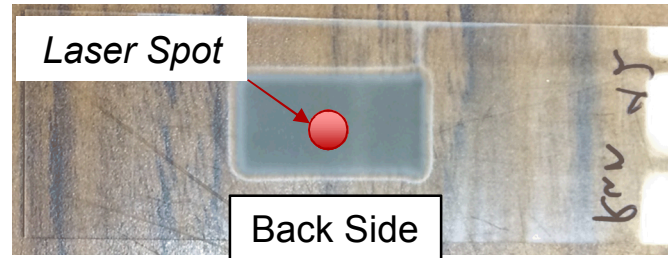
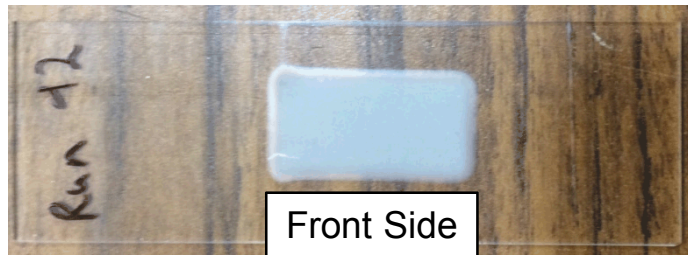
3-4 μm BaTiO_3 deposited onto soda lime glass

Collected Data

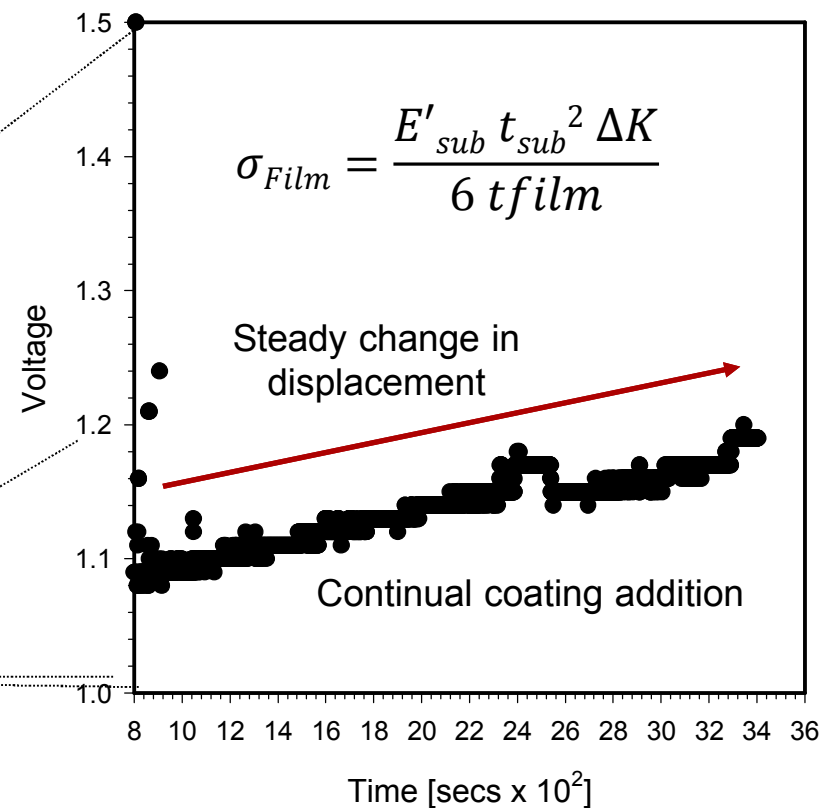
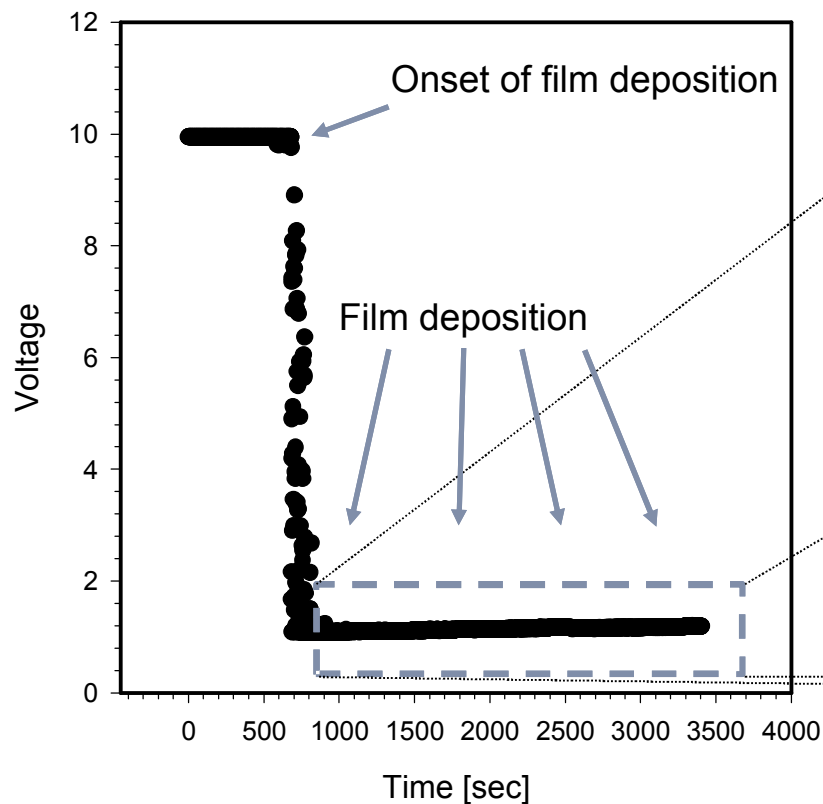


- Linear substrate curvature is observed with AD film deposition
- No thermally induced substrate curvature after deposition

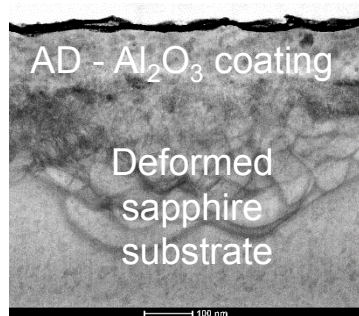
Preliminary Experimental Results – Deposition



BaTiO₃ on 25 x
75mm Glass Slide

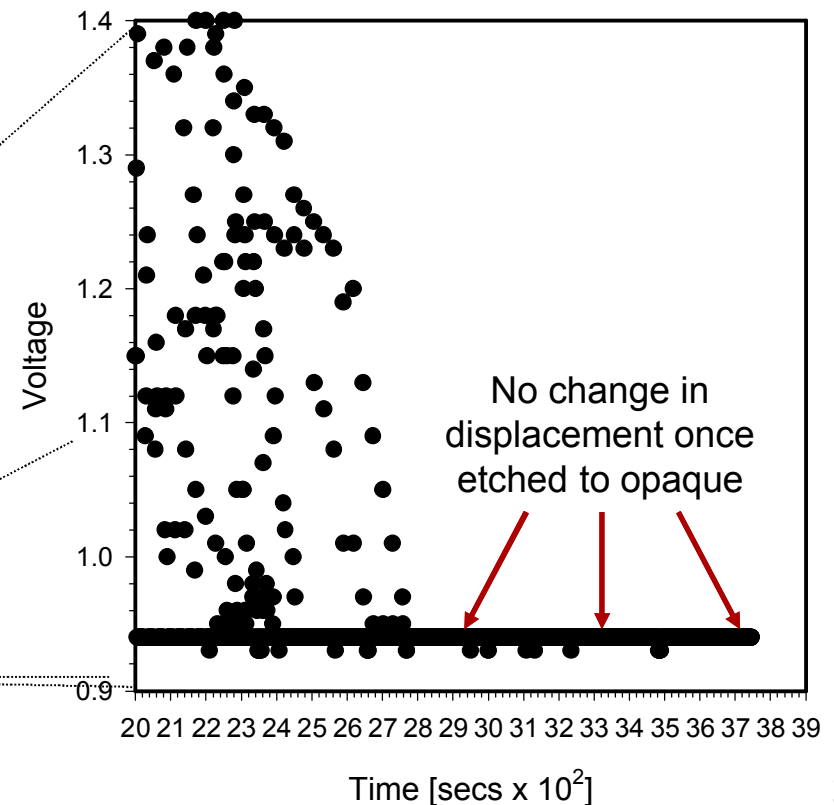
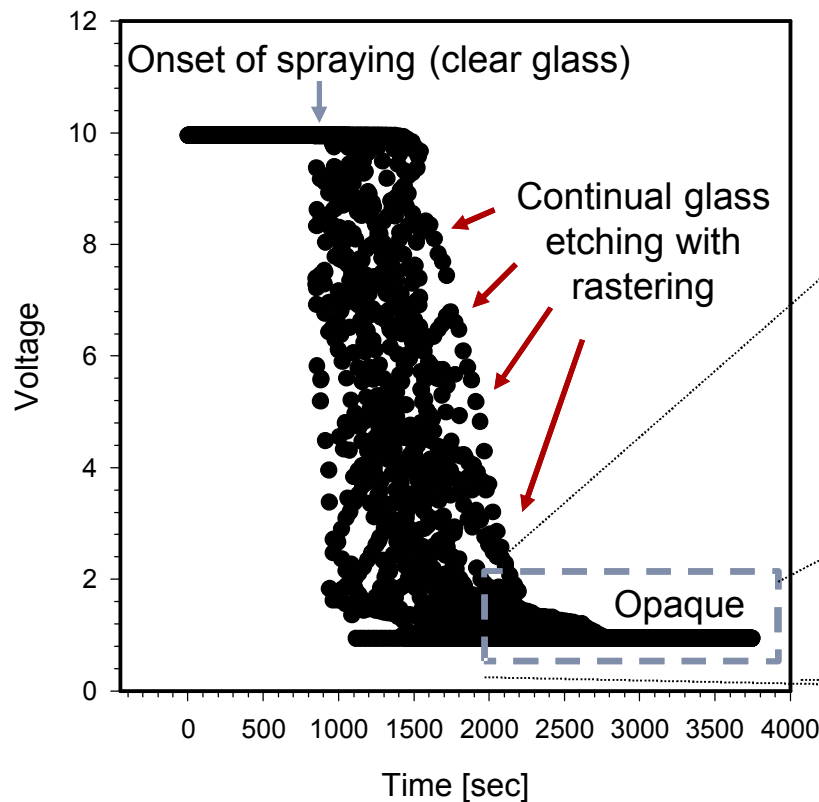


Preliminary Experimental Results – Etching



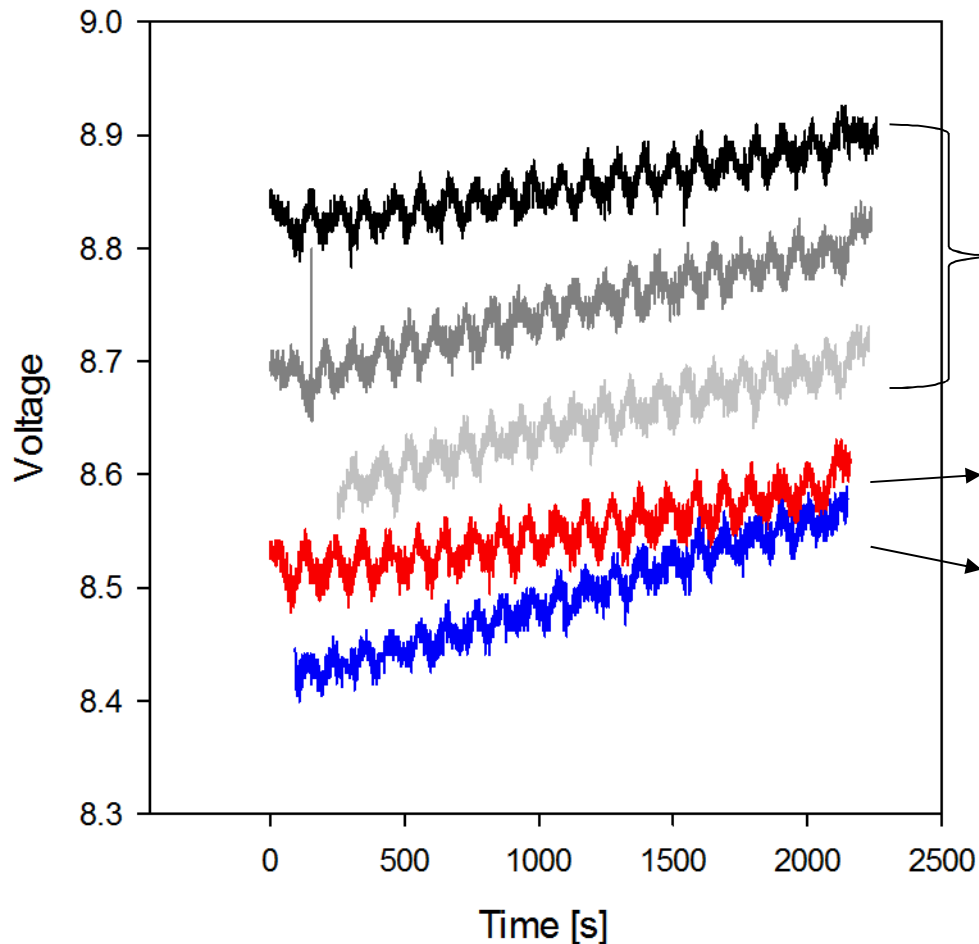
Al_2O_3 on Glass

- Highly damaging to substrate – Etches glass
- Self limiting film growth – Requires process modification for deposition



Substrate Deflection Measurements of AD Deposition

BaTiO₃ on Glass



6 psig Nozzle
Pressure (Repeats)

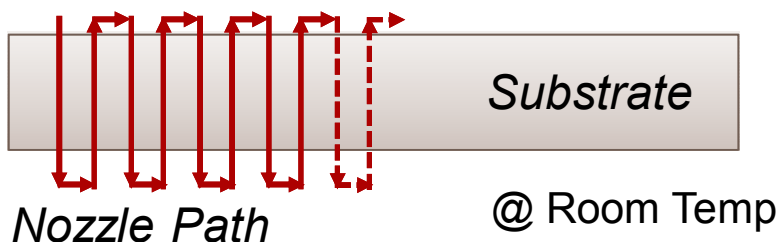
10.5 psig Nozzle Pressure

1 psig Nozzle Pressure

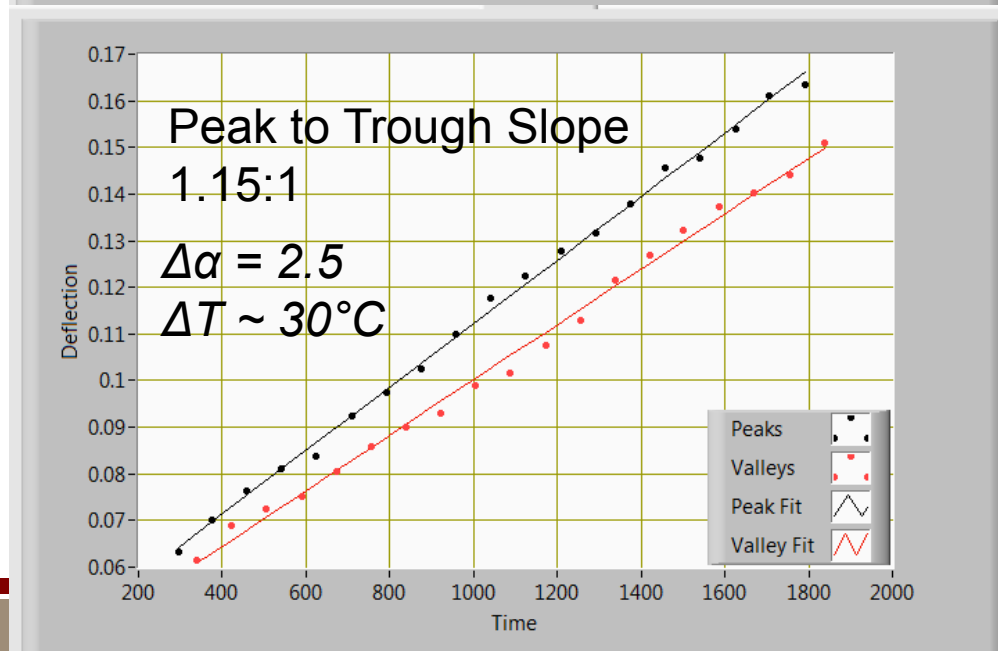
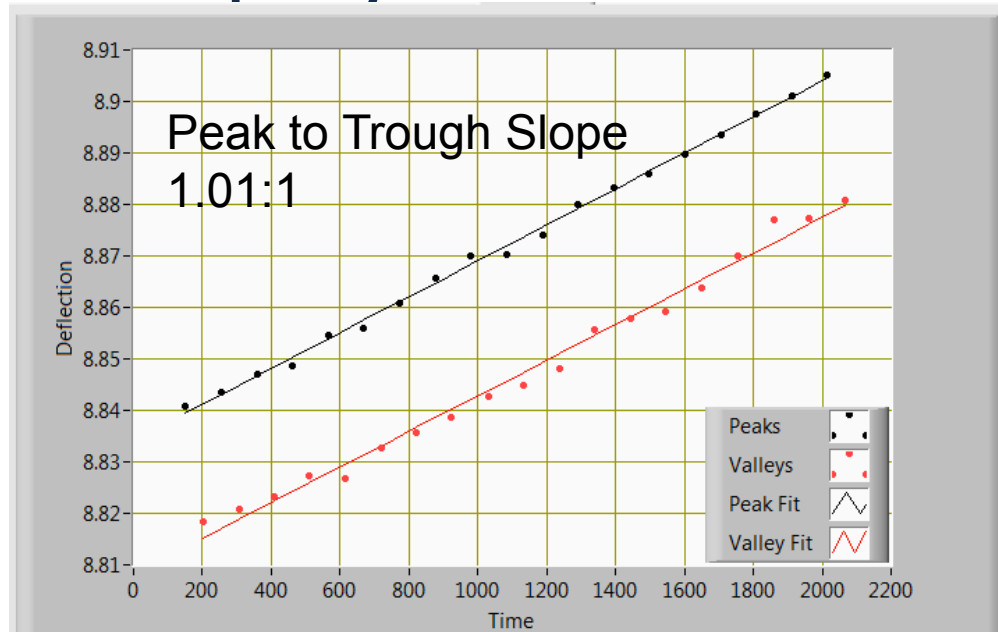
- 1 Torr Chamber pressure
- ~3-4 μm Coating thickness
- Glass Slide Substrates (60mm x 12.5mm)

Comparison to Thermal Spray

- AD has linear deflection accumulation with film growth
- Peak and Trough of deflection data correspond to raster pattern

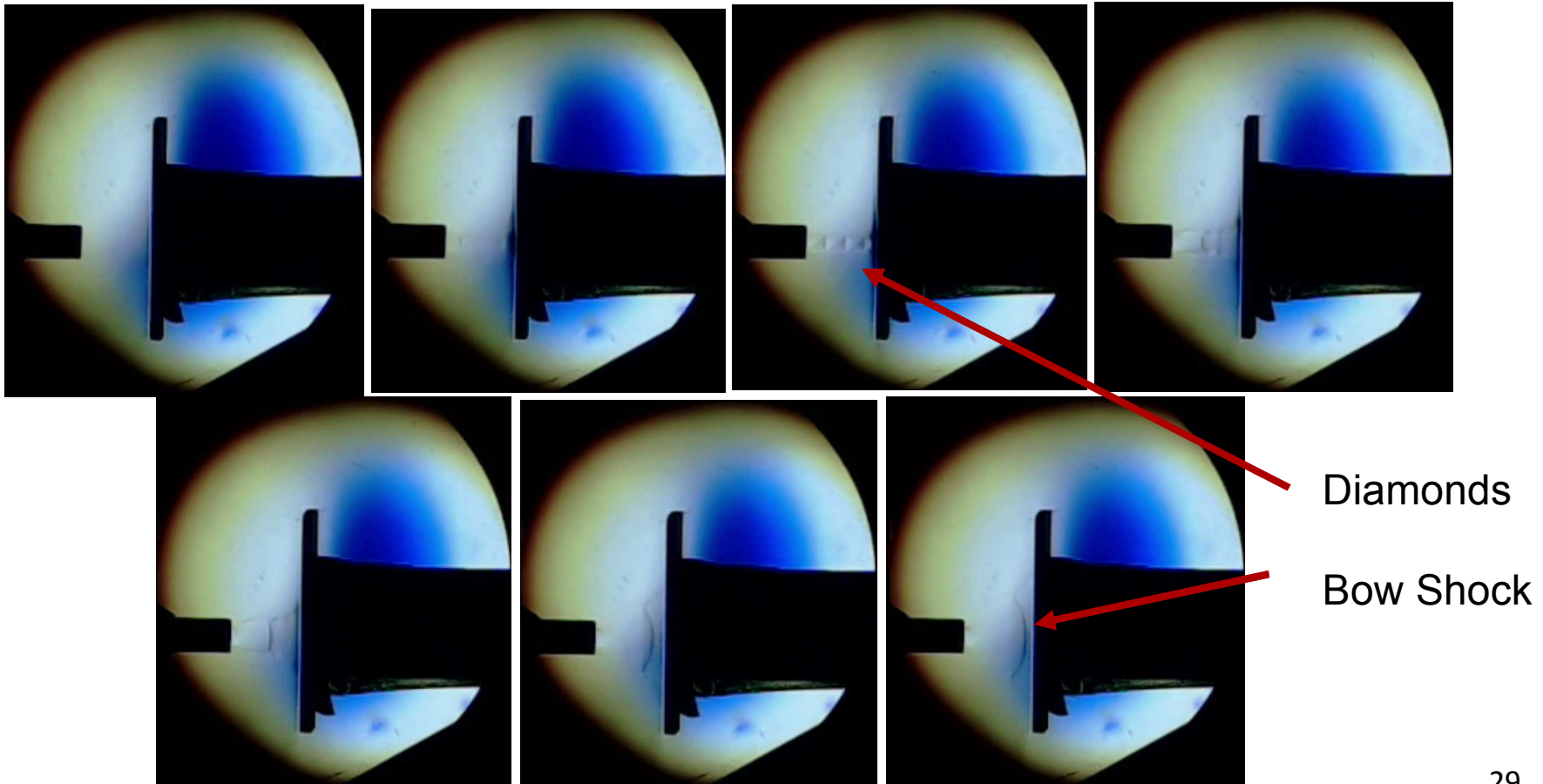


- TS has linear deflection accumulation with film growth
- Peak and Trough of deflection data diverge with film growth due to CTE mismatch and temperature undulations with each layer addition



Schlieren Imaging of AD

We are using Schlieren imaging to better understand the dynamics of AD to improve process control. Note Shock Diamonds and Bow Shock visible as pressure is varied from vacuum to 15 psig



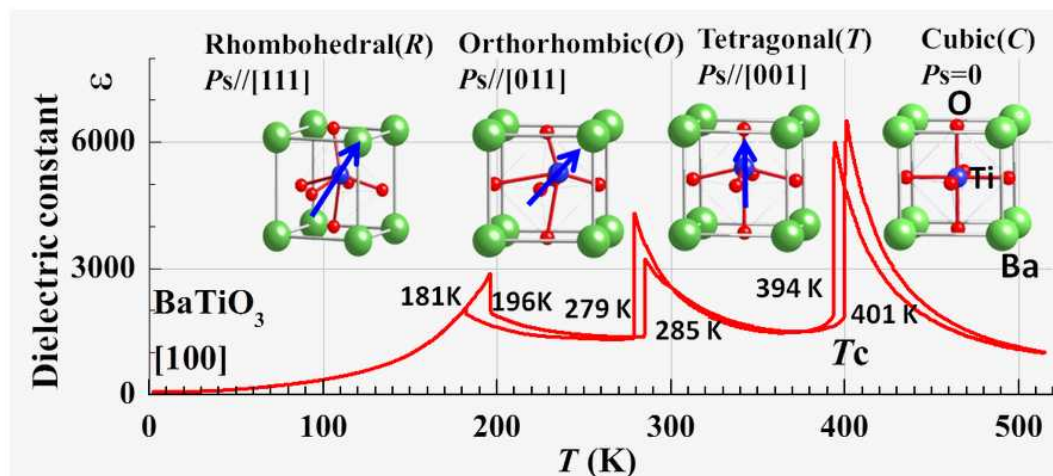
BaTiO₃ Aerosol Deposited Film

Why BaTiO₃?

- Ferroelectric with high dielectric constant (up to 7,000) with spontaneous polarization
- Well studied and used material

Why AD?

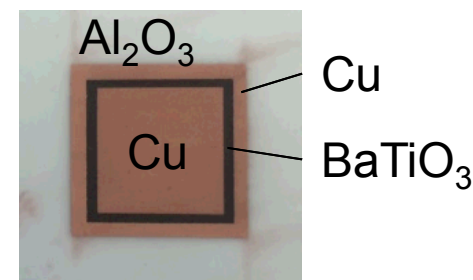
- No feedstock heating -> *Preservation of material stoichiometry and phase*
- Room temperature process -> *Integration with low melting temperature materials*



Desheng Fu and Mitsuru Itoh DOI: 10.5772/61017

BaTiO₃ case study:

- Phase and grain size from deposition and heat treatment
- Residual stress by XRD and substrate curvature
- Electrical properties

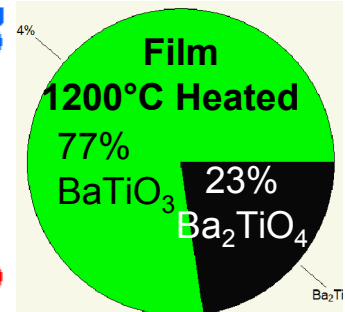
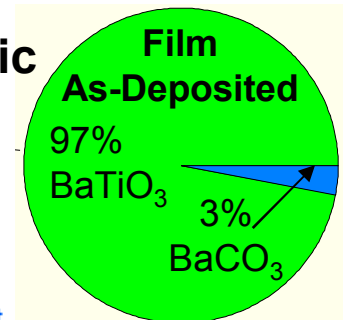
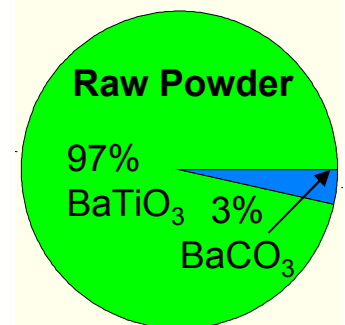
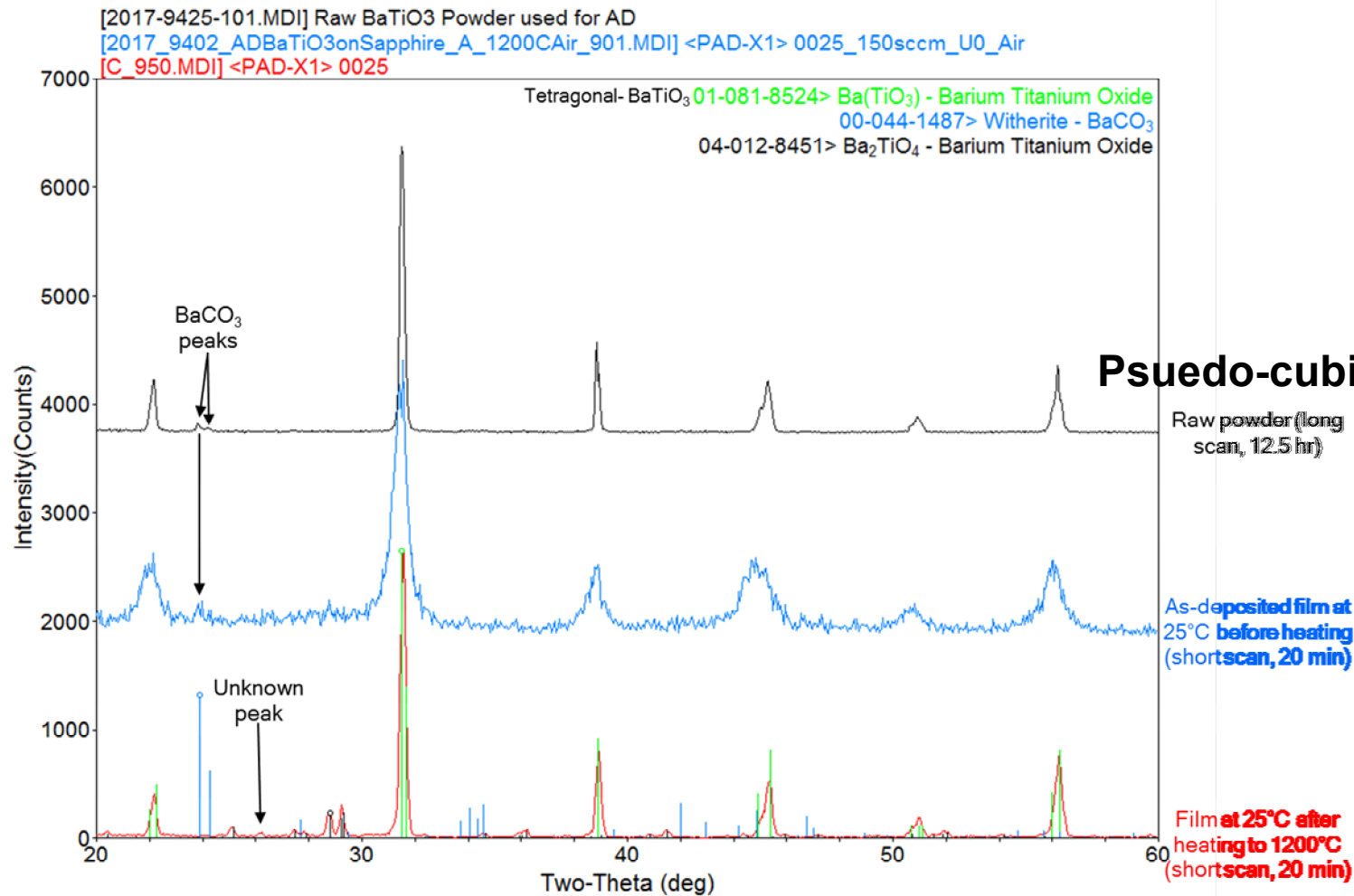


AD built Cu and BaTiO₃ capacitor

XRD results – Composition & Phase

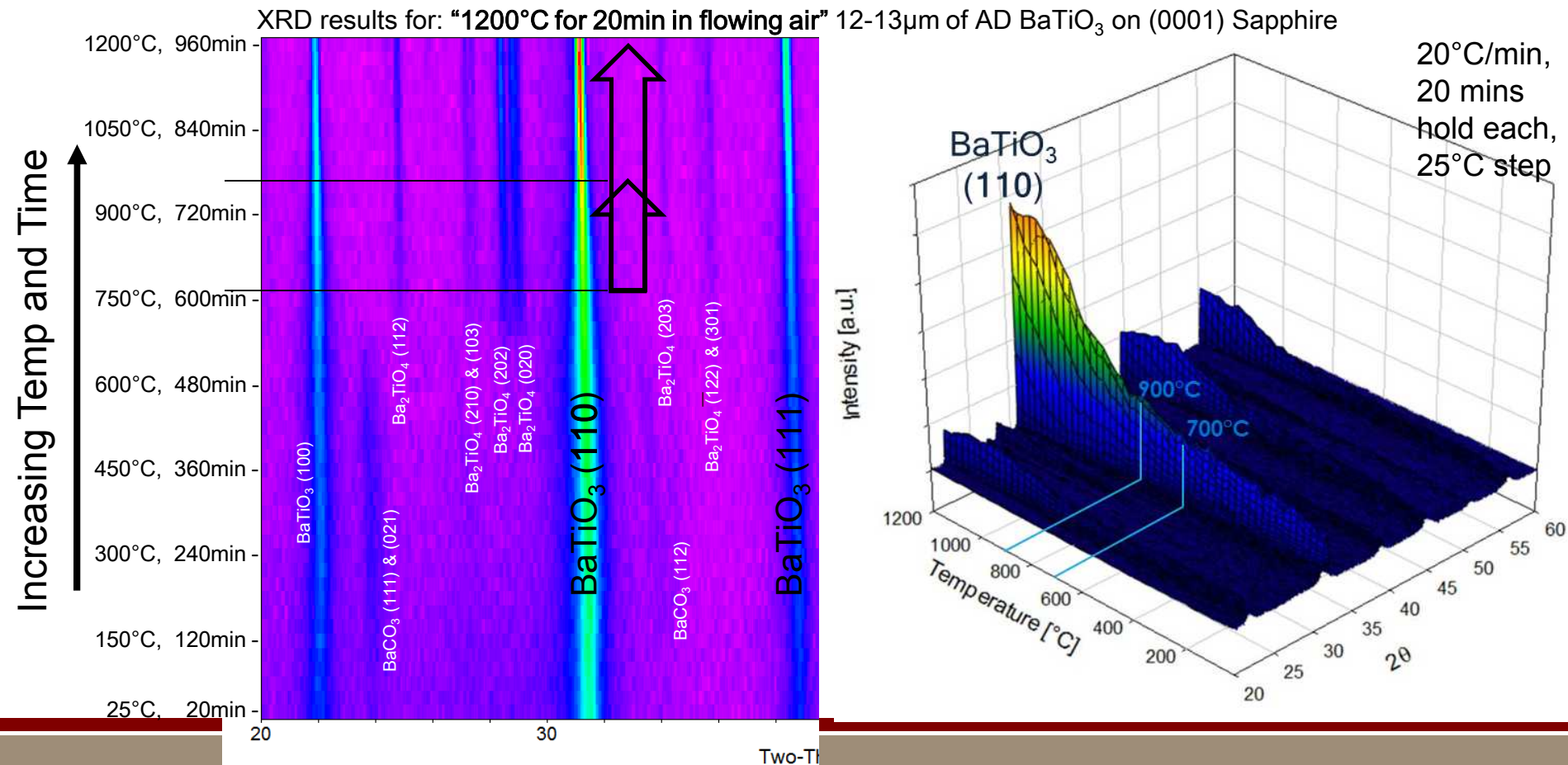
Commercially available “BaTiO₃” 0.4μm powder

wt% based on relative intensity



XRD Measurement – Grain growth

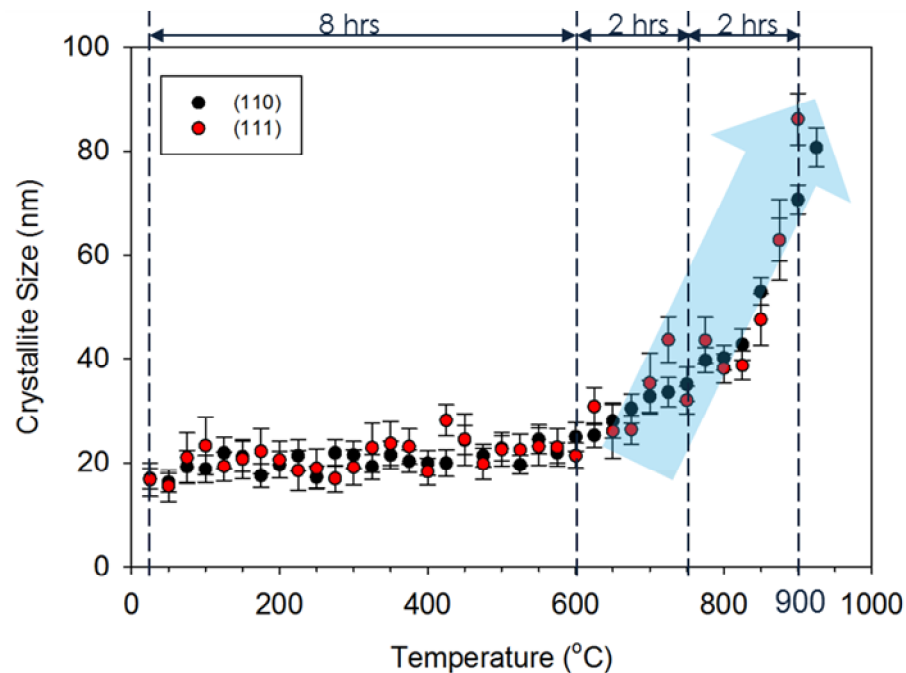
- $>700^{\circ}\text{C}$, BaCO_3 decomposes & Ba_2TiO_4 forms
- Band narrowing & increased intensity – Grain growth
- $>900^{\circ}\text{C}$, see significant grain growth



XRD Measurement – Grain growth

INCREASING TEMPERATURES

- Crystallite size from (110) & (111) peaks
- 15-20 nm as-deposited vs. 80-90 nm 900°C
- Significant grain growth occurred >600°C
- After 1,000°C, > 100 nm detection limit



ISOTHERMAL HOLD

- Very little grain growth, even when held at 900°C for 16 hrs

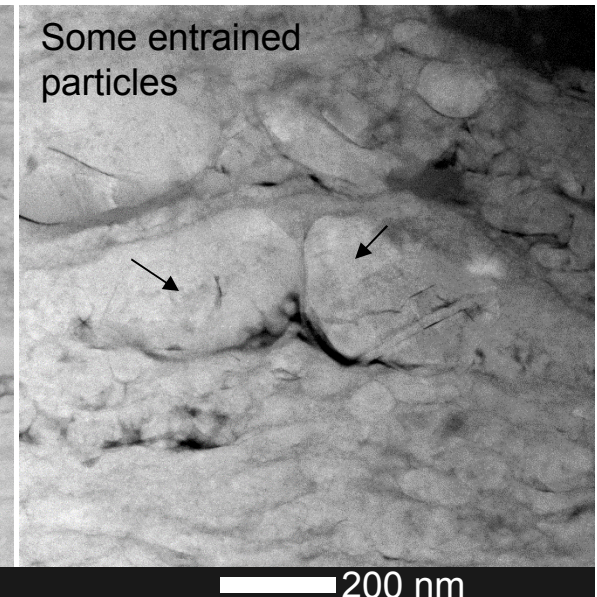
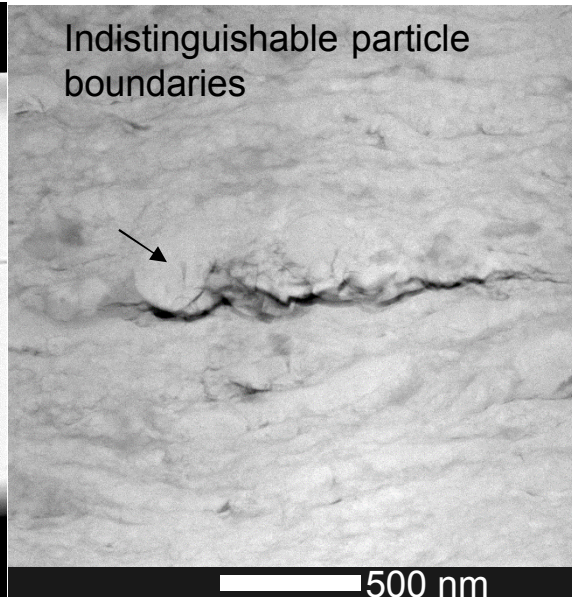
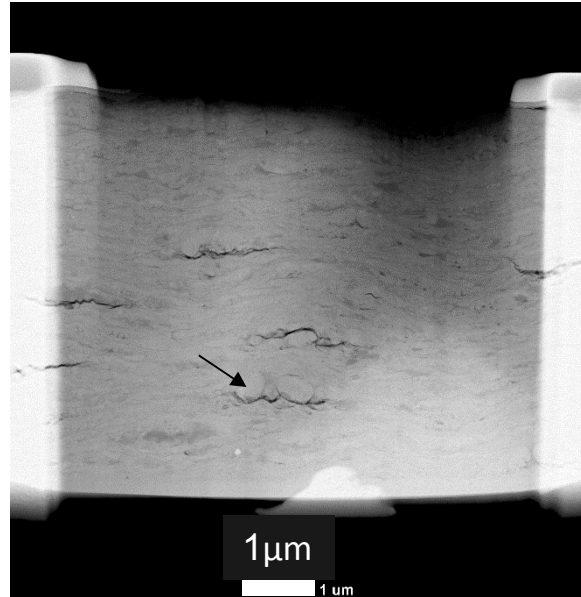
Starting Grain Size (nm)	Annealing Temperature (°C)	Time (hrs)	At Temperature Grain Size (nm)
24	650	16	31
33	700	2	35
41	800	16	55
64	900	16	90

Isothermal hold at 900°C did not result in significant grain growth. Ramping temperatures appears to be more effective, providing higher growth rate.

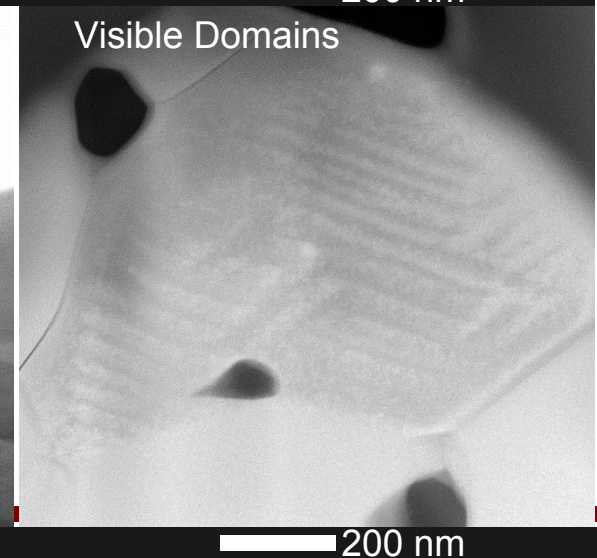
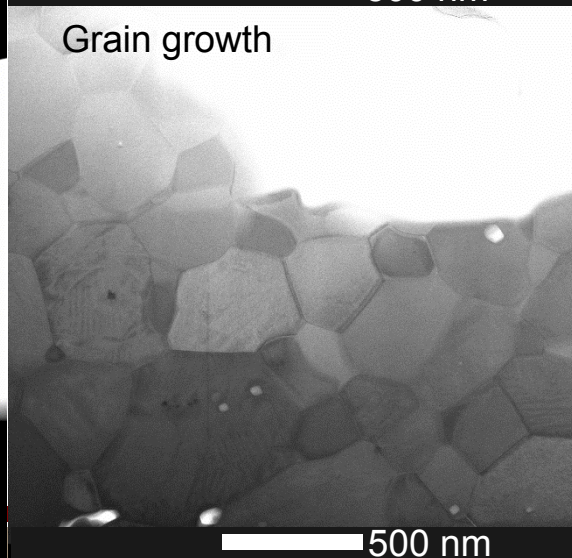
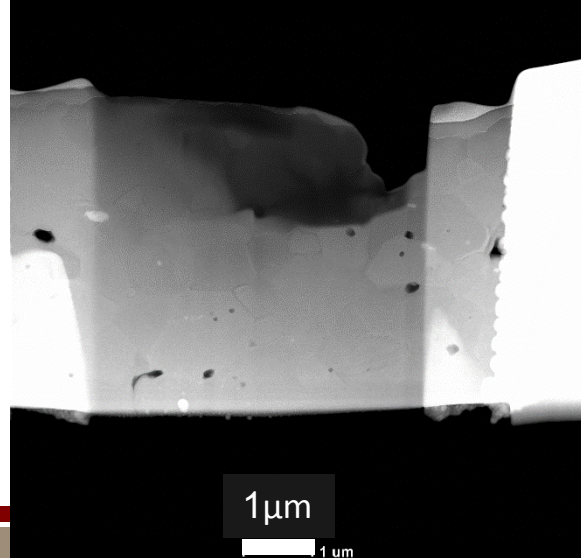
We recognized the high temperatures needed to grow the grains and are currently exploring other treatment methods to effectively integrate with Cu (T_m 1083°C).³

Film Microstructures - FIB / TEM

As-deposited

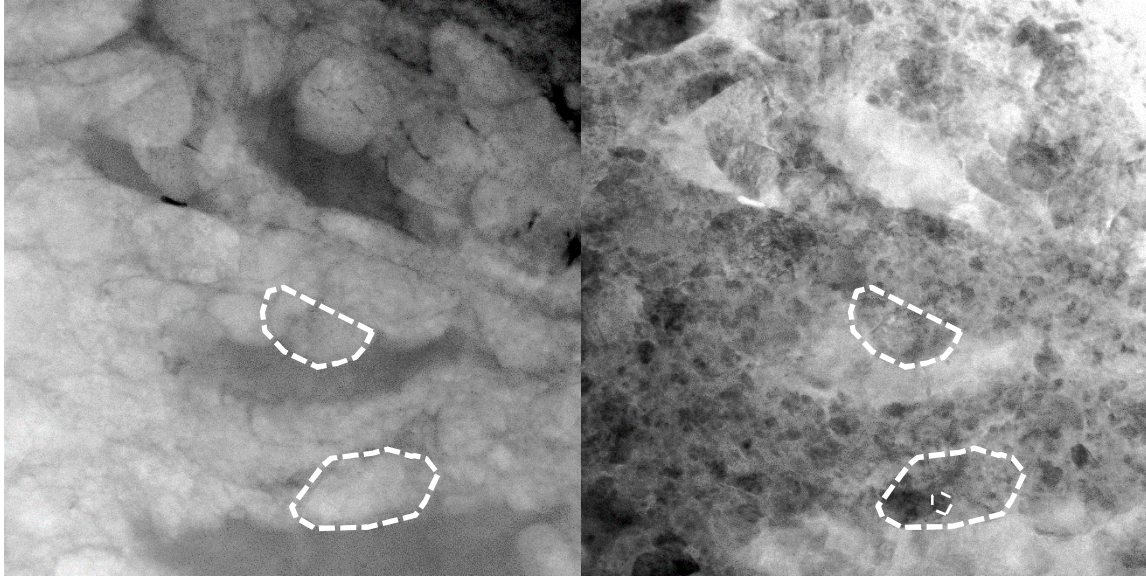


Heated 1200°C

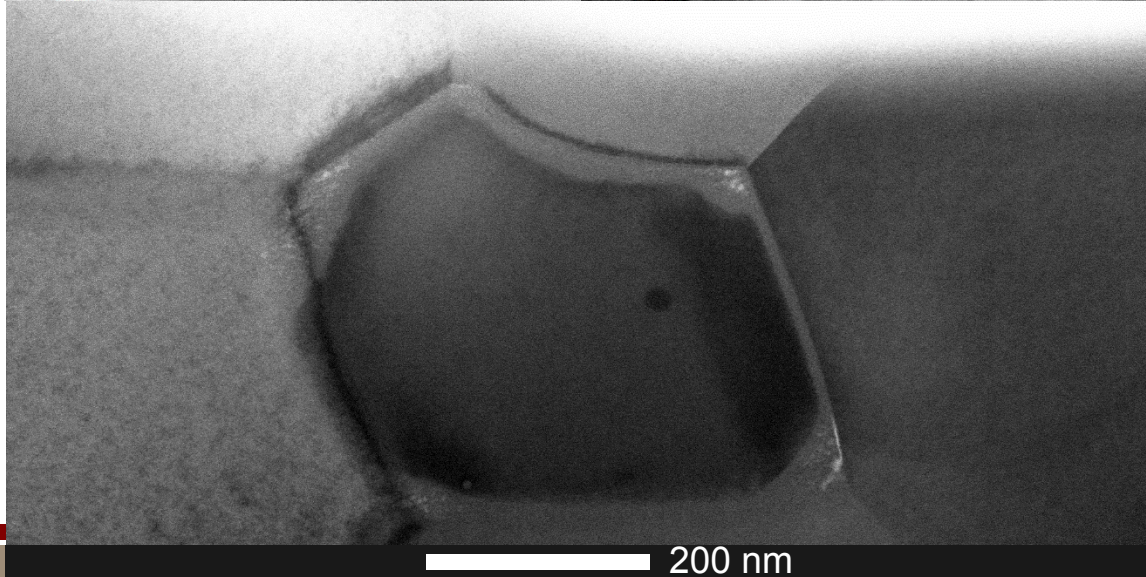


Film Microstructures - FIB / TEM

As-deposited



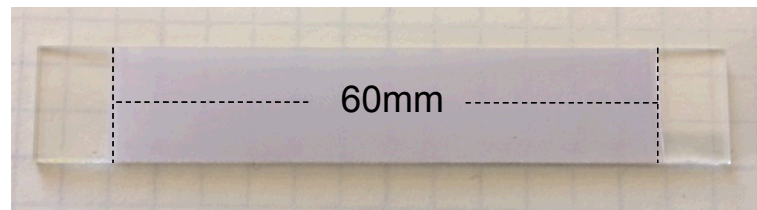
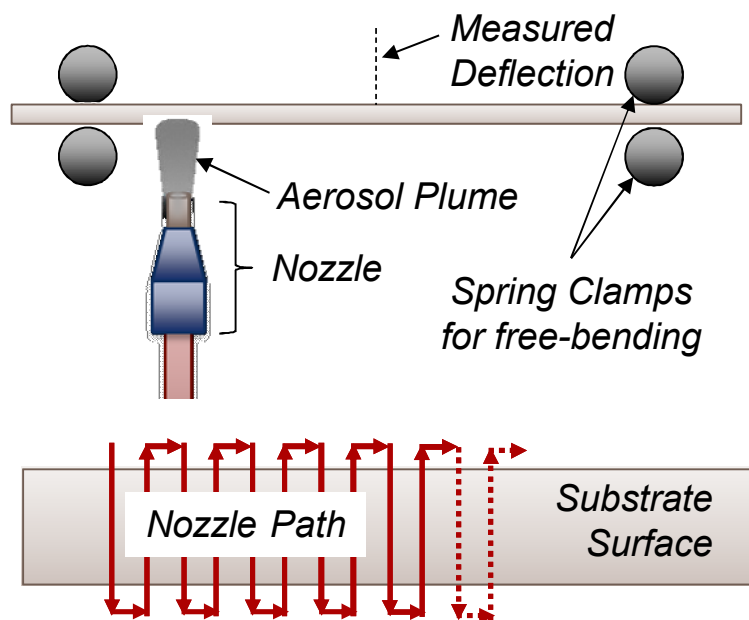
Heated 1200°C



- As-deposited films showed
 - undefined particle boundaries
 - polycrystalline with crystallite size <30 nm
 - some entrained particles (not significantly deformed)
 - cracks
- After 1200° C heating
 - Ba_2TiO_4 segregation to grain boundaries
 - Grain growth
 - pores

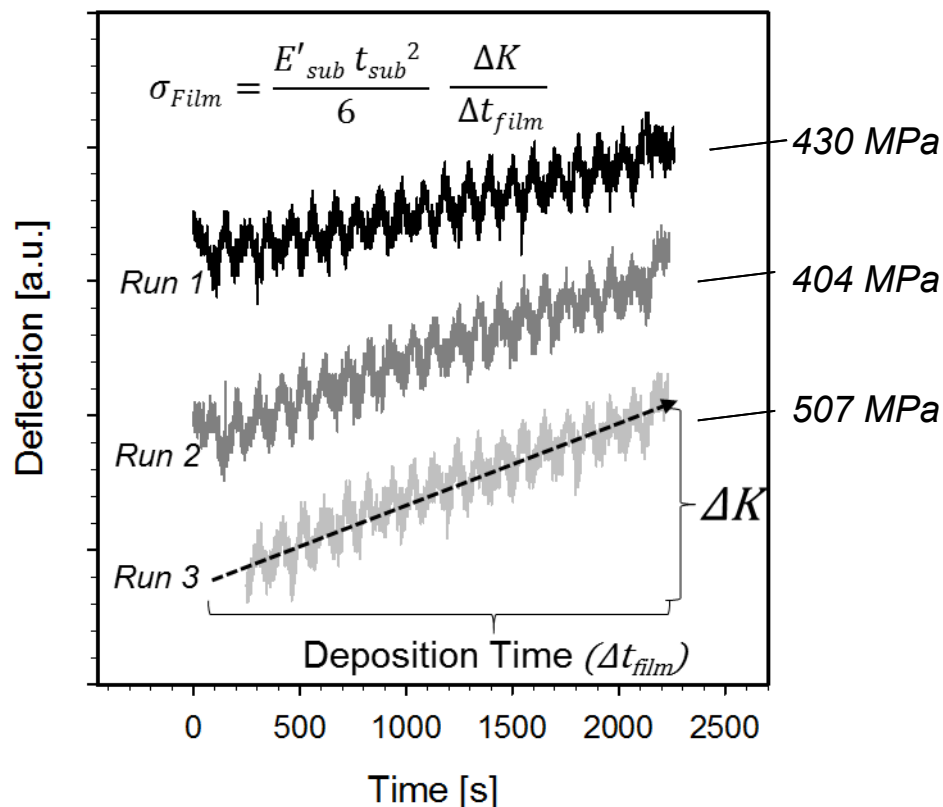
Residual Stress in BaTiO₃ on Glass

Experiment Schematic



3-4 μm BaTiO₃ deposited onto soda lime glass

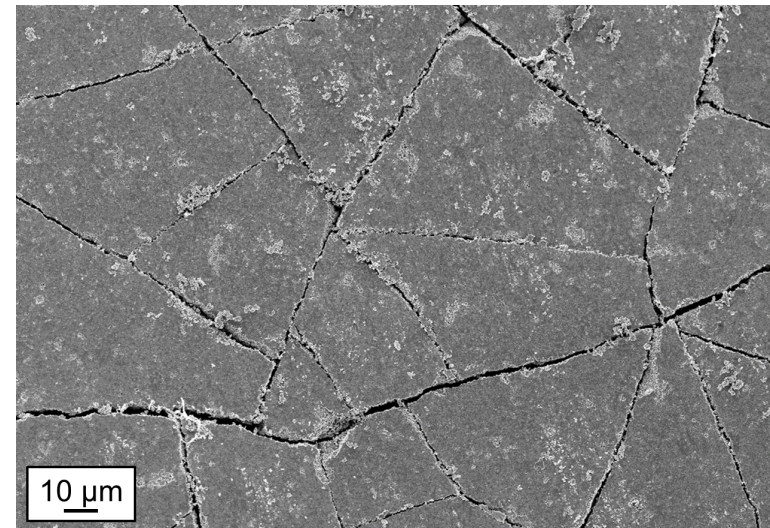
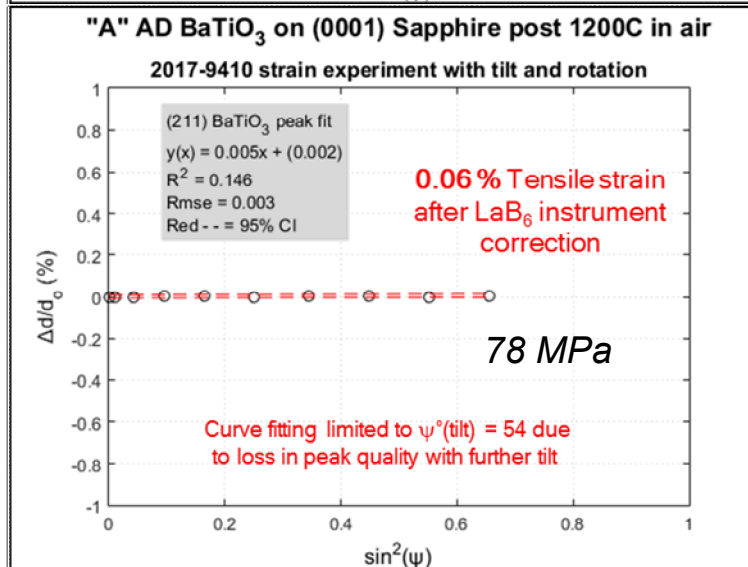
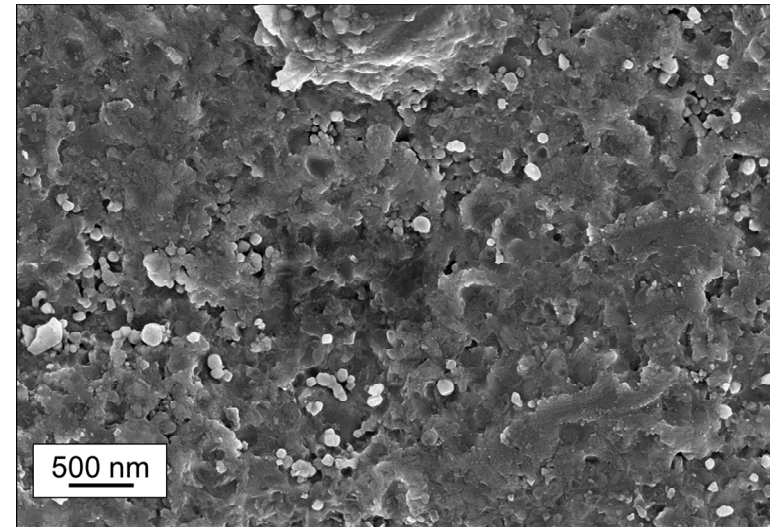
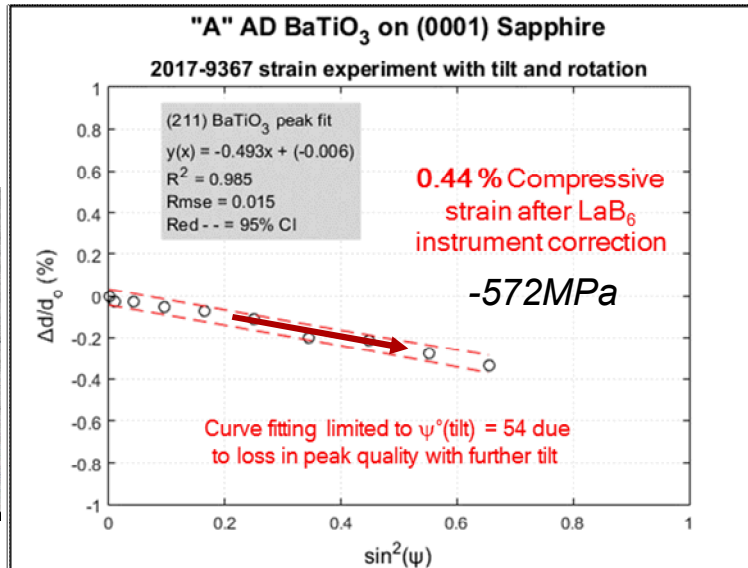
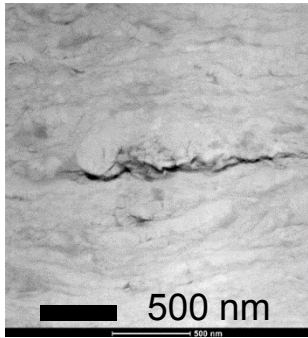
Collected Data



- Linear substrate curvature is observed with AD film deposition
- No thermally induced substrate curvature after deposition

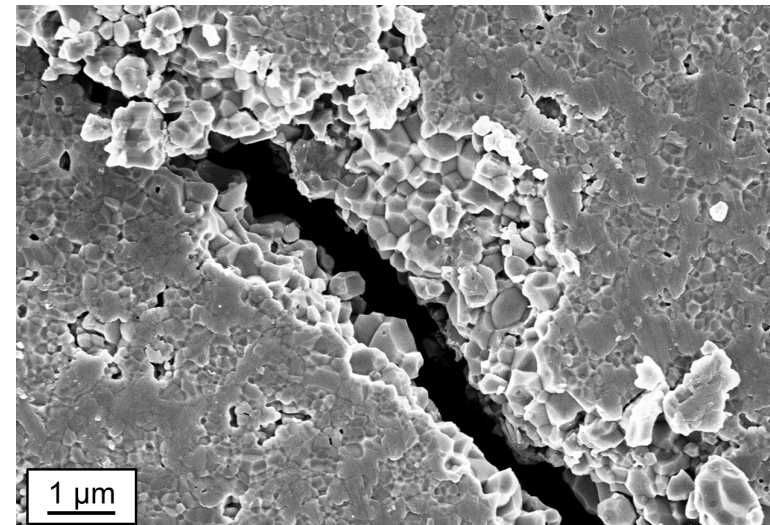
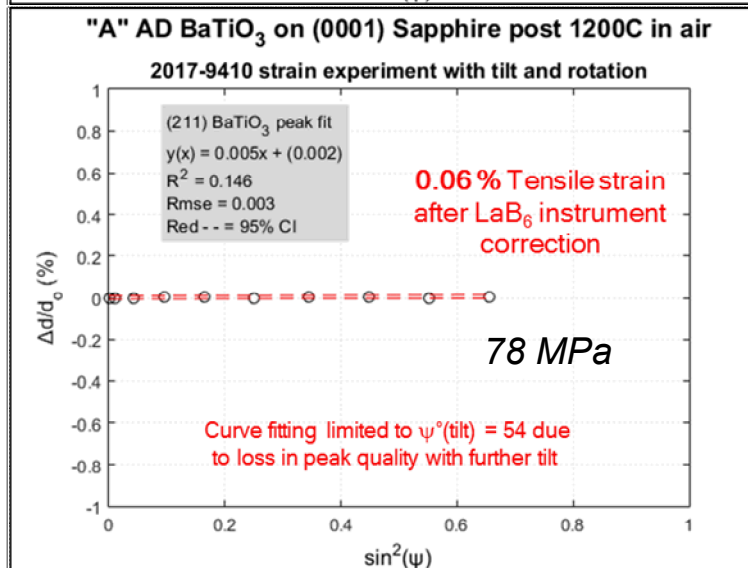
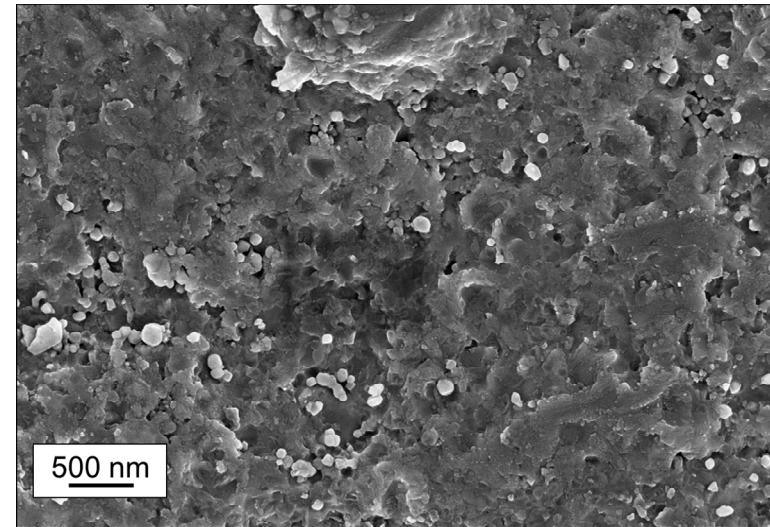
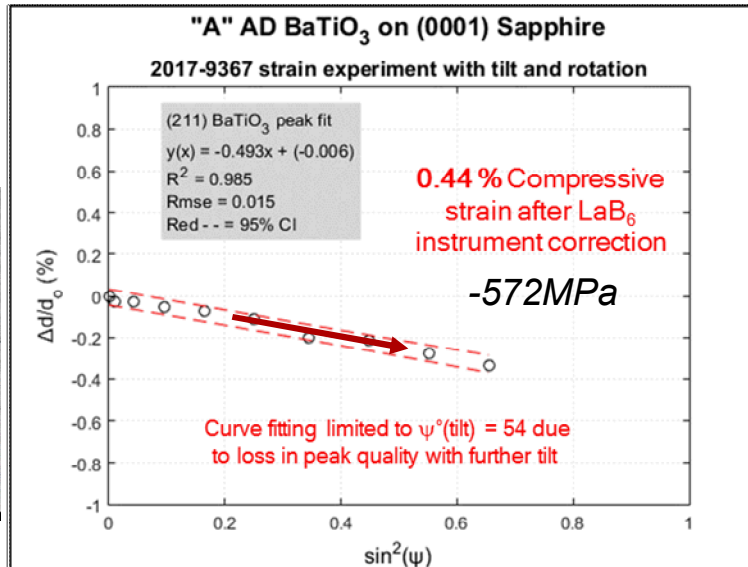
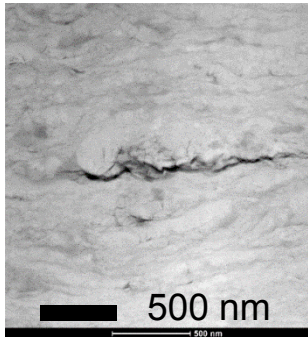
Sin²ψ XRD Measurement - Strain

8-10μm films on
Sapphire



Sin²ψ XRD Measurement - Strain

8-10μm films on
Sapphire

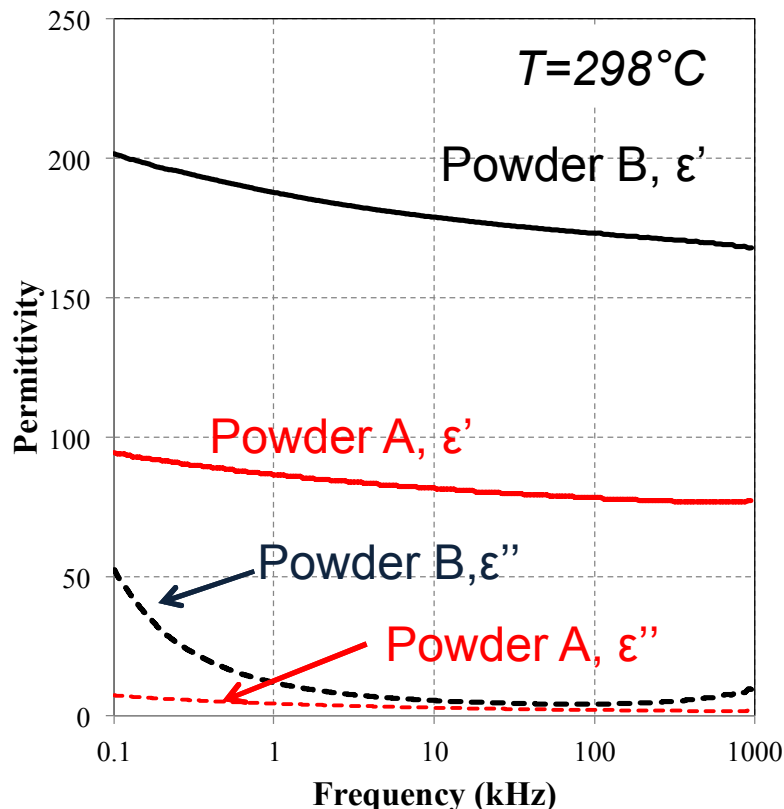


Electrical Properties – As-Deposited Feedstock Comparison

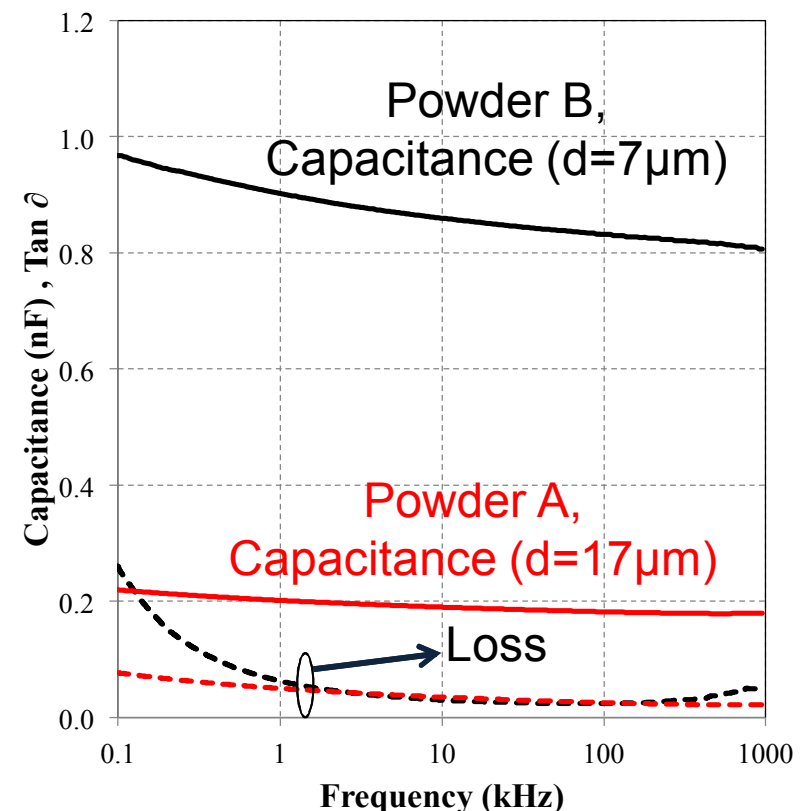
- 2 different powders, 2 different responses
 - Powder A – psuedo cubic**
 - Powder B – tetragonal?
- As deposited films exhibit $k < 200$
- Low frequency loss (space charge) observed in Powder B films

$$C = \epsilon_0 \epsilon_r \frac{A}{d}$$

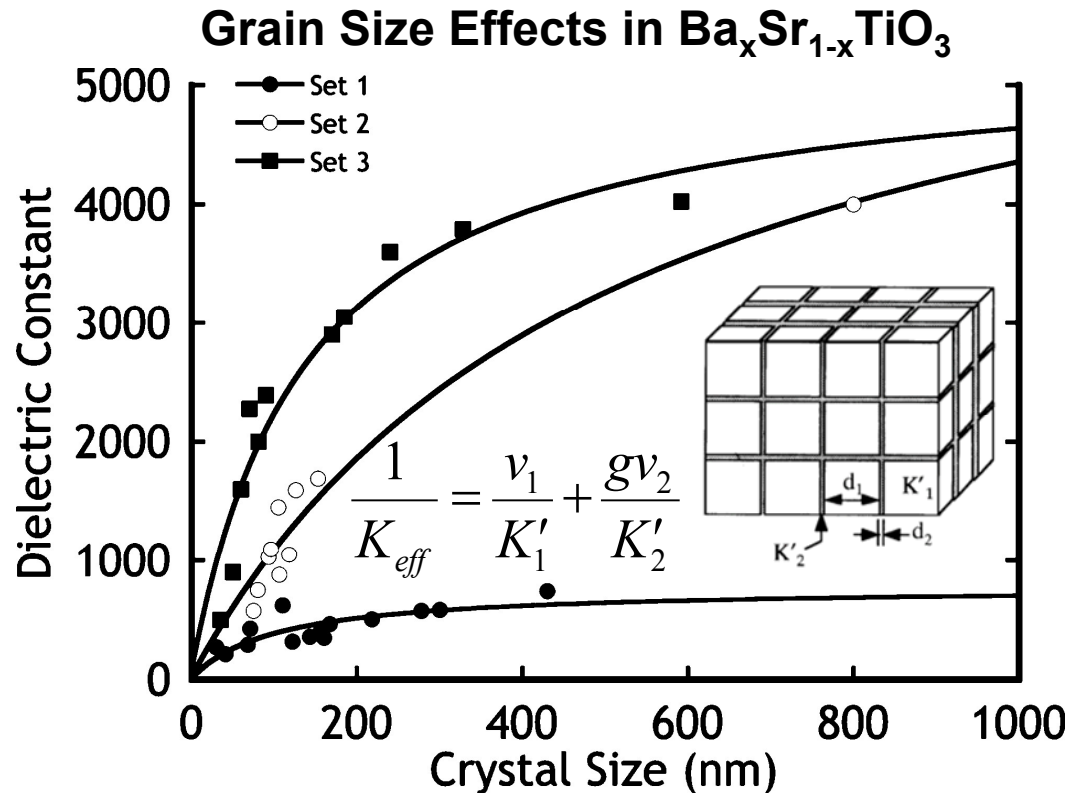
Dielectric Permittivity



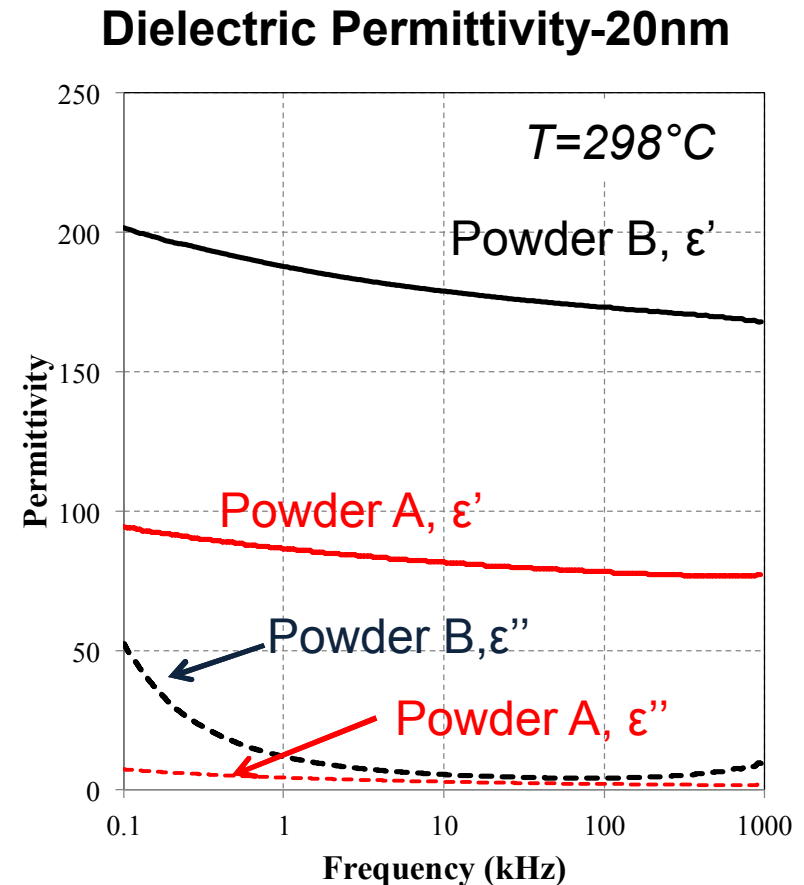
Capacitance and Loss



Brick-wall model and size effects



Aygün, Ihlefeld, Borland, and Maria, *Journal of Applied Physics* **109** [3] (2011).
Frey, Xu, Han, and Payne, *Ferroelectrics* **206** [337] (1998).



- A permittivity of the AD BaTiO_3 ($k \sim 100$ -200) agrees well with brick-wall theory
- Significant dilution from grain boundaries. Grain growth is required to increase permittivity.

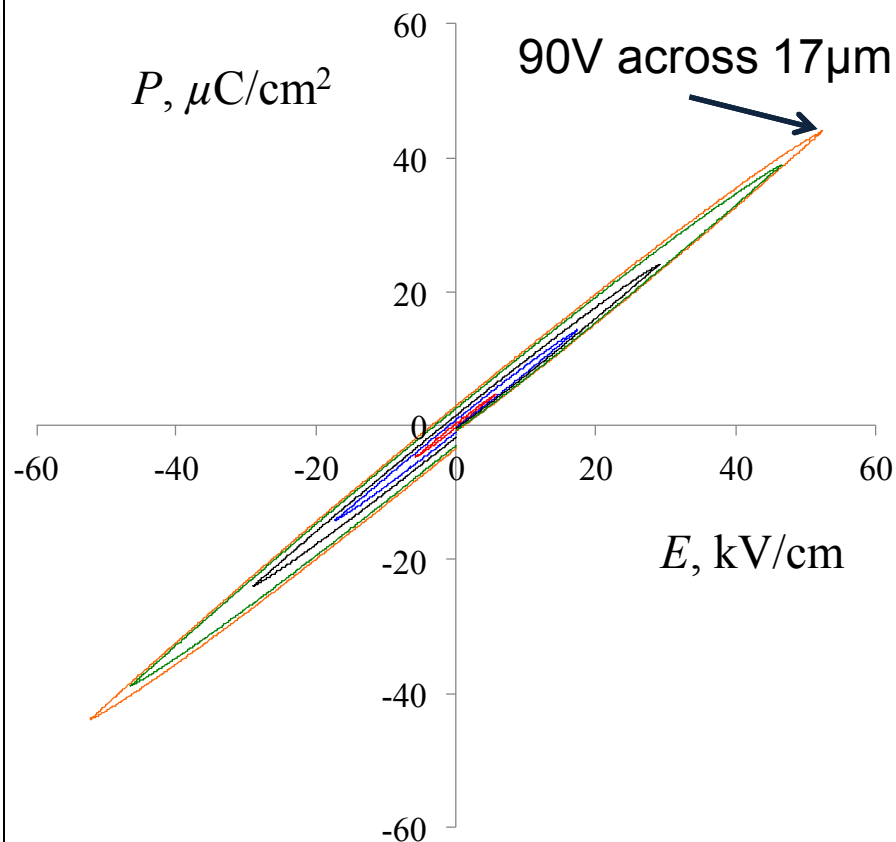
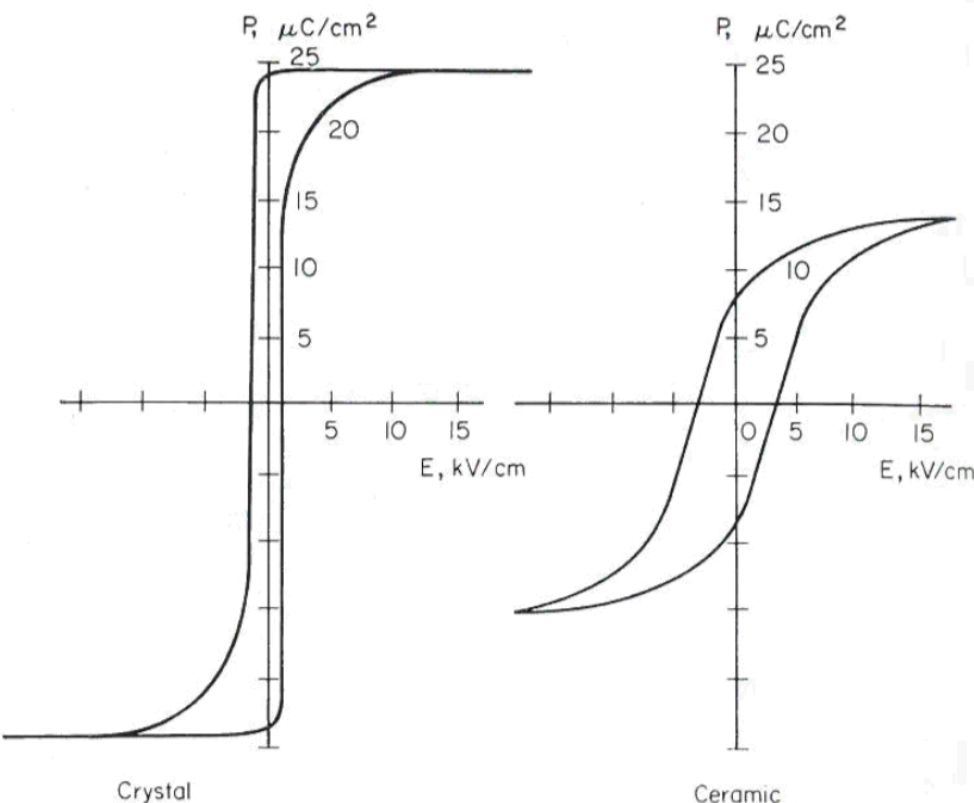
P-E Loops indicate paraelectricity

- Pseudocubic nanocrystallinity generates linear dielectric response
- Nested loops show negligible hysteresis that is caused by conduction
- Voltage withstanding suggests no thru cracks are present

BaTiO₃ (100) Crystal

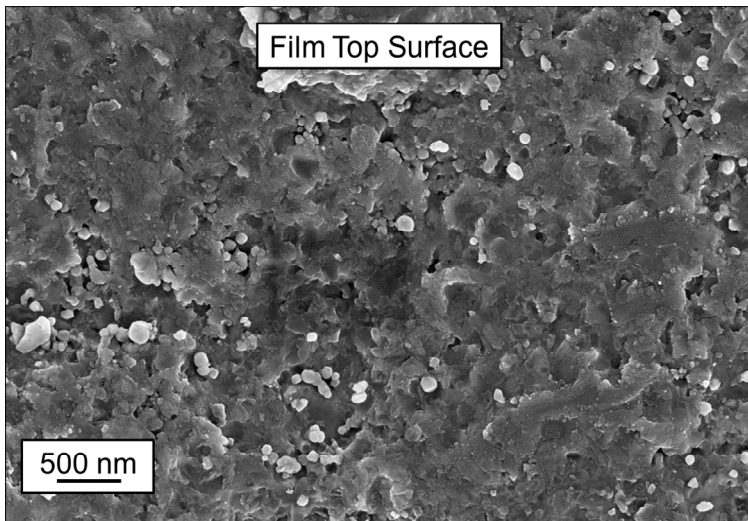
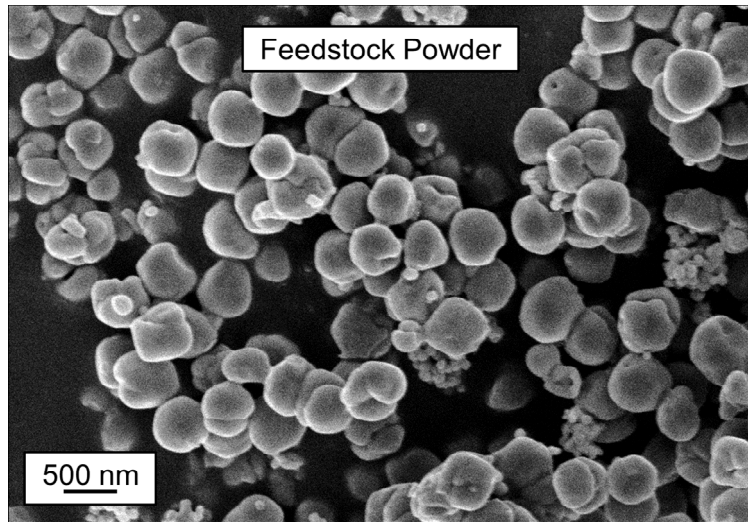
BaTiO₃ Ceramic

17μm BaTiO₃ AD Film, Powder A

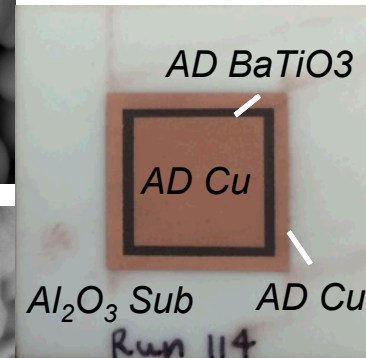
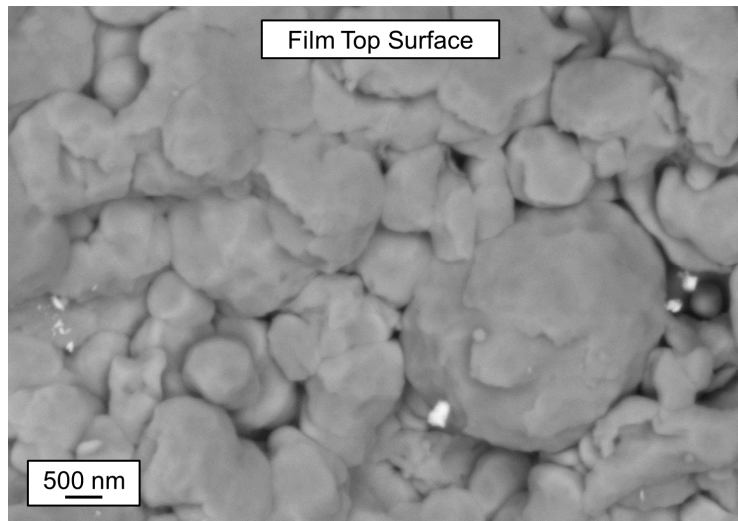
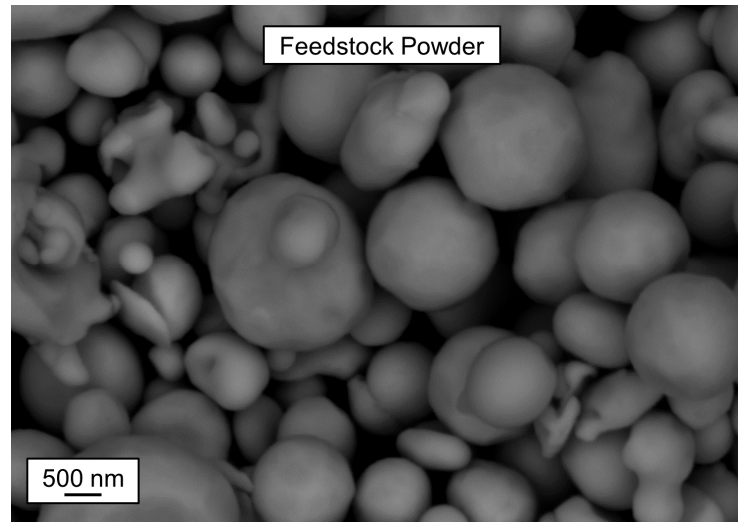


Other AD materials - Cu

BaTiO_3

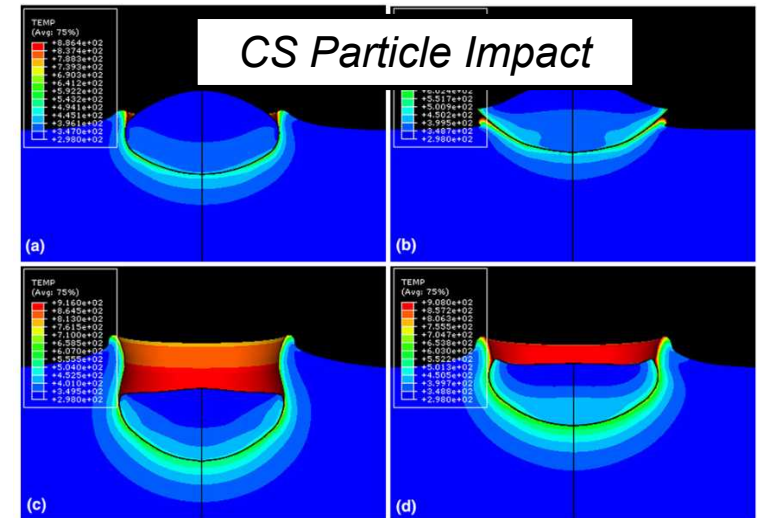


Cu

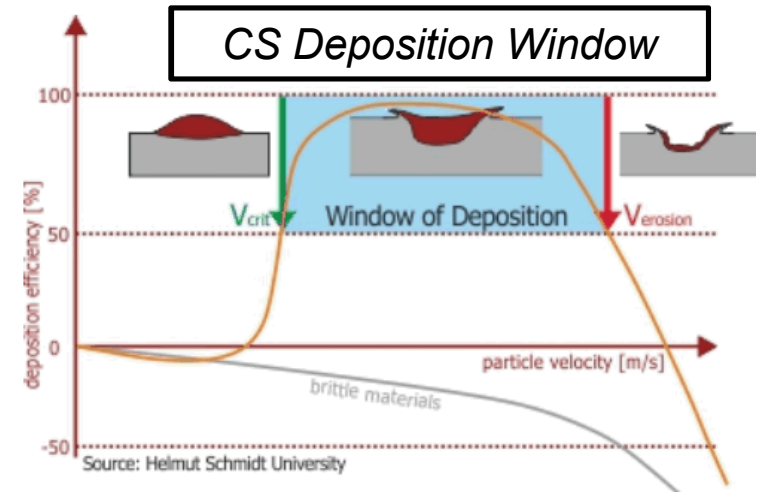
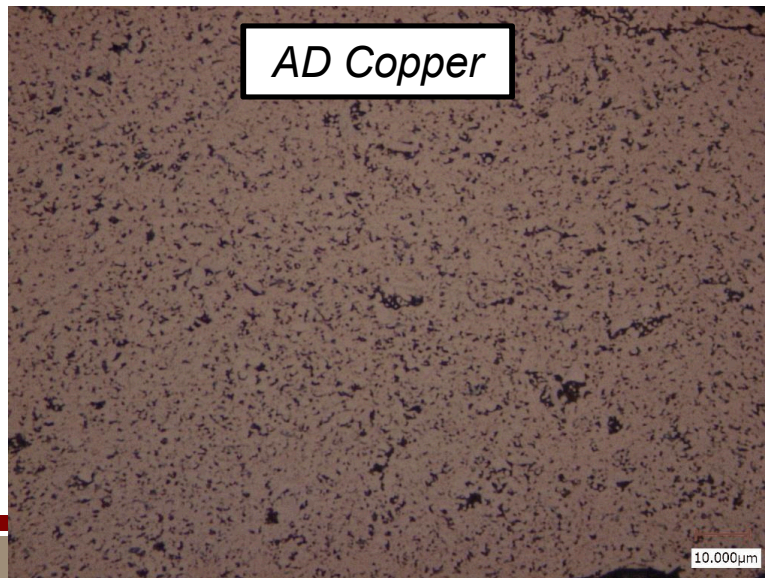


Similarities and Contrast to Cold Spray (CS)

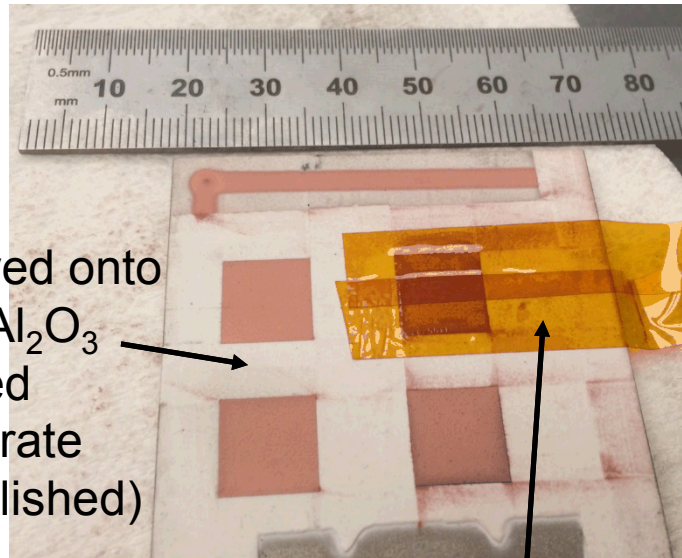
- Relies on ductility of material to bond particles at high velocity – CS uses warmed particles for softening
- Substrate heating
 - CS warms substrates
 - AD remains at room temperature
- Particle Sizes
 - CS 5-25 μm
 - AD 0.1-5 μm
- Higher resistivity (10-25x) than bulk



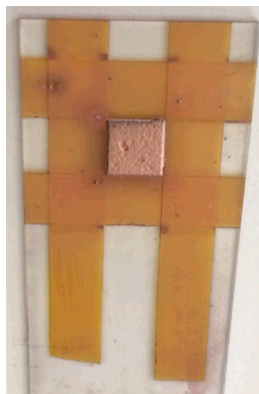
King, Peter C., et al. "An experimental and finite element study of cold spray copper impact onto two aluminum substrates." *Journal of thermal spray technology* 19.3 (2010): 620-634.



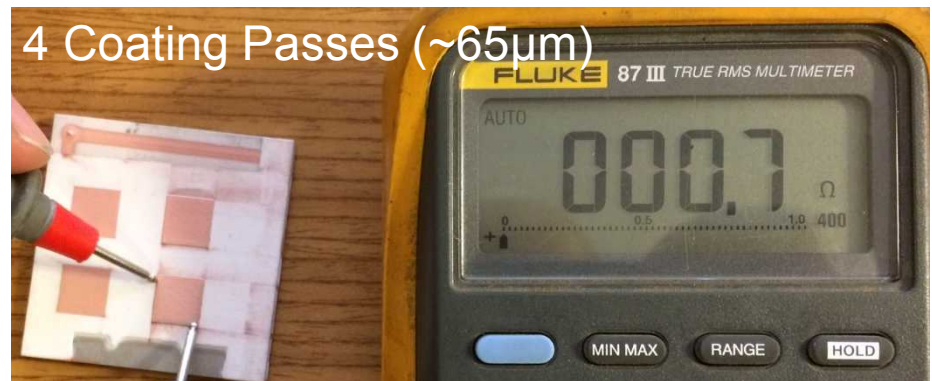
Adhesion and Resistivity



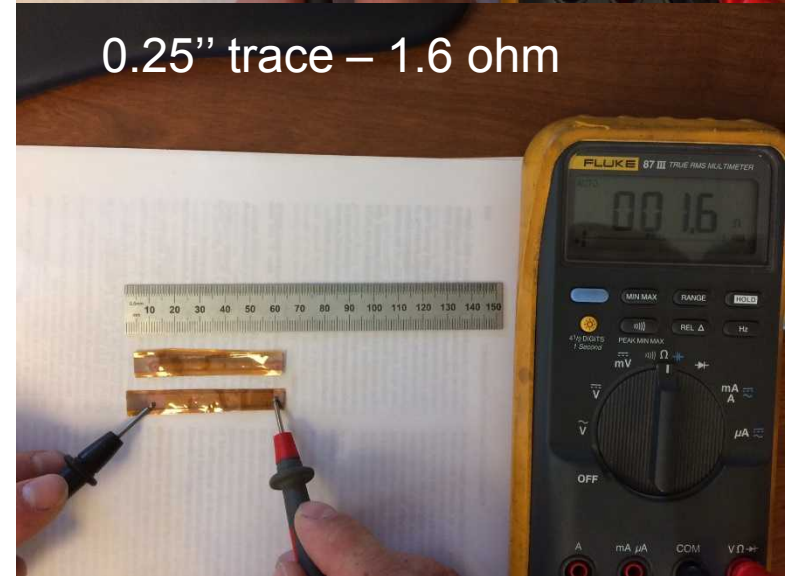
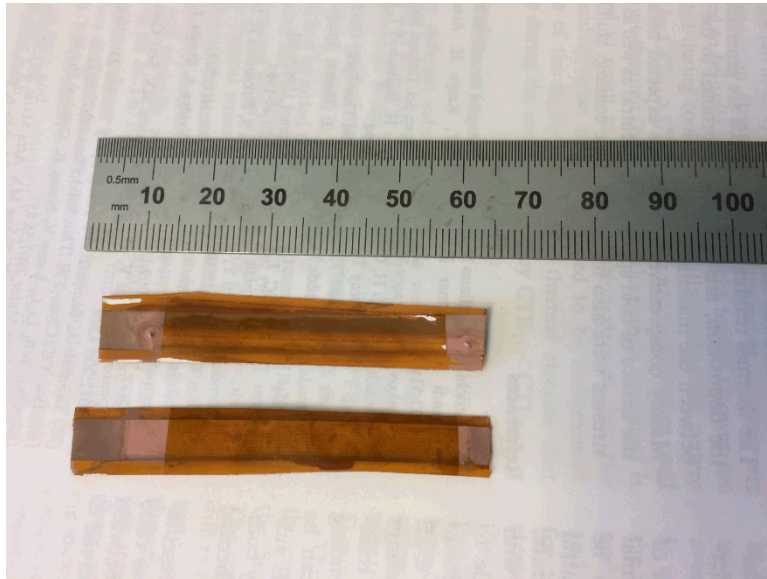
Tape test with Kapton
- Passed



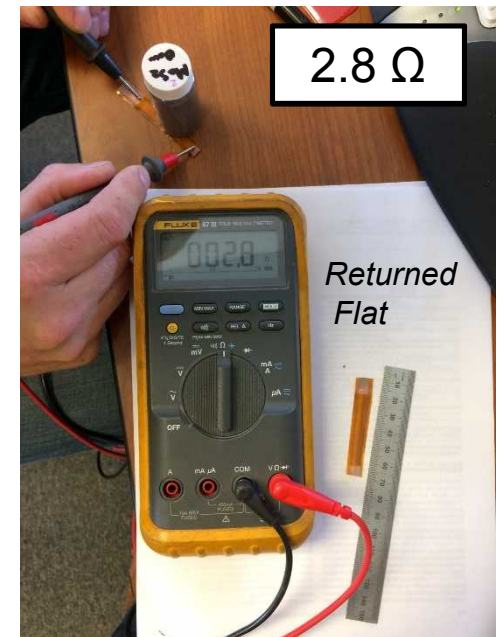
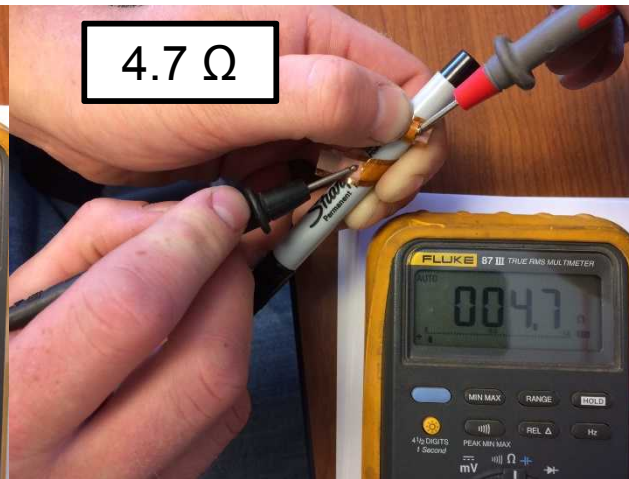
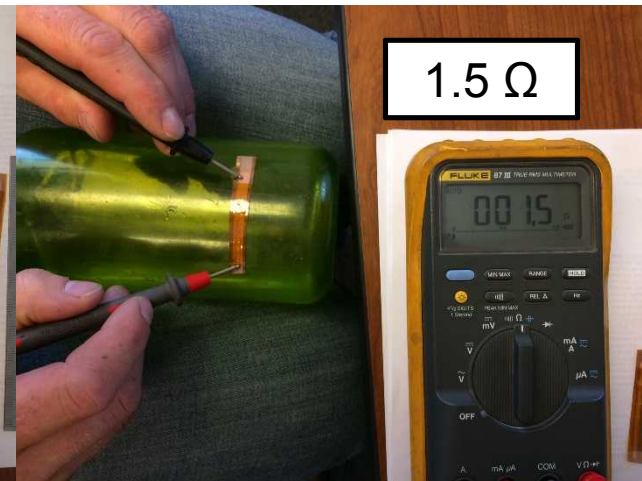
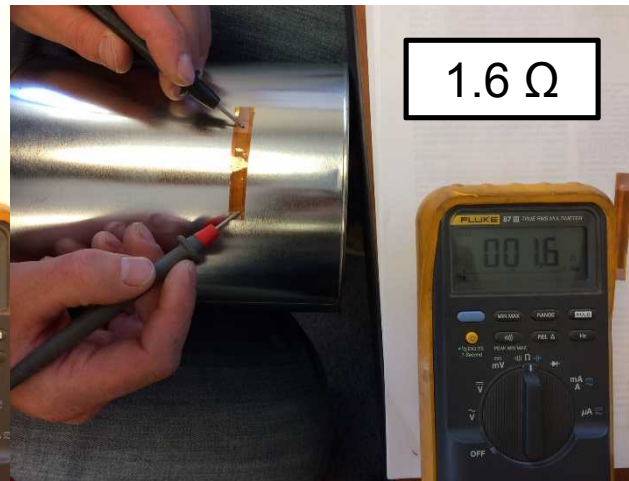
500 μm sprayed onto
glass – delaminated
with masking removal



Cu trace in Kapton tape



Cu in Kapton – Curvature vs Resistance



Cu on APS Ceramic

2 pass, 8.9Ω

10 pass, 2.4Ω

1 pass, 42.8Ω

2 pass

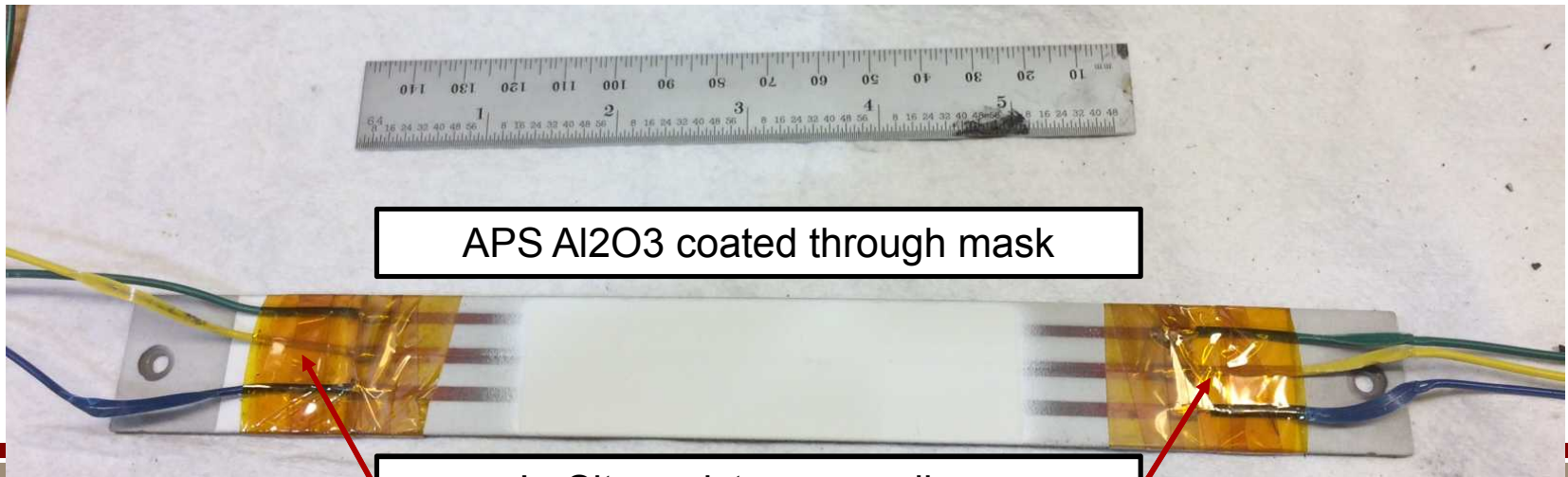
10 Pass

1 Pass

Measured by multi-meter probes



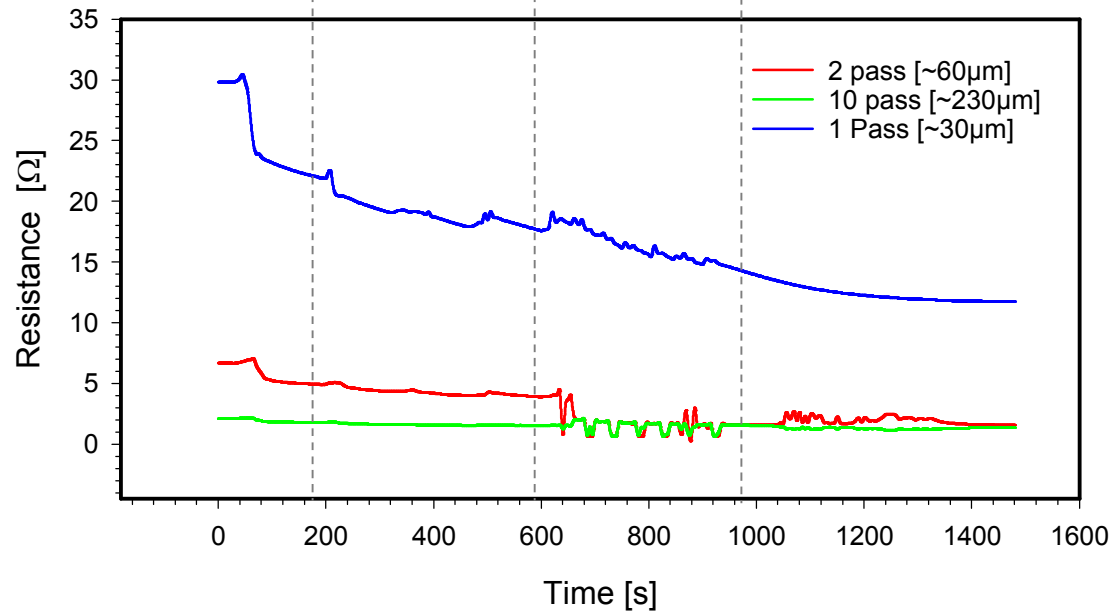
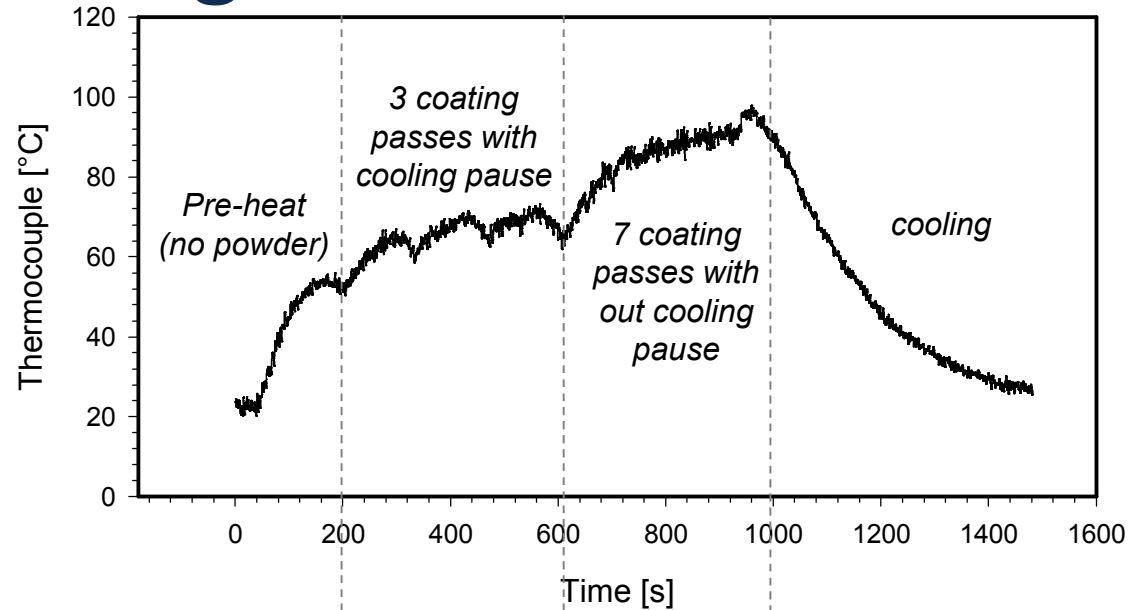
Thermocouple on backside



APS Al₂O₃ coated through mask

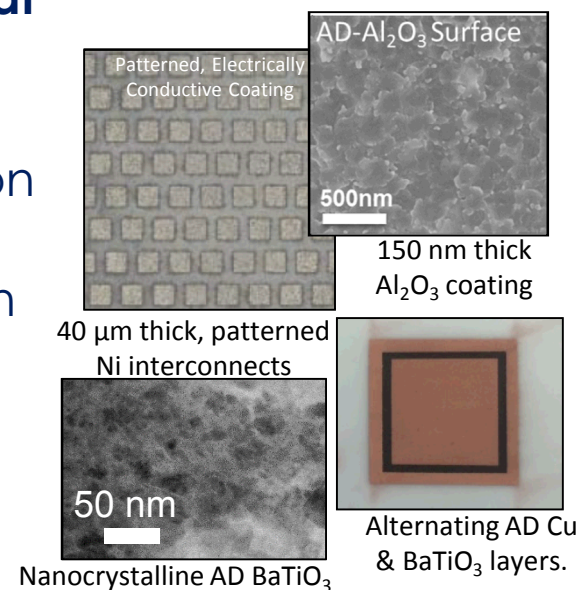
In-Situ resistance readings

Embedding Cu traces



Summary

- **AD produces dense nanocrystalline functional films at room temp, enabling integration with low temp materials.**
 - Great for structural and environmental protection applications.
 - Grain size can be tuned after deposition through heat treatment.
- Submicron sized ceramic particles can undergo dislocation plasticity under quasi-static loading and high strain-rate loading.
- Aerosol Deposition (AD) leverages use of submicron particles that are accelerated, impacted, deformed, and consolidated as films.
- Utilize substrate deflection and Schlieren to understand role of process parameters
- AD BaTiO₃ for capacitor application: In progress
- AD Copper for conductive film: In progress





Questions ?



Sandia
National
Laboratories