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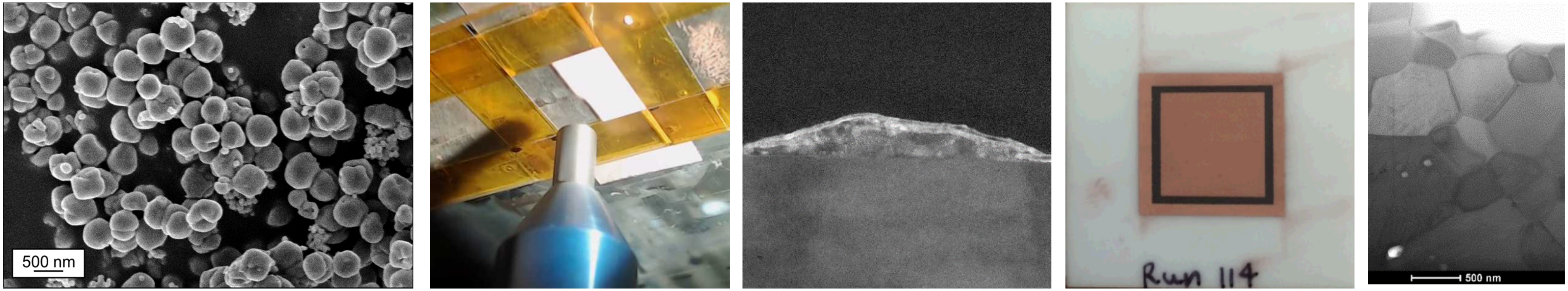

# Synthesis and Characterization of Aerosol Deposited Materials

Andrew Vackel, Pylin Sarobol, Jesse Adamczyk, Harlan Brown-Shaklee

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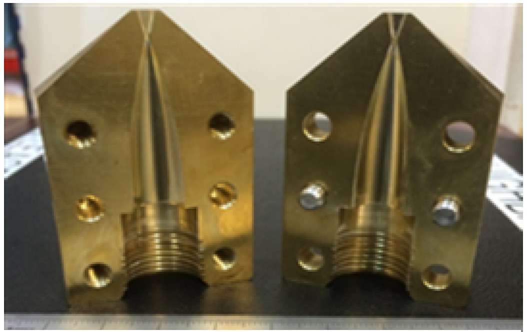
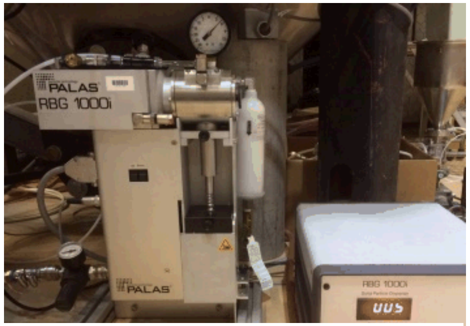
# Aerosol Deposition (AD)

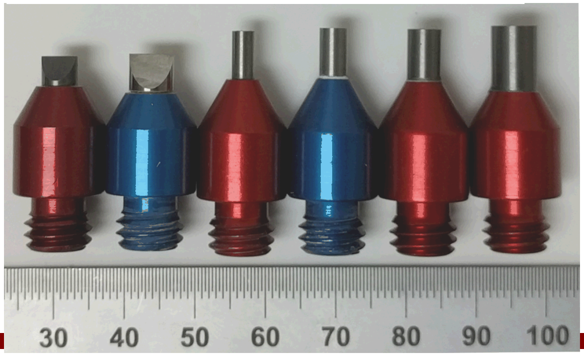
- Room temperature, solid state deposition process for thick films (>1µm)
- Relies on aerosolized fine powder accelerated to high speeds (>300m/s) within a vacuum environment for coating consolidation
- Capable of depositing ceramics, carbides, and metals with no feedstock melting or substrate heating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

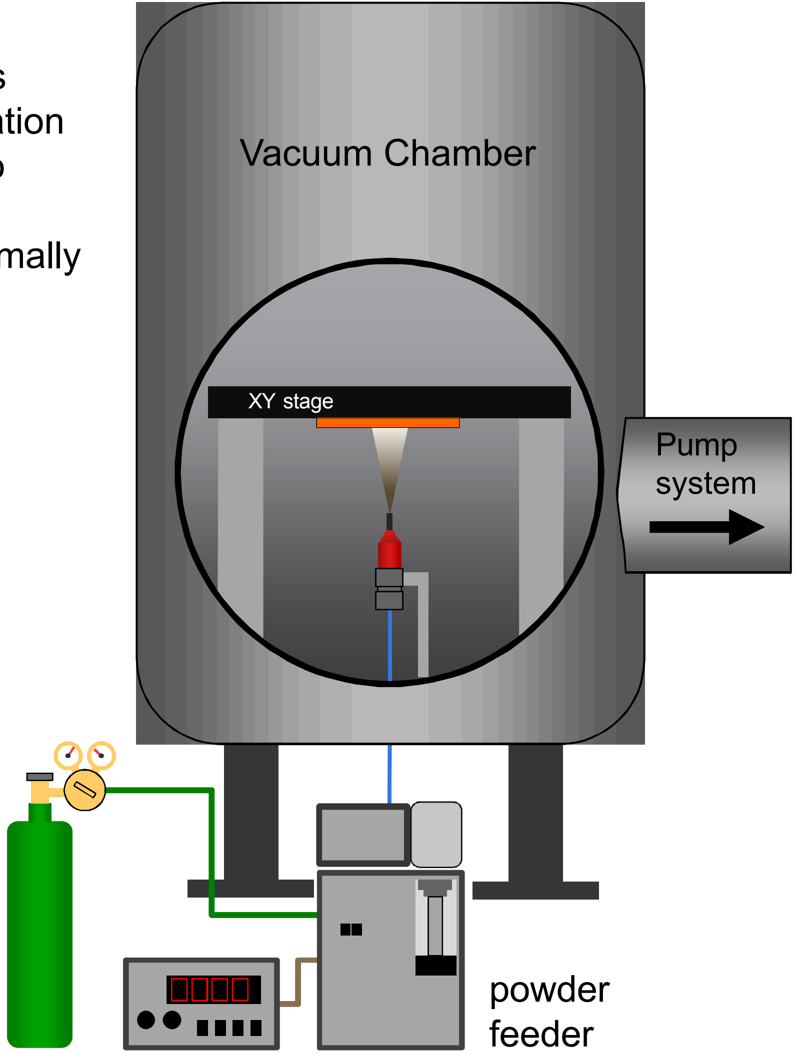


Nozzles for achieving supersonic particle flow



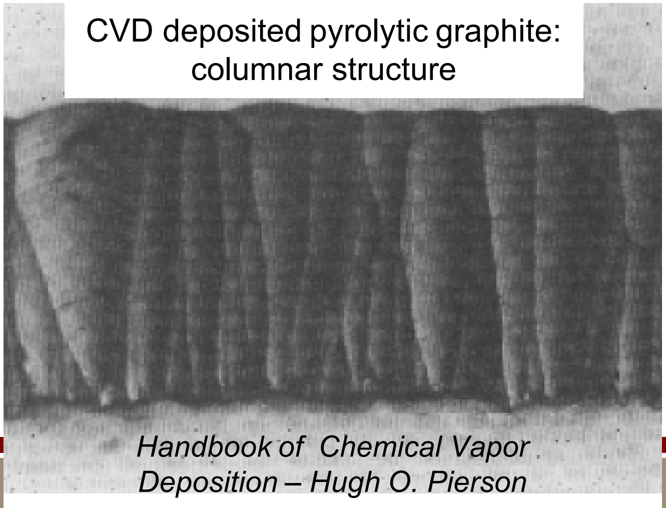
Aerosol Generator for controlled powder feed





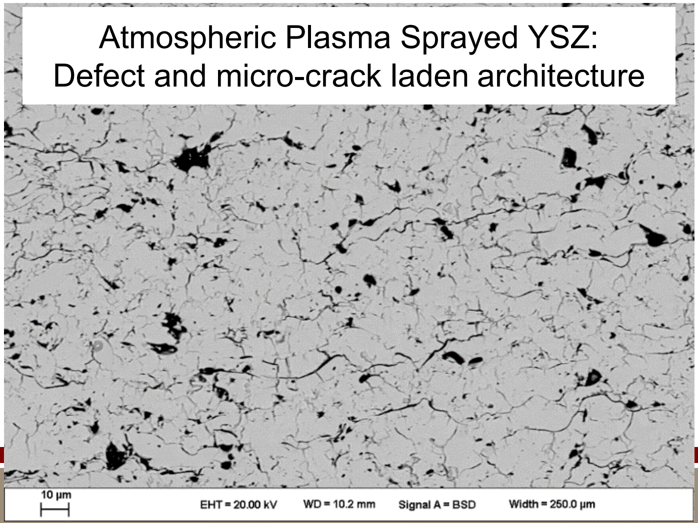
# Film processing comparison

|  | CVD | Air Plasma Spray | Aerosol Deposition |
|---|---|---|---|
| Film Thickness | <10µm | 10µm – 1mm | 10s µm |
| µstructure/density | Columnar, equiax/Dense | Lamellar/ Porous, micro-cracked | Lamellar/ Near theoretical |
| Grain Size | Fine to coarse | Nano/10s µm | 10-100nm |
| Substrate Temp | >500°C | 100-300°C | Room Temp |
| Film Stresses | Tensile or Compressive | Tensile or Compressive | Compressive |

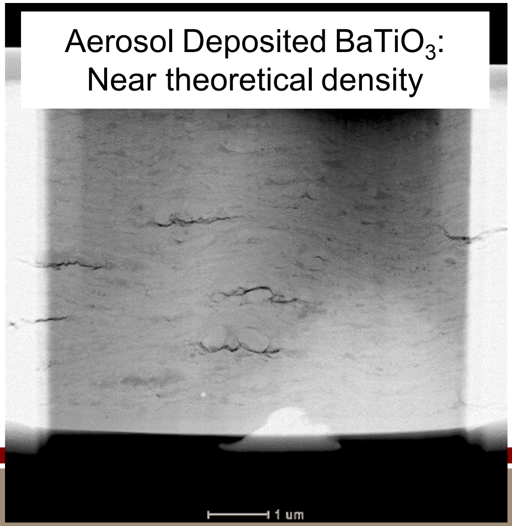


CVD deposited pyrolytic graphite: columnar structure

*Handbook of Chemical Vapor Deposition – Hugh O. Pierson*



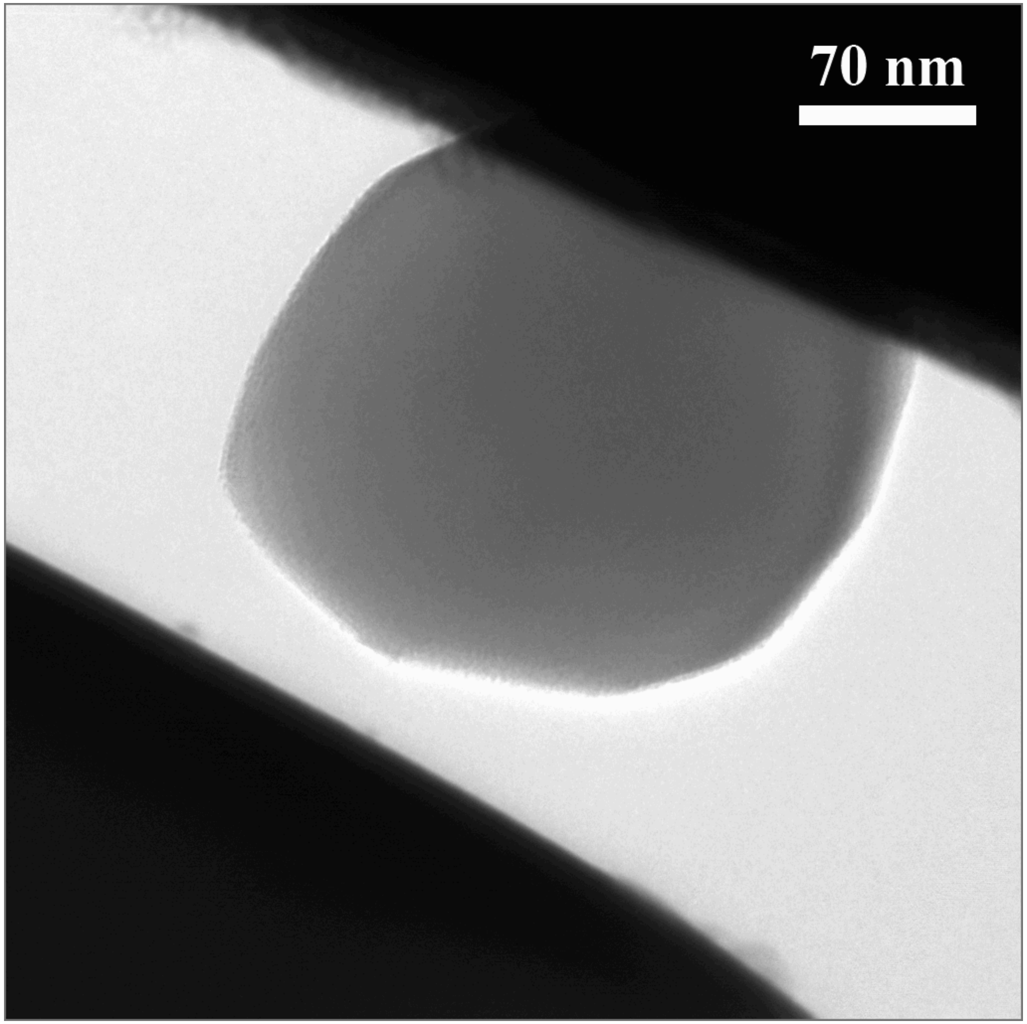
Atmospheric Plasma Sprayed YSZ: Defect and micro-crack laden architecture



Aerosol Deposited $BaTiO_3$: Near theoretical density

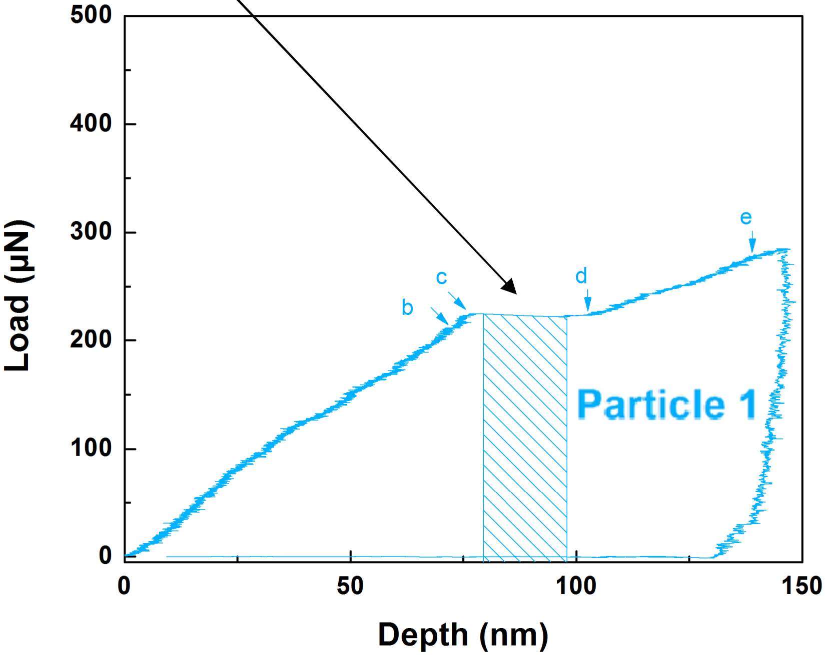
# *In Situ* TEM Compression Results

Diameter ~ 0.24 µm, Open loop, Strain rate ~ 0.009 $s^{-1}$



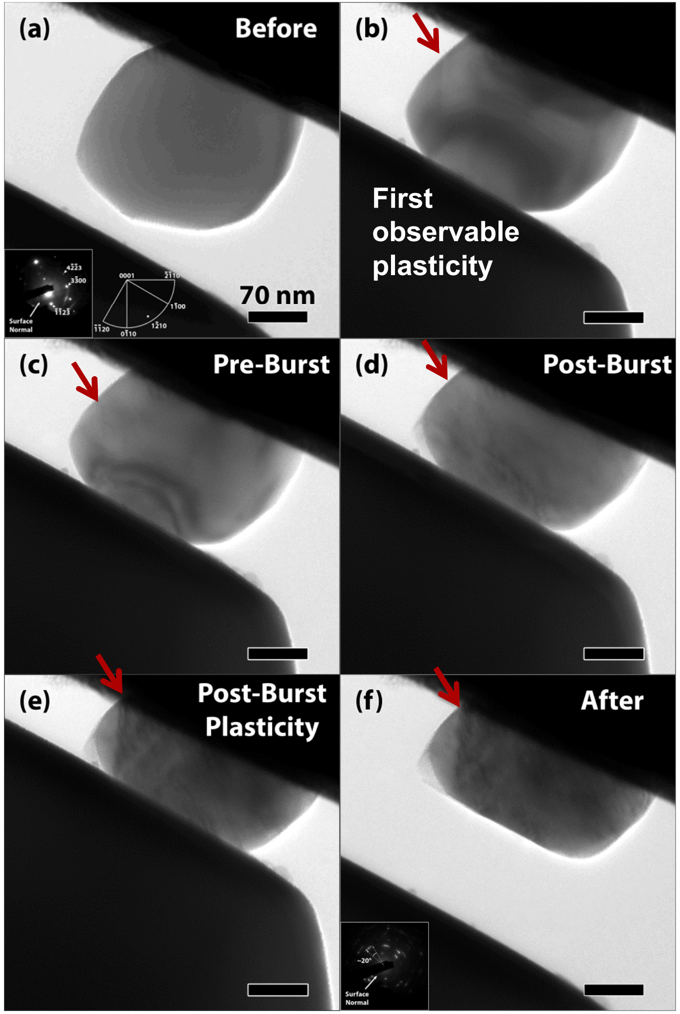
**Observed dislocation nucleation & movement. Dislocation plasticity preceded fracture.**

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

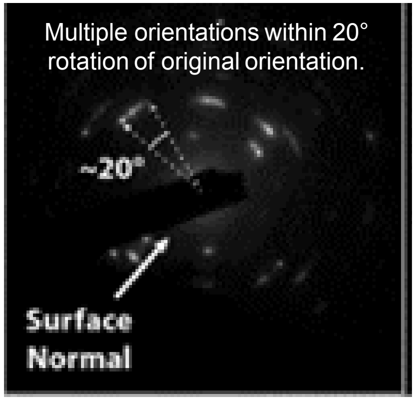


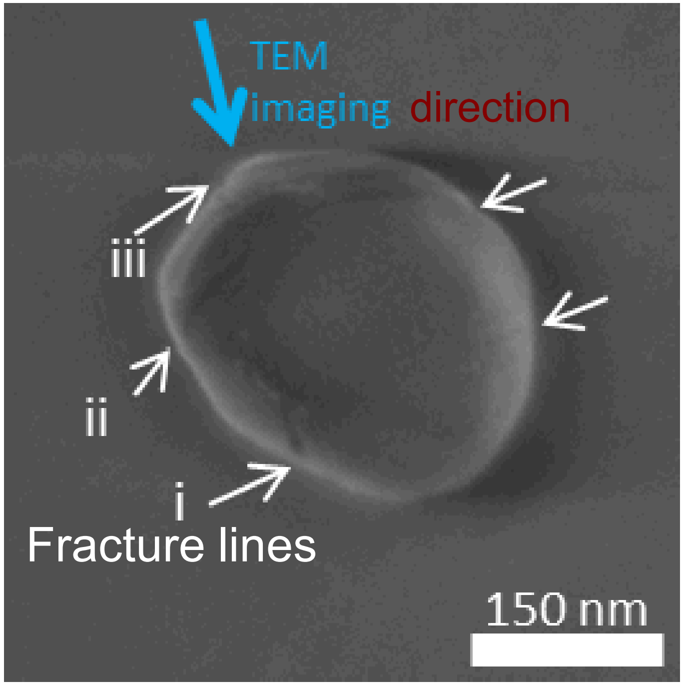
# *In Situ* TEM Compression Results

Zone axis near $[\bar{9}\,\bar{9}\,18\,6]$



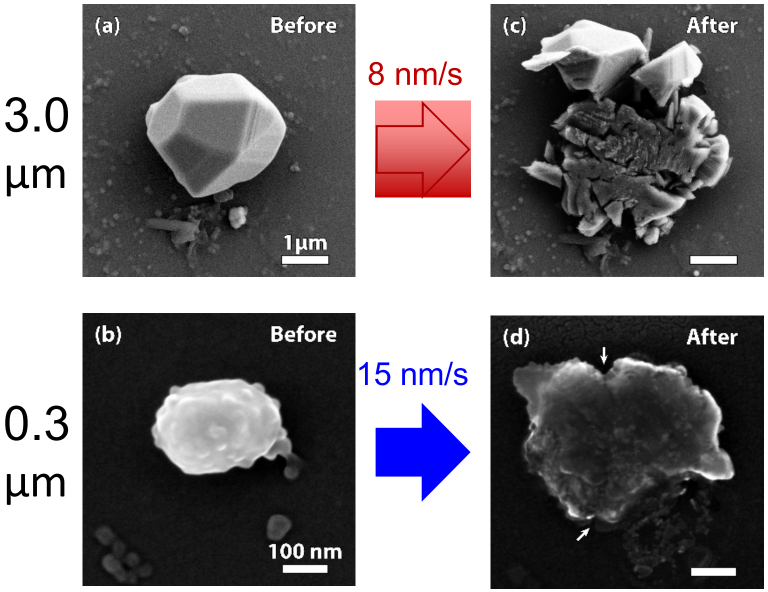
**Observed dislocation nucleation & movement.**
**Dislocation plasticity preceded fracture.**


Multiple orientations within 20° rotation of original orientation.



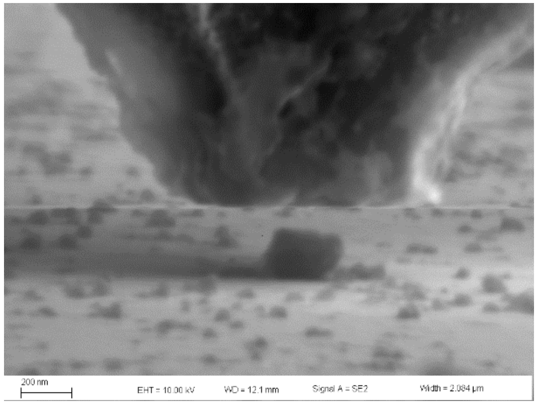
- Pre-burst plasticity—small regime with low dislocation activity
- Crack nucleation & propagation → through-particle fracture
- Post-burst plasticity—high dislocation activities
- **Polycrystalline, Mosaicity**—a 20 degree orientation spread

# Micro-Compression Results



| Particle Identifier | Diameter (µm) | Nominal Strain Rate ($s^{-1}$) | Strain Energy before Fracture ($MJ/m^3$) | Strain at Fracture (%) |
|---|---|---|---|---|
| **Large Particles** | | | | |
| SEM-LP1 | 2.9 | 0.03 | 47 | 5 |
| SEM-LP2 | 2.6 | 0.006 | 106 | 5 |
| SEM-LP4 | 2.9 | 0.005 | 70 | 5 |
| SEM-LP5 | 2.9 | 0.003 | 203 | 7 |
| **Avg Large Particles** | **2.8** | - | 🟥 | 🟥 |
| **Small Particles** | | | | |
| SEM-SP2 | 0.17 | 0.09 | 494 | 11 |
| SEM-SP3 | 0.29 | 0.05 | 366 | 12 |
| SEM-SP4 | 0.28 | 0.05 | 607 | 13 |
| SEM-SP5 | 0.29 | 0.05 | 675 | 16 |
| *TEM-SA2 | 0.38 | *0.005 | 573 | 32 |
| *TEM-SB1 | 0.24 | *0.009 | 1066 | 27 |
| **Avg Small Particles** | **0.26** | - | 🟦 | 🟦 |

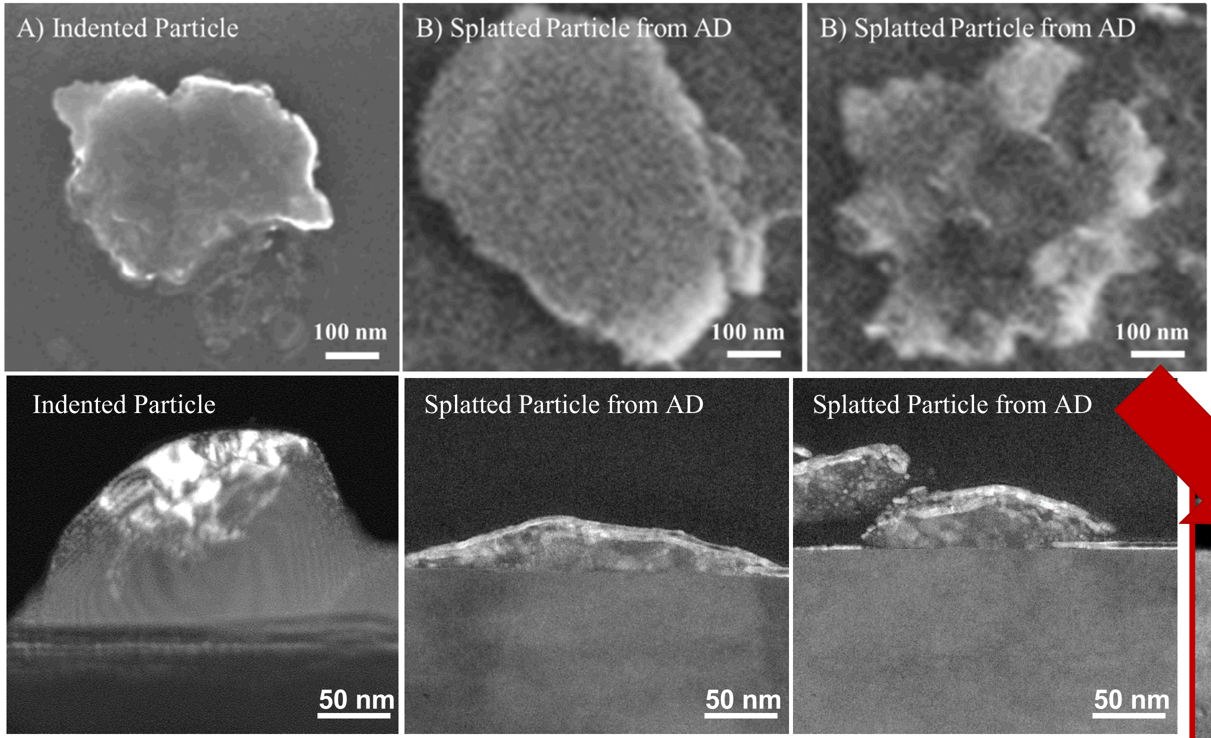
- Micron sized particles - brittle fracture
- Sub-micron sized particles - substantial plastic deformation before fracture.
  - **6x** higher strain energy density input
    - dislocation nucleation
  - **3x** higher accumulated strain
  - In some cases, became **polycrystalline**.
- Takes more energy to nucleate dislocations and move them for deformation.



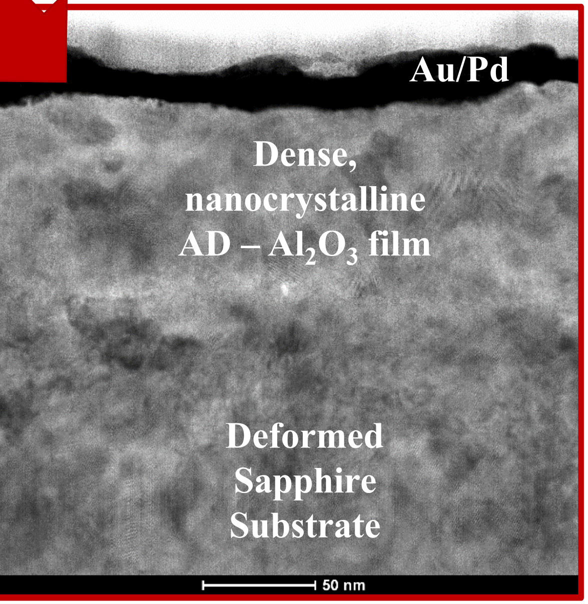
Sarobol et al.

# Mechanisms Underlying AD

INDENTATION SINGLE-PARTICLES DEPOSITION



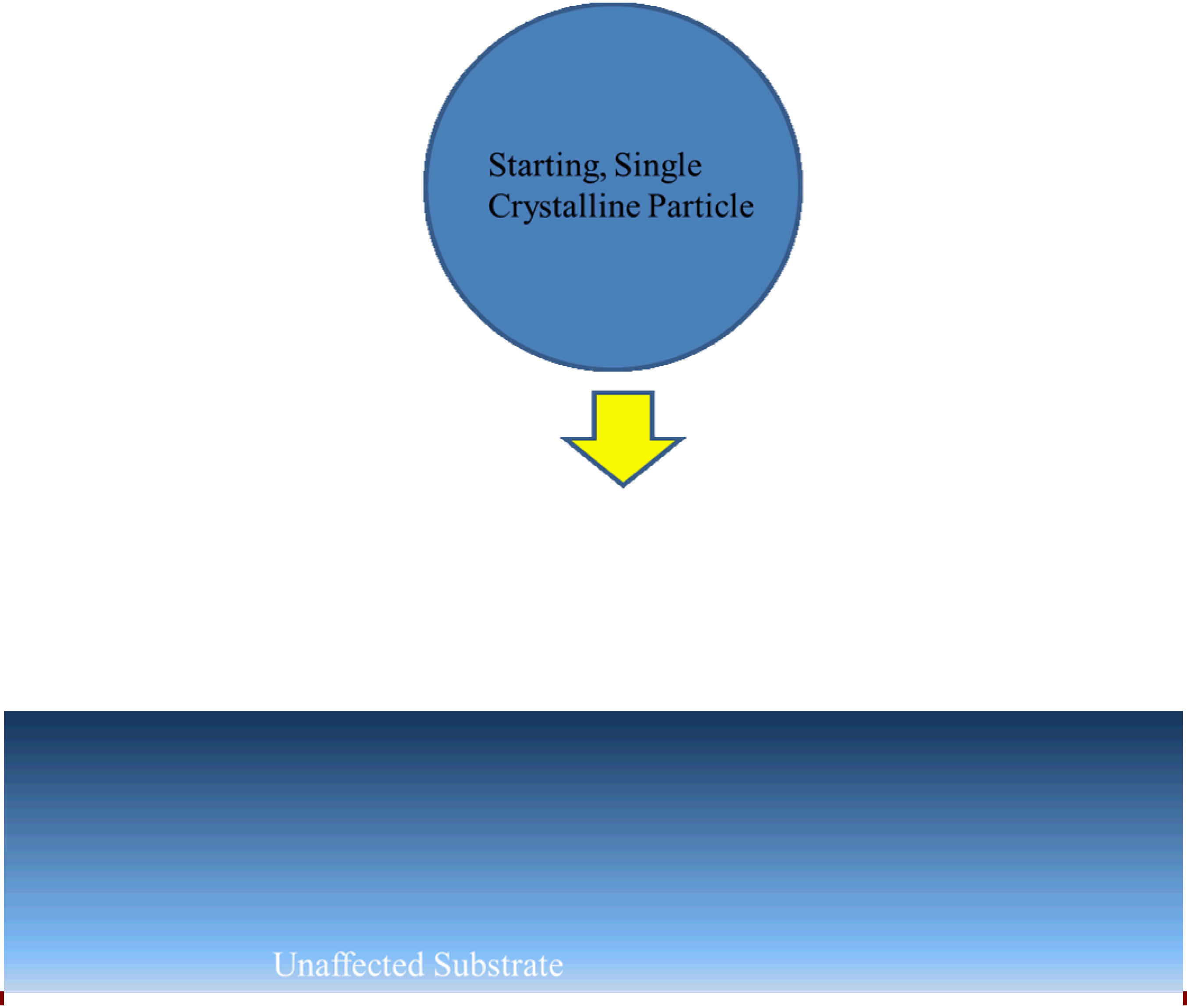
- **Kinetic energy → Absorbed strain energy**
- **Dislocation plasticity**
- **Fracture without fragmentation**
- **Tamping from subsequent impacting particles → building up dense coating**



In both quasi-static and high strain-rate loadings, 0.3 µm $Al_2O_3$ 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



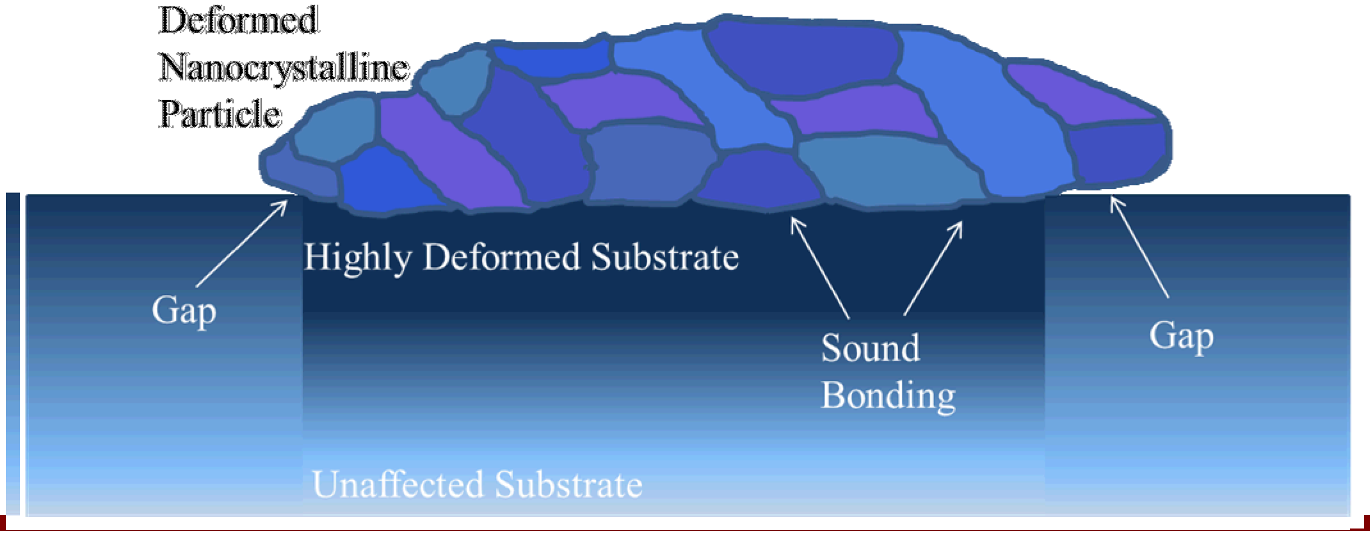
Starting, Single Crystalline Particle

Unaffected Substrate

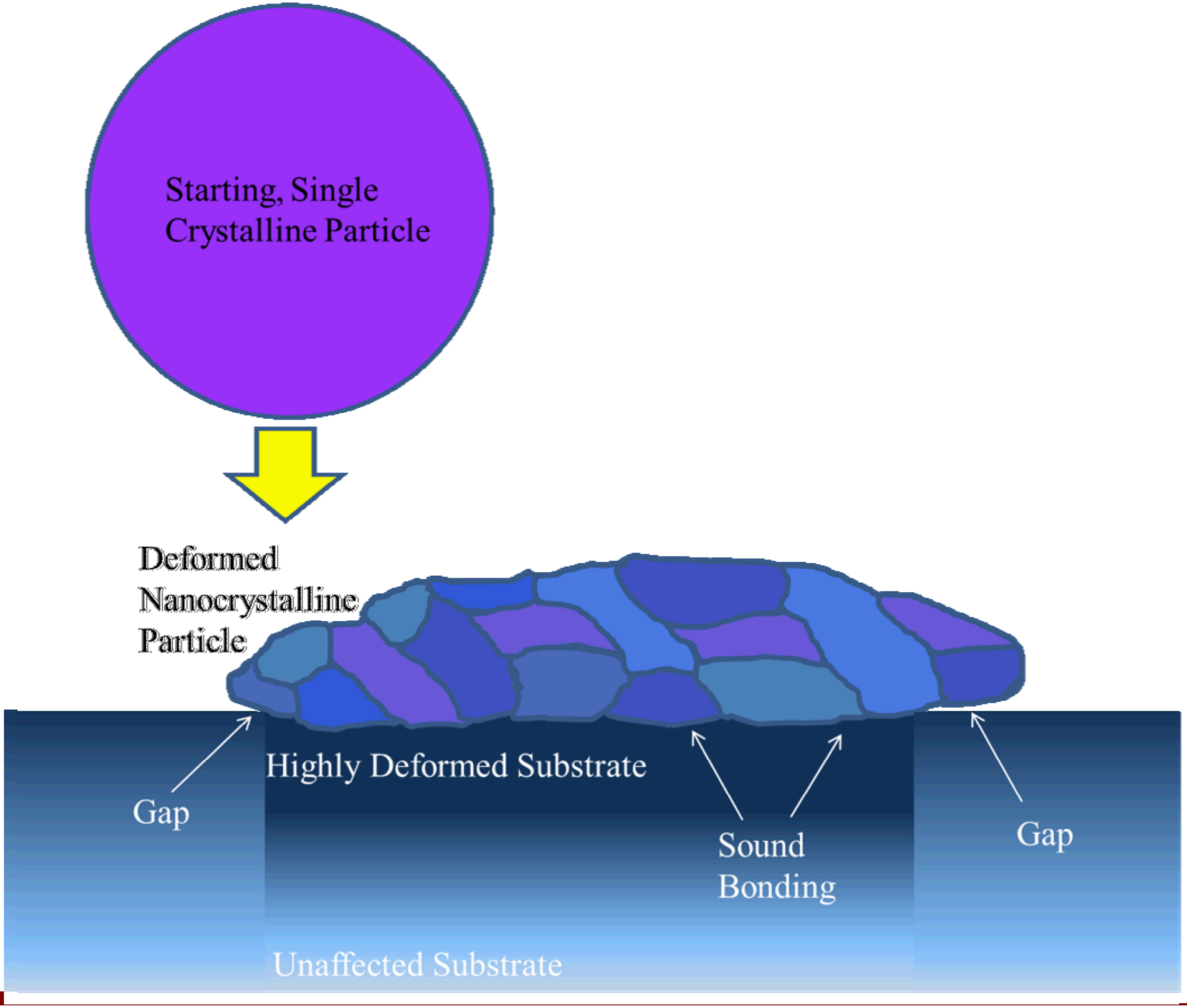
# RT Deformation & Bonding Mechanisms

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



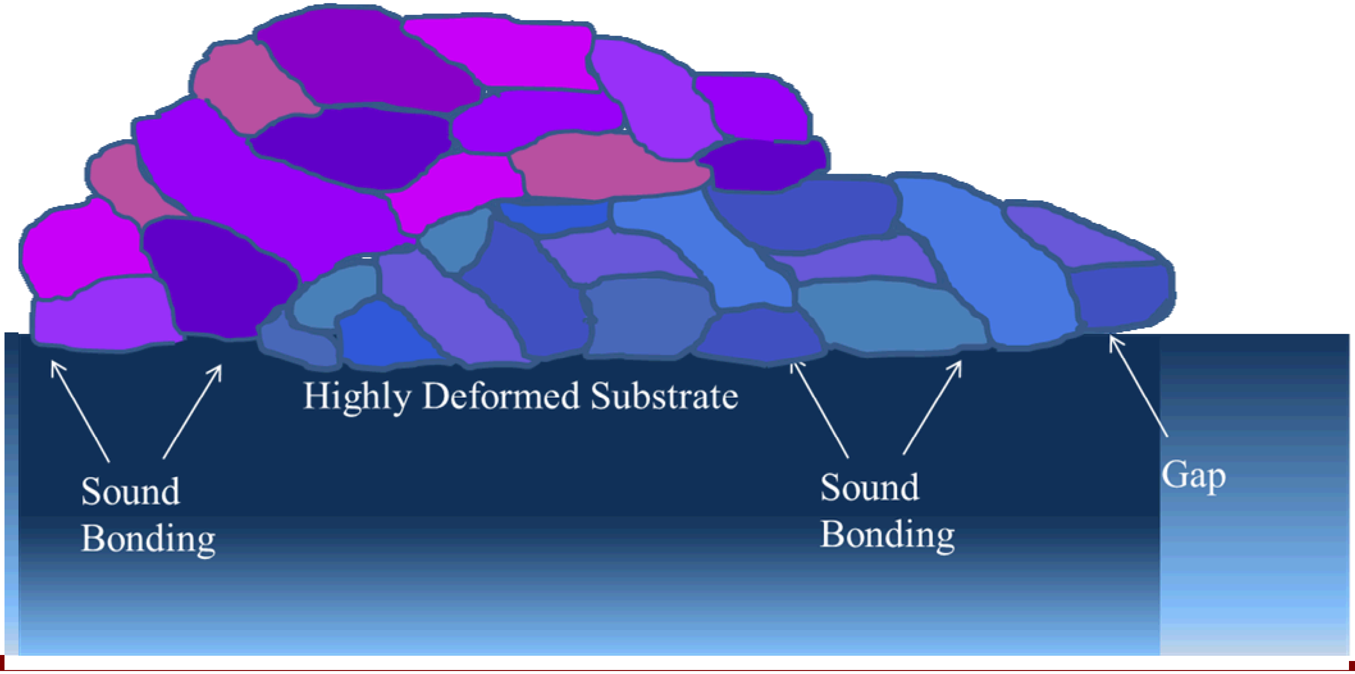
# RT Deformation & Bonding Mechanisms



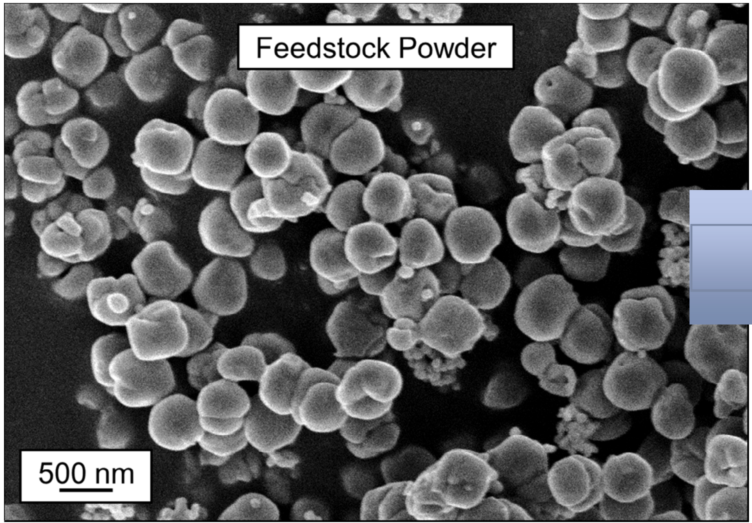
# RT Deformation & Bonding Mechanisms

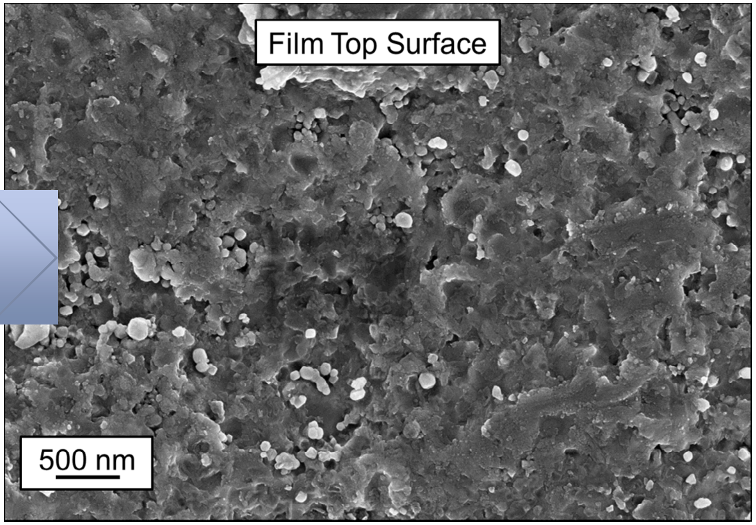
Subsequent impacting particle imparts sufficient energy to

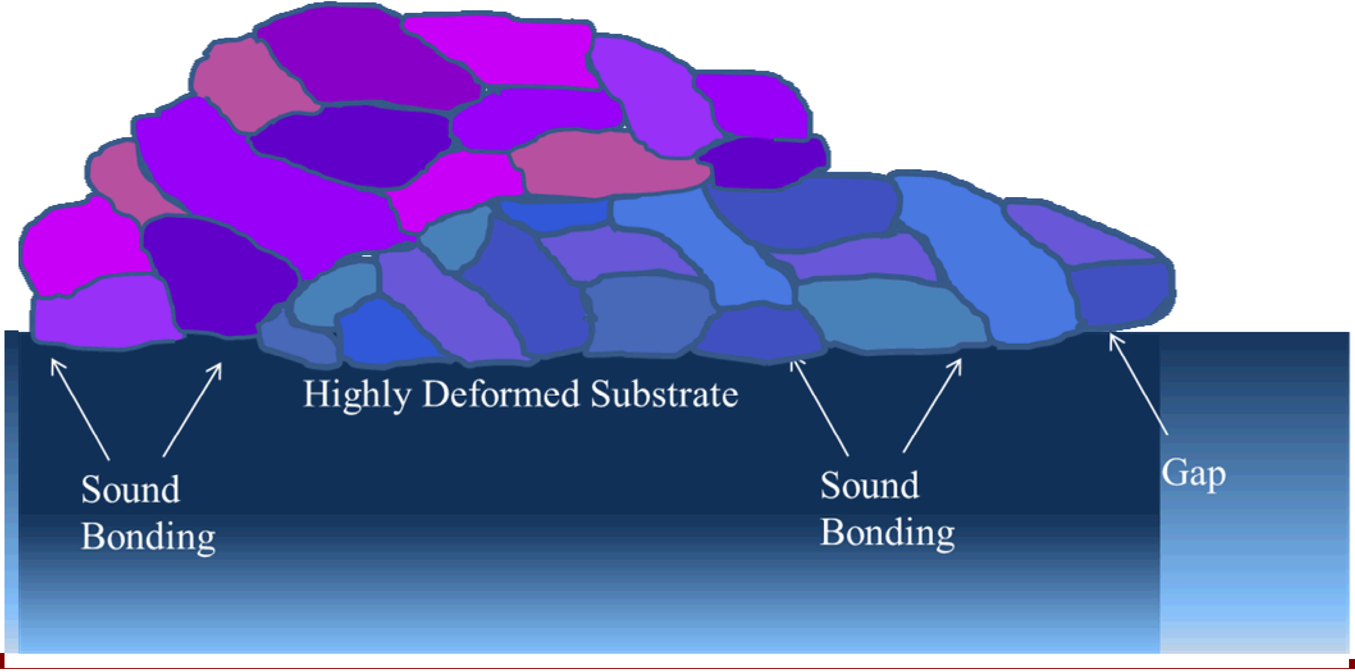
- Further deform splatted particle
- Provide further bond formation between splatted particle-substrate from "tamping effect"
- Compaction and densification of deposited coating from "tamping effect"



# RT Deformation & Bonding Mechanisms



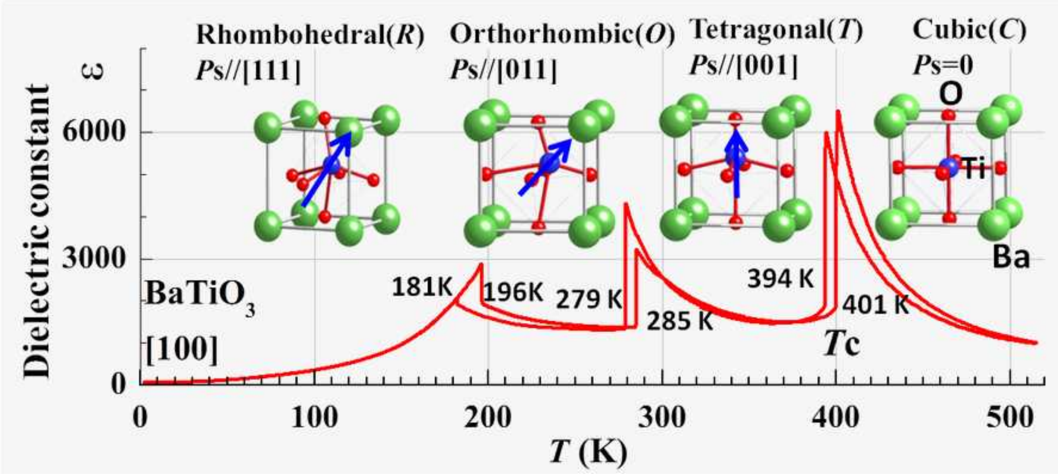




# $BaTiO_3$ Aerosol Deposited Film

**Why $BaTiO_3$?**

- Ferroelectric with high dielectric constant (up to7,000) with spontaneous polarization
- Well studied and used material



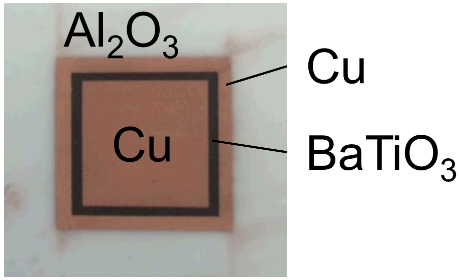
*Desheng Fu and Mitsuru Itoh DOI: 10.5772/61017*

**Why AD?**

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

**$BaTiO_3$ case study:**

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

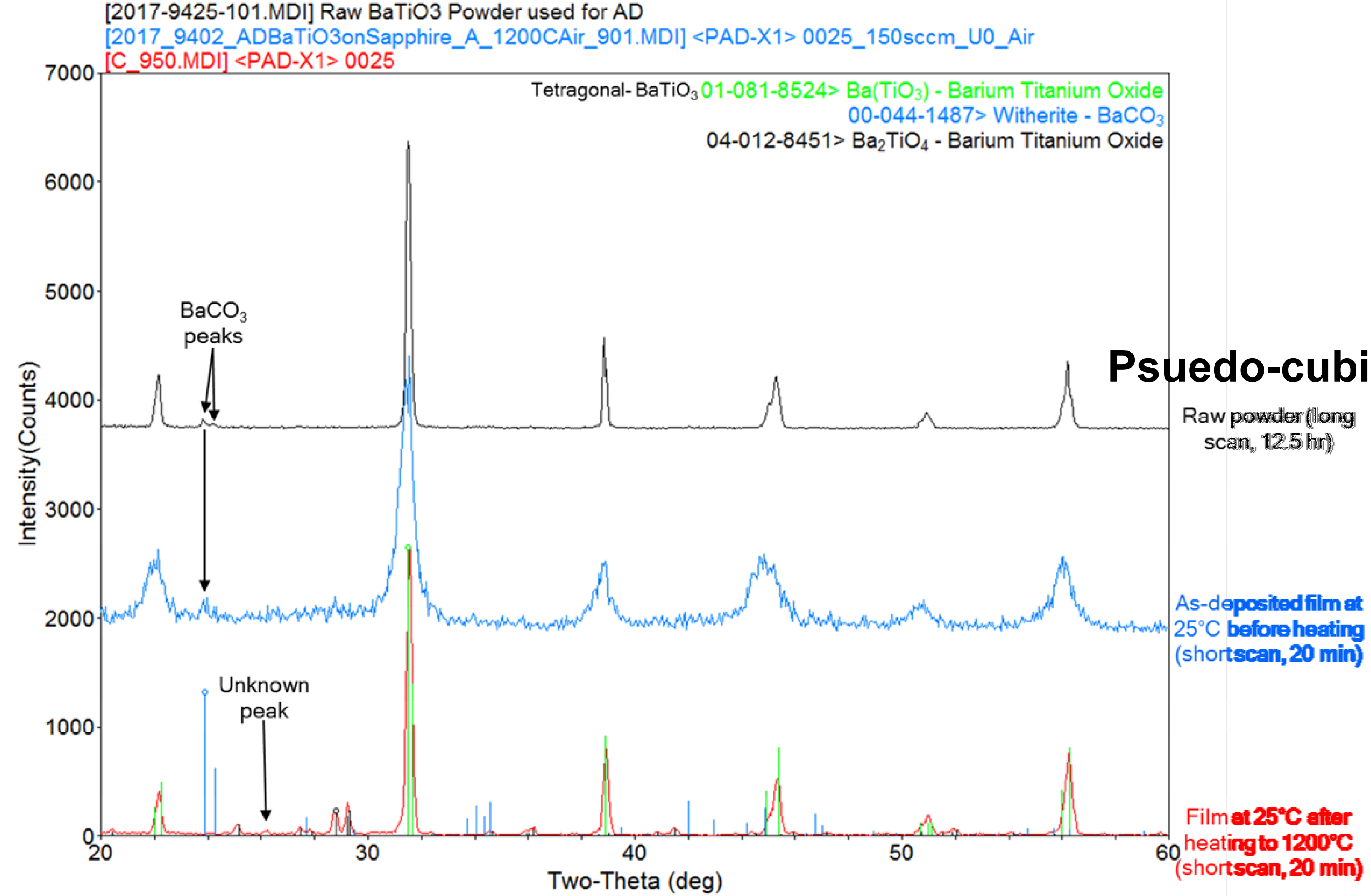


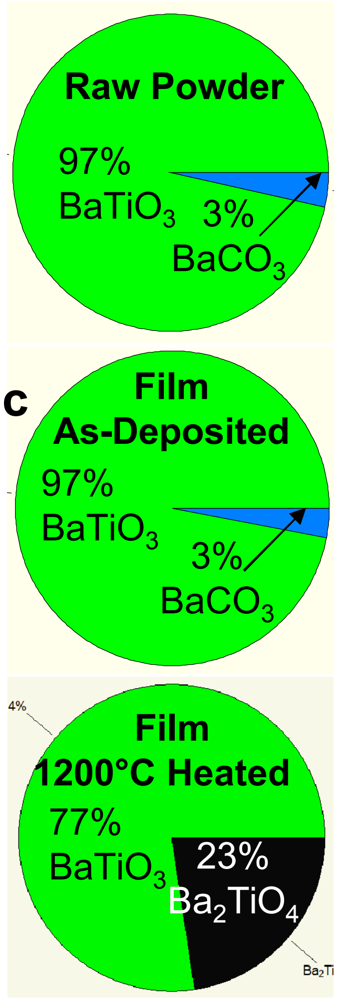
*AD built Cu and $BaTiO_3$ capacitor*

# XRD results – Composition & Phase

Commercially available “$BaTiO_3$” 0.4µm powder

wt% based on relative intensity





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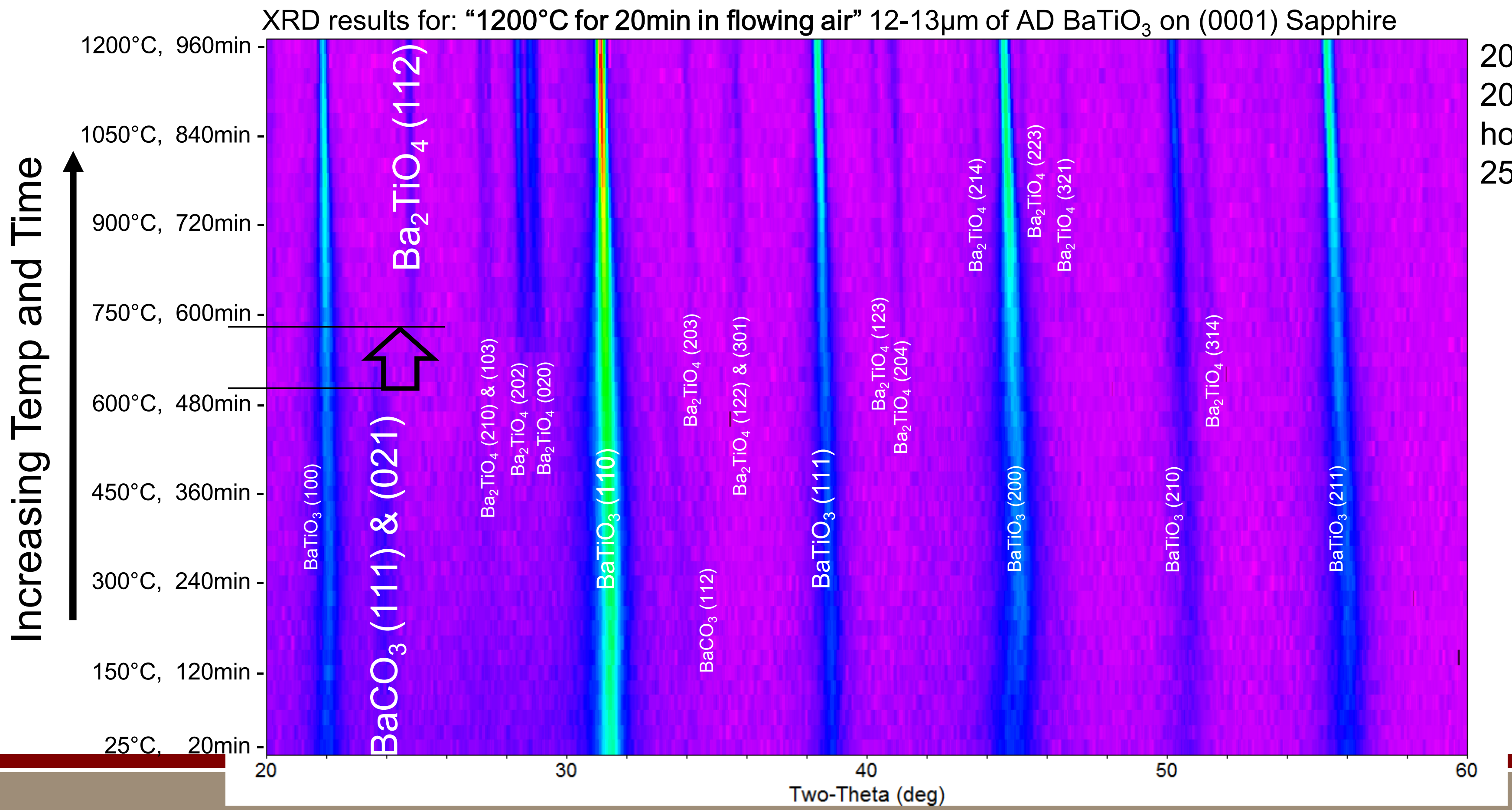
# XRD Measurement – Grain growth

- >700°C, $BaCO_3$ decomposes & $Ba_2TiO_4$ forms



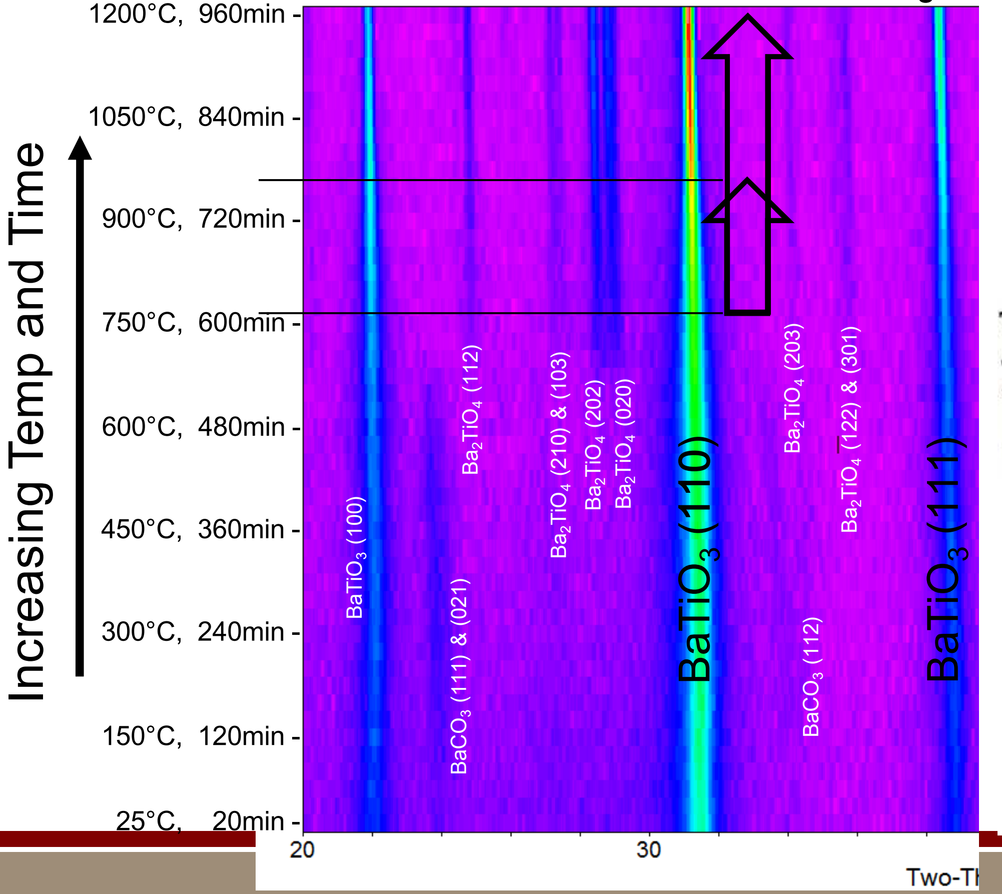
XRD results for: **“1200°C for 20min in flowing air”** 12-13µm of AD $BaTiO_3$ on (0001) Sapphire

20°C/min, 20 mins hold each, 25°C step

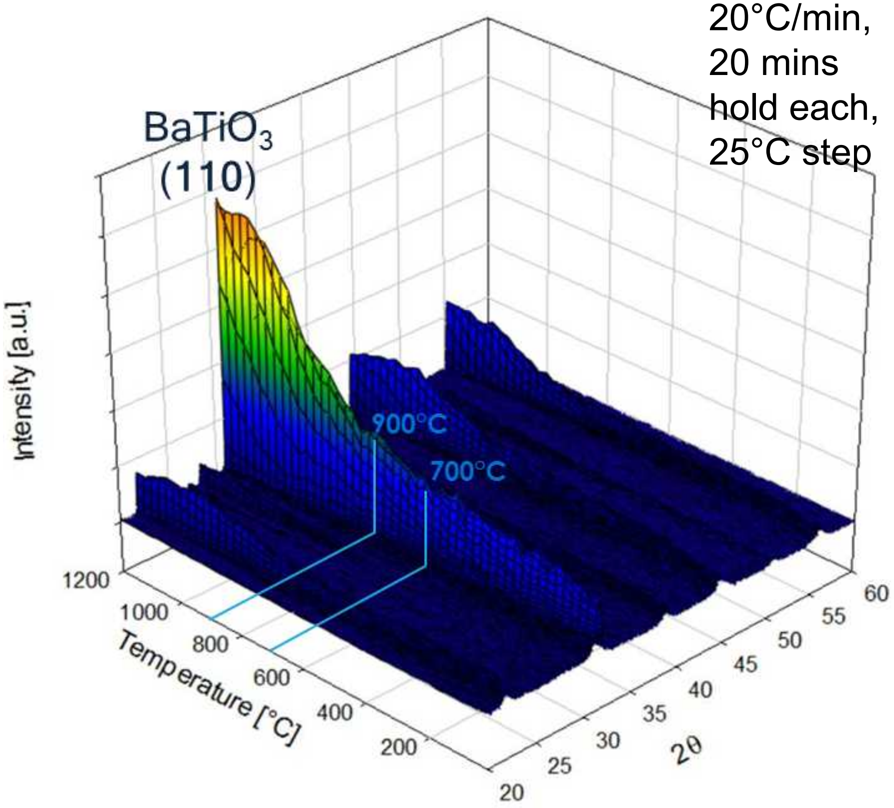
# XRD Measurement – Grain gr

- >700°C, $BaCO_3$ decomposes & $Ba_2TiO_4$ forms
- Band narrowing & increased intensity – Grain growth
- >900°C, see significant grain growth

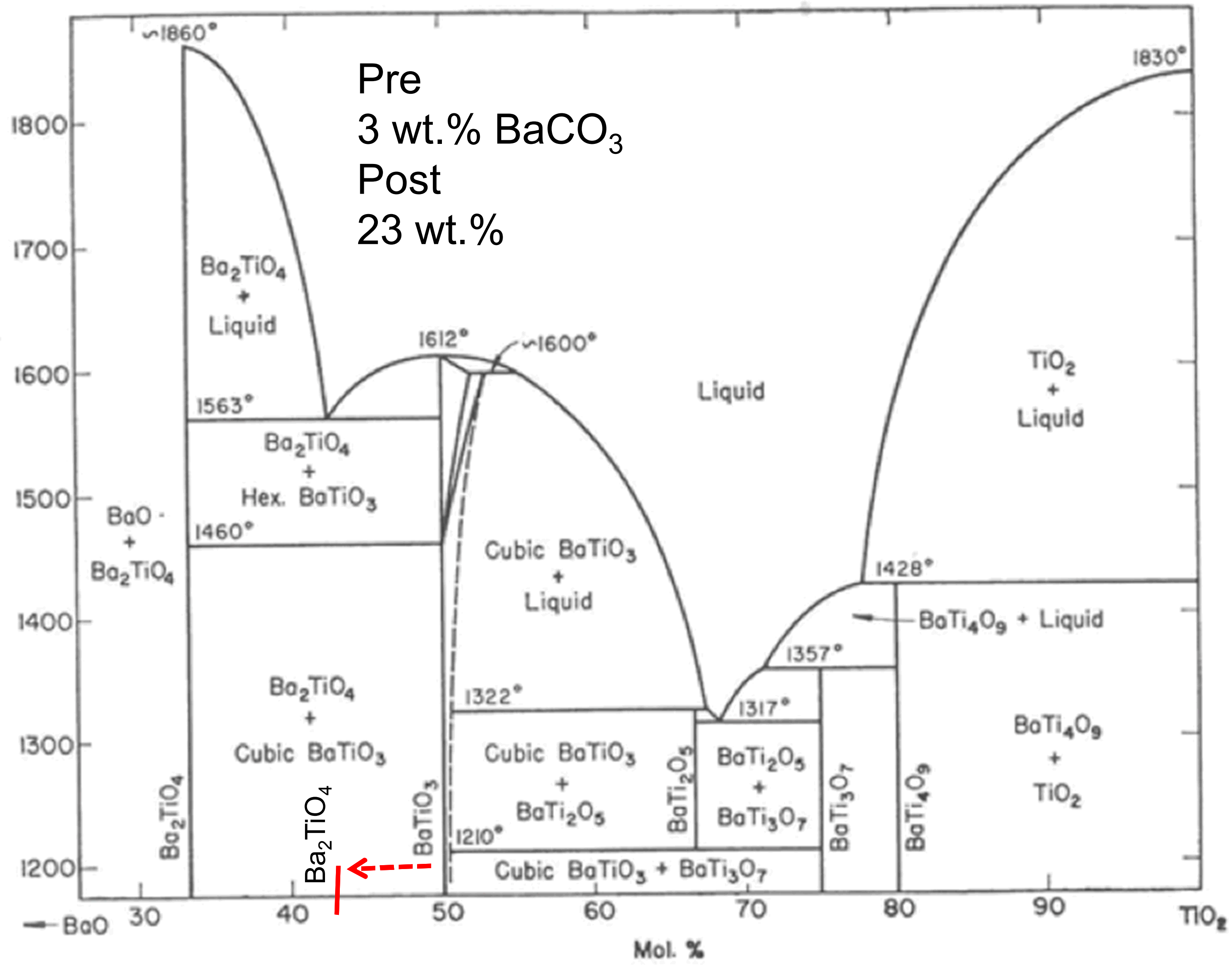
XRD results for: **"1200°C for 20min in flowing air"** 12-13µm of AD $BaTiO_3$ on (0001) Sapphire



20°C/min,
20 mins
hold each,
25°C step



# Only 1 at. % $BaCO_3$ excess produces $Ba_2TiO_4$



Pre

3 wt.% $BaCO_3$

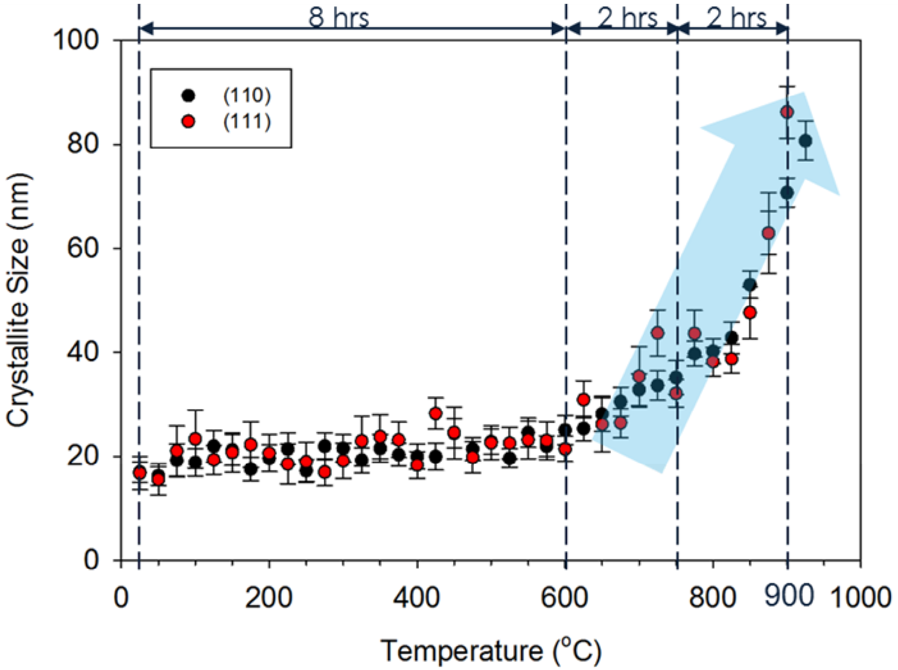
Post

23 wt.%

# 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

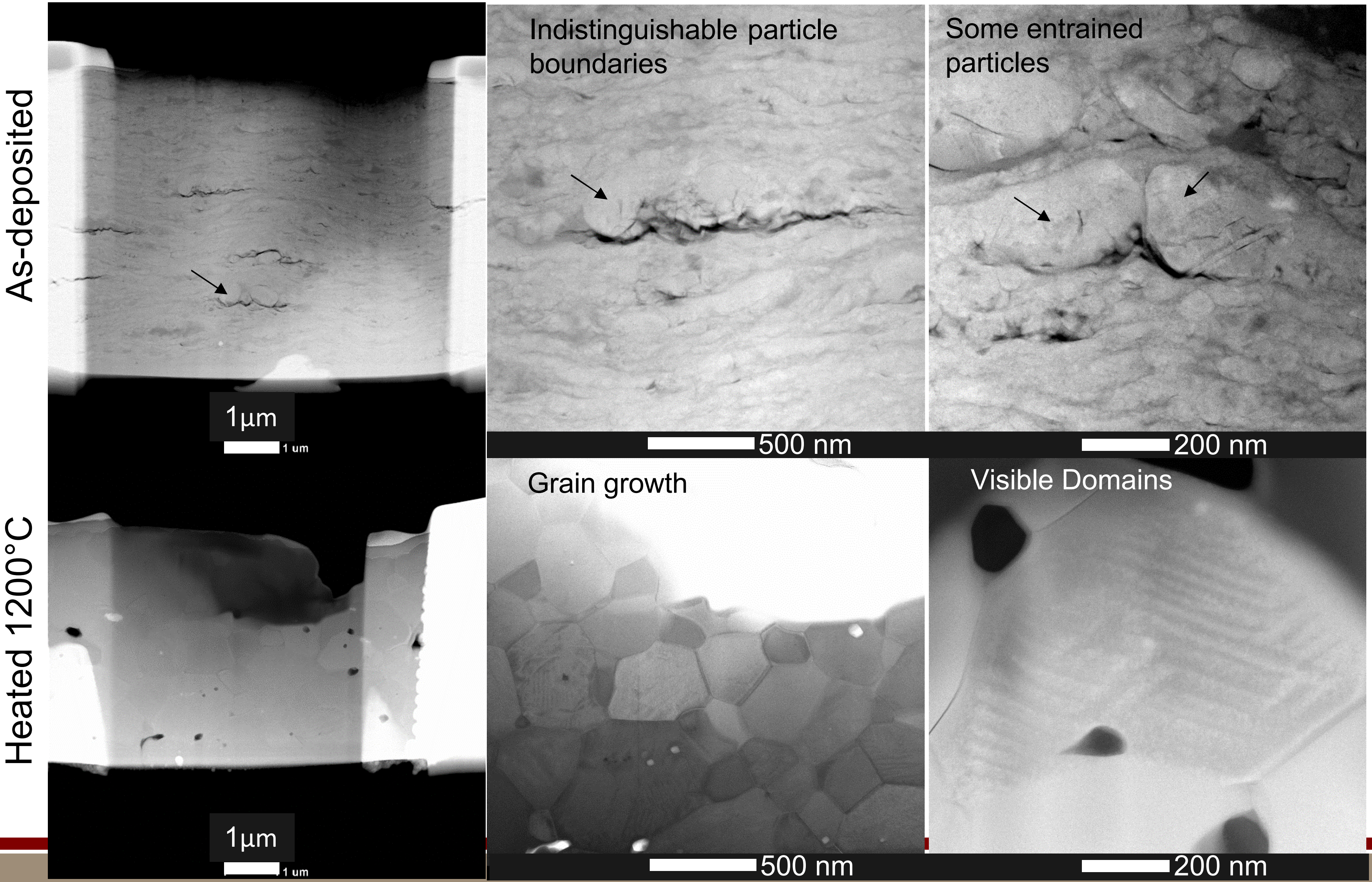
- Very little grain growth, even when held at 900°C for 16 hrs

| 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 |

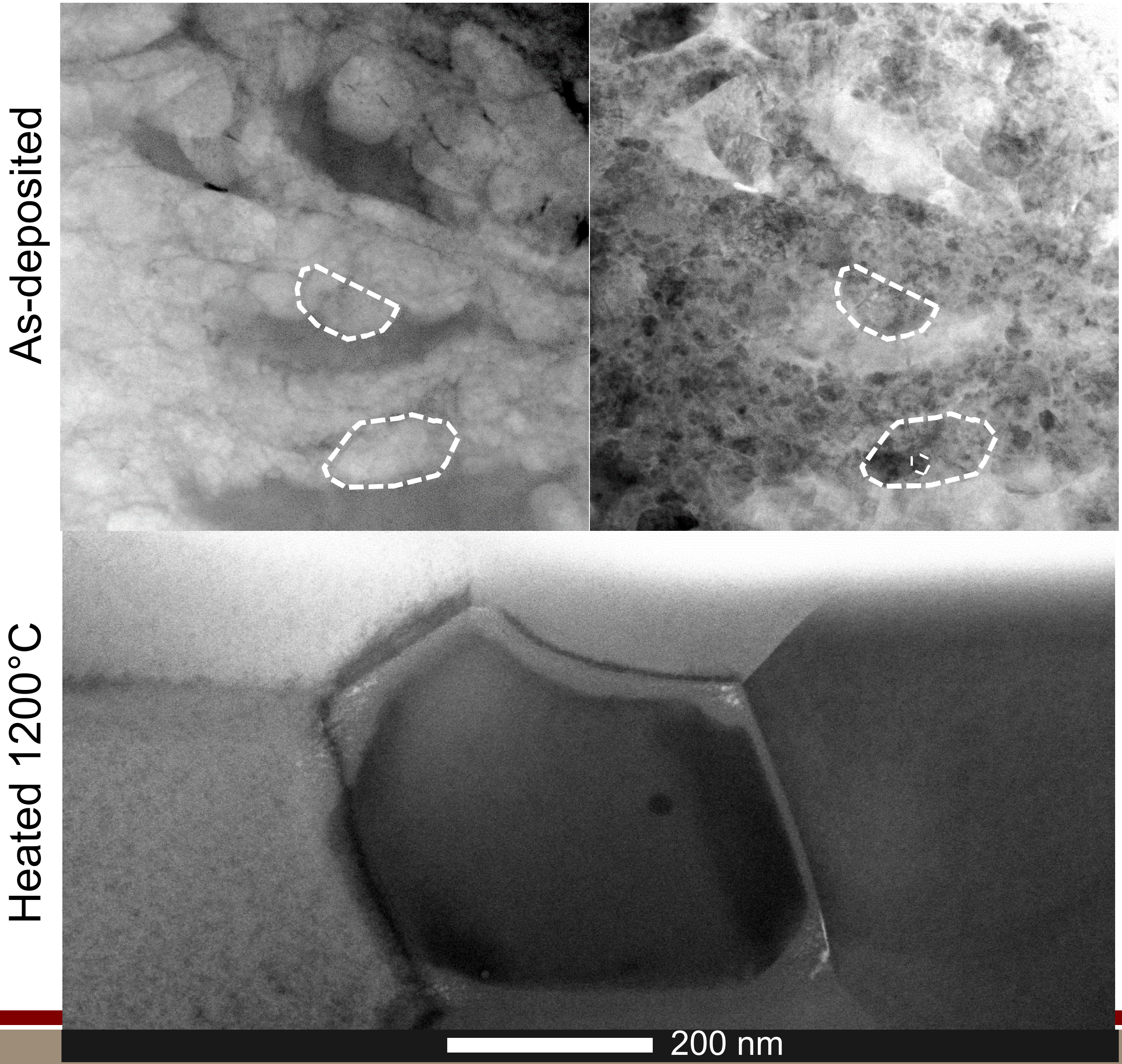
Isothermal hold at 900°C did not result in significant grain growth. Ramping temperatures appears to be more effective, providing higher growth rate.

**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).**

# Film Microstructures - FIB / TEM



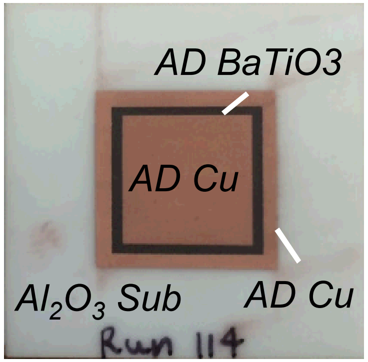
# Film Microstructures - FIB / TEM



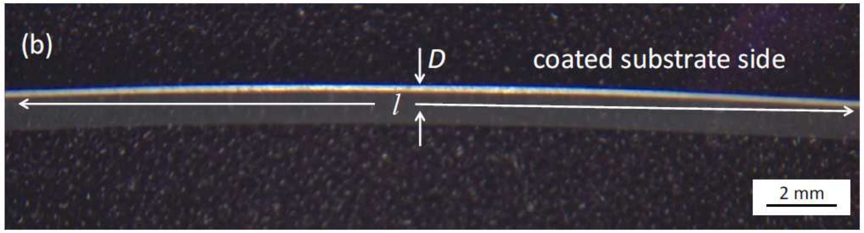
- As-deposited films showed
  - undefined particle boundaries
  - polycrystalline with crystallite size <30 nm
  - some entrained particles (not significantly deformed)
  - cracks
- After 1200° C heating
  - $Ba_2TiO_4$ segregation to grain boundaries
  - Grain growth
  - pores

# Residual Stress in AD films

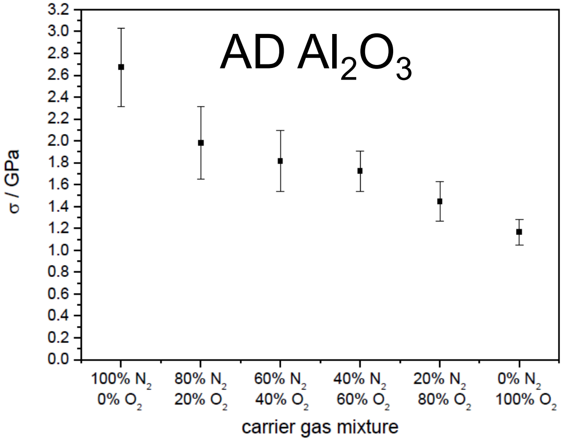
- Motivation for study
  - Multi-layer integration, device building utilizing AD films
  - Understand process parameter influence on stress, coating formation dynamics, and resultant properties
  - Additional method for accessing repeatability of process



- Common measurement techniques for thin/thick films
  - X-Ray diffraction ($\Psi^2$ 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

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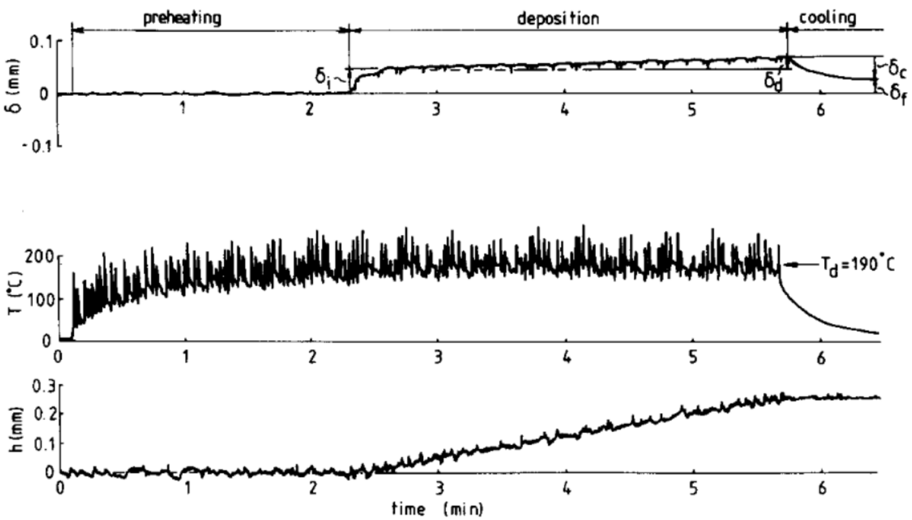
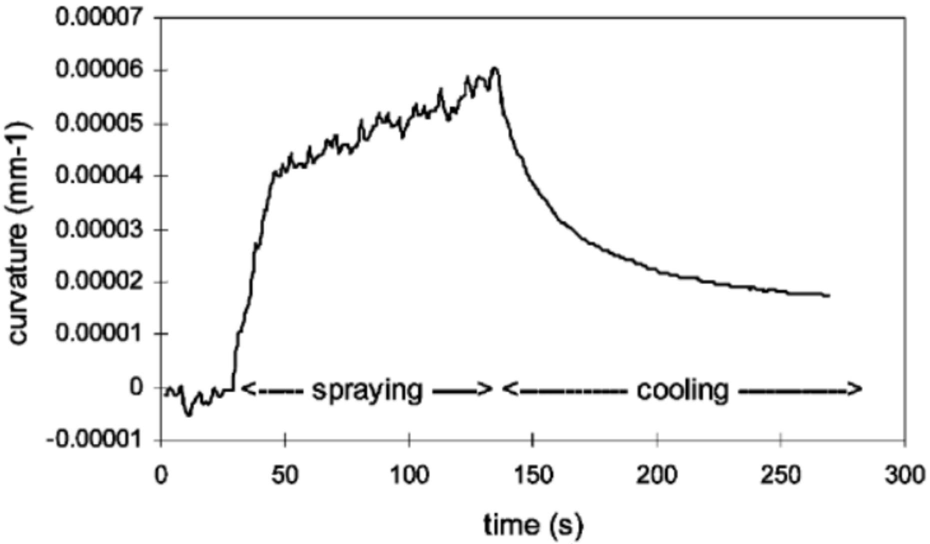
- Allows observation of coating dynamics in real time
- Discrete measurements of stress during deposition and cooling
- Response of stress to processing conditions


Image from ReliaCoat Technologies



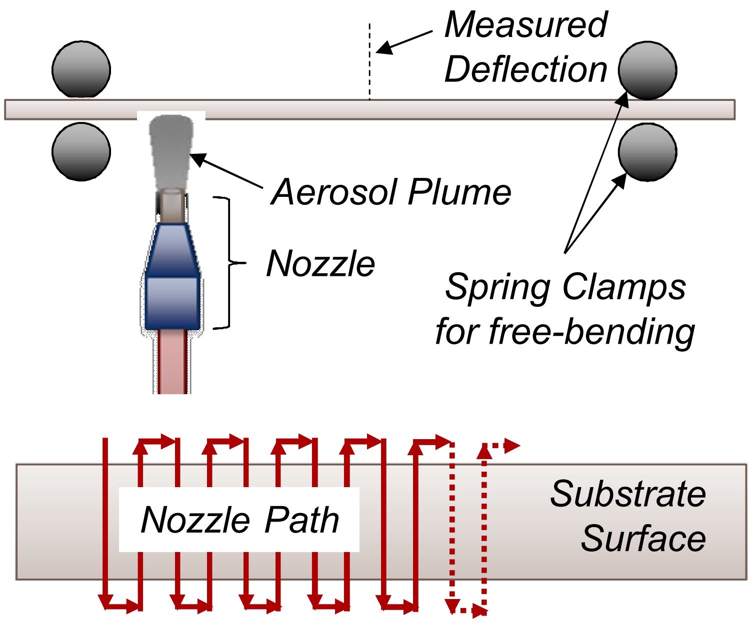
Kuroda, S., T. Fukushima, and S. Kitahara. "Simultaneous measurement of coating thickness and deposition stress during thermal spraying." Thin solid films 164 (1988): 157-163.

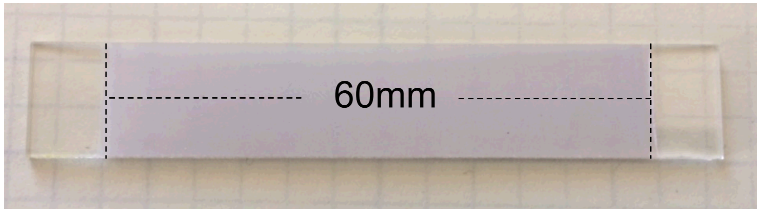


*Matejicek, J., et al. "In situ measurement of residual stresses and elastic moduli in thermal sprayed coatings: Part 2: processing effects on properties of Mo coatings." Acta Materialia 51.3 (2003): 873-885.*

# In-situ deflection monitoring of AD films

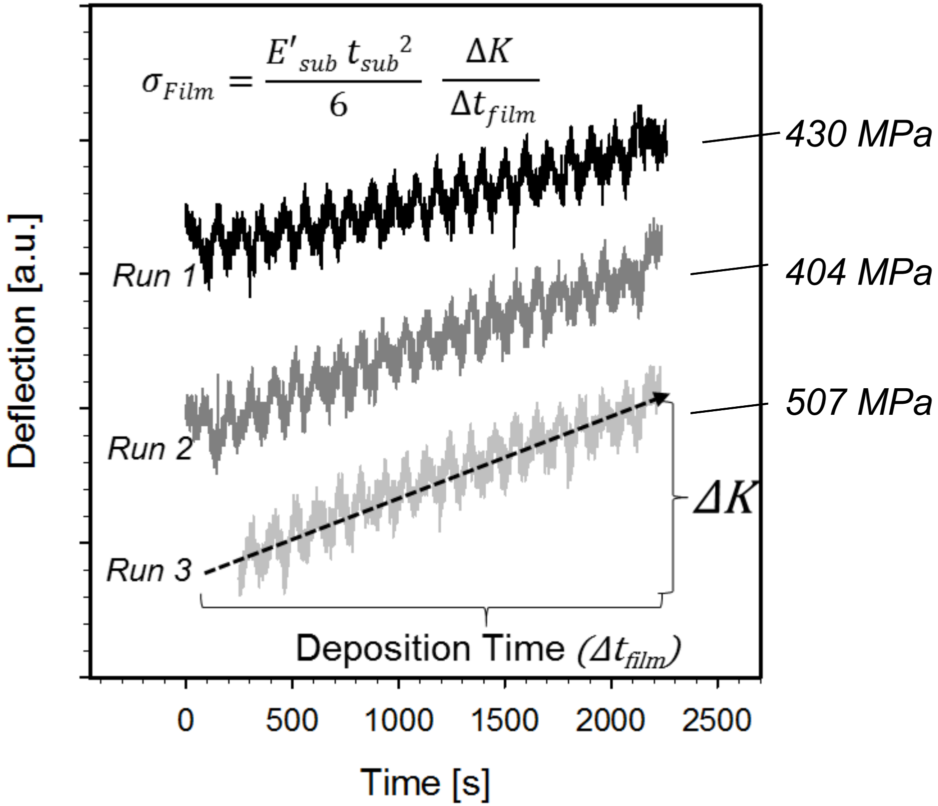
## Experiment Schematic





3-4 μm $BaTiO_3$ deposited onto soda lime glass

## Collected Data

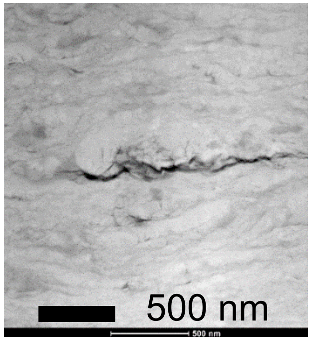


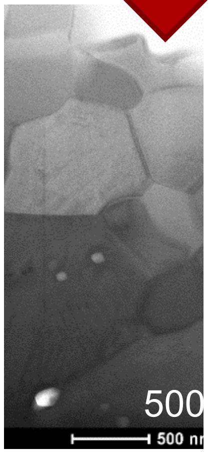
$$\sigma_{Film} = \frac{E'_{sub}\, t_{sub}^{2}}{6} \frac{\Delta K}{\Delta t_{film}}$$

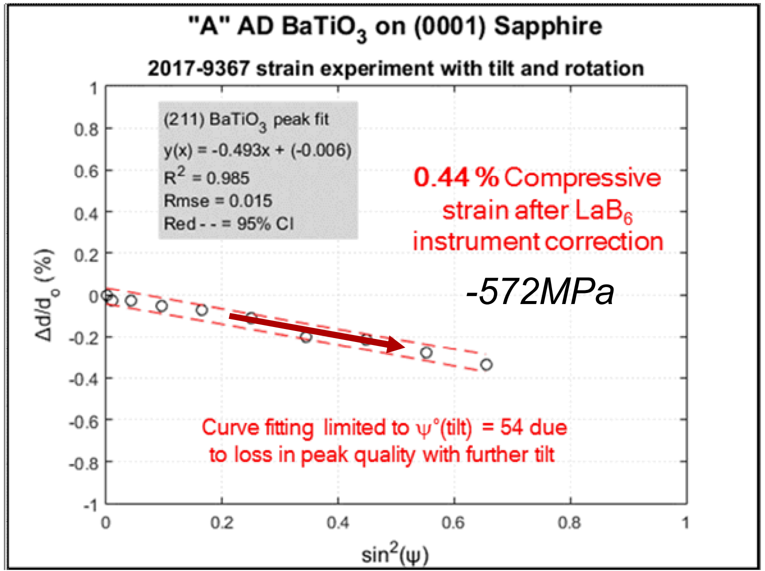
- *Linear substrate curvature is observed with AD film deposition*
- *No thermally induced substrate curvature after deposition*

# $\mathrm{Sin}^2\Psi$ XRD Measurement - Strain

8-10µm films on Sapphire






"A" AD $BaTiO_3$ on (0001) Sapphire

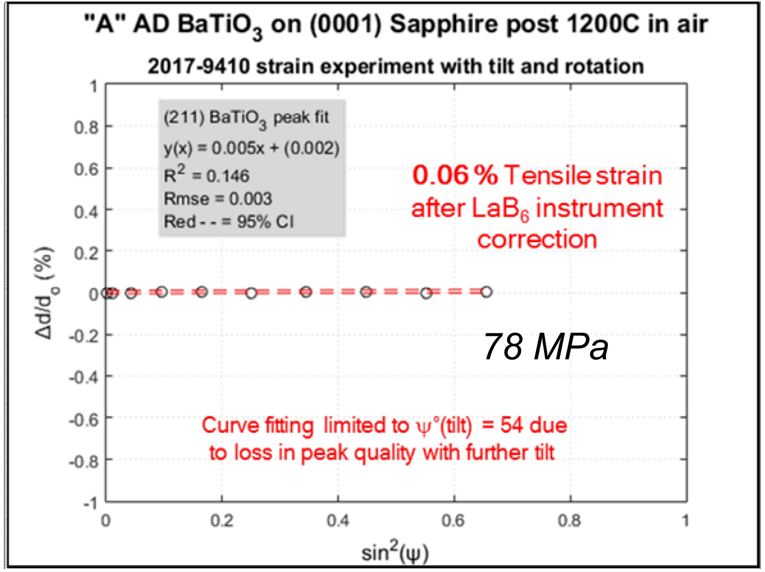
2017-9367 strain experiment with tilt and rotation

(211) $BaTiO_3$ peak fit
y(x) = -0.493x + (-0.006)
$R^2$ = 0.985
Rmse = 0.015
Red - - = 95% CI

0.44 % Compressive strain after $LaB_6$ instrument correction

-572MPa

Curve fitting limited to ψ°(tilt) = 54 due to loss in peak quality with further tilt


"A" AD $BaTiO_3$ on (0001) Sapphire post 1200C in air

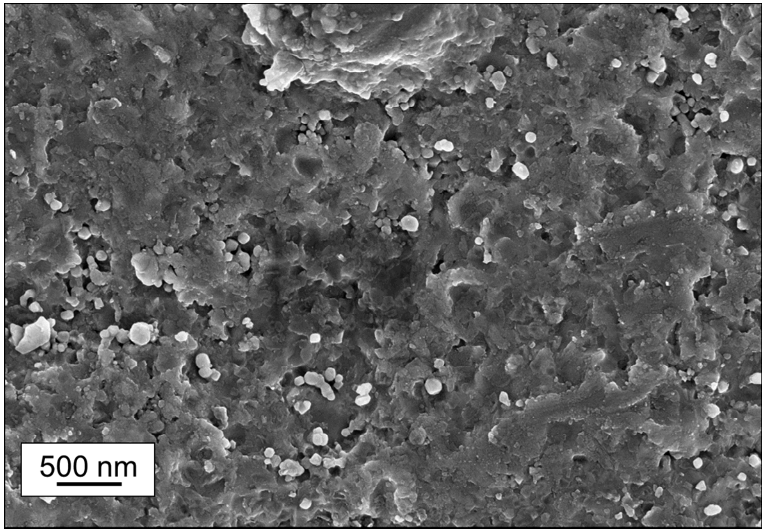
2017-9410 strain experiment with tilt and rotation

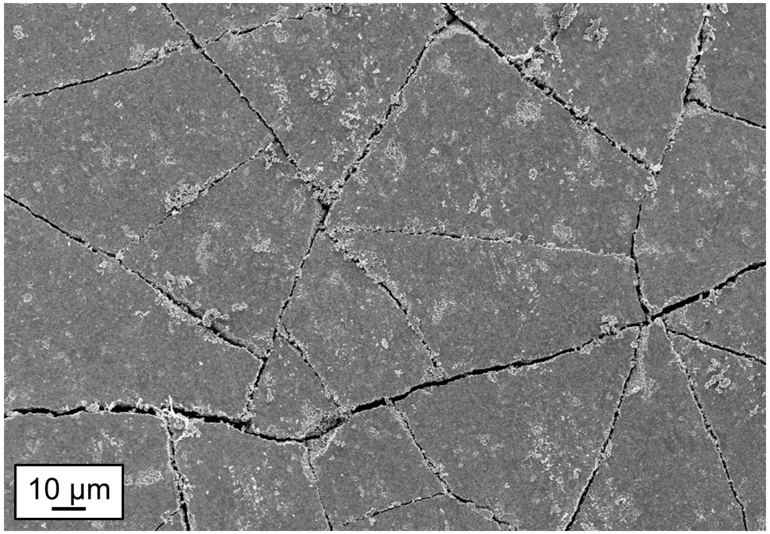
(211) $BaTiO_3$ peak fit
y(x) = 0.005x + (0.002)
$R^2$ = 0.146
Rmse = 0.003
Red - - = 95% CI

0.06 % Tensile strain after $LaB_6$ instrument correction

78 MPa

Curve fitting limited to ψ°(tilt) = 54 due to loss in peak quality with further tilt

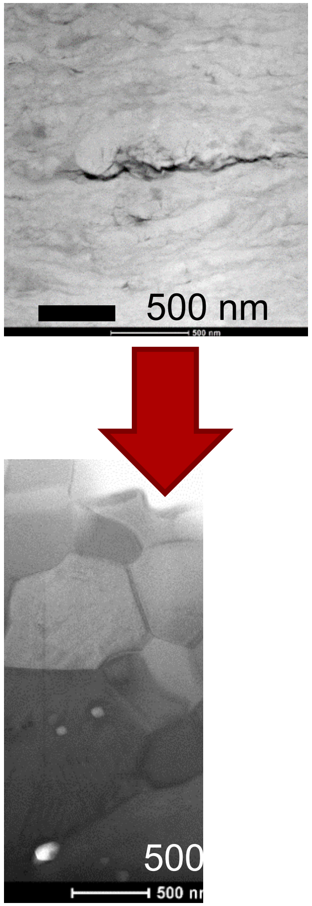


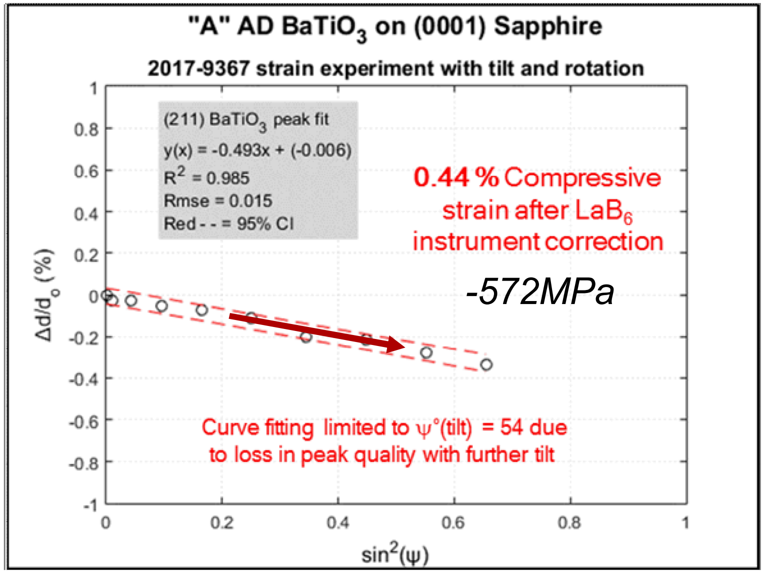


(211)

# $Sin^2\Psi$ XRD Measurement - Strain

8-10μm films on Sapphire

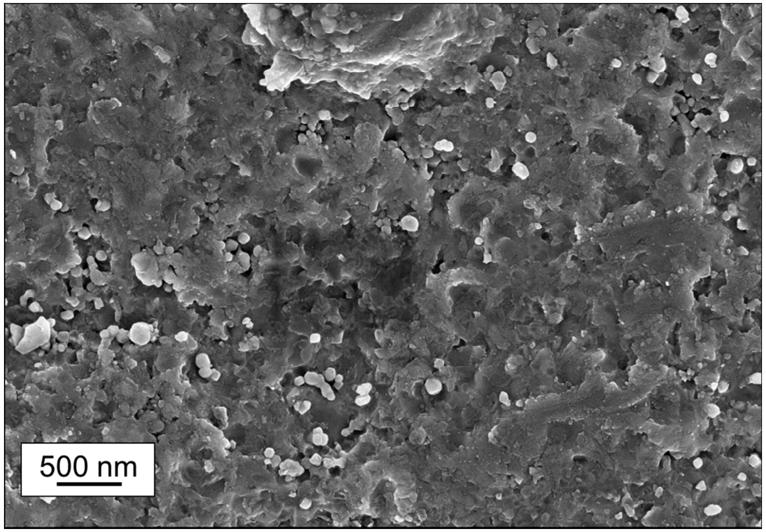


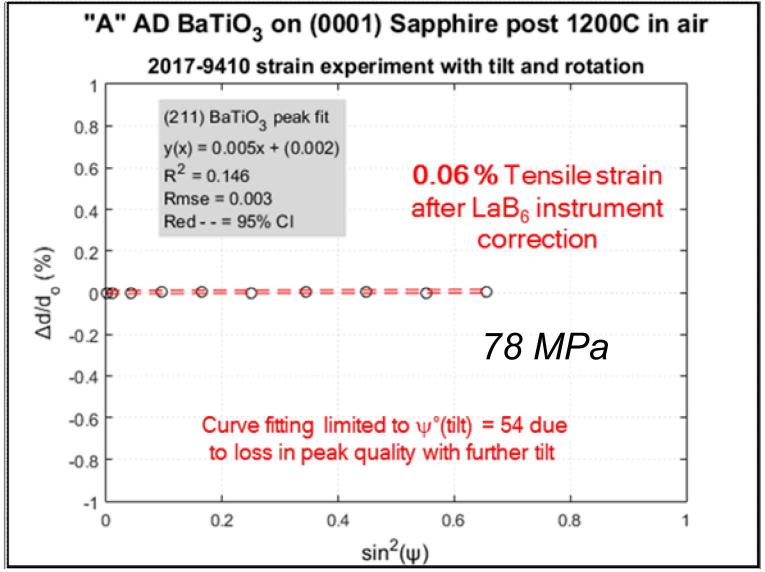


0.44 % Compressive strain after $LaB_6$ instrument correction

-572MPa

Curve fitting limited to ψ°(tilt) = 54 due to loss in peak quality with further tilt

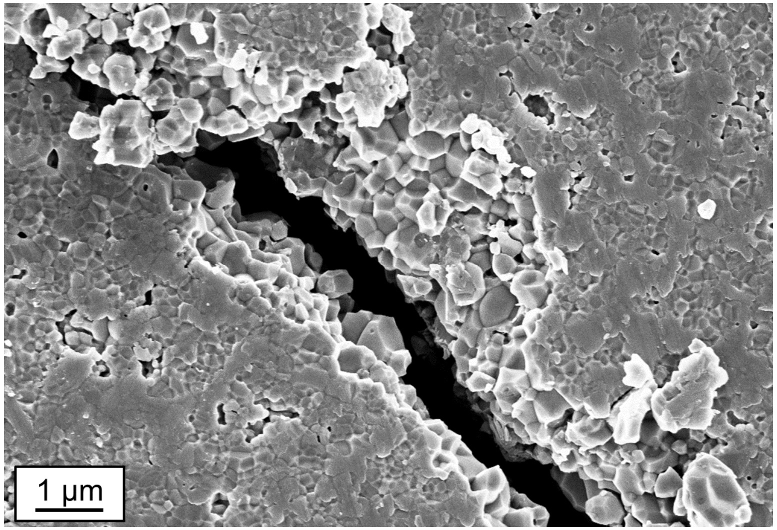




0.06 % Tensile strain after $LaB_6$ instrument correction

78 MPa

Curve fitting limited to ψ°(tilt) = 54 due to loss in peak quality with further tilt



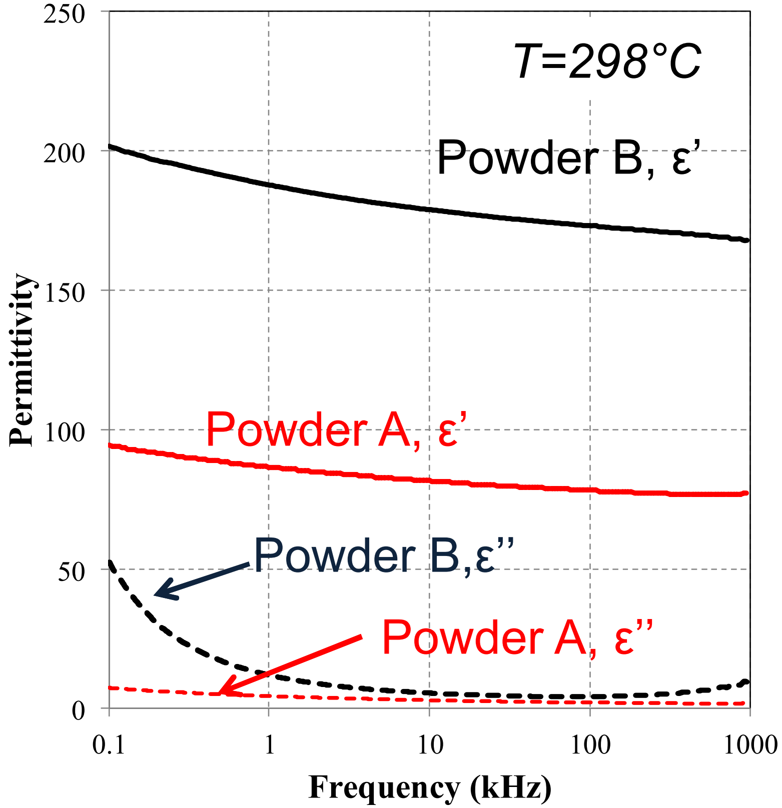
(211)

# Electrical Properties – As-Deposited Feedstock Comparison

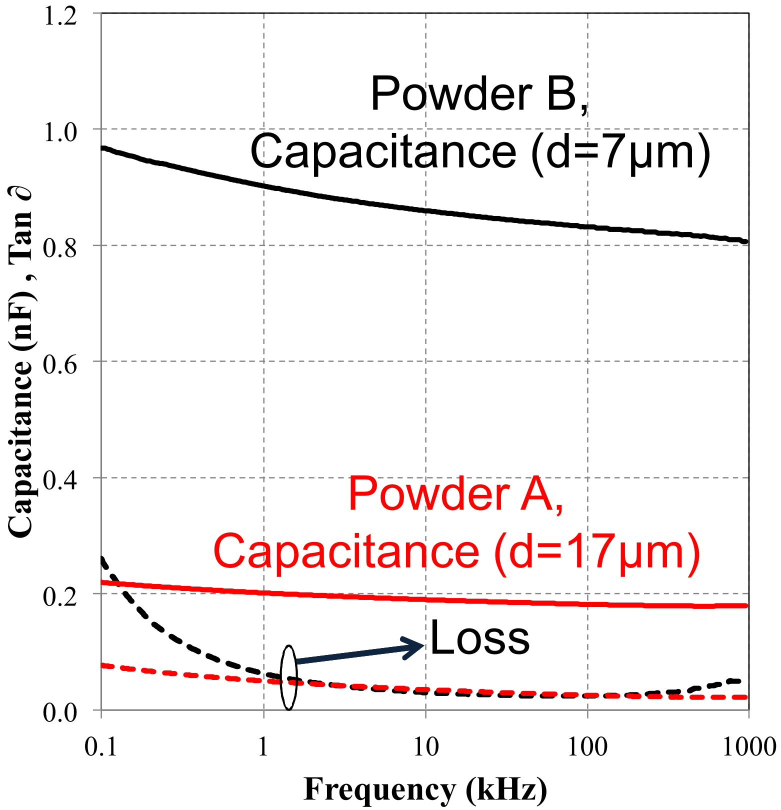
- 2 different powders, 2 different responses
  - Powder A – psuedo cubic
  - Powder B – tetragonal?
- As deposited films exhibit k<200
- Low frequency loss (space charge) observed in Powder B films

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

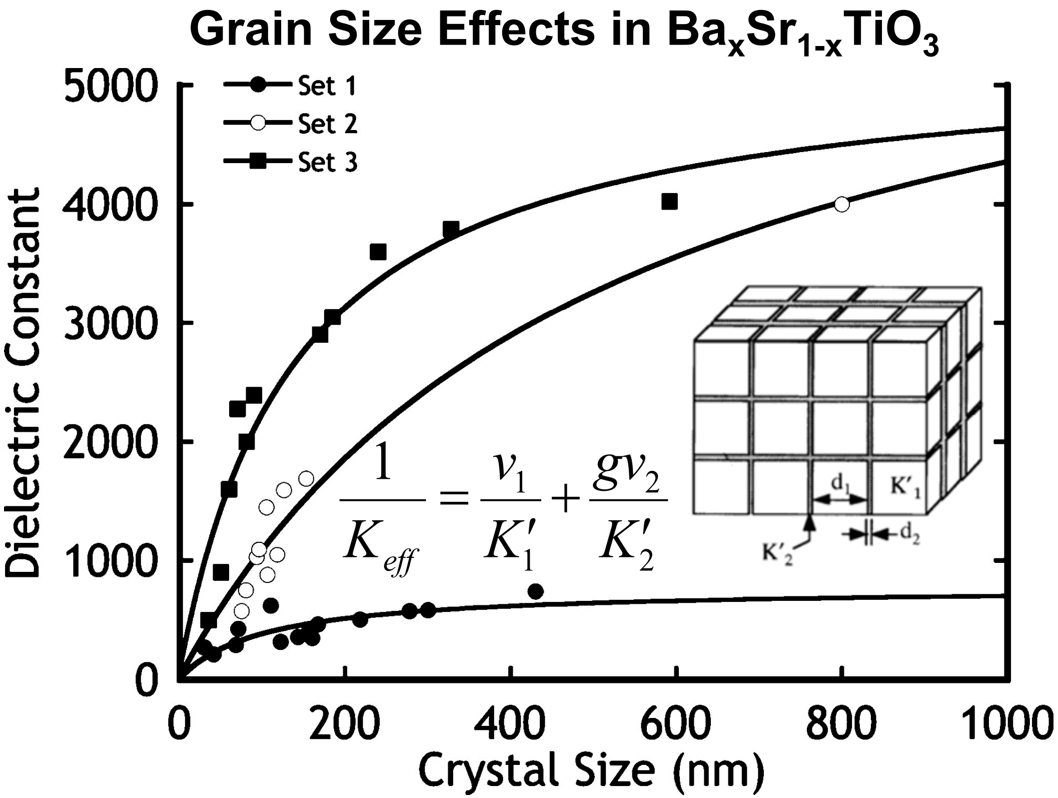
**Dielectric Permittivity**



**Capacitance and Loss**



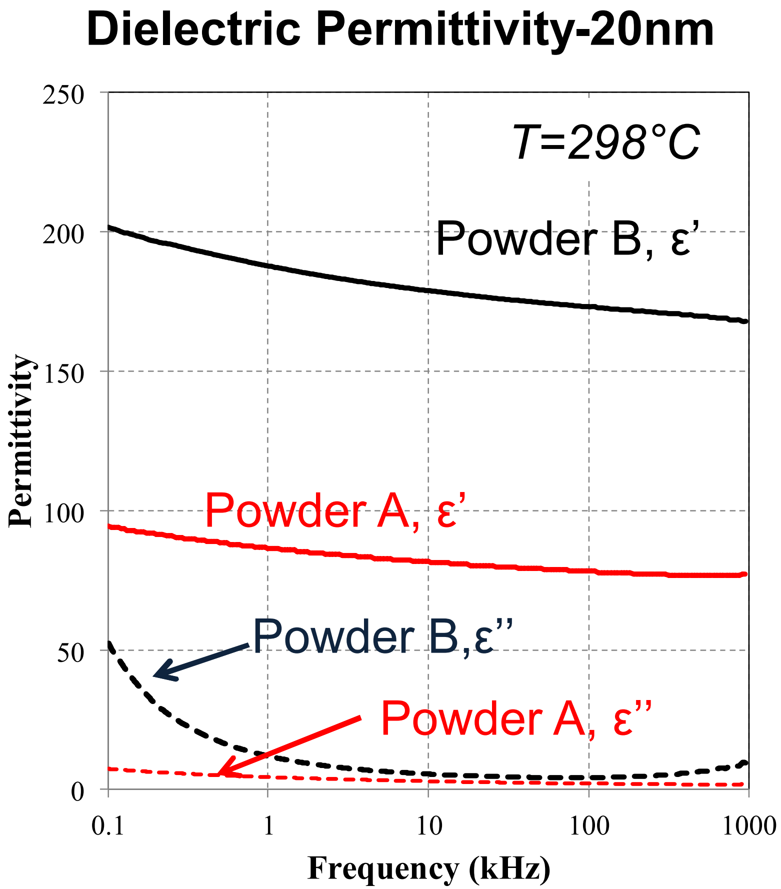
# Brick-wall model and size effects



Grain Size Effects in $Ba_xSr_{1-x}TiO_3$

$$\frac{1}{K_{eff}} = \frac{v_1}{K'_1} + \frac{g v_2}{K'_2}$$

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



Dielectric Permittivity-20nm

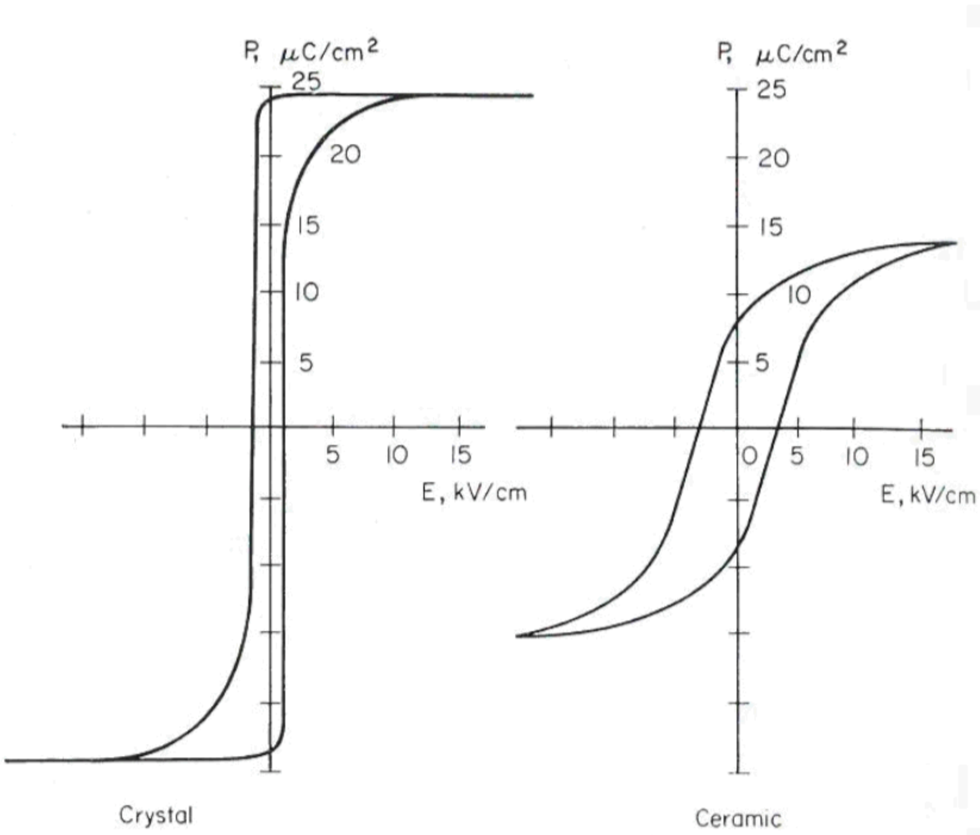
- A permittivity of the AD $BaTiO_3$ (k~100-200) agrees well with brick-wall theory
- Significant dilution from grain boundaries. Grain growth is required to increase permittivity.

# P-E Loops indicate paraelectricity

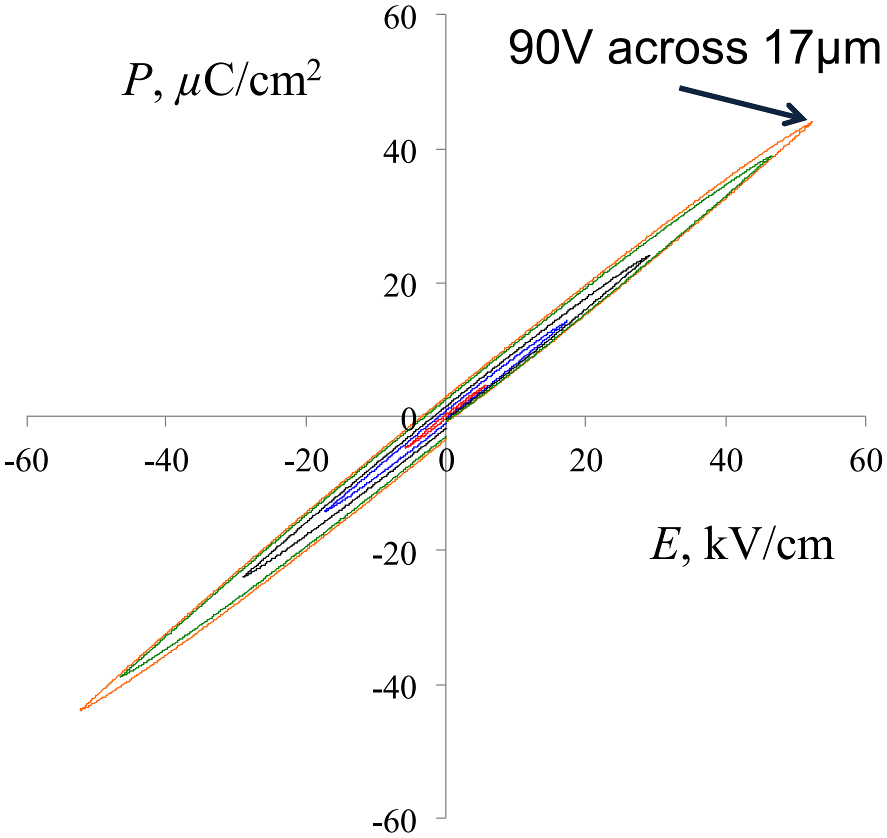
- Pseudocubic nanocrystallinity generates linear dielectric response
- Nested loops show negligible hysteresis that is caused by conduction
- Voltage withstanding suggests no thru cracks are present

$BaTiO_3$ (100) Crystal

$BaTiO_3$ Ceramic



17µm $BaTiO_3$ AD Film, Powder A



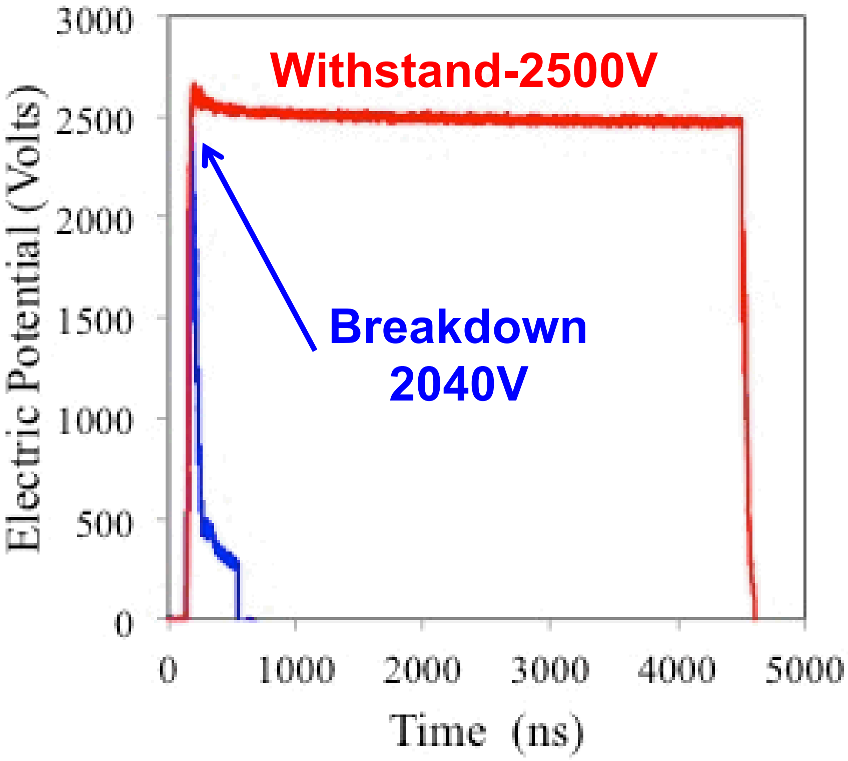
90V across 17µm

Jaffe, Cook and Jaffe, *Piezoelectric Ceramics pp. 78 (1971).*

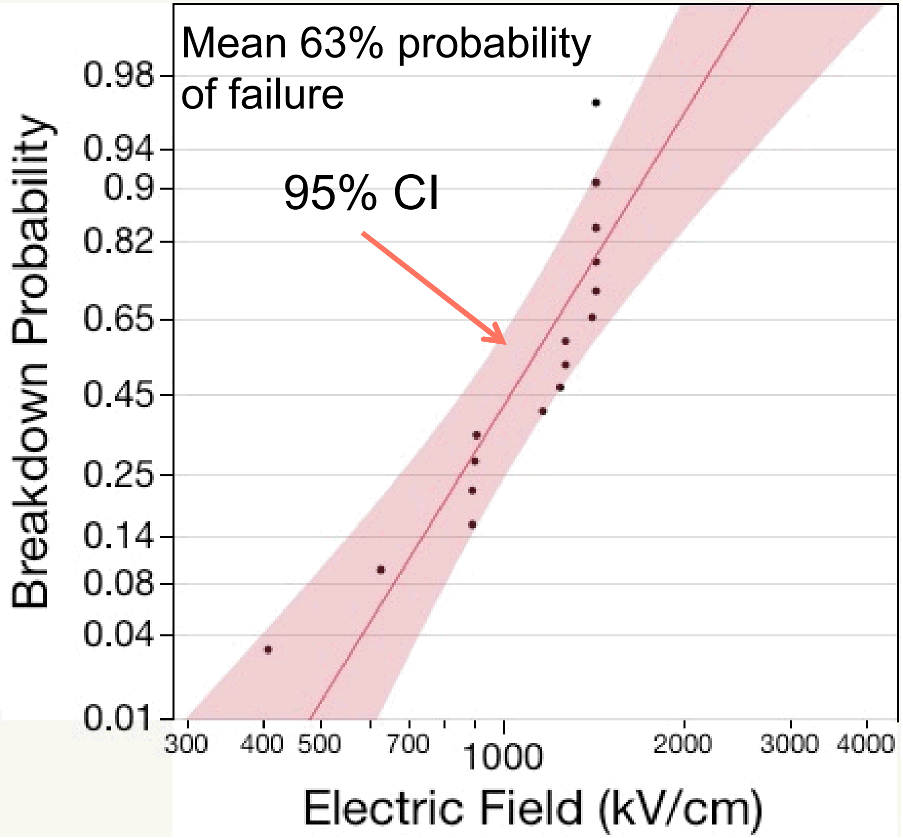
# Fast Rise Breakdown (FRB) of As-Deposited Films

FRB is a fast voltage transient measurement-100ns rise and 4.5µs pulse width

FRB Voltage Transient



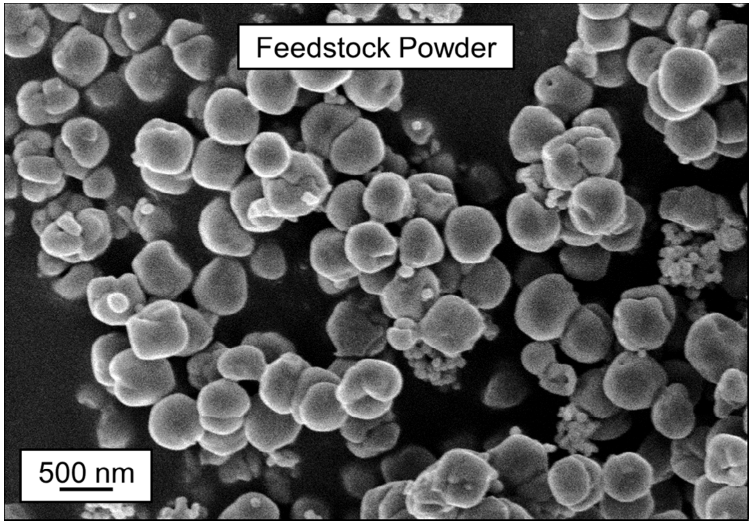
17µm Thickness
Weibull Failure Statistics n=16, 95%CI

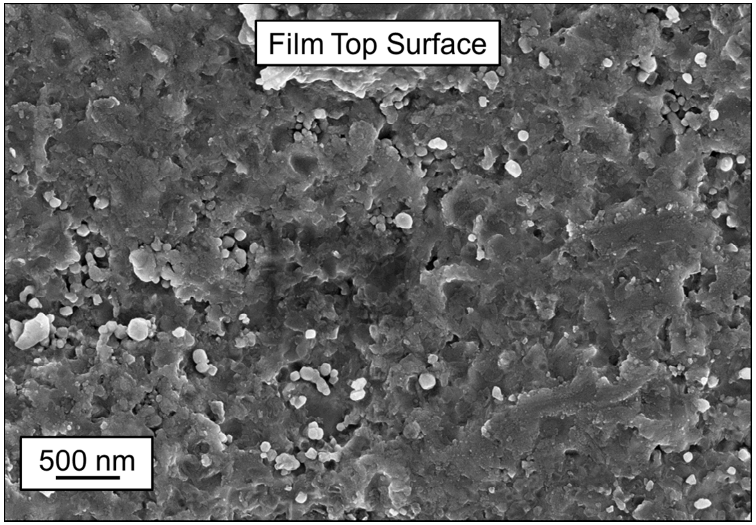


Breakdown strength is very high, 400 - 1400 kV/cm for a 17 µm film.
**FRB energy densities range from ~0.75 $\text{J/cm}^3$ to >9.1 $\text{J/cm}^3$
**Note, ***not*** a DC measurement.

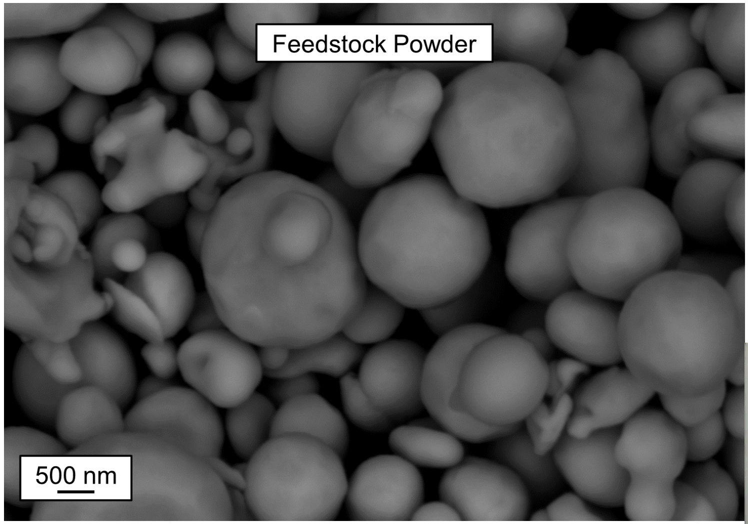
# Other AD materials - Cu

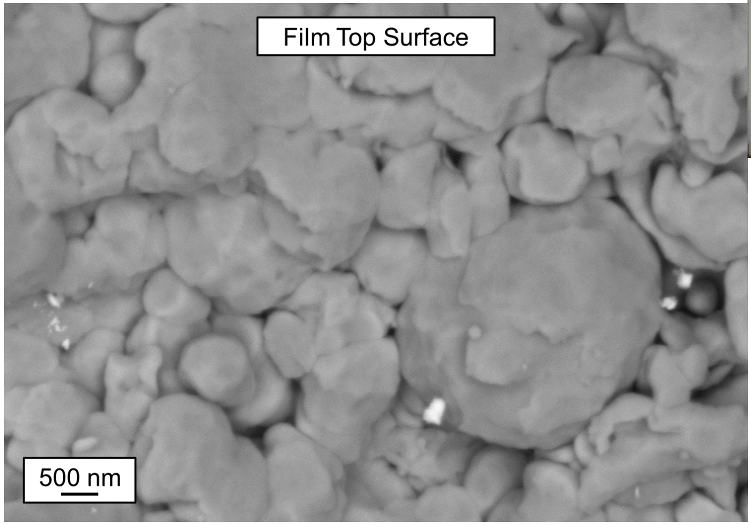
**$BaTiO_3$**

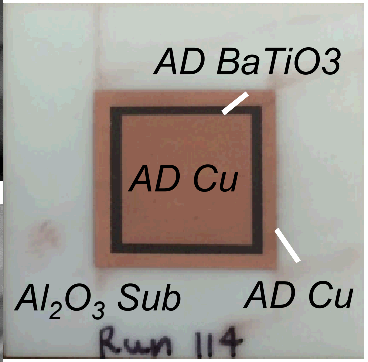




**Cu**

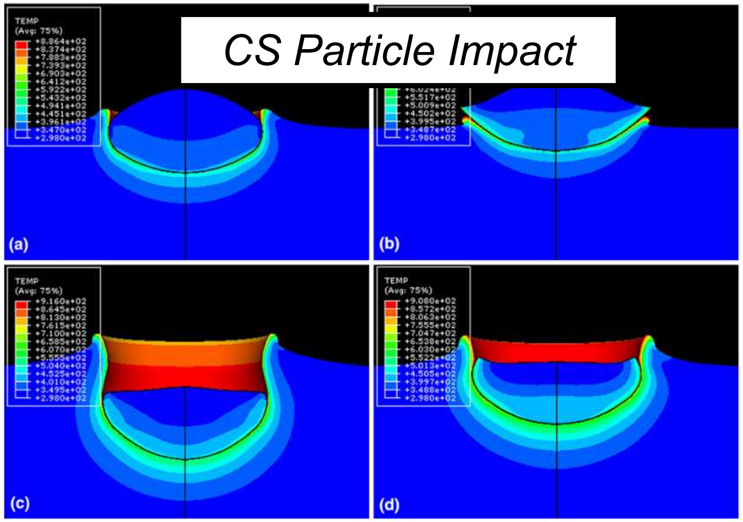




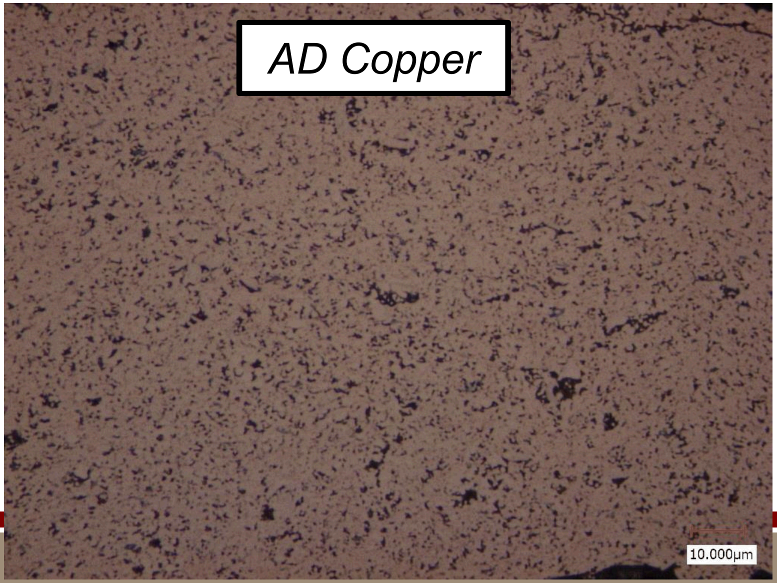


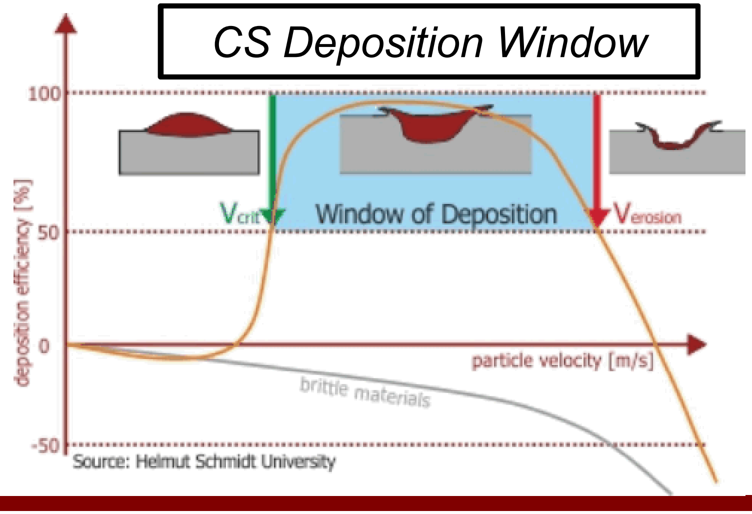
# Similarities and Contrast to Cold Spray (CS)

- 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 5-25μm
    - AD 0.1-5μm
- Higher resistivity (10-25x) than bulk


*CS Particle Impact*

*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.*


*AD Copper*


*CS Deposition Window*

# Summary

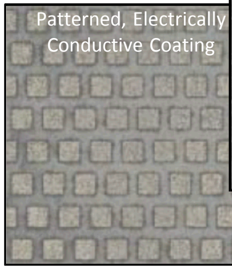
a) **AD produces dense nanocrystalline functional films at room temp, enabling integration with low temp materials.**
   i. Great for structural and environmental protection applications.
   ii. Grain size can be tuned after deposition through heat treatment.

b) Submicron sized ceramic particles can undergo dislocation plasticity under quasi-static loading and high strain-rate loading.

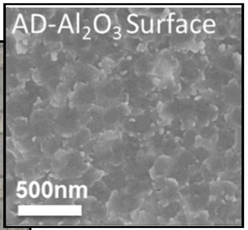
c) Aerosol Deposition (AD) leverages (b)—submicron particles accelerated, impacted, deformed, and consolidated as films.

d) AD $BaTiO_3$ for capacitor application: In progress

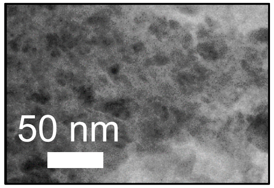
e) AD Copper for conductive film: In progress



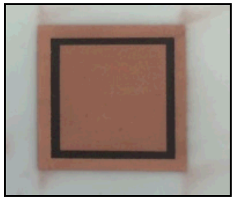
40 µm thick, patterned Ni interconnects



150 nm thick $Al_2O_3$ coating



Nanocrystalline AD $BaTiO_3$

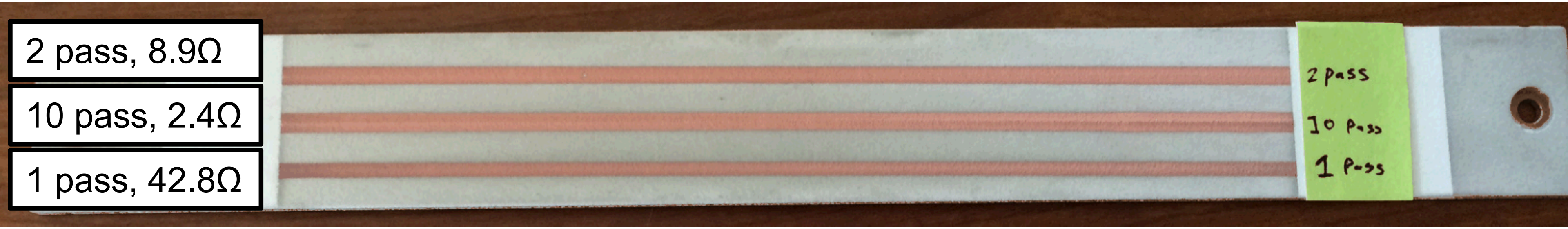

Alternating AD Cu & $BaTiO_3$ layers.

| | **As-Deposited** | **Annealed** | **Note** |
|---|---|---|---|
| Grain size | 15-30 nm | 90 nm (900°C, 16 hrs)<br>>500 nm (ramp to 1200°C) | Need >100nm. Significant growth @>900°C |
| In-plane Strain | Comp 0.4% | Comp 0.06% (ramp to 1200°C) | Strain relaxation from annealing. |
| K | <200 | FUTURE WORK | Will increase with annealing |
| P-E Loop | Lossy linear dielectrics | FUTURE WORK | Will exhibit ferroelectricity with annealing |
| FRB | 400 - 1400 kV/cm | FUTURE WORK | Extremely high compared to 70-100 kV/cm! |

# extras

$$\sigma = \frac{4Ed^2}{3(1-\nu)l^2} \cdot \frac{D}{t}$$

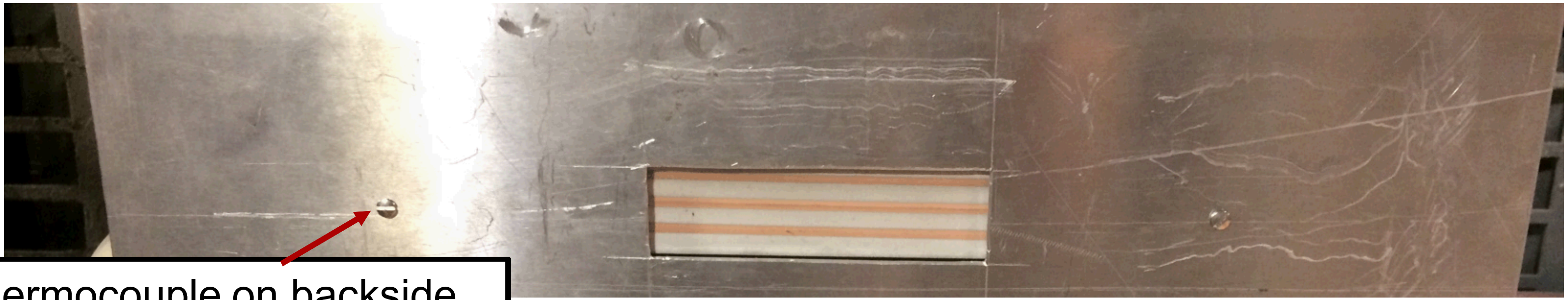
# Cu on APS Ceramic

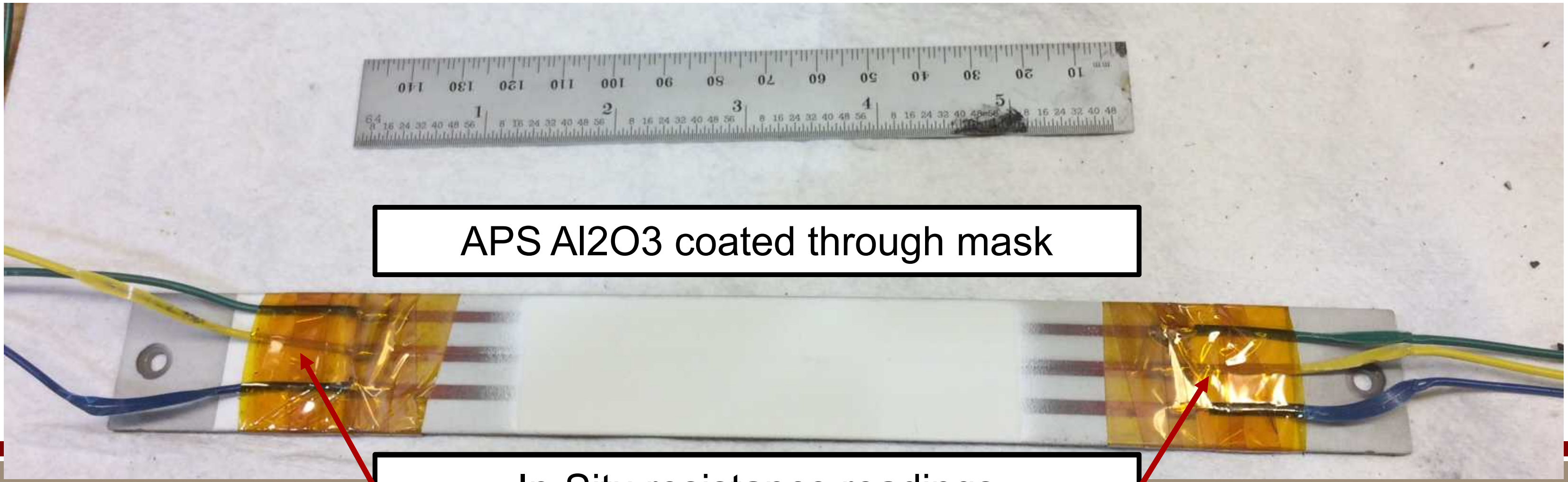

2 pass, 8.9Ω

10 pass, 2.4Ω

1 pass, 42.8Ω

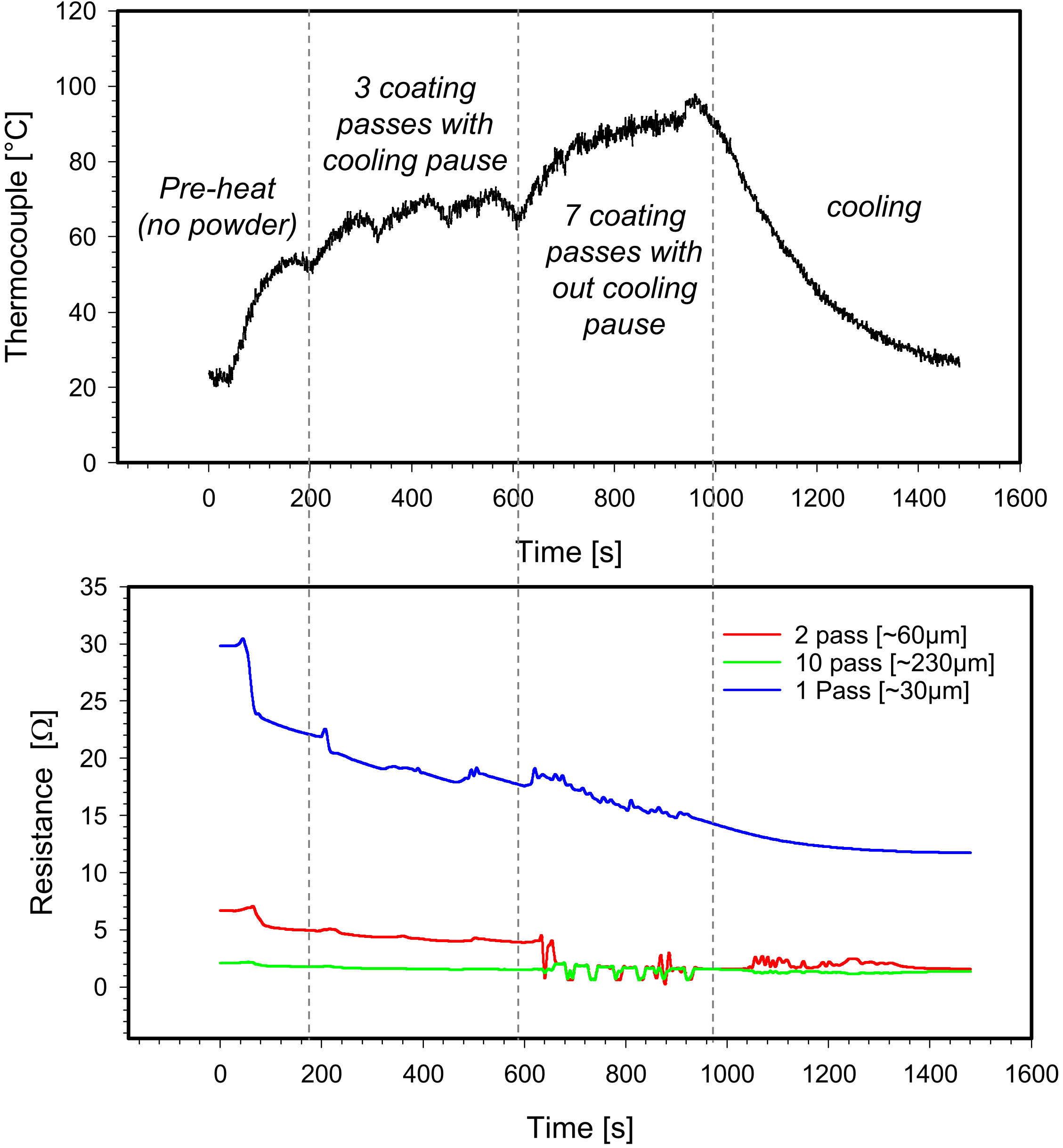
*Measured by multi-meter probes*


Thermocouple on backside

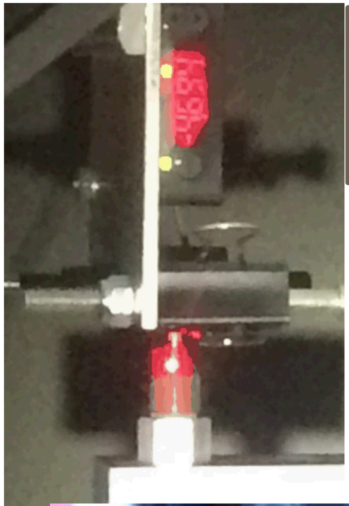

APS Al2O3 coated through mask

In-Situ resistance readings

# Embedding Cu traces

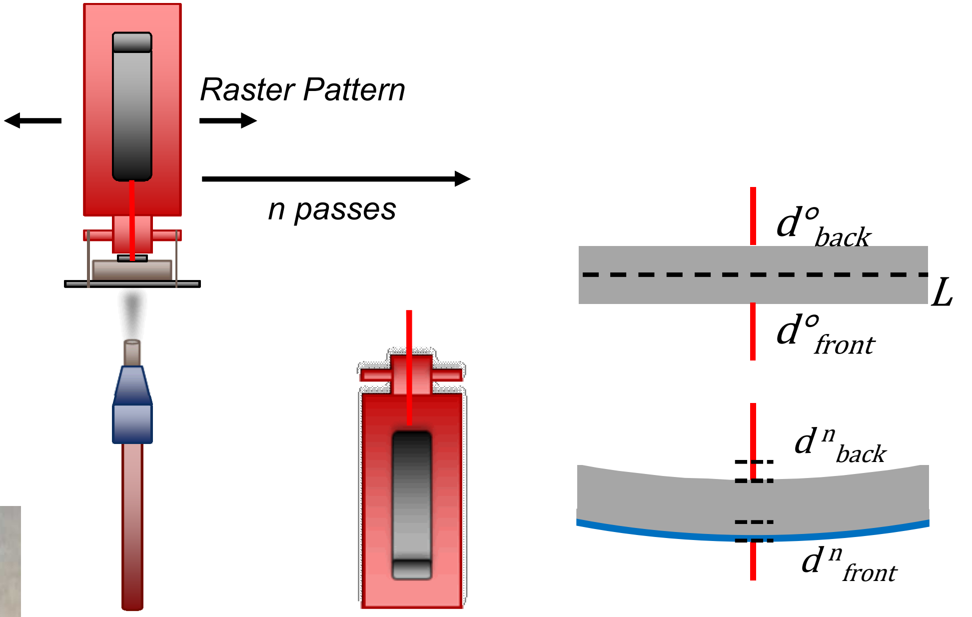


# Experimental setup for substrate deflection from AD films



Center Point : 30mm
Range : ± 4mm
Resolution: ± 1µm

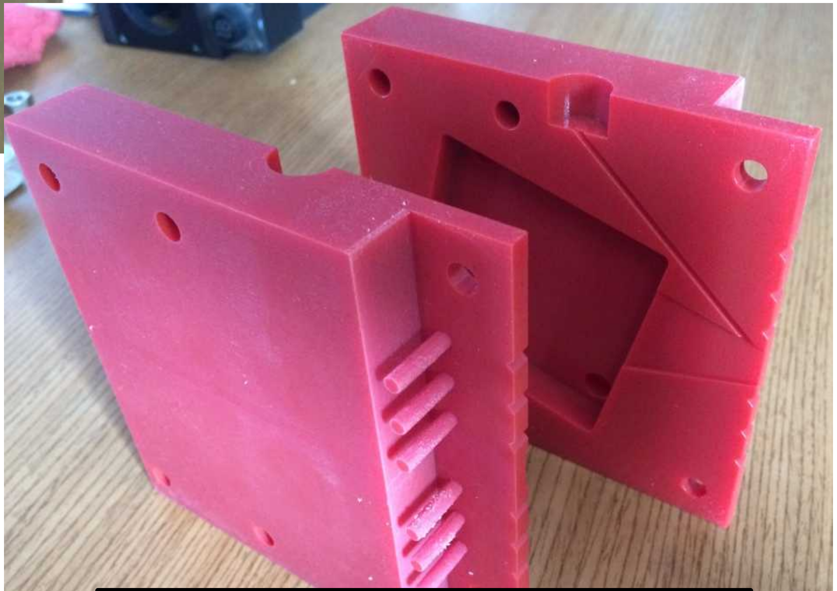
Preliminary measurements and feasibility



$$t^n_{film} = d^o_{front} - d^n_{front} - d^n_{back}$$

$$K^n = \frac{2\ dnfront}{{d^n_{front}}^2 + \frac{L^2}{4}}$$

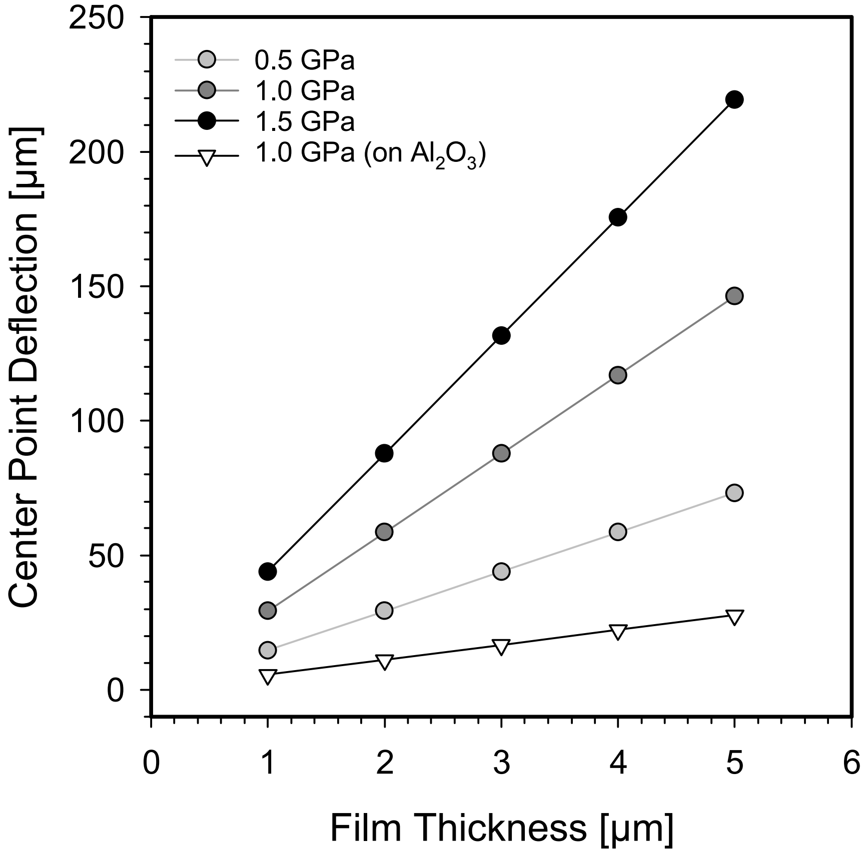
$$Stoney\ \sigma_{Film} = \frac{E'_{sub}\ {t_{sub}}^2\ (Kn - K^\circ)}{6\ tnfilm}$$



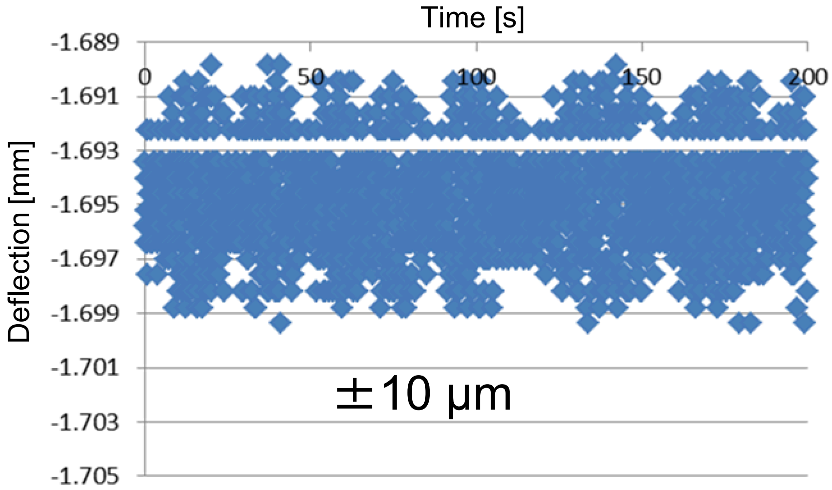
Designed and 3D printed substrate holder/laser measurement fixture

# Expected substrate deflection in AD

- Back calculations of expected deflection based on expected film stress, substrate dimensions and stiffness, and film thickness



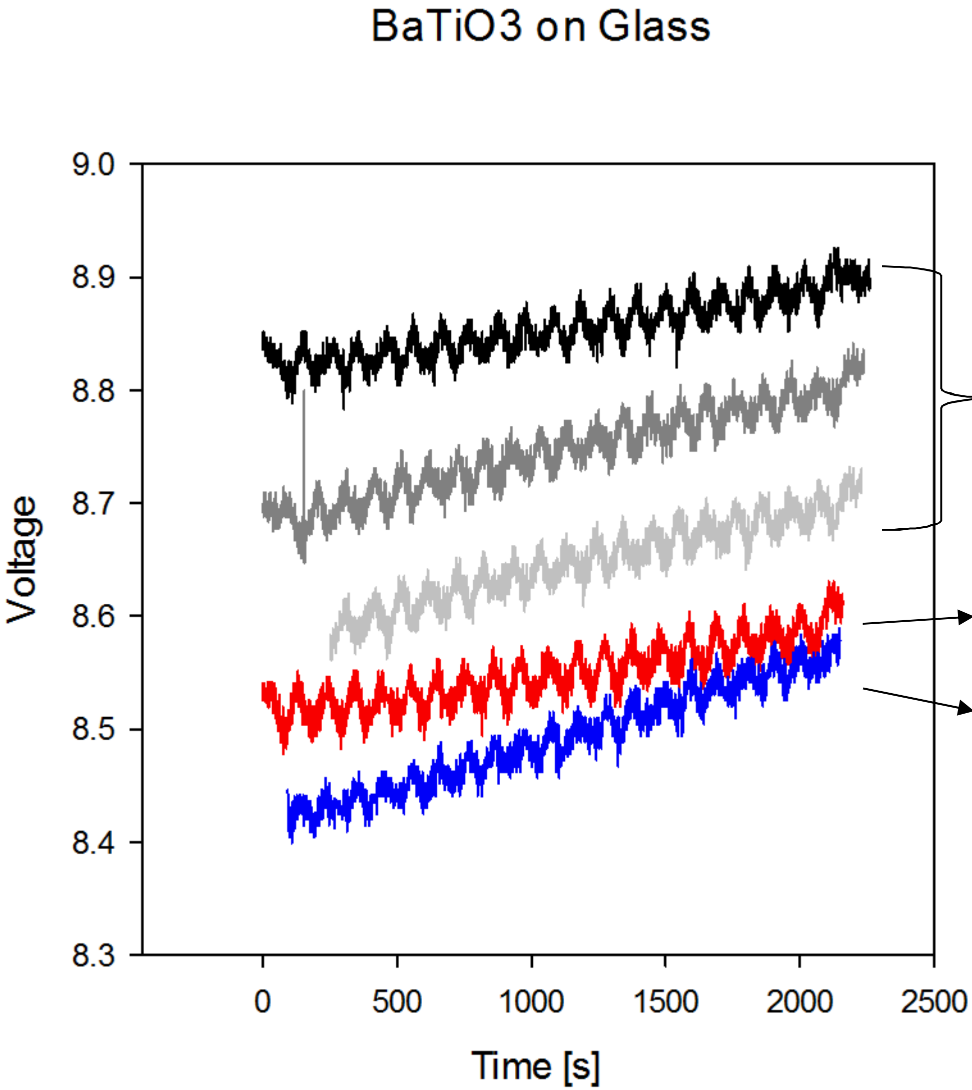
Laser measurement background noise



±10 µm

Based on 1mm thick soda-lime glass substrates

# Substrate Deflection Measurements of AD Deposition


BaTiO3 on Glass

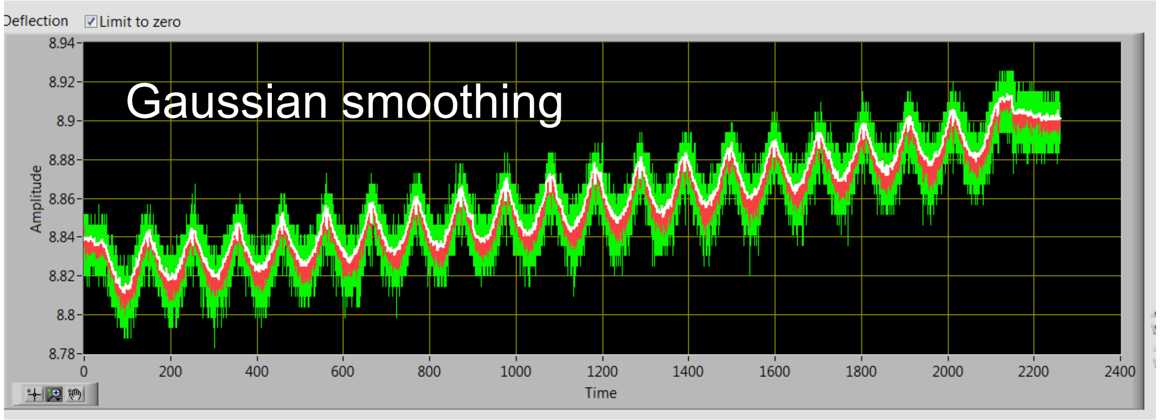
6 psig Nozzle Pressure (Repeats)

10.5 psig Nozzle Pressure

1 psig Nozzle Pressure

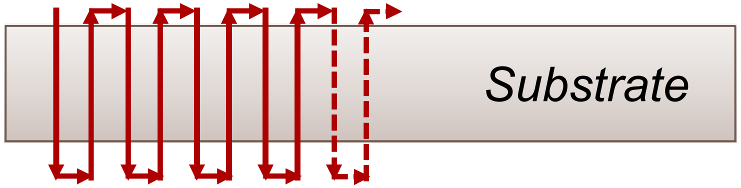
- 1 Torr Chamber pressure
- ~3-4 μm Coating thickness
- Glass Slide Substrates (60mm x 12.5mm)

# Substrate Deflection Measurements of AD Deposition – Analysis

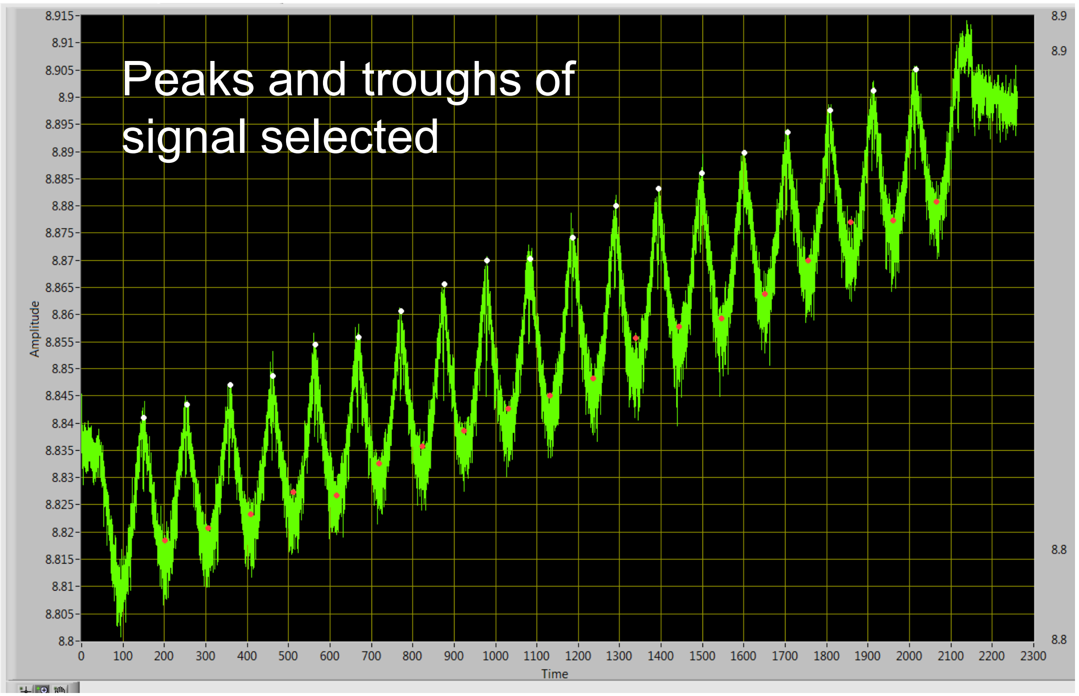


Gaussian smoothing

Spray path over substrate creates undulating deflection signal



*Nozzle Path*

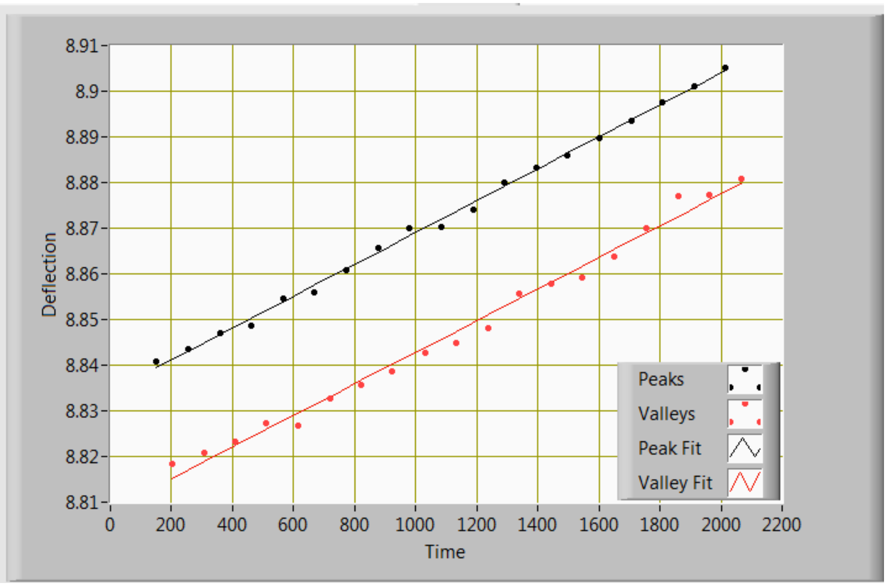


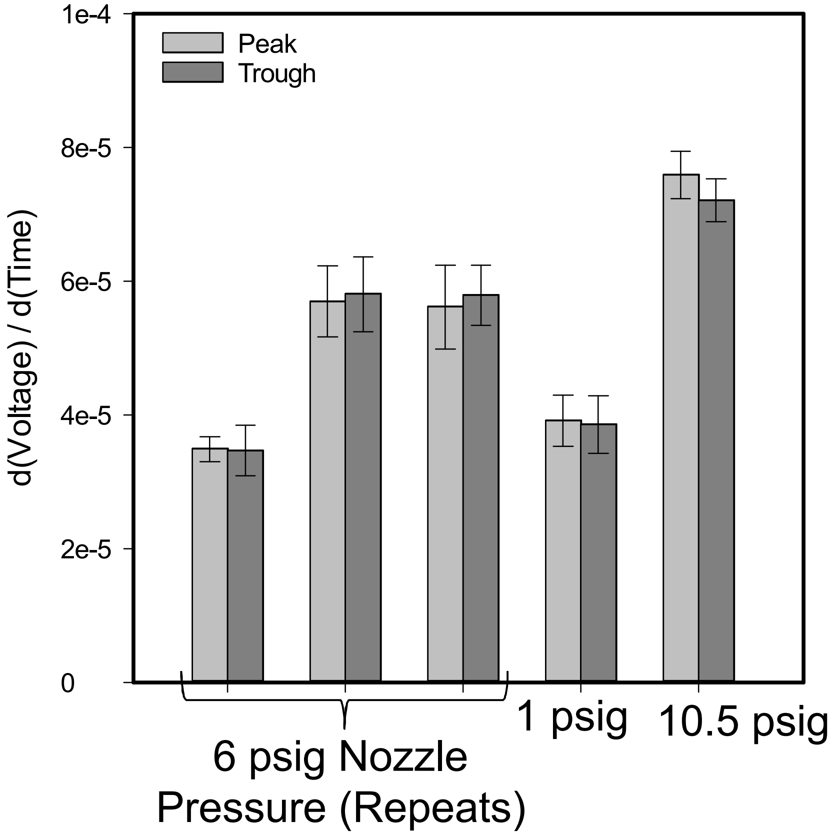
Peaks and troughs of signal selected

# Substrate Deflection Measurements of AD Deposition – Analysis

Plot of Peak Heights and Troughs

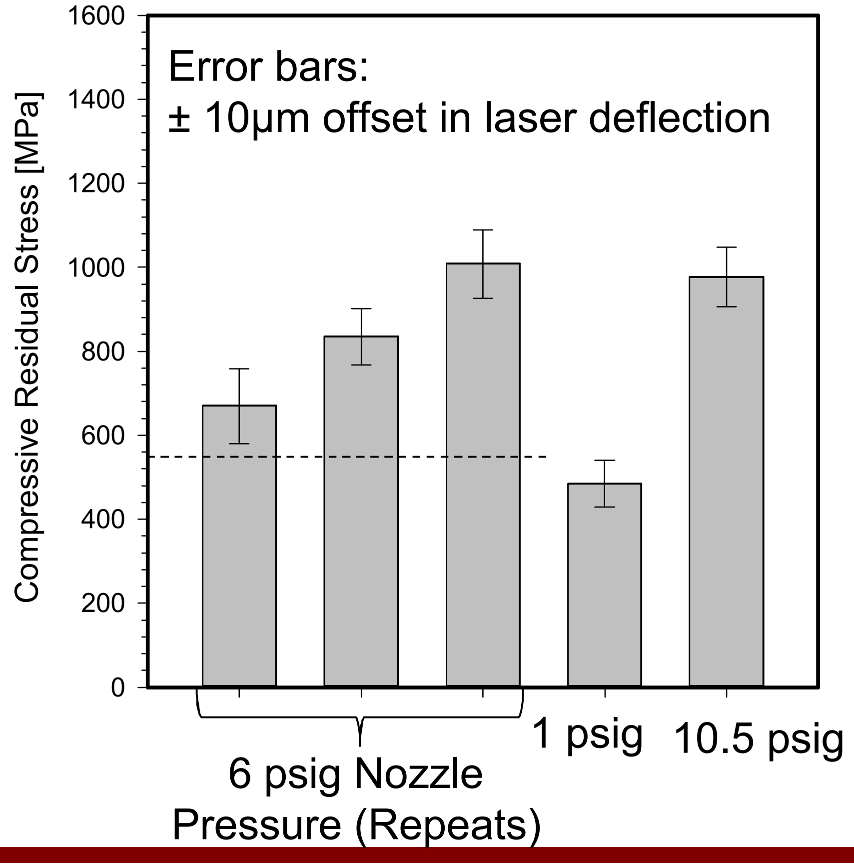
- Linear Accumulation of Deflection with Film Growth
- Little divergence between peak height and trough

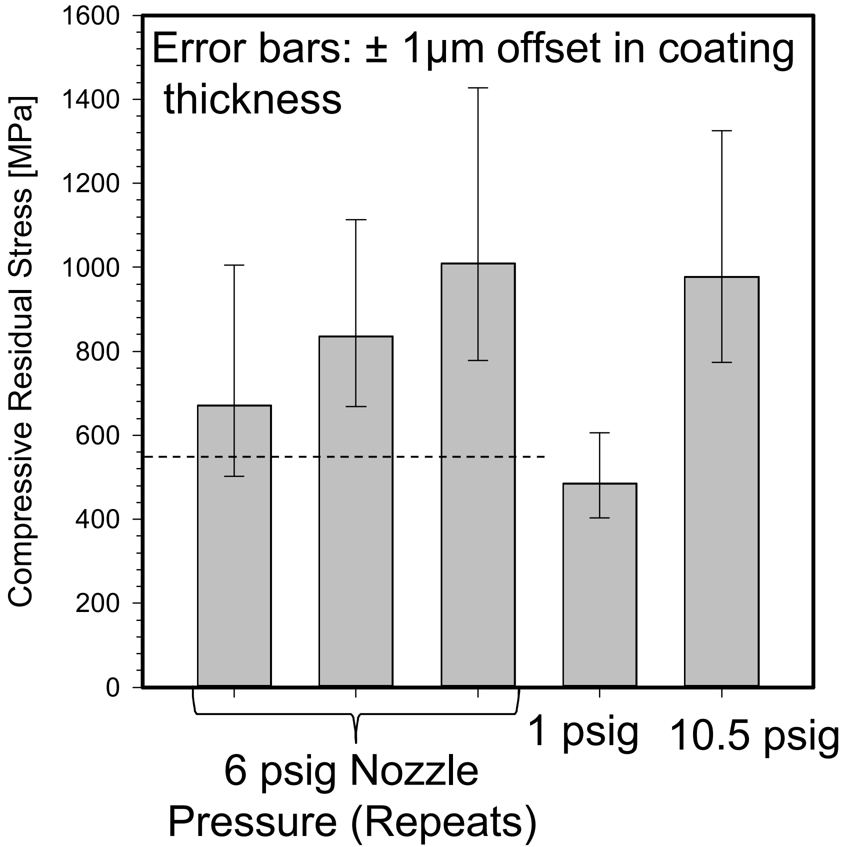




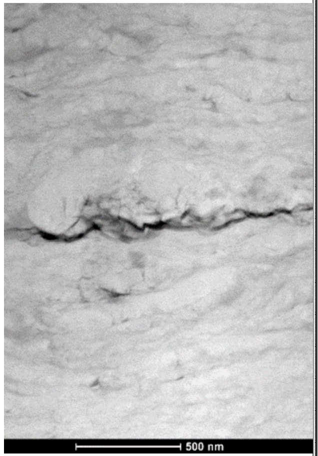
# Stress Calculations

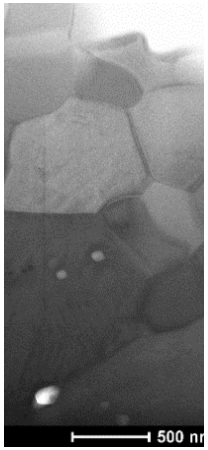
- Prone to error – laser measurement and coating thickness
- Limited repeatability

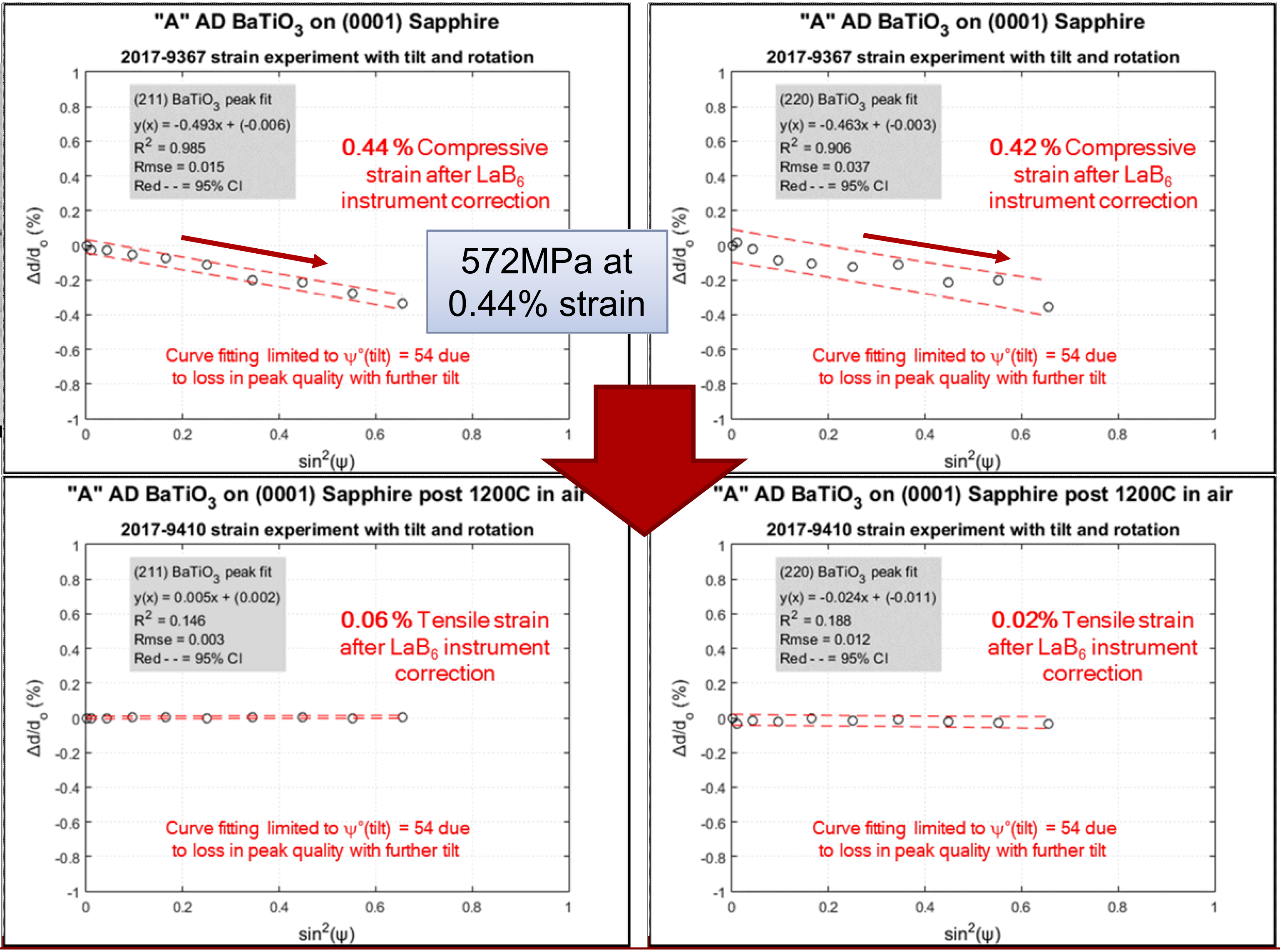




# Stress Calculations







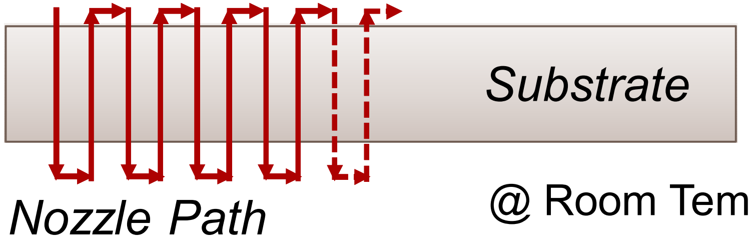
572MPa at 0.44% strain

(211)

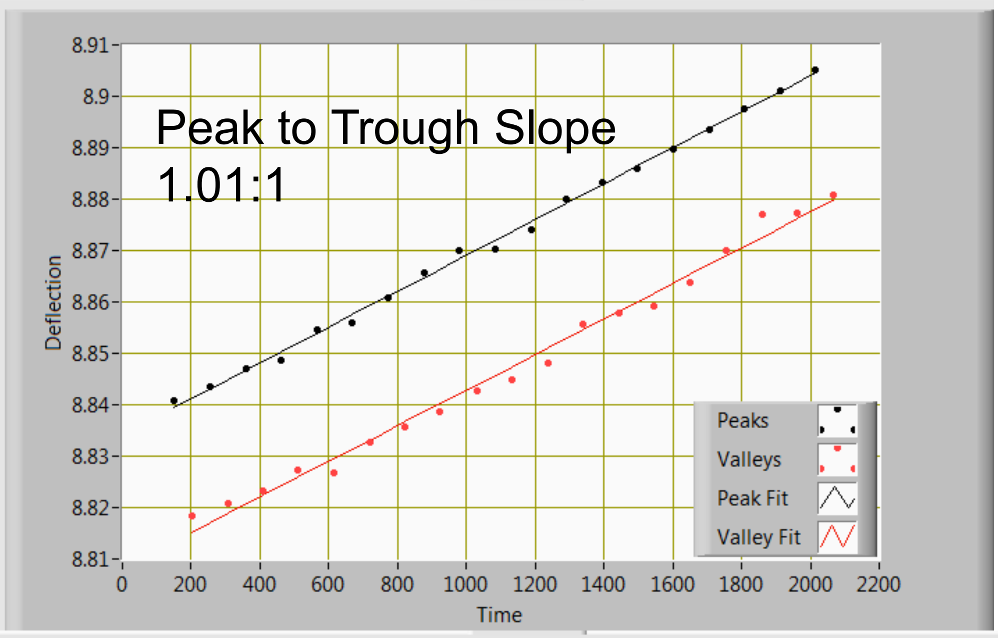
(220)

# Comparison to Thermal Spray

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

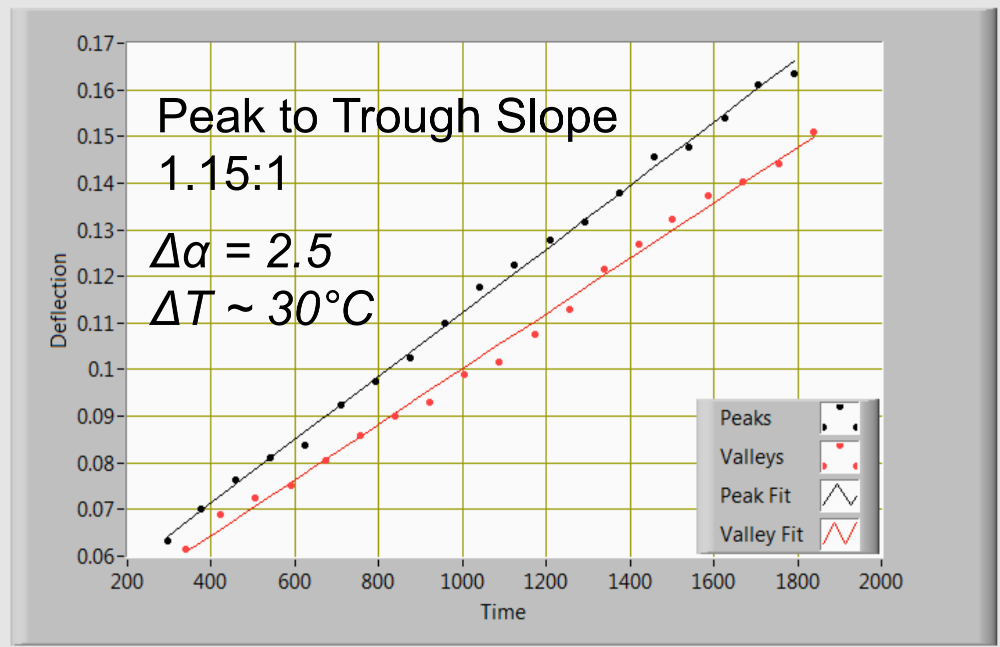


@ Room Temp



Peak to Trough Slope
1.01:1

- 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



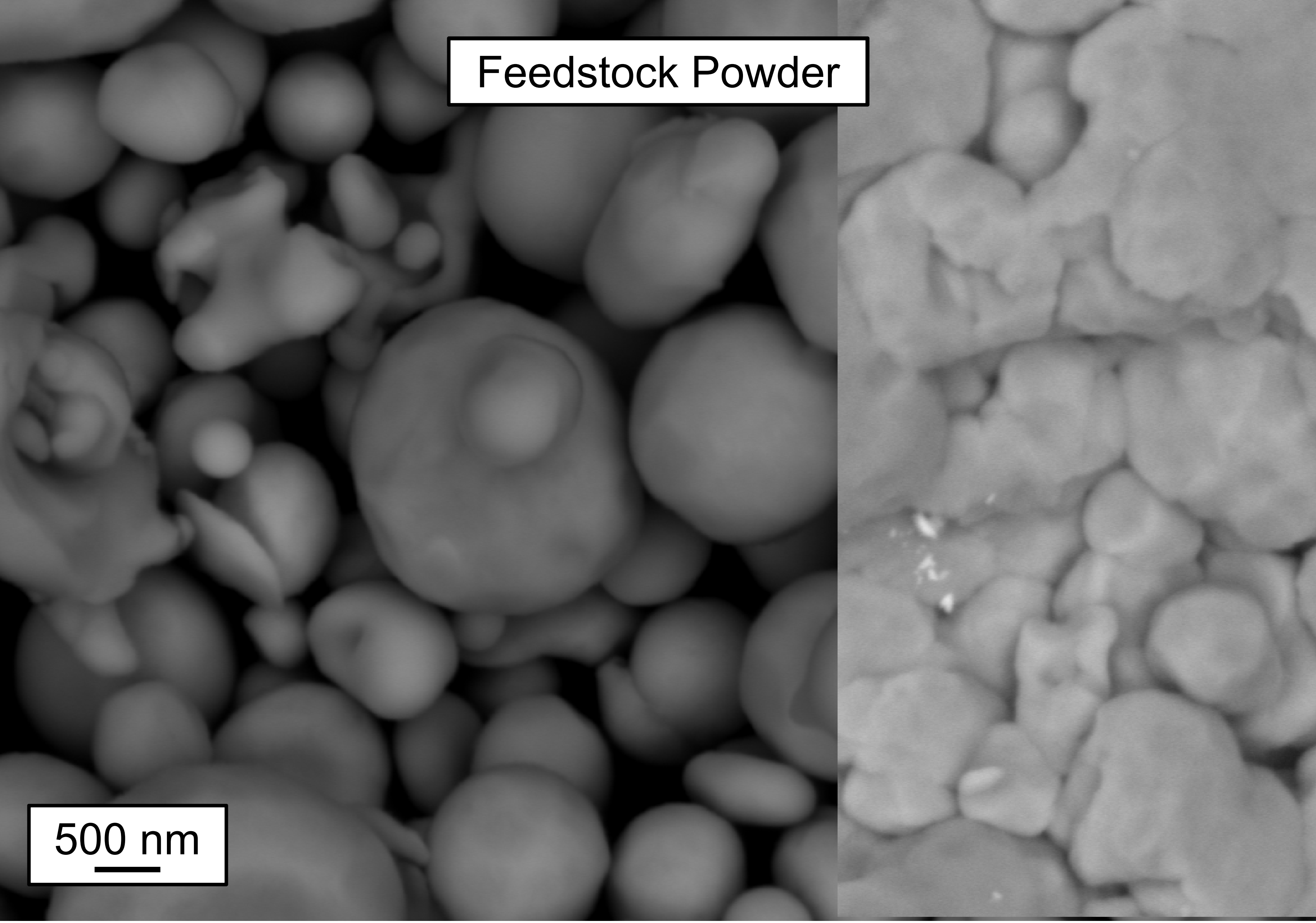
Peak to Trough Slope
1.15:1

*Δα = 2.5*
*ΔT ~ 30°C*

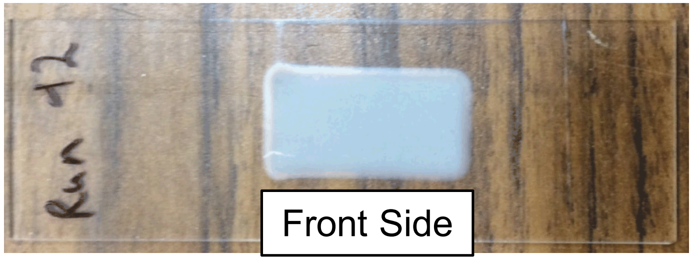
# Summary

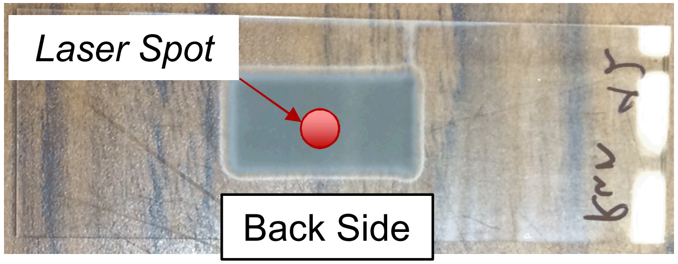
- AD Films under considerable compressive stress
- In-situ substrate deflection measurement possible
  - Linear deflection accumulation with film growth
  - No fluctuations from temperature observed
  - Somewhat responsive to parameter differences
- With better measurement resolution, possibly a more rapid way to measure film stress
- Enables further in-situ investigation of films based on process parameters (gas pressures, nozzle geometries, stand off distance etc.)
- Enables in-situ detection of film growth, delamination

Thank you - Question?

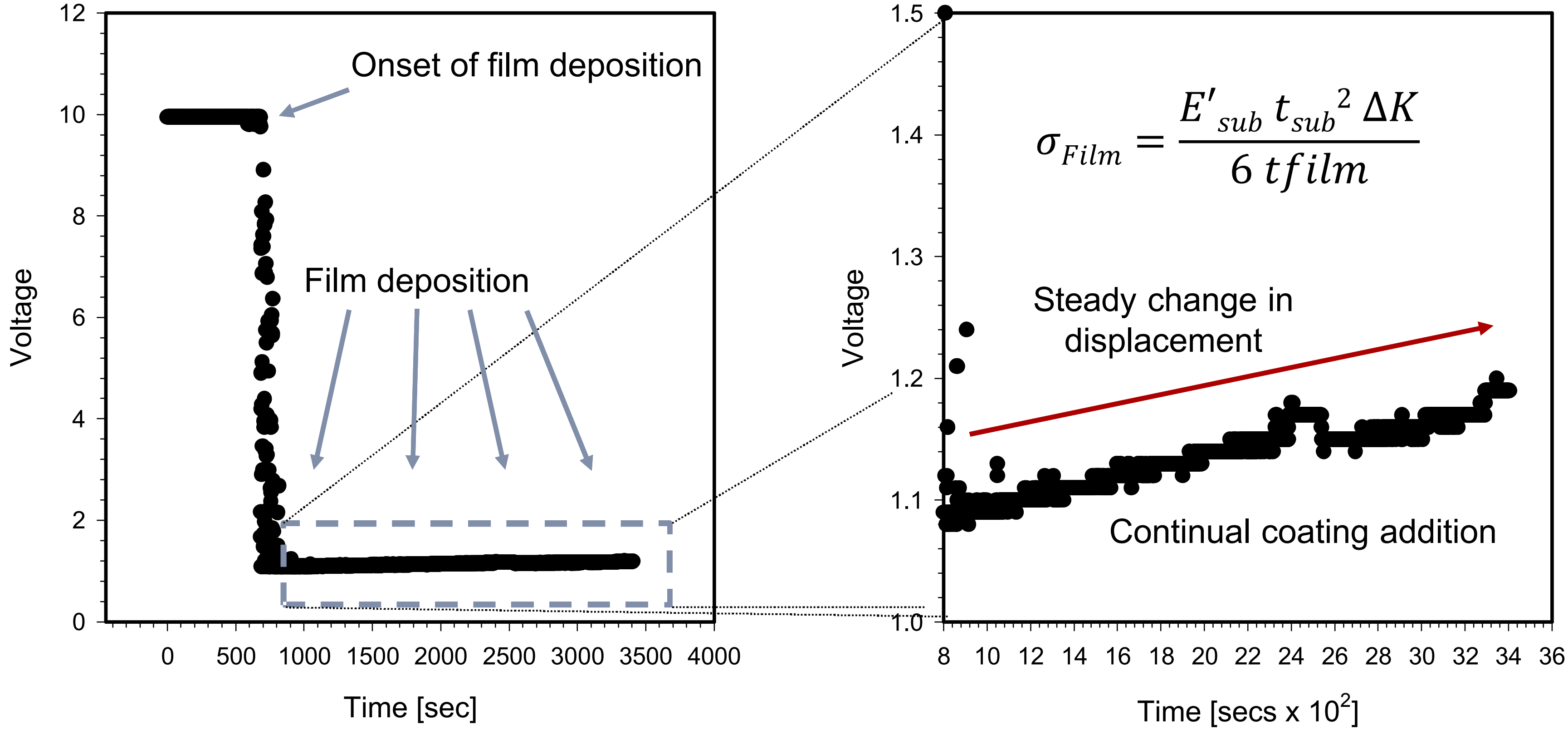

Feedstock Powder
500 nm

# Preliminary Experimental Results – Deposition



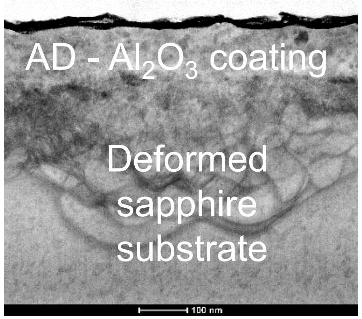


BaTiO$_3$ on 25 x 75mm Glass Slide



$$\sigma_{Film} = \frac{E'_{sub}\, t_{sub}{}^{2}\, \Delta K}{6\, tfilm}$$

# Preliminary Experimental Results – Etching



$Al_2O_3$ on Glass
- Highly damaging to substrate – Etches glass
- Self limiting film growth – Requires harder substrate for deposition