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Intrinsic Stress in Aerosol Deposited TiO_2 Films Measured by Substrate Bending

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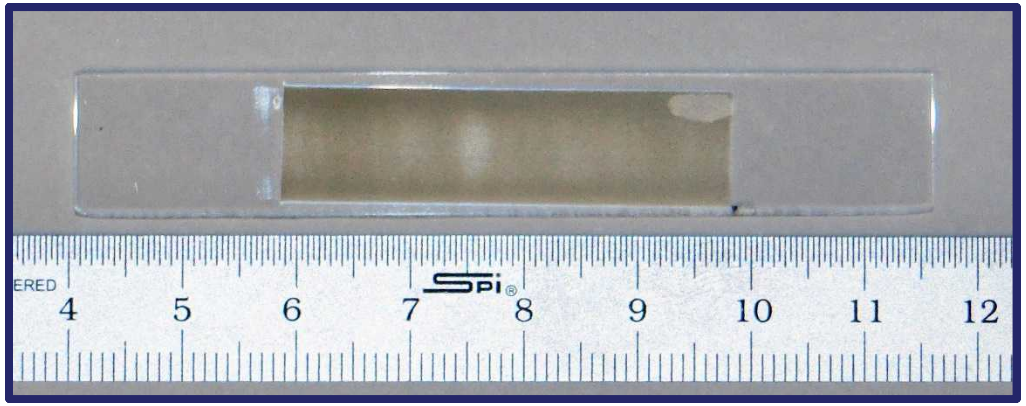
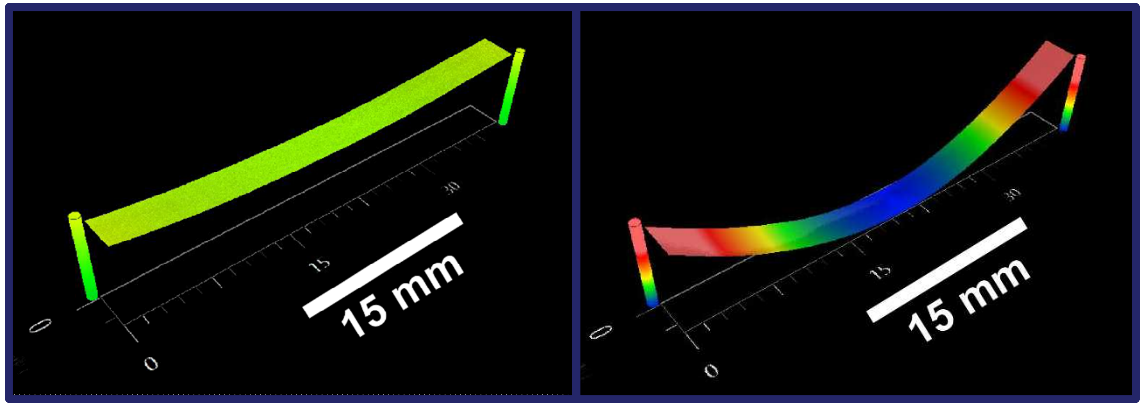


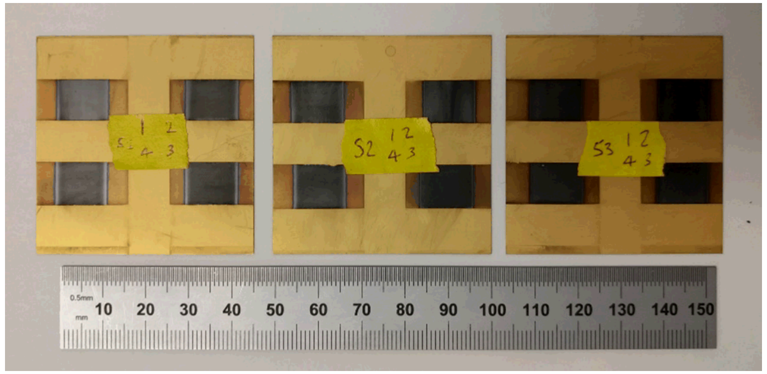


Introduction

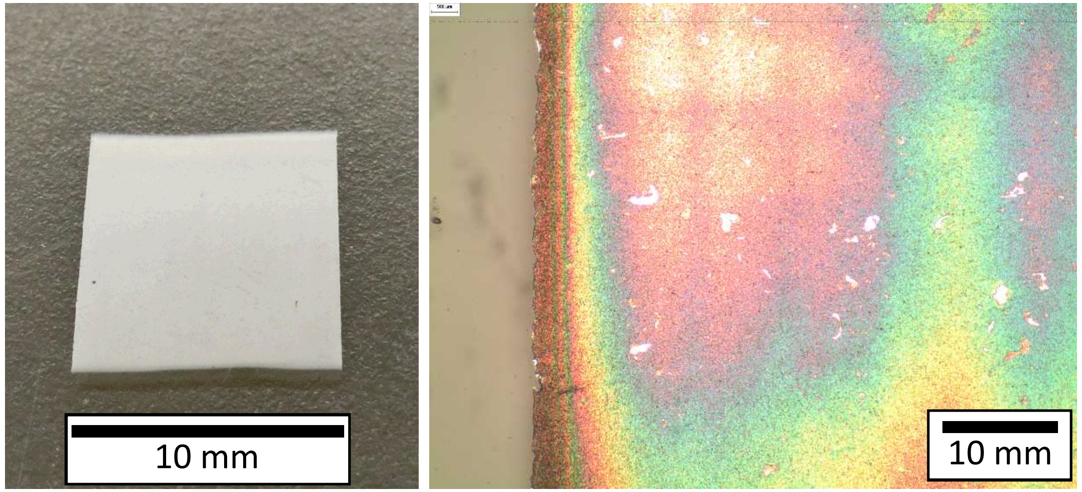
Introduction to Aerosol Deposition (AD)

- Room temperature thick-film deposition
- Nanocrystalline structure with high density
- Variety of applications for TiO_2
  - Dye sensitized solar cells
  - Hydrophobic/hydrophilic coatings
  - Scratch/corrosion resistance

- AD research worldwide
  - USA
  - Germany
  - Japan
  - Korea



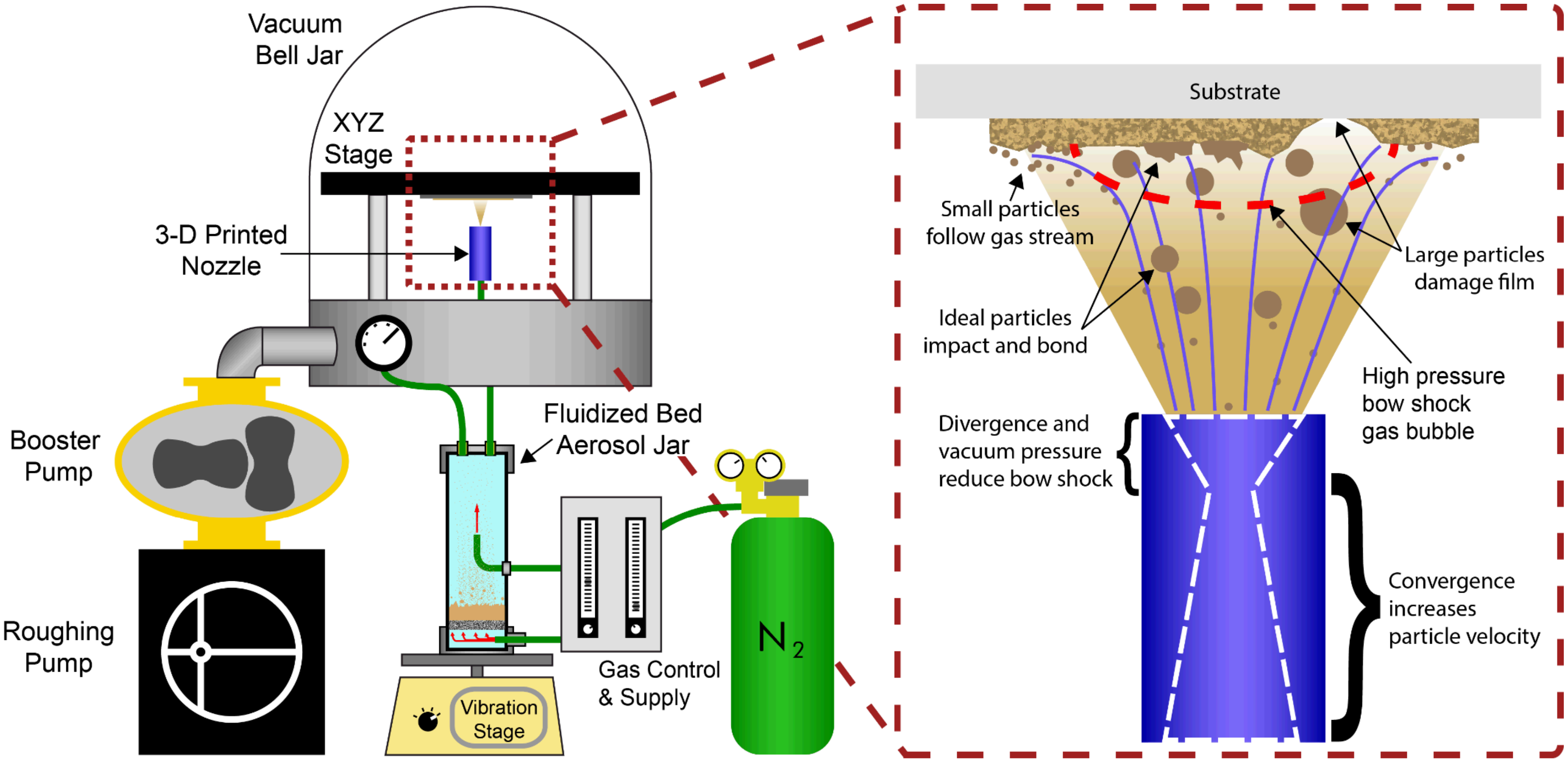
Aerosol Deposited $LiCoO_2$



Aerosol Deposited TiO_2

AD System

- Fluidized bed powder system
- Vacuum system
  - Velocity
  - Bow shock
- Small particle size required for deposition

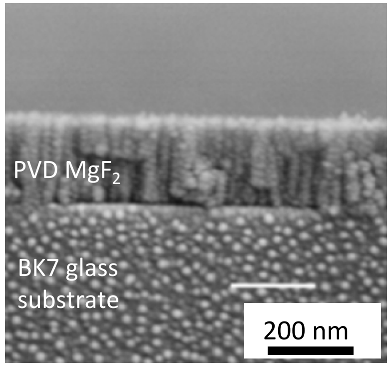


AD Process Comparison

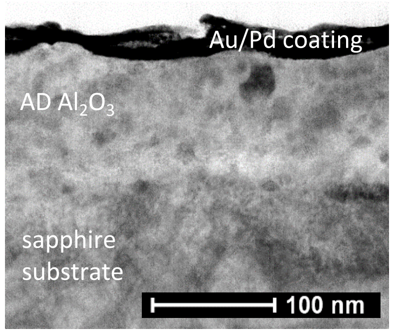
- Film Characteristics of Various Processes

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

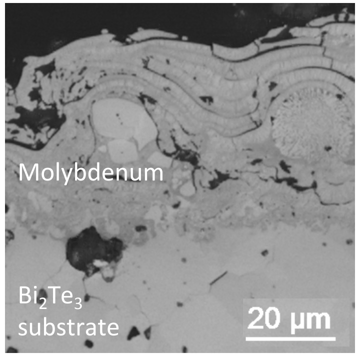
Microstructures of PVD, AD, and TS coatings



Physical Vapor deposited columnar MgF_2 [2]



Aerosol deposited Al_2O_3 on Sapphire substrate



Thermal sprayed Mo On Bi_2Te_3 Substrate

Stoney's Equation

- G. G. Stoney, 1909
- Utilizes curvature to calculate stress
- Assumptions give confidence to calculated values
- Substrate elastic properties only

Stoney's Equation Assumptions [3]

- Deposited film is very thin compared to the substrate.
- Film and substrate thickness are smaller than the lateral dimensions.
- Edge and interface effects are ignored.
- Film and substrate are uniform, homogenous, isotropic, and linear elastic.
- Substrate and film have the same or similar elastic moduli.
- Radius of curvature is equal in all directions.
- Stress and radius of curvature are constant across the entire area.

$$\sigma = \frac{E_S}{6(1-\nu_s)} \cdot \frac{h_s^{\,2}}{h_f}\left(\frac{1}{R} - \frac{1}{R_0}\right)$$

σ Film stress

E_s Substrate modulus

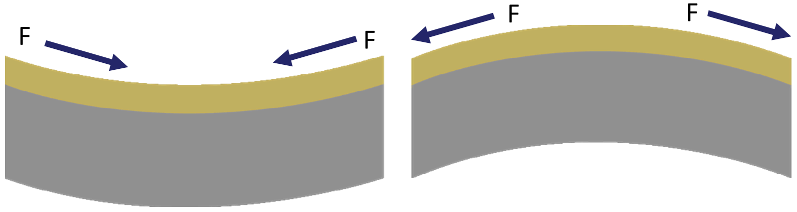
ν_s Substrate Poisson's ratio

$h_s^{\,2}$ Substrate thickness

h_f Film thickness

R_0 Initial curvature

R Final curvature

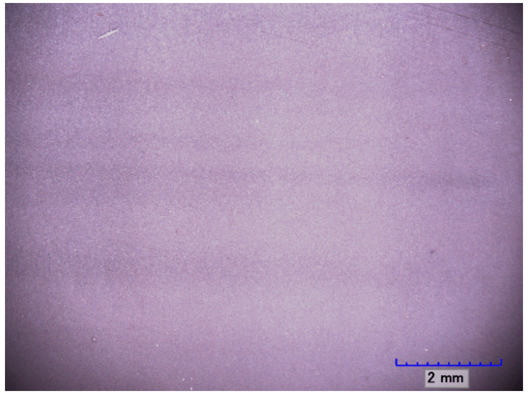


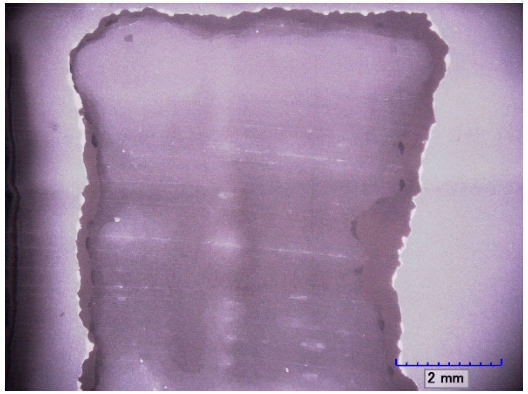
Tensile Stress

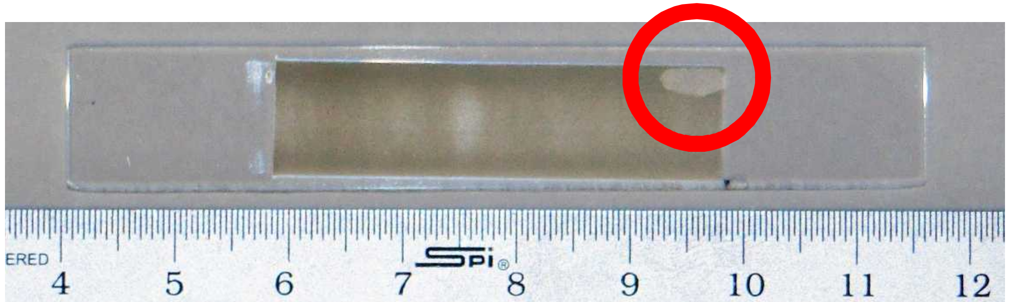
Compressive Stress

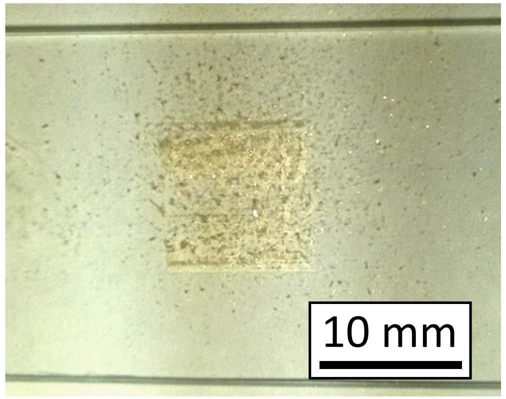
Stress in AD Films

- Results in delamination of films
  - Stress is higher than adhesion strength
  - Results in free standing "flakes"
- Damages substrates
  - Very high adhesion strength
  - Film stress higher than substrate strength
- Insight into deposition mechanism
- Ignore thermal effects

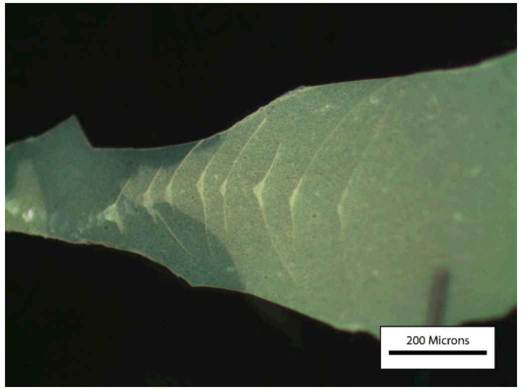

Uniform Film


Delaminated Film


Delaminated corner of beam substrate



Delaminated Film



Delaminated Flake

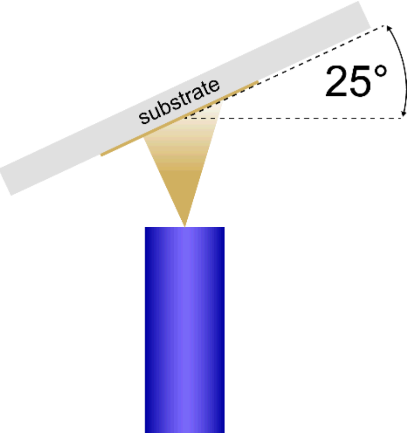
Objective

- Quantify stress in AD TiO_2
- Investigate a shape effect of substrates
  - Beam and square substrates
  - Most AD samples prepared are square

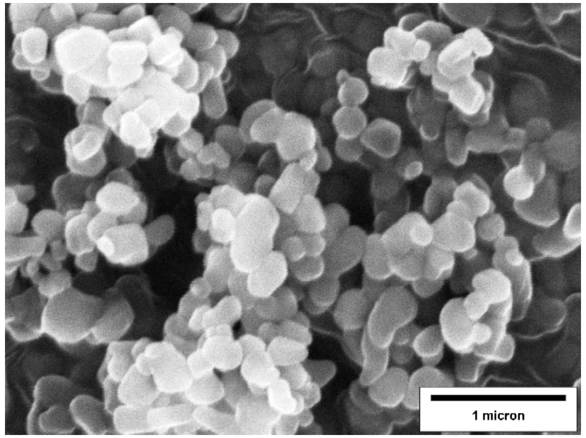
Experimental

Angle of Deposition

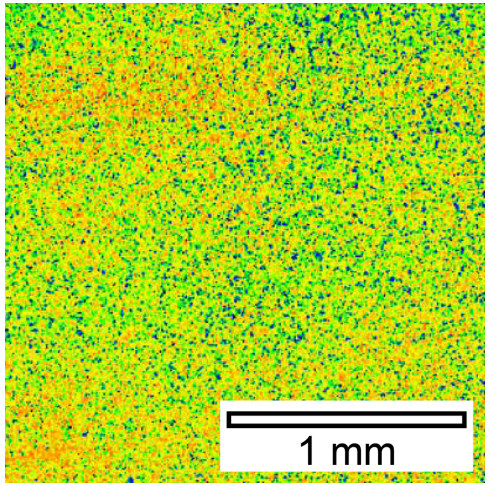
- Produce smoother and more uniform films
  - Stoney’s equation assumptions
- Reduce damage from large agglomerates
- Lowers deposition efficiency [4]



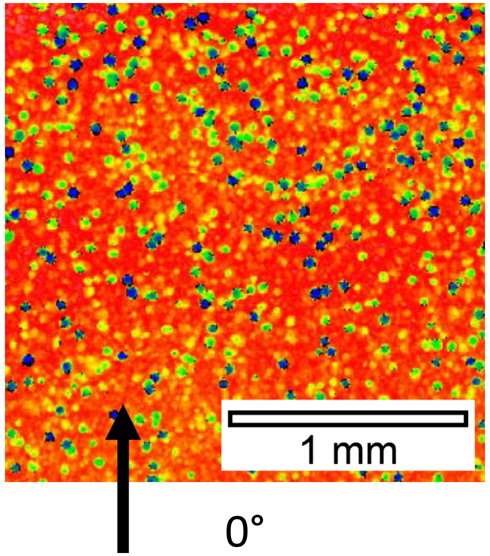
Angle of deposition



250 nm primary particles

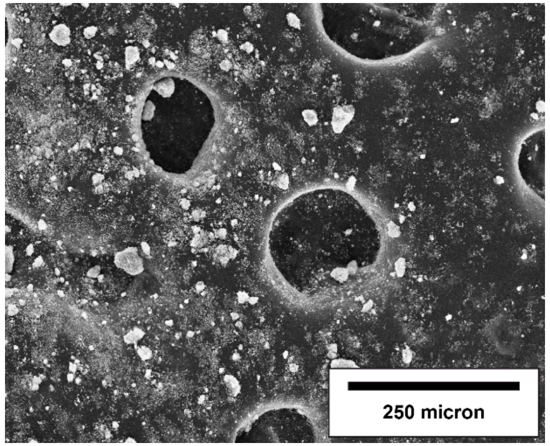


25°

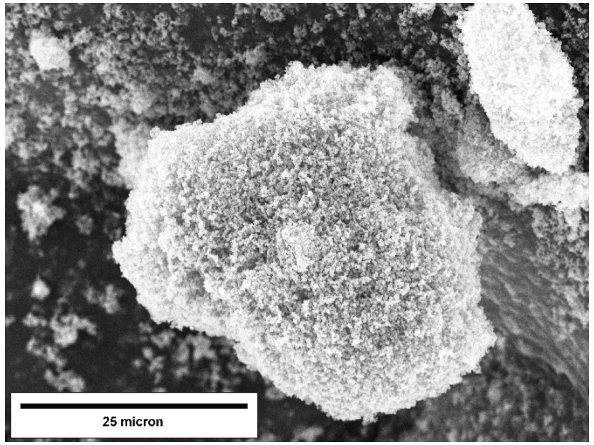


0°

40 µm craters



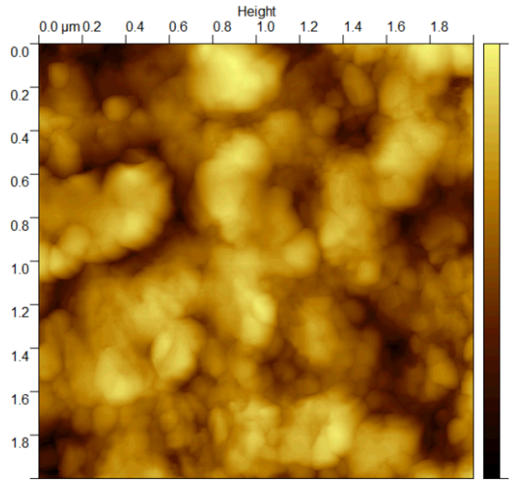
Agglomerated particles on carbon tape

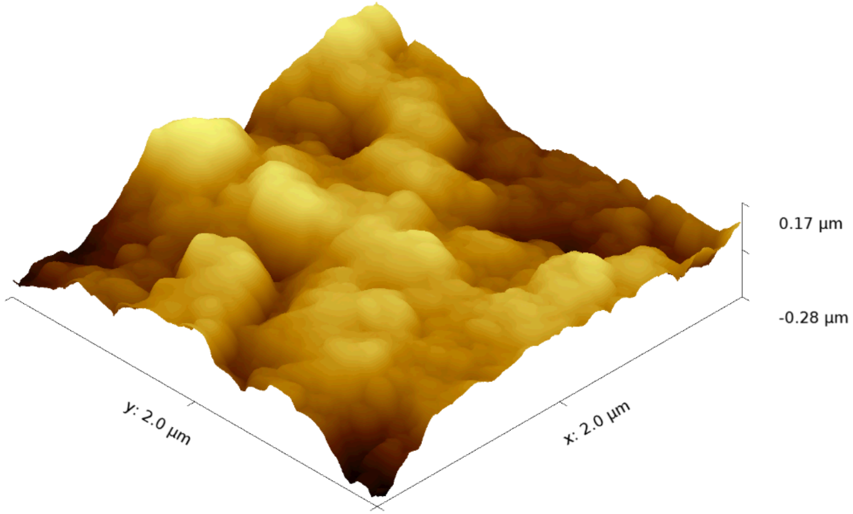


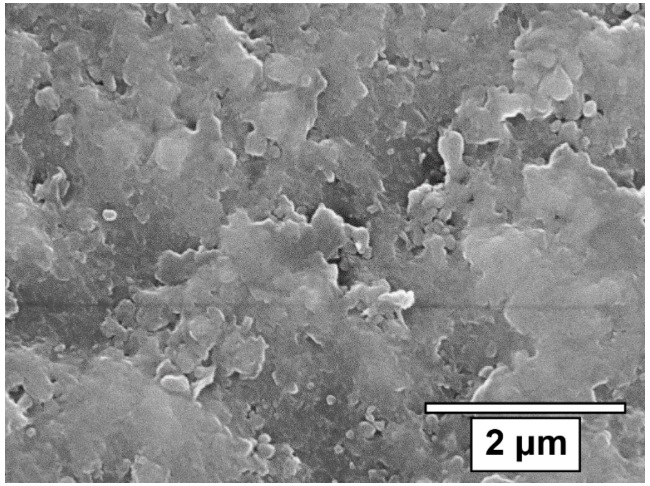
40 µm secondary particle agglomerate.

SEM/AFM Characterization

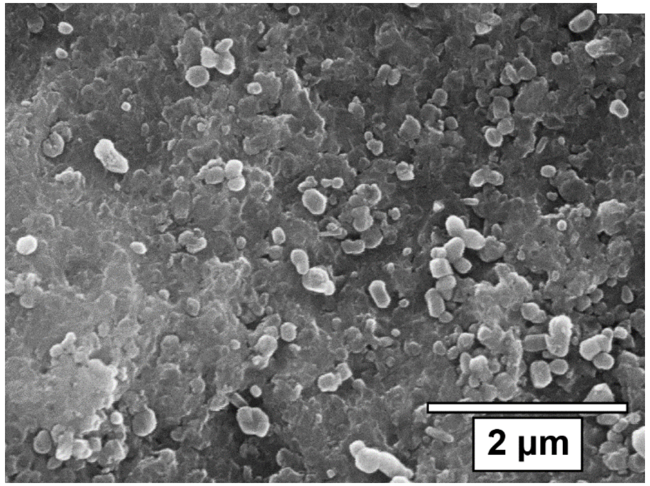
- Roughness increases
- Minimal voids
- Plastic deformation
- Small grain sizes



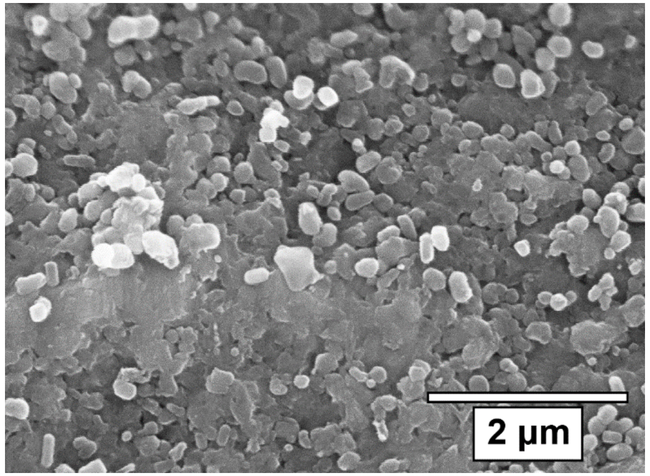




1 µm



5 µm



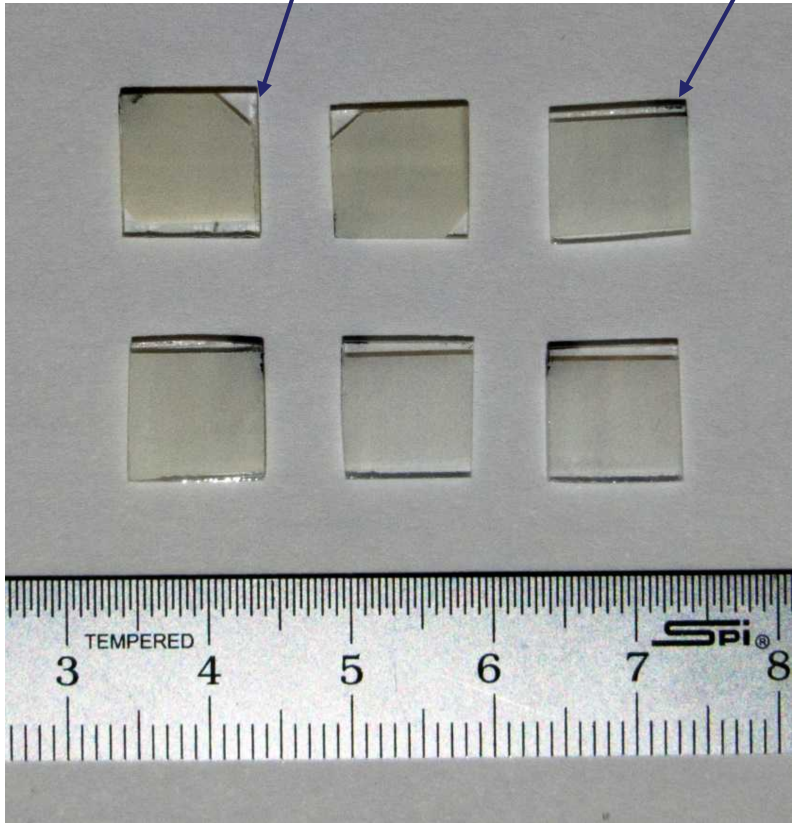
10 µm

Deposition Experiments

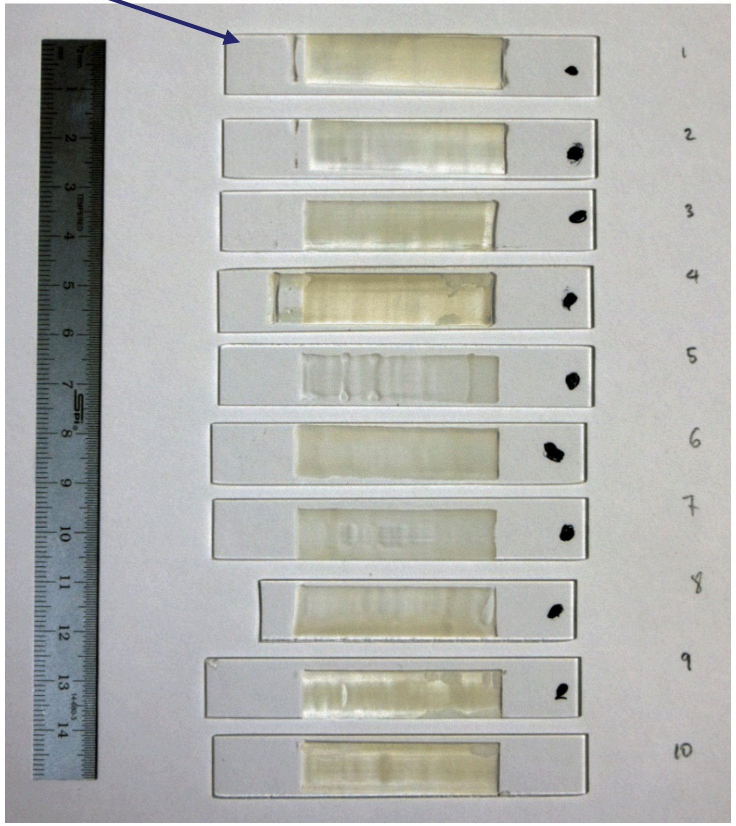
- 9 squares and beam shaped substrates
- 3 different thicknesses
- Masking for film measurement
- Substrates marked and measured before deposition
- Same deposition parameters for all samples

Masked region

Laser cut glass microscope slide substrates



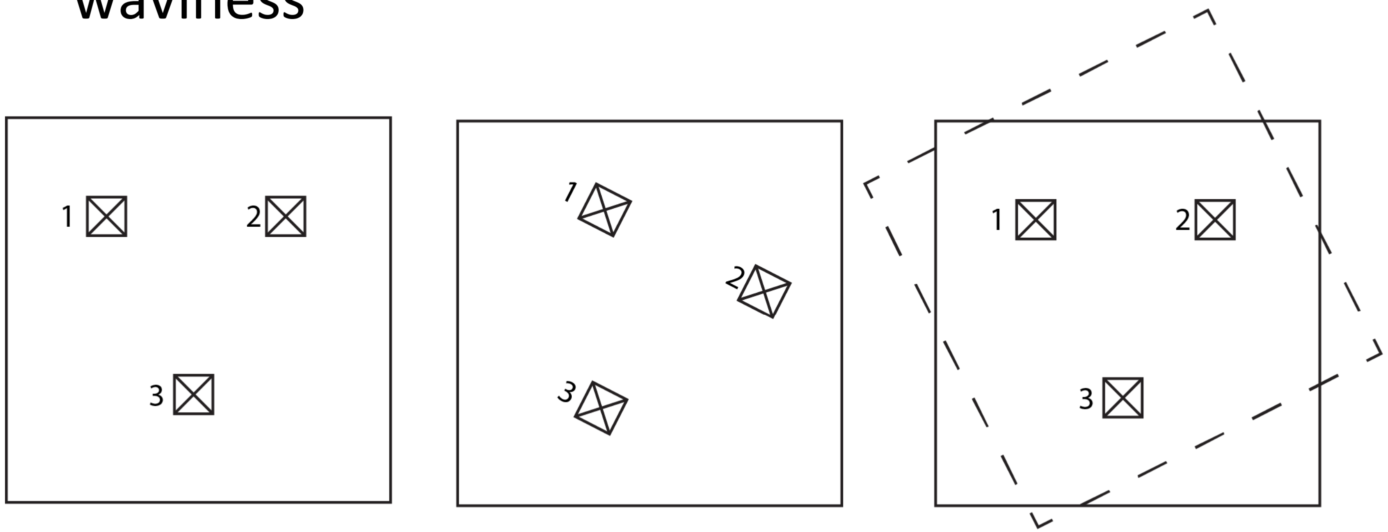
Square Samples



Beam Samples

Substrate Reference Marking

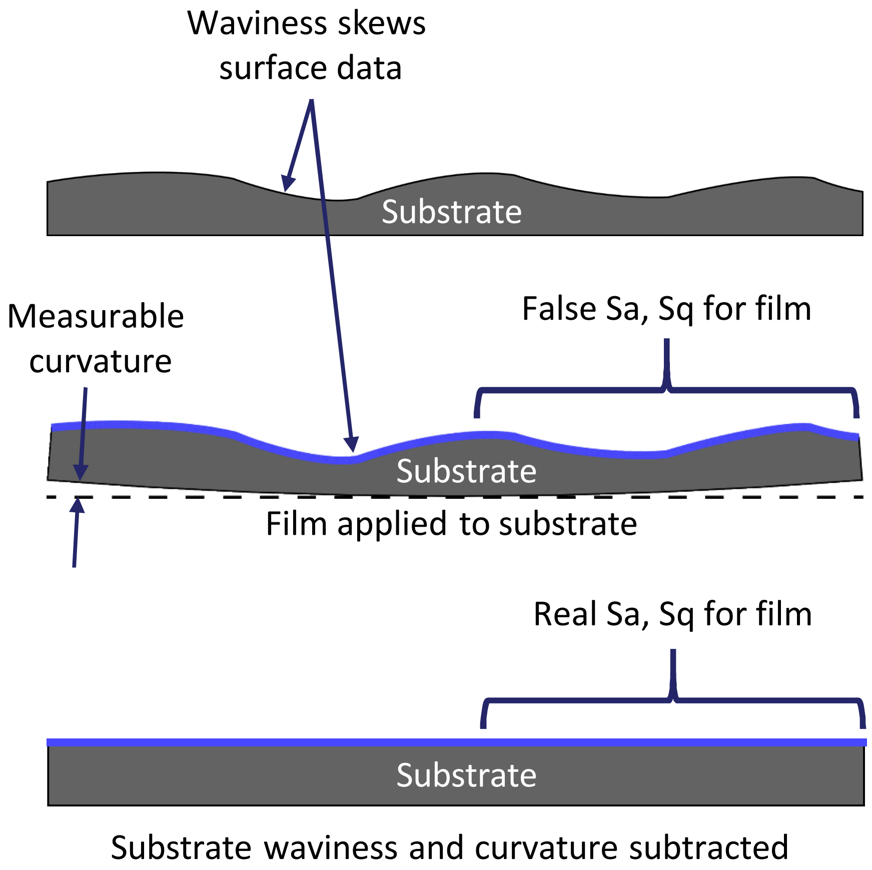
- Micro hardness indentations as fiducials
- Alignment and subtraction of data
- Measure deflection lower than substrate waviness



Pre-Spray Measurement Region

Post-Spray Measurement Region

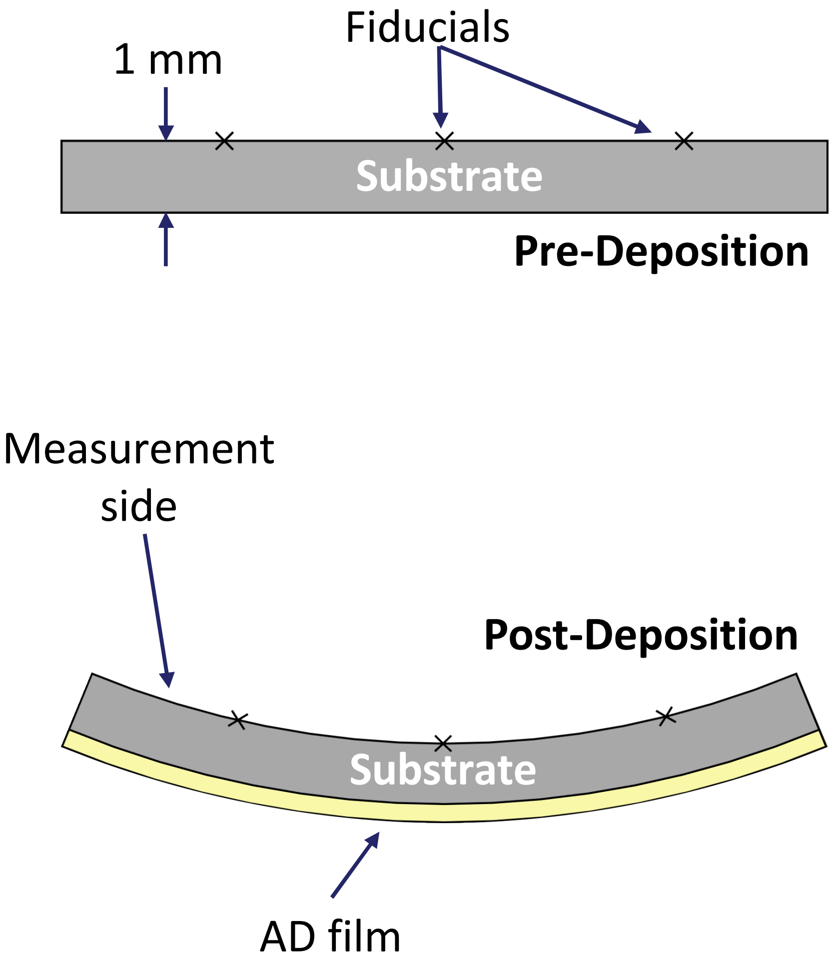
Fiducial Alignment

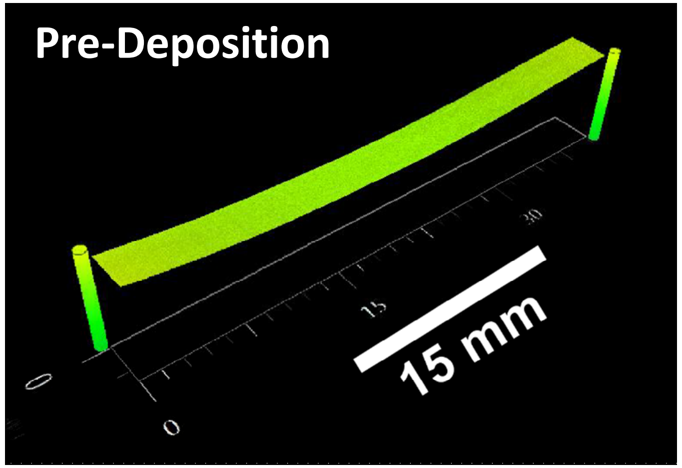


Substrate Curvature

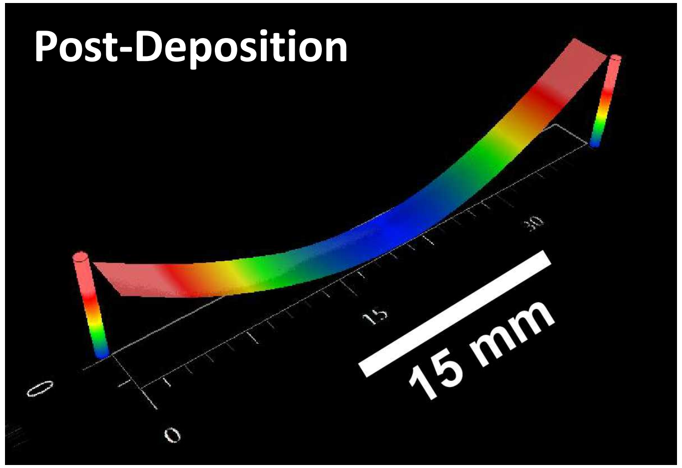
- 3-D maps
- Change in RadCrv
  - Cylindrical calculation
  - Spherical calculation
- Optical profiler

Zygo Optical Profiler





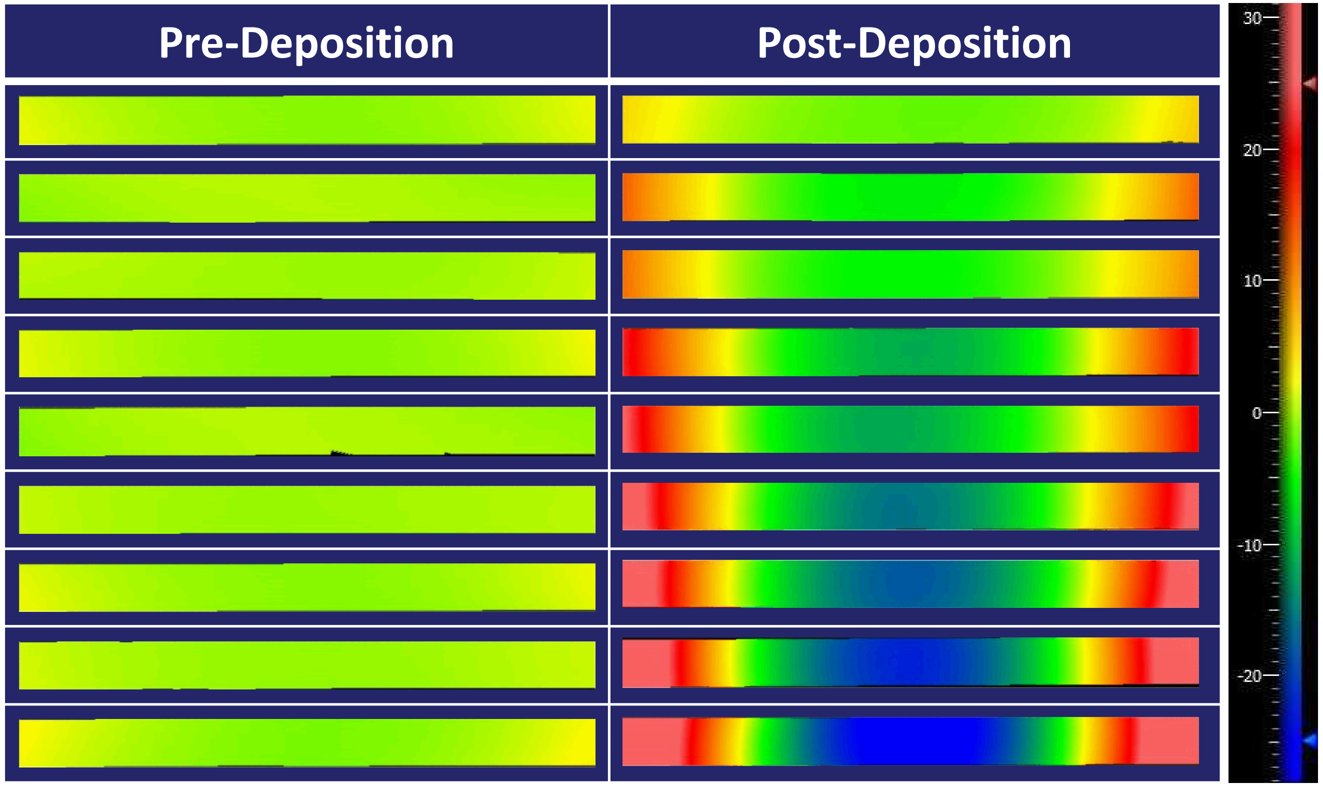
RadCrv = 116.361 m



RadCrv = 2.548 m

Curvature and Stress Results

Beam Substrates



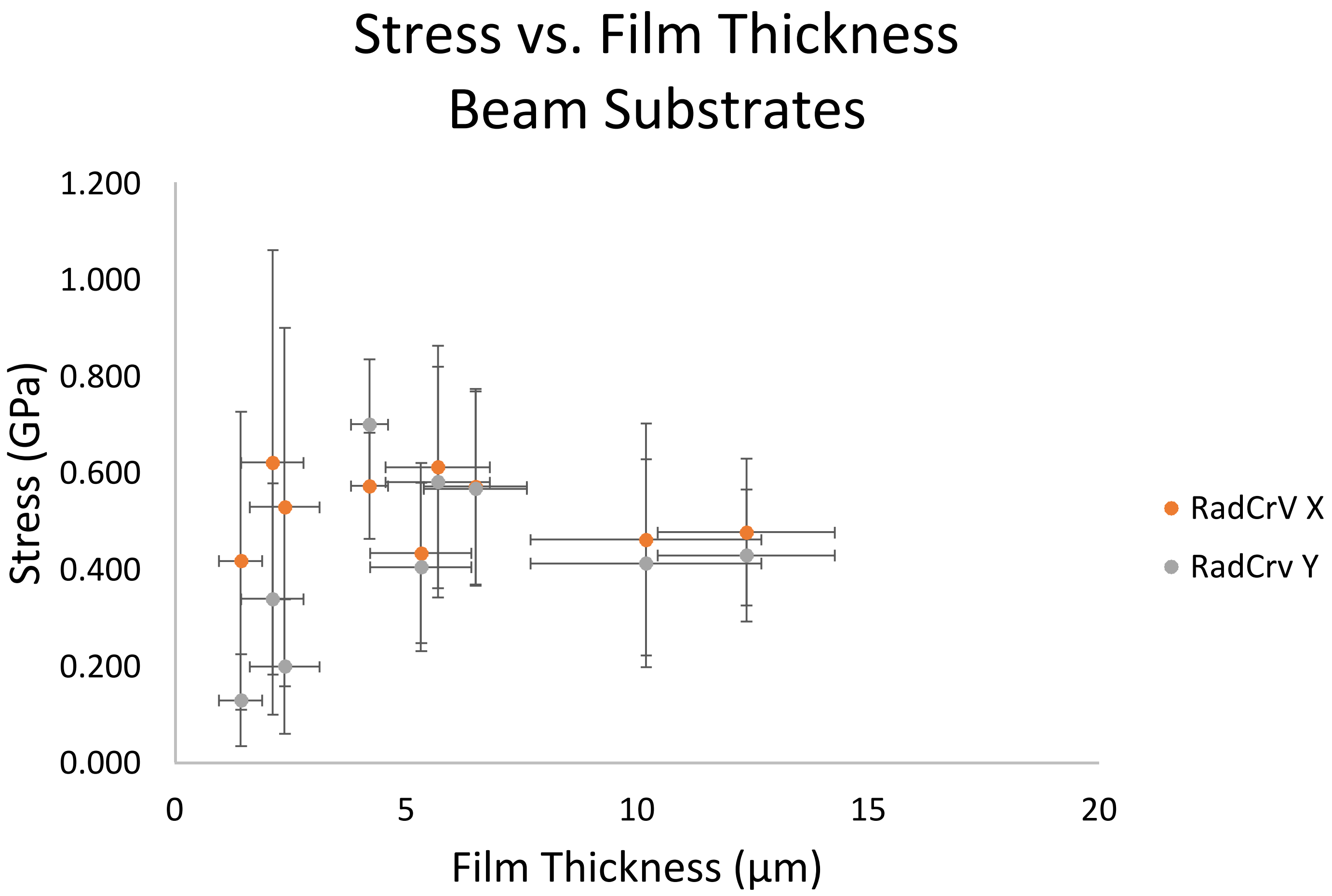
±25 µm

Film Thickness (µm)	RadCrv X (m)	RadCrv Y (m)
1.43	-29.5	-39.1
2.12	-10.9	-11.3
2.38	-12.4	-11.6
4.21	-6.2	-5.3
5.33	-6.1	-5.9
5.69	-4.5	-4.6
6.51	-3.8	-3.8
10.20	-3.1	-4.4
12.37	-2.5	-2.9

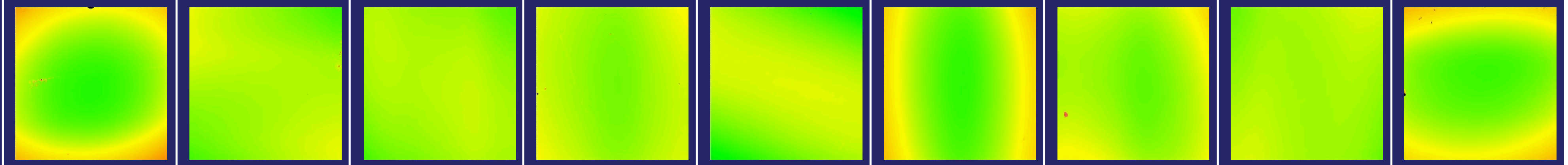
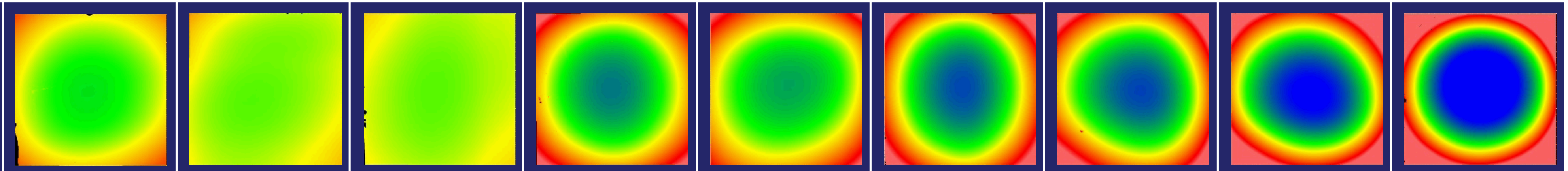
Converges towards spherical

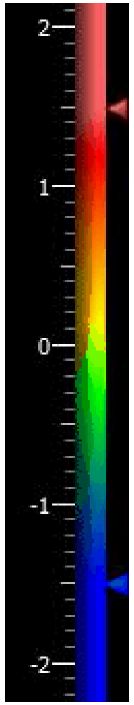
Stress vs. Film Thickness – Beams

- High variation in data
- Obvious trend not present
- 0.522 GPa average stress in X
- 0.418 GPa average stress in Y
- Large deposition area
  - 40 mm x 10 mm



Square Substrates

Pre-Deposition									
Post-Deposition									
Thickness (µm)	1.07	1.44	1.59	5.82	6.58	7.12	8.03	14.34	26.81
RadCrv X (m)	-13.3	-30.8	-32.9	-5.8	-7.9	-4.2	-4.6	-3.6	-2.5
RadCrv Y (m)	-11.9	-46.1	-53.8	-5.7	-6.6	-5.3	-4.5	-2.9	-2.2



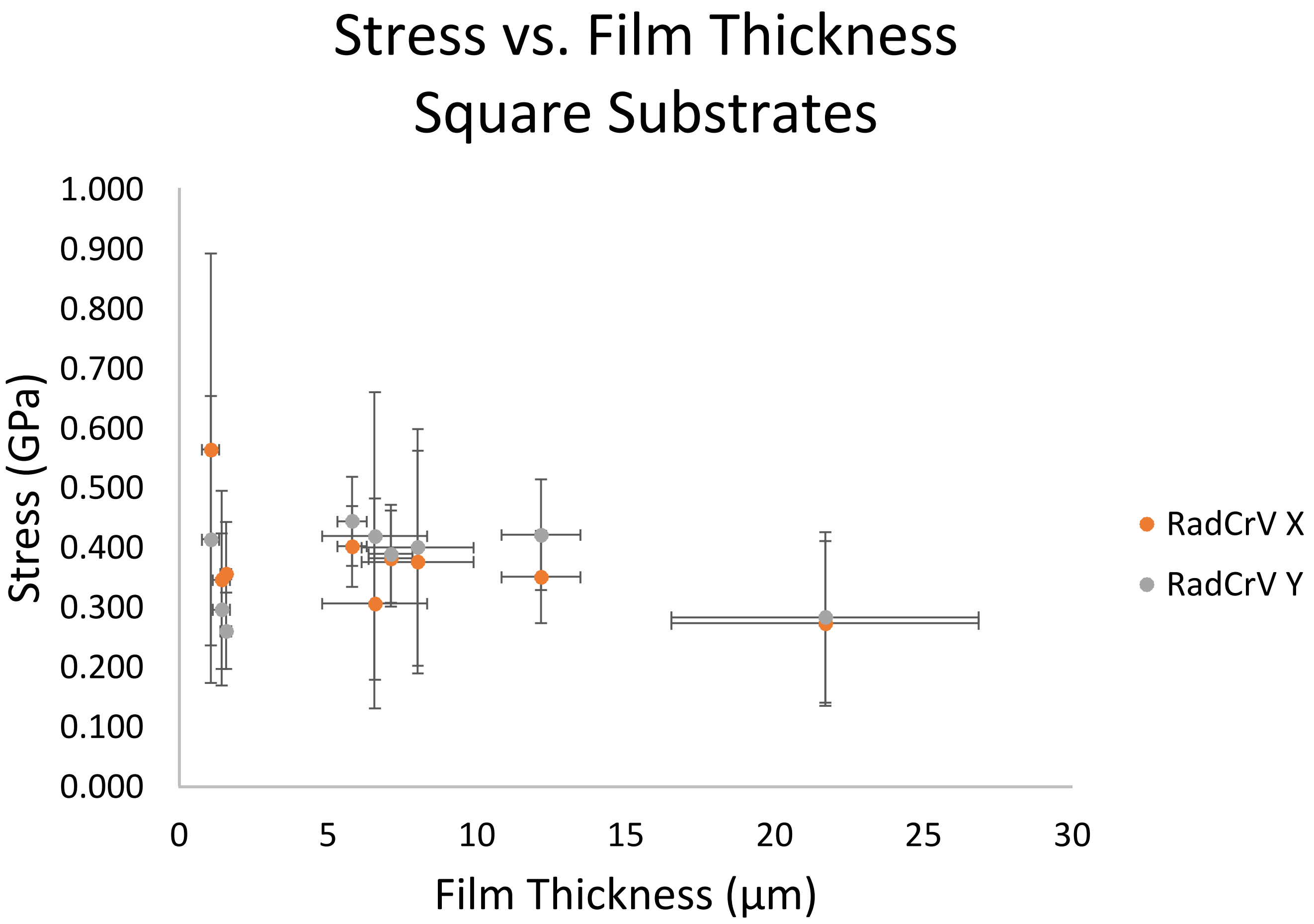
±1.5 µm

Increasing Film Thickness

Converges towards spherical

Stress vs. Film Thickness – Squares

- Obvious trend not present
- 0.373 GPa average stress in X
- 0.370 GPa average stress in Y
- Smaller deposition area
  - 10 mm x 10 mm
- Comparable to literature values [5]



Conclusion

- An intrinsic stress value for AD TiO_2 was calculated
  - 0.418-0.522 GPa for beams
  - 0.373-0.370 GPa for squares
- Substrate shape factor may affect stress measurements
- Future work
  - Investigate trends in stress vs. thickness of films
  - Develop an understanding of bonding mechanisms
  - Control film stress with process parameters

References

[1] D. M. Mattox, *Handbook of Physical Vapor Deposition (PVD) Processing*. Park Ridge, N.J.: Noyes Publications, 1998.

[2] C. Guo, et al., “Microstructure-related properties of magnesium fluoride films at 193nm by oblique-angle deposition,” *Opt. Express*, vol. 21, no. 1, pp. 960-967, 2013.

[3] G. G. Stoney, “The tension of metallic films deposited by electrolysis,” *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences,* vol. 82, no. 553, pp. 172-175, May 1909.

[4] D. Lee, S. Nam, “Factors affecting surface roughness of Al2O3 films deposited on Cu substrates by an aerosol deposition method”, *Journal of Ceramic Processing Research*, vol. 11, No. 1, pp. 100-106, 2010.

[5] M. Schubert, J. Exner and R. Moos, “Influence of Carrier Gas Composition on the Stress of Al_2O_3 Coatings Prepared by the Aerosol Deposition Method”, Materials, Vol. 7, no. 8, pp.5633-5642, 2014.

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