

Chemically Homogeneous Complex Oxide Thin Films via Improved Substrate Metallization: *Processing Matters*

Jon Ihlefeld

Sandia National Laboratories

Albuquerque, NM, USA

jihlefe@sandia.gov



Collaborators

Sandia National Labs

- Paul Kotula
- Geoff Brennecka
- Bryan Gauntt
- Chris T. Shelton
- Dara Gough
- Ping Lu
- Erik Spoerke
- Bonnie McKenzie
- Michael Rye
- Kelsey Meyer

North Carolina State University

- Jon-Paul Maria
- Brian Laughlin
- Peter Lam

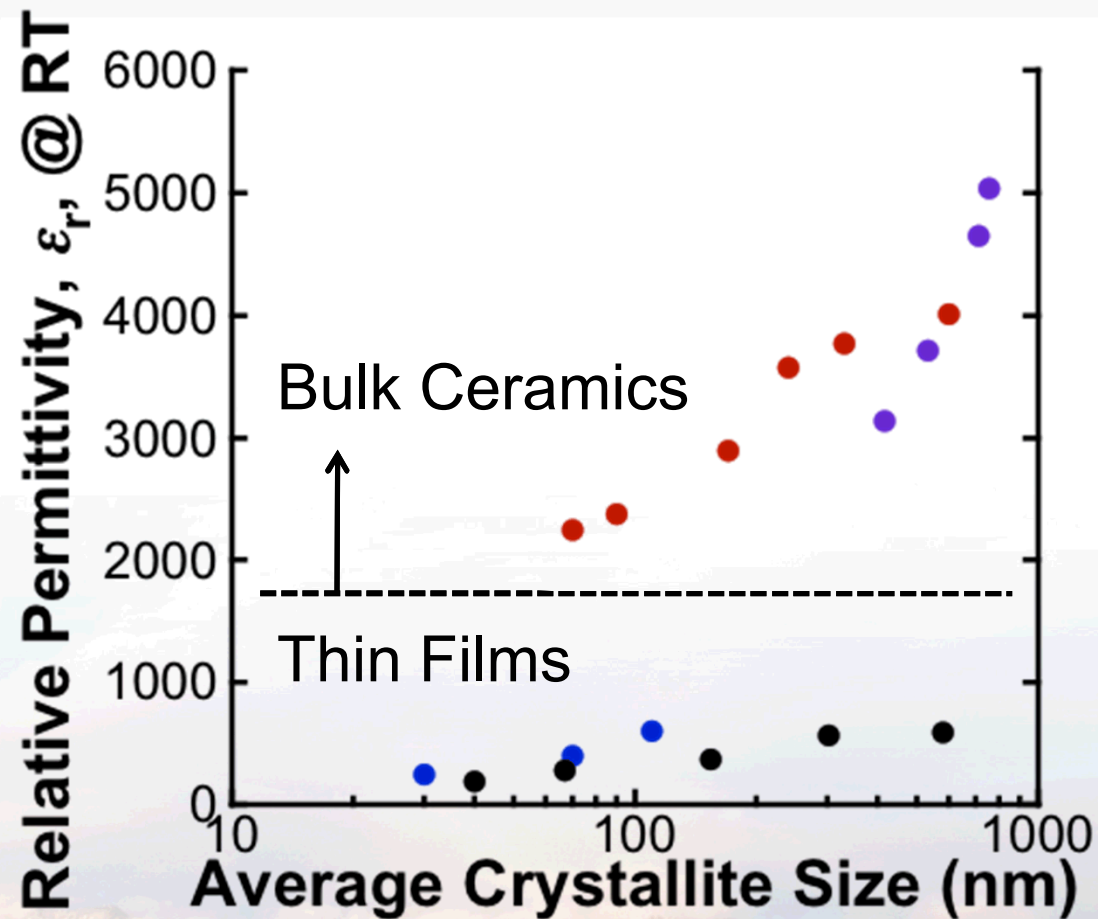
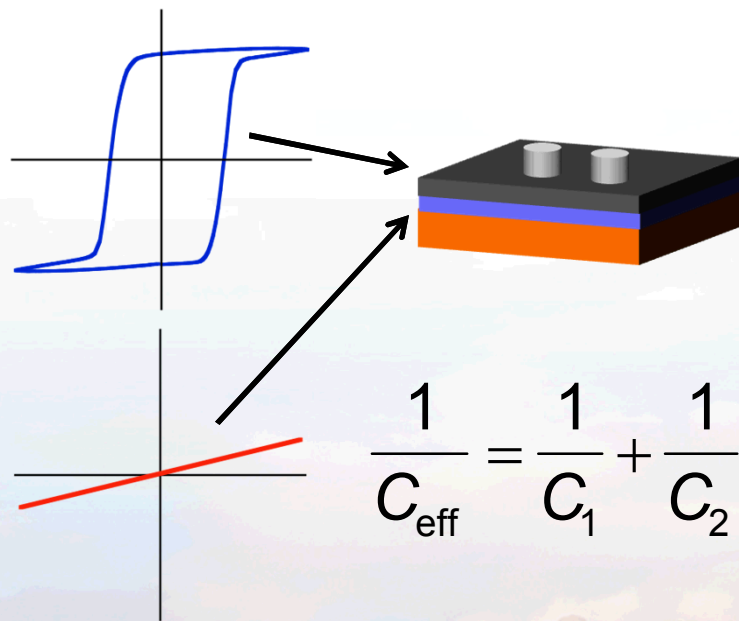
Oregon State University

- Brady Gibbons



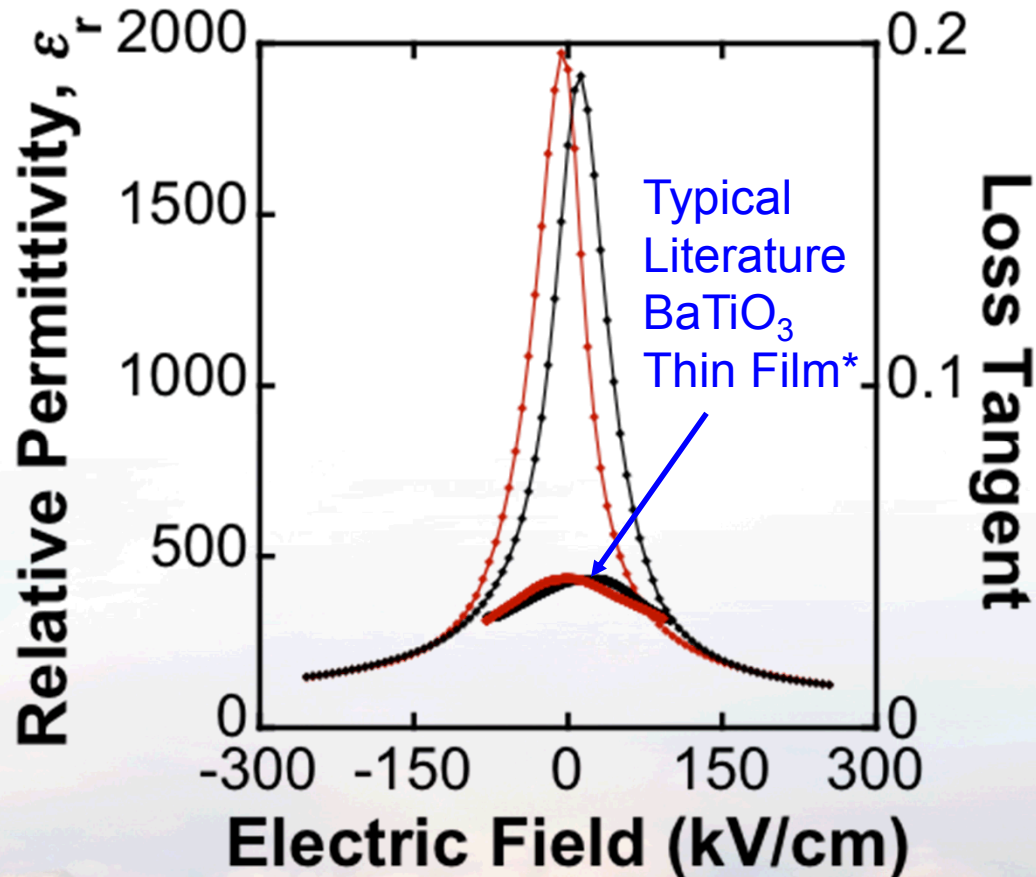
Scaling Effects in Ferroelectric Films

- Severely diminished properties in films
- Traditionally blamed on 'size effects'



BaTiO₃ Processed on Copper

- Films fired to 900° C in a reducing atmosphere
- Dielectric Constant approaching 2000
- > 80 % Dielectric Tunability
- $\tan \delta$ consistent with FE BaTiO₃
- Clear evidence of Extrinsic Ferroelectric contributions
- *This represents a breakthrough in Ferroelectric Thin Film Technology*



10 kHz, 0.77 kV/cm Oscillator

J. Ihlefeld *et al.* *J. Electroceram.* (2005)

*Thomas *et al.* *J. Appl. Phys.* (2001)



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Impact of Crystallization Temperature

700 °C

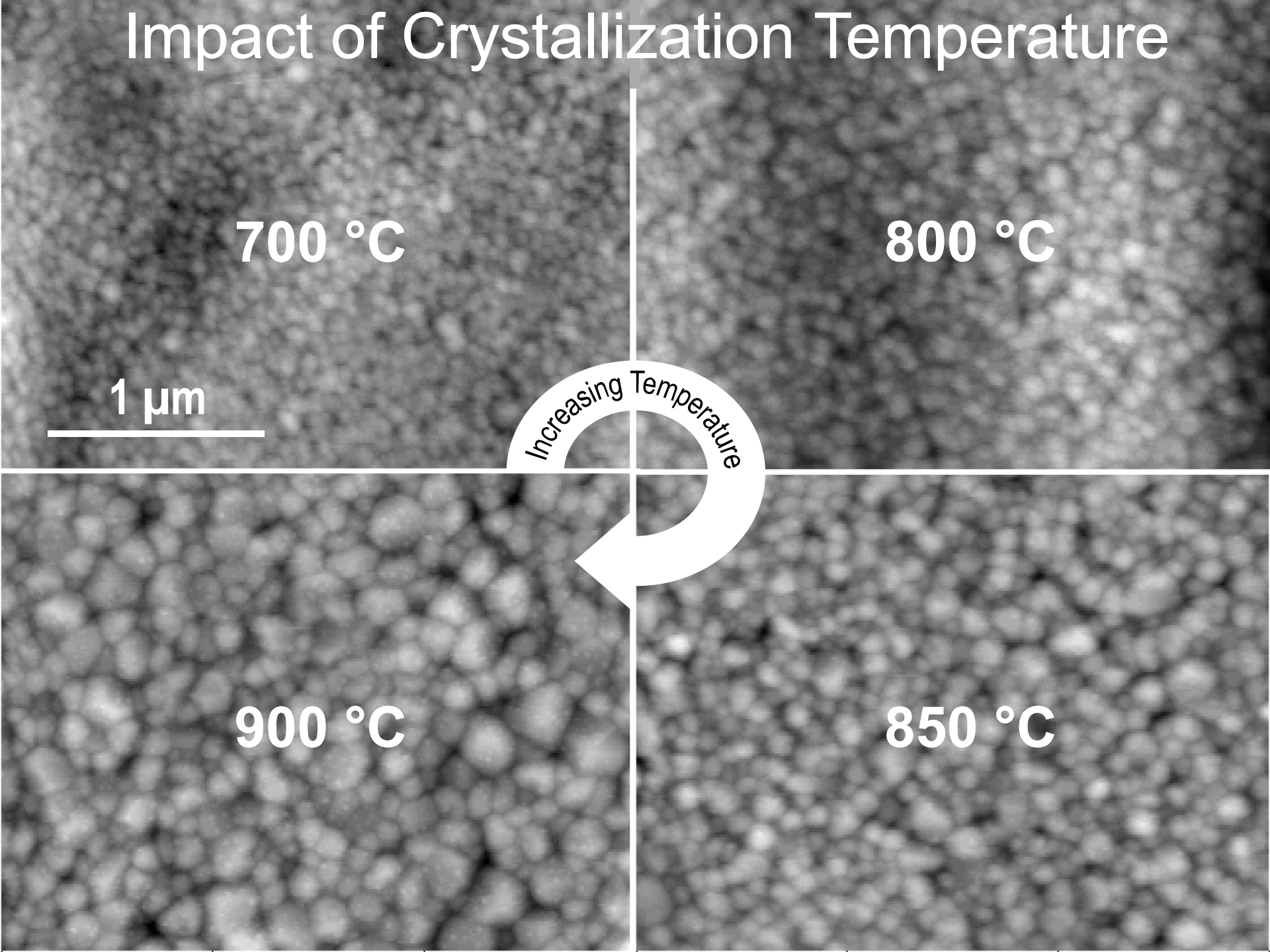
800 °C

1 μm

Increasing Temperature

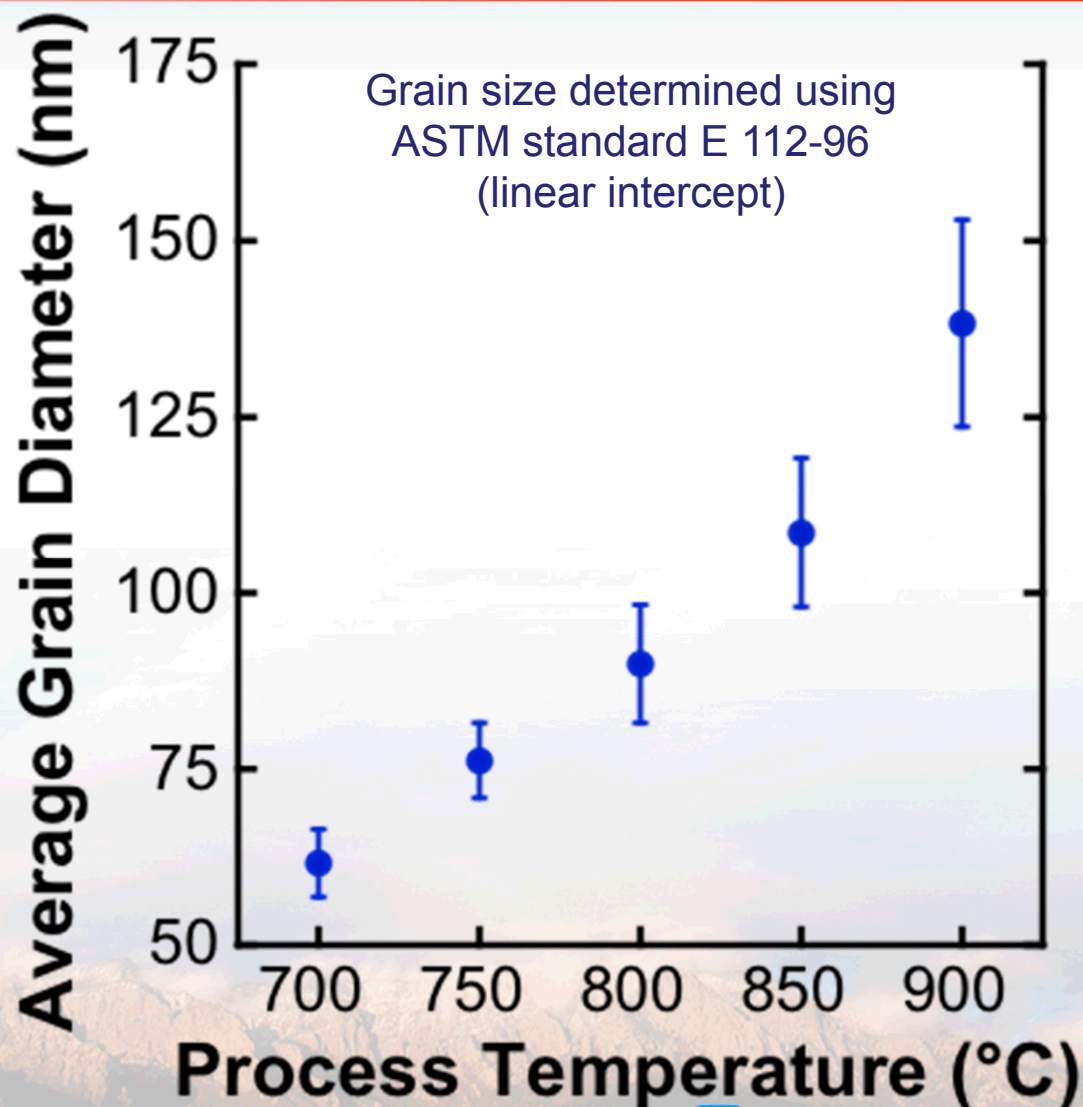
900 °C

850 °C



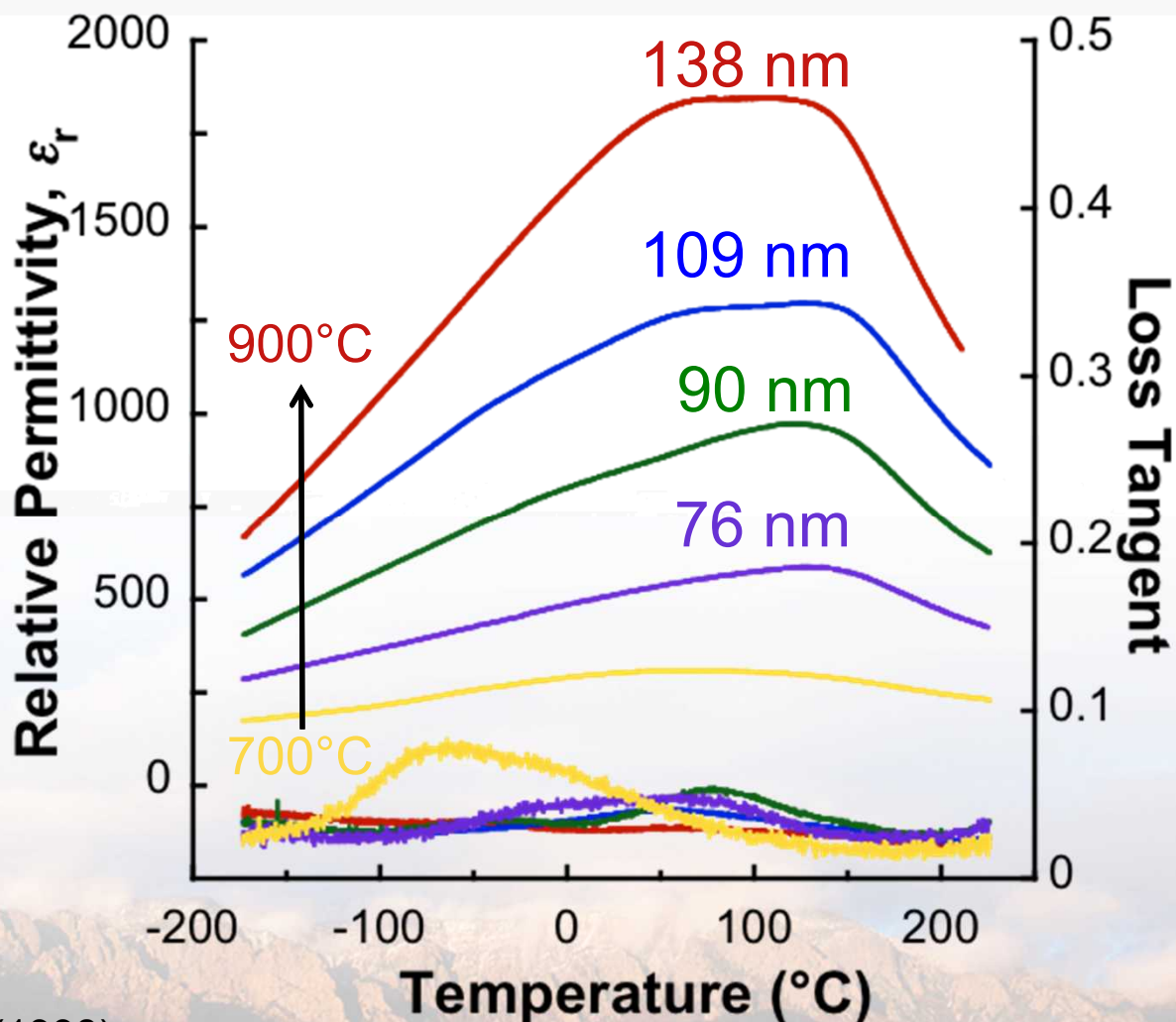
Grain Size Modification

- Process Temperature Modifies Grain Size
- Higher Temperature Anneal
- Larger Average Grain Size



Processing Temperature Effects on Permittivity

- Strong Permittivity Dependence on Processing Temperature
- T_c Does Not Change
 - Consistent with Brick-Wall Model
 - Agrees with bulk BaTiO_3 of similar purity*
 - T_c shifts for finest grained material†



* Frey *et al. Ferroelectrics* (1998)

† McCauley *et al. J. Amer. Cer. Soc.* (1998)

J.F. Ihlefeld *et al. J. Appl. Phys.* (2008)



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Crystallite vs. Grain Size: Processing Matters!

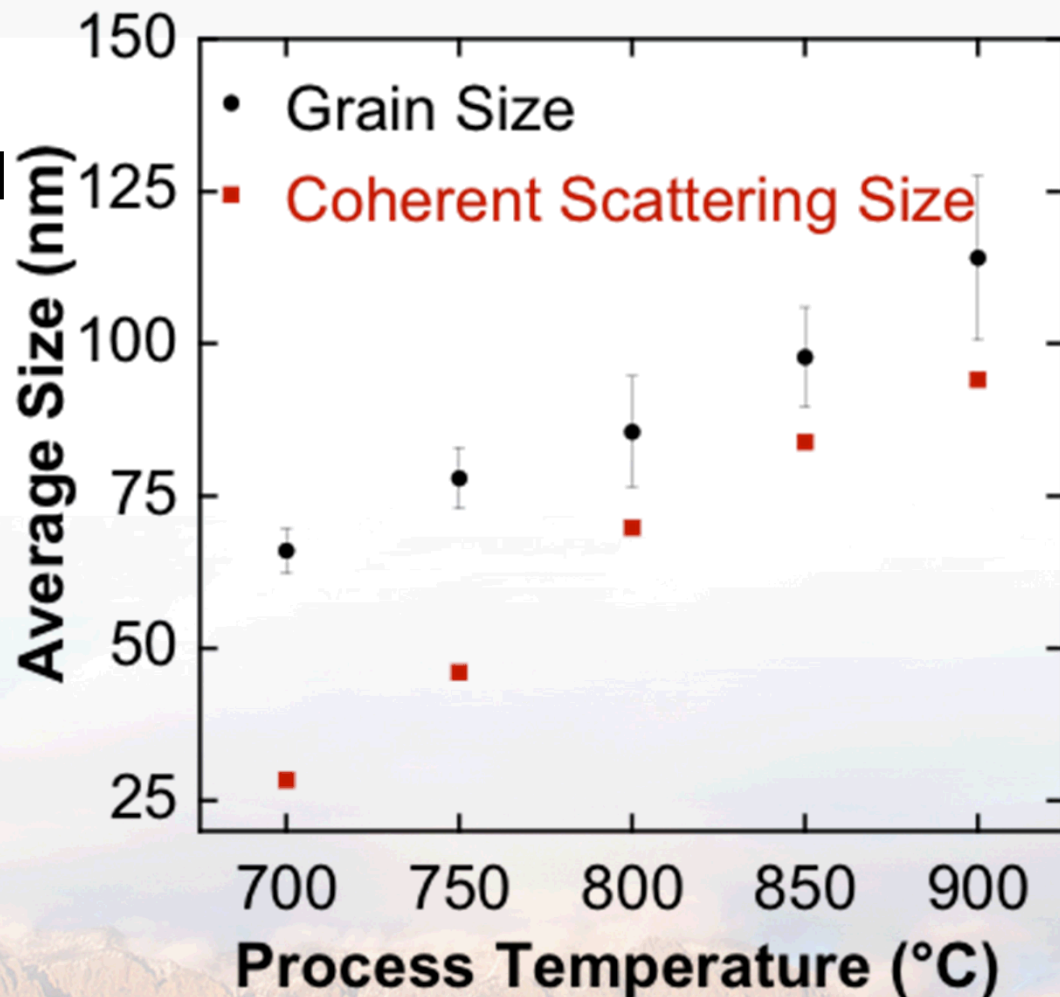
Grain Size

- AFM and FE-SEM
- 95% confidence interval

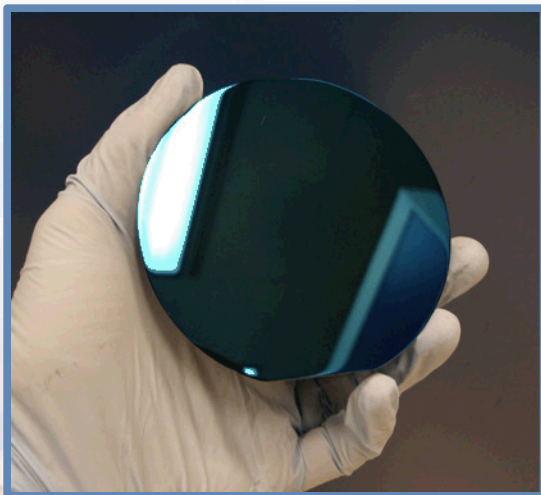
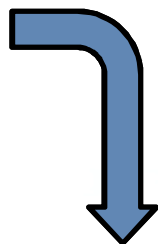
Coherent Scattering Size

- CHES
- Scherrer's Formula on 111 reflections

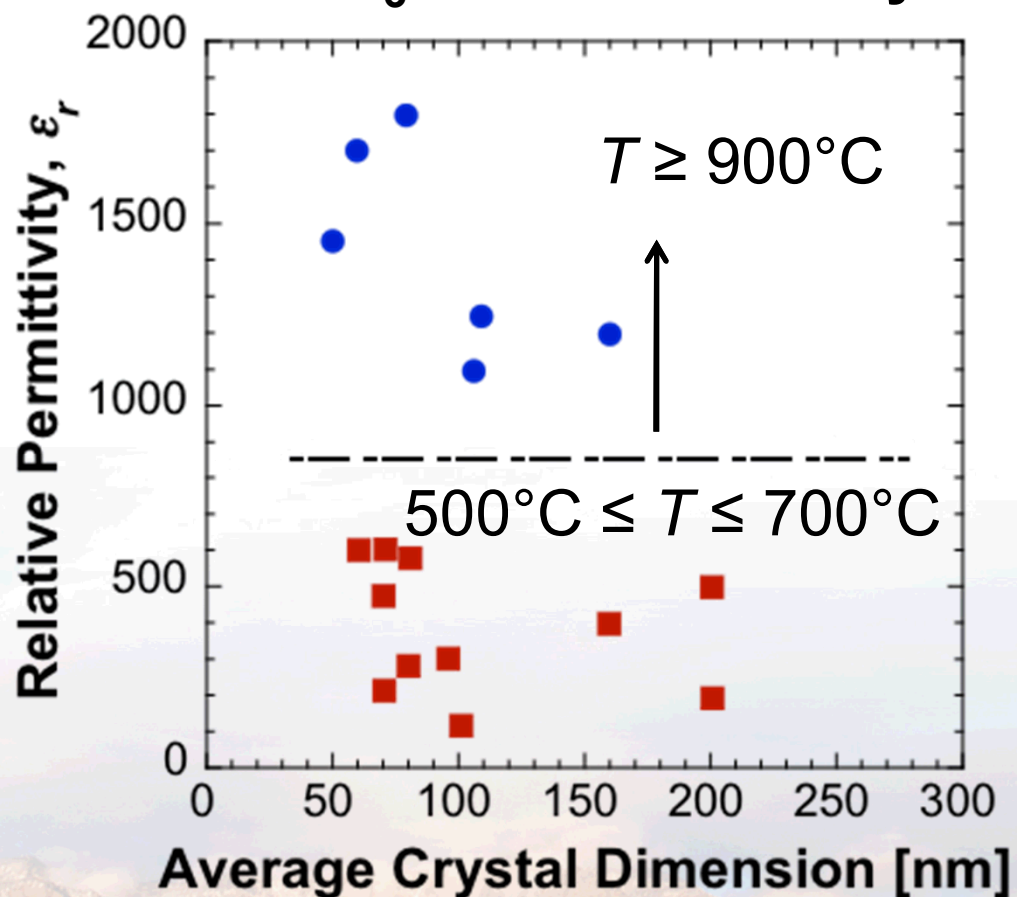
***Higher Processing
Temperature Gives
Improved Crystalline
Quality***



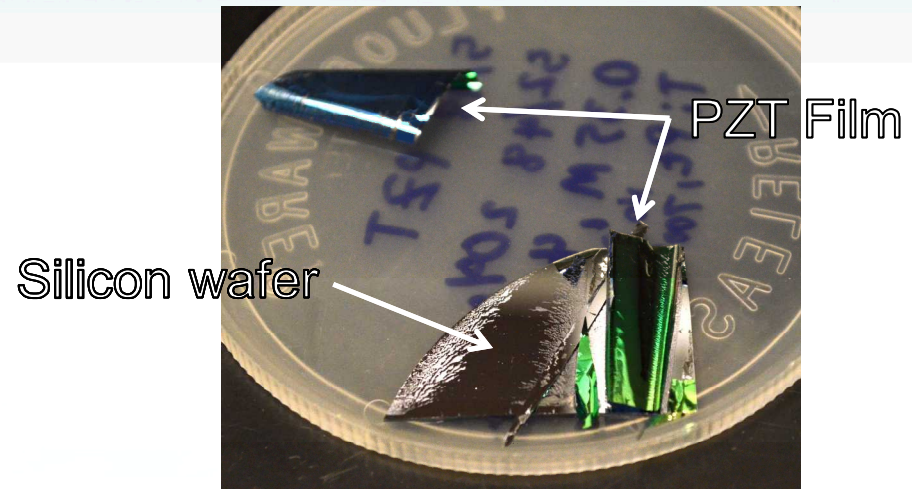
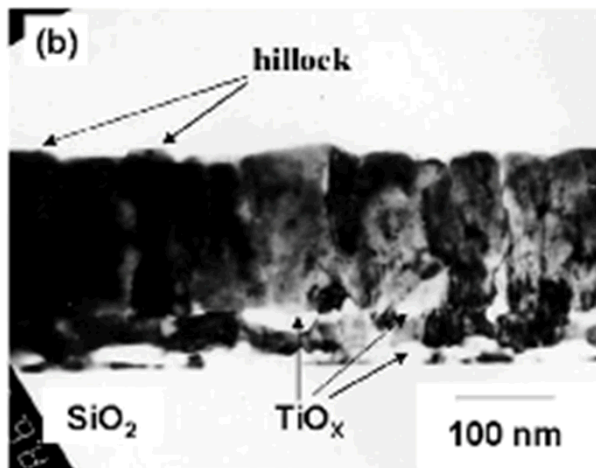
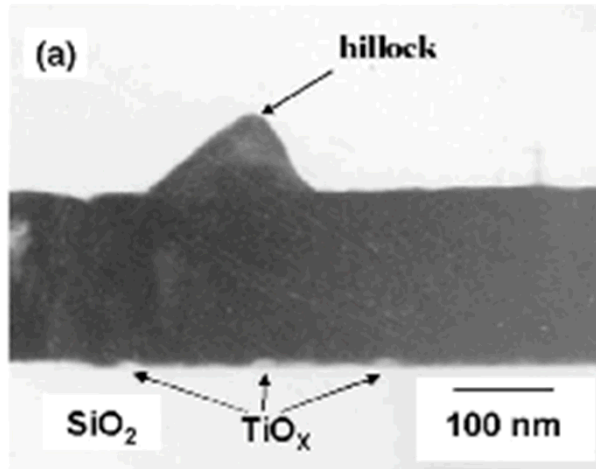
Processing Effects on K vs d



BaTiO₃ Film Permittivity



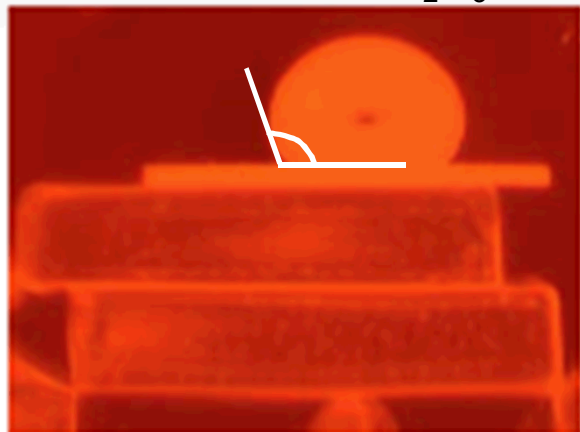
Issues with Platinized Silicon Substrates



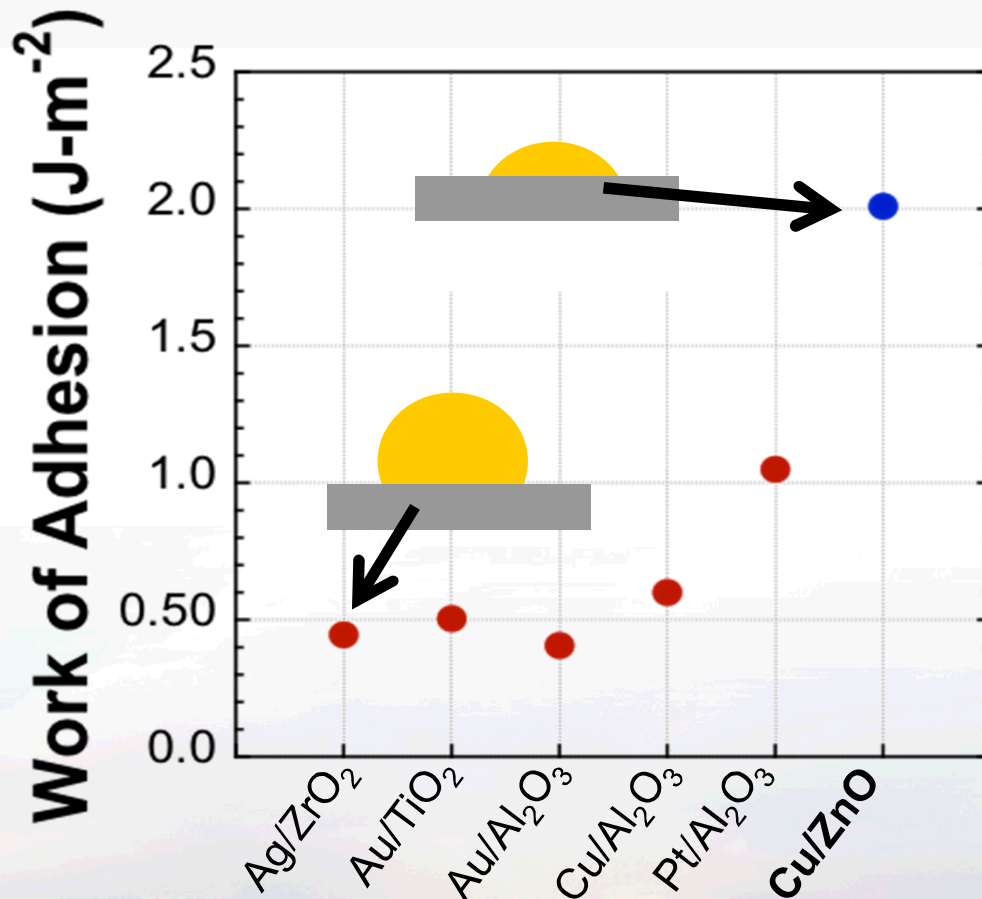
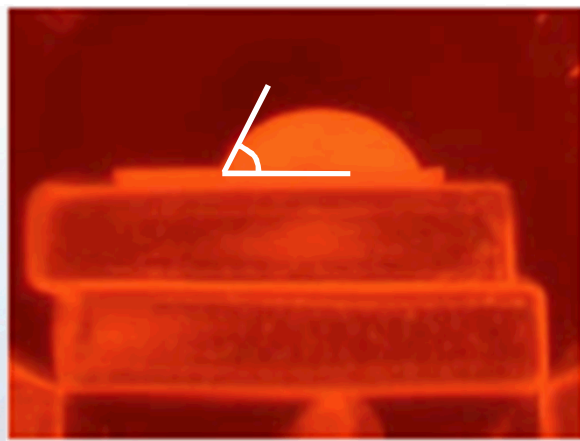
- Titanium 'adhesion' layers by far the most common
- Titanium expands upon oxidation causing hillocks
- Adhesion layers fail with large temperature swings ($>700^\circ$)

Metal Wetting and Adhesion

Molten Cu on Al_2O_3



Molten Cu on ZnO



Can we use ZnO as an adhesion layer for Pt?

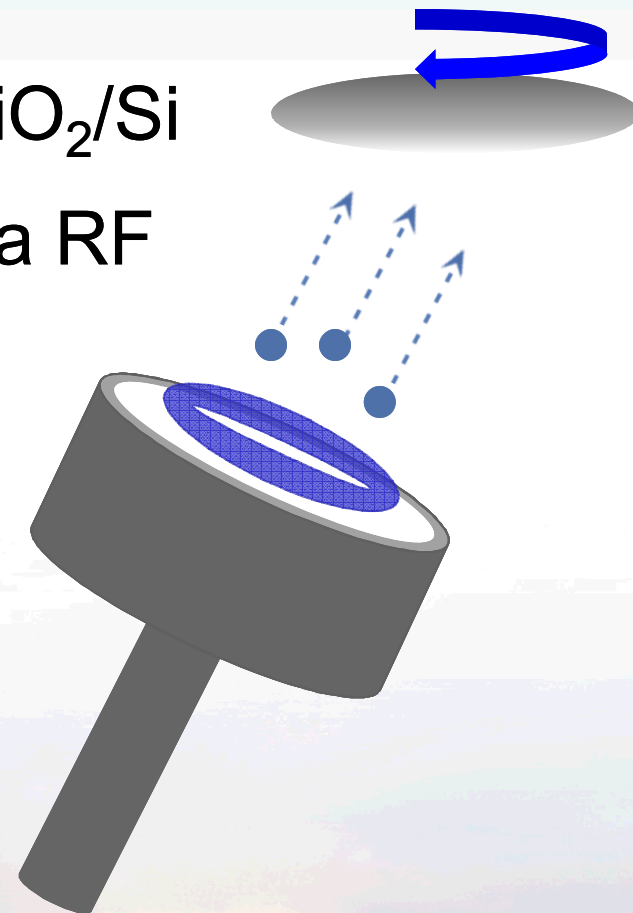
Cu and Pt both $Fm\bar{3}m$ metals



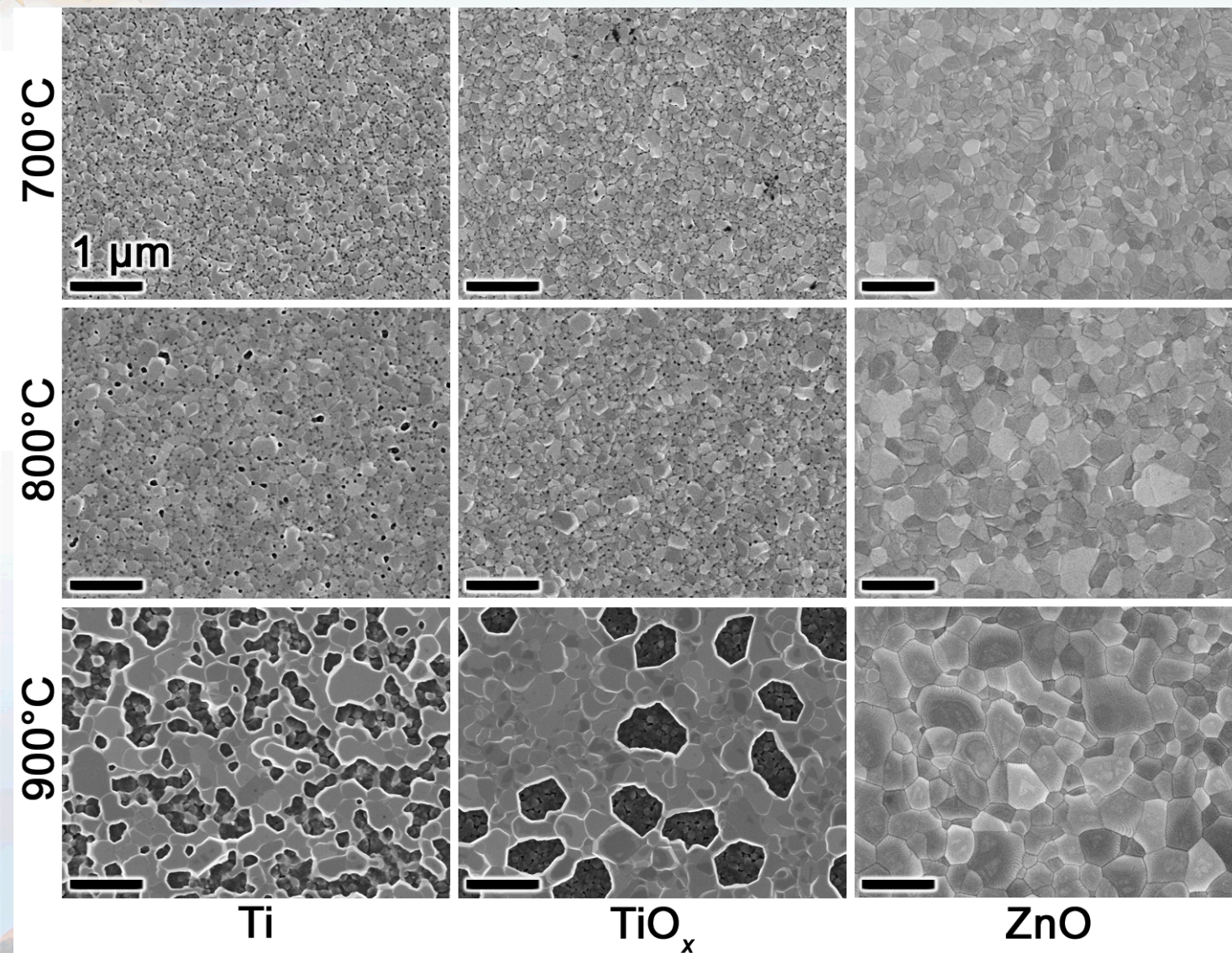
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Pt/Si Substrate Preparation

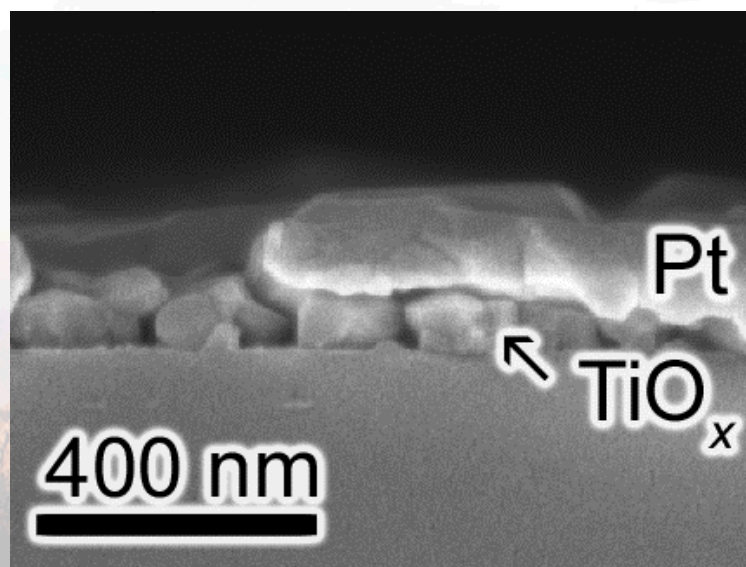
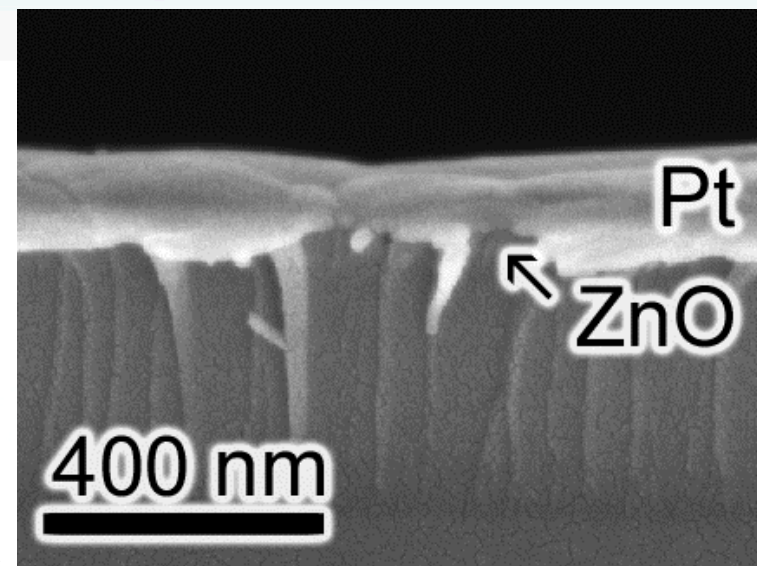
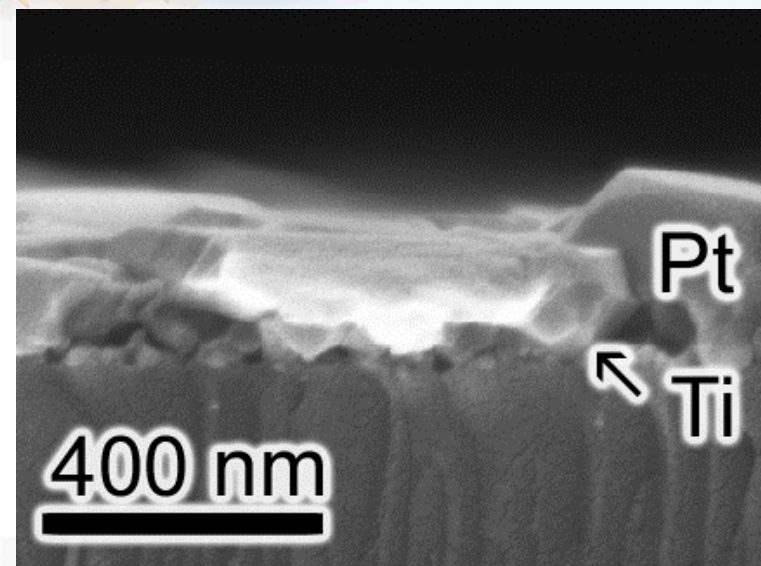
- 100 nm Pt/40 nm buffer/40 nm SiO₂/Si
- Ti, TiO_x, ZnO, and Pt prepared via RF magnetron sputtering
 - 30° off-axis geometry
 - Ti: Ar atmosphere
 - TiO_x: Ar sputter, O₂ anneal
 - ZnO: 1:1 Ar:O₂ atmosphere
 - Pt: Ar Atmosphere



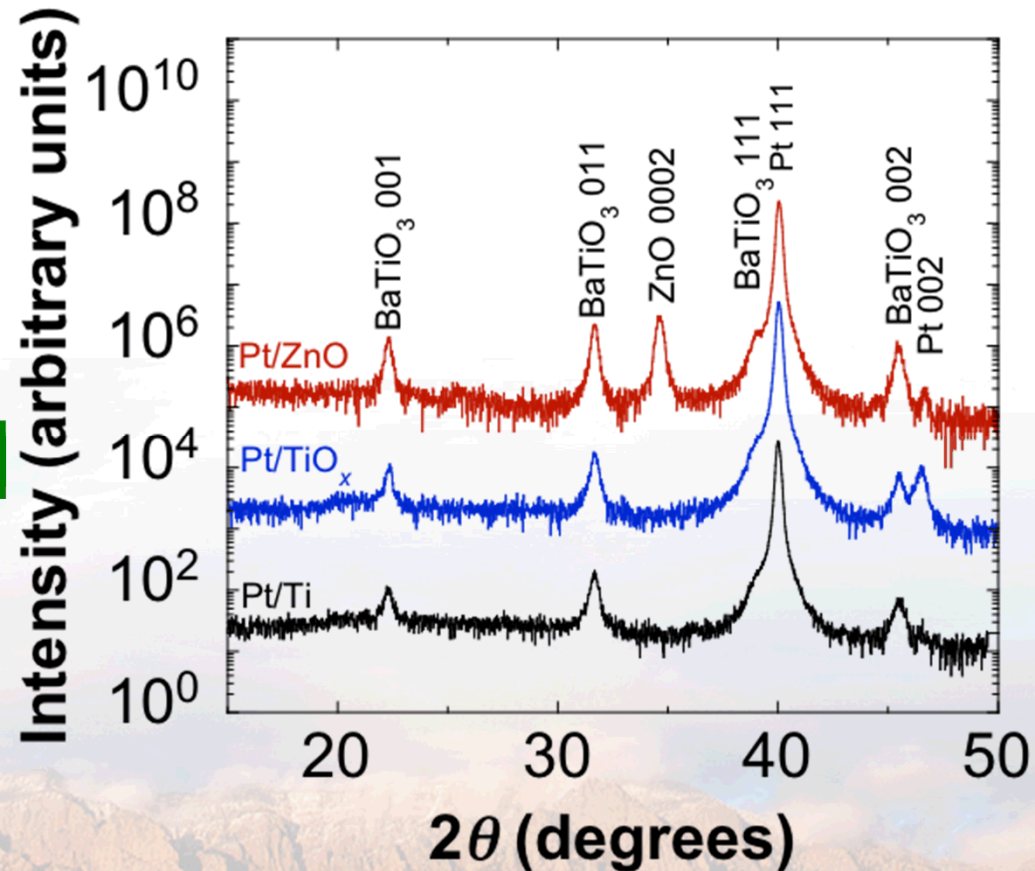
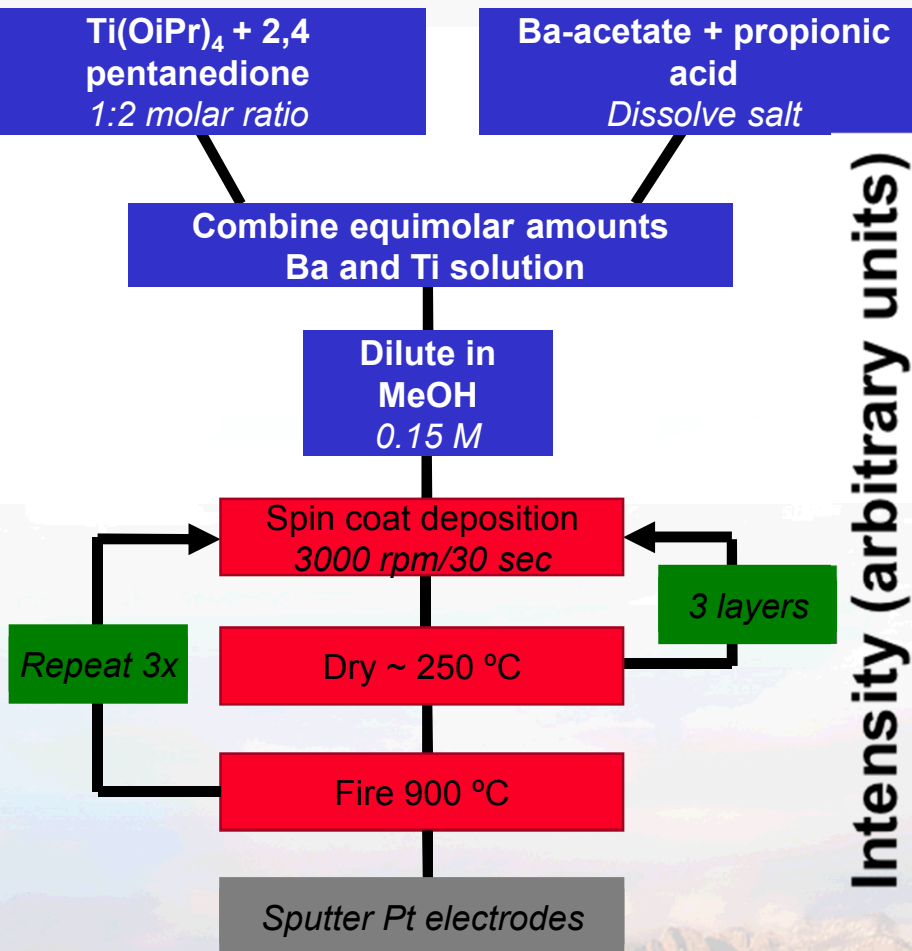
Electrode Temperature Stability



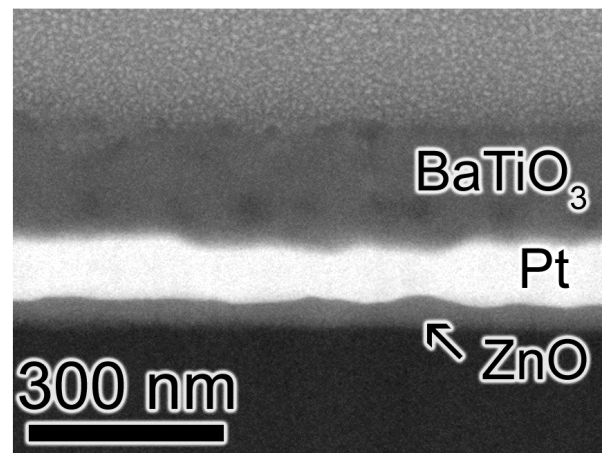
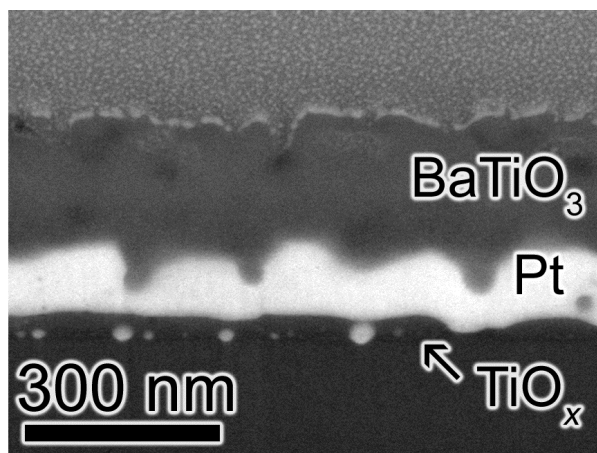
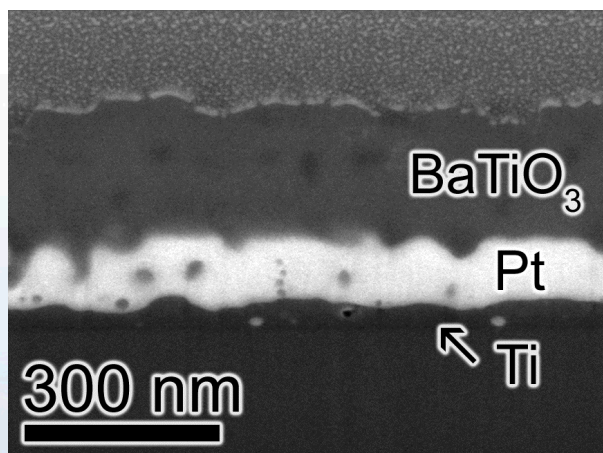
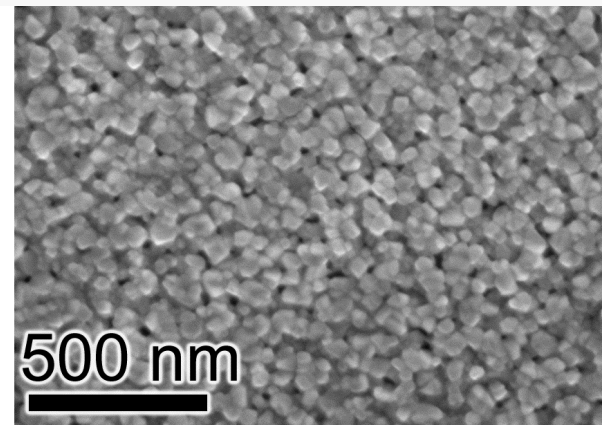
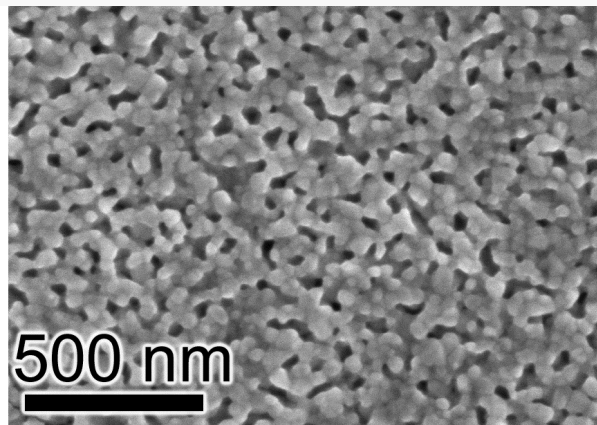
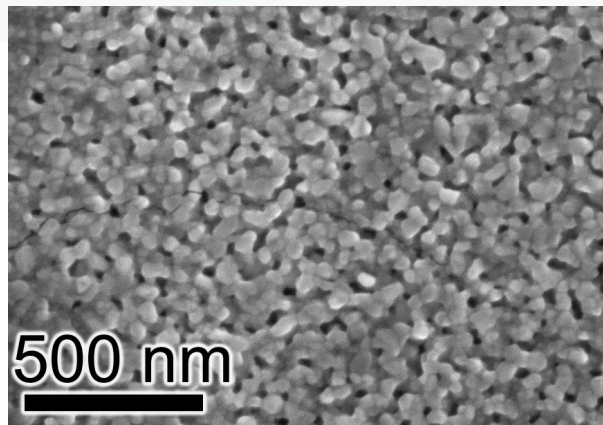
Electrode Stability: 900° C



High Temperature Test Case: CSD BaTiO₃ on Platinized Silicon



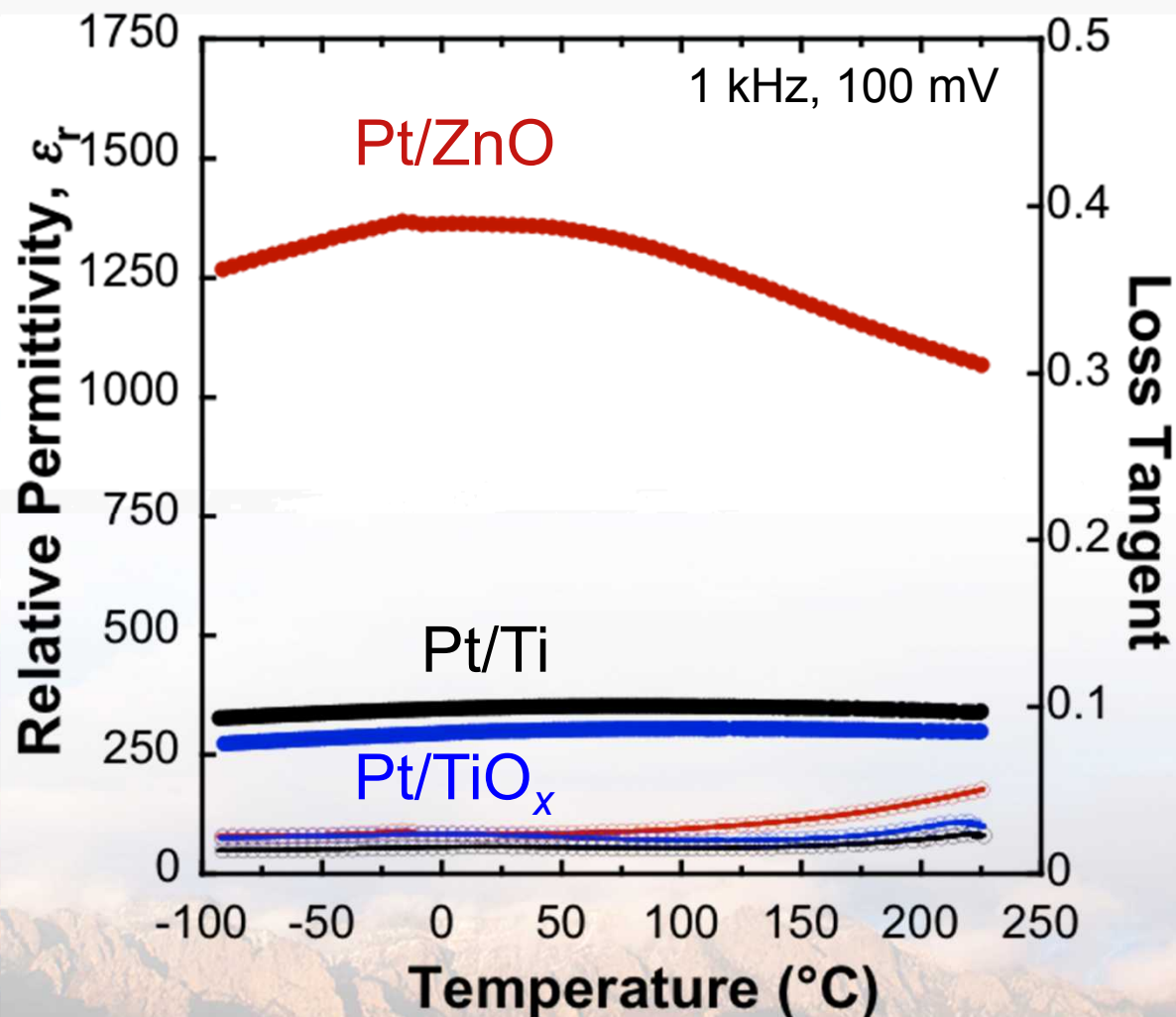
BaTiO₃ Topography and Microstructure



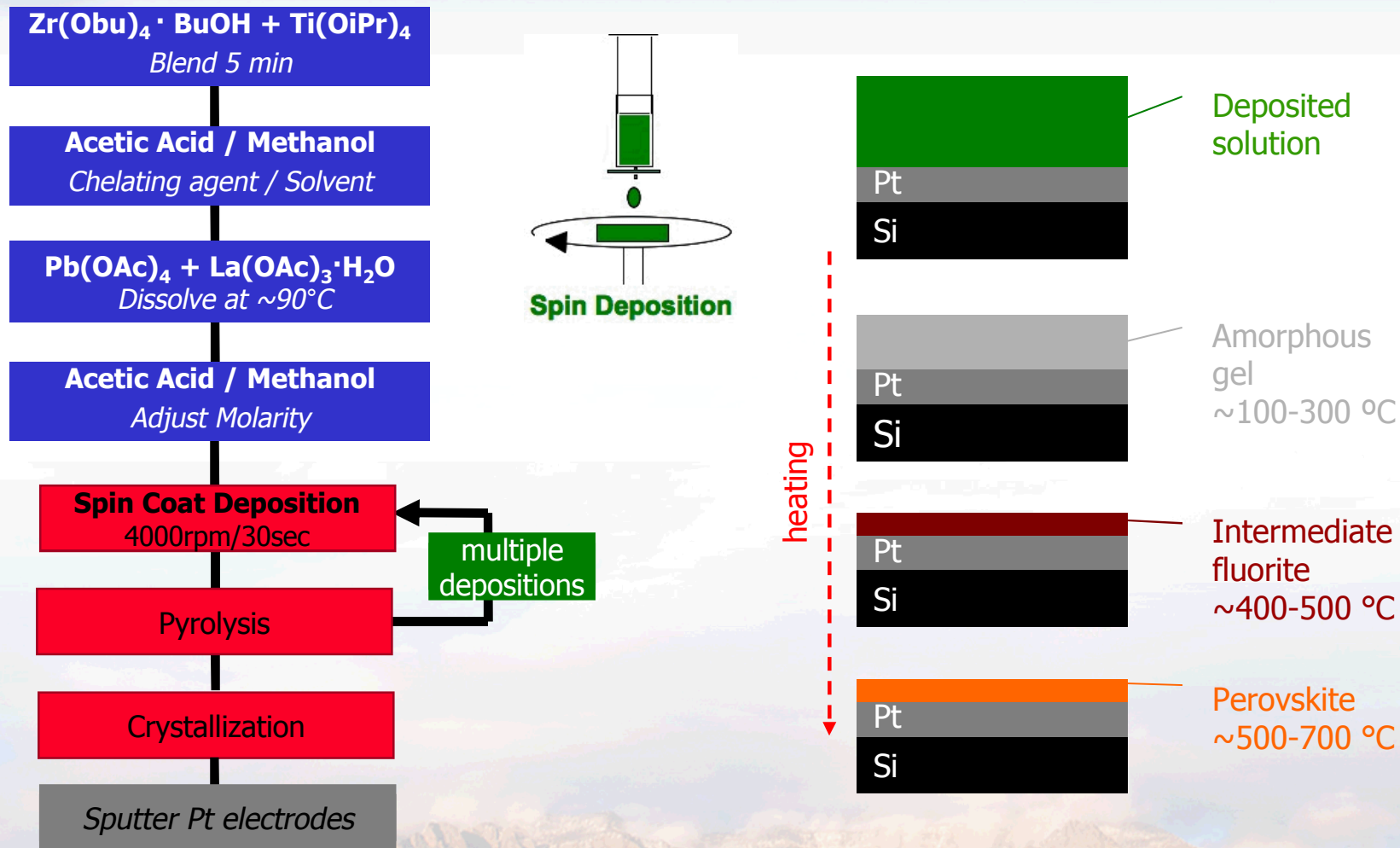
BaTiO₃ Microstructures Virtually Identical
Electrode Integrity Dependent on Adhesion Layer

BaTiO₃ Dielectric Properties: Pt/ZnO Substrates Superior

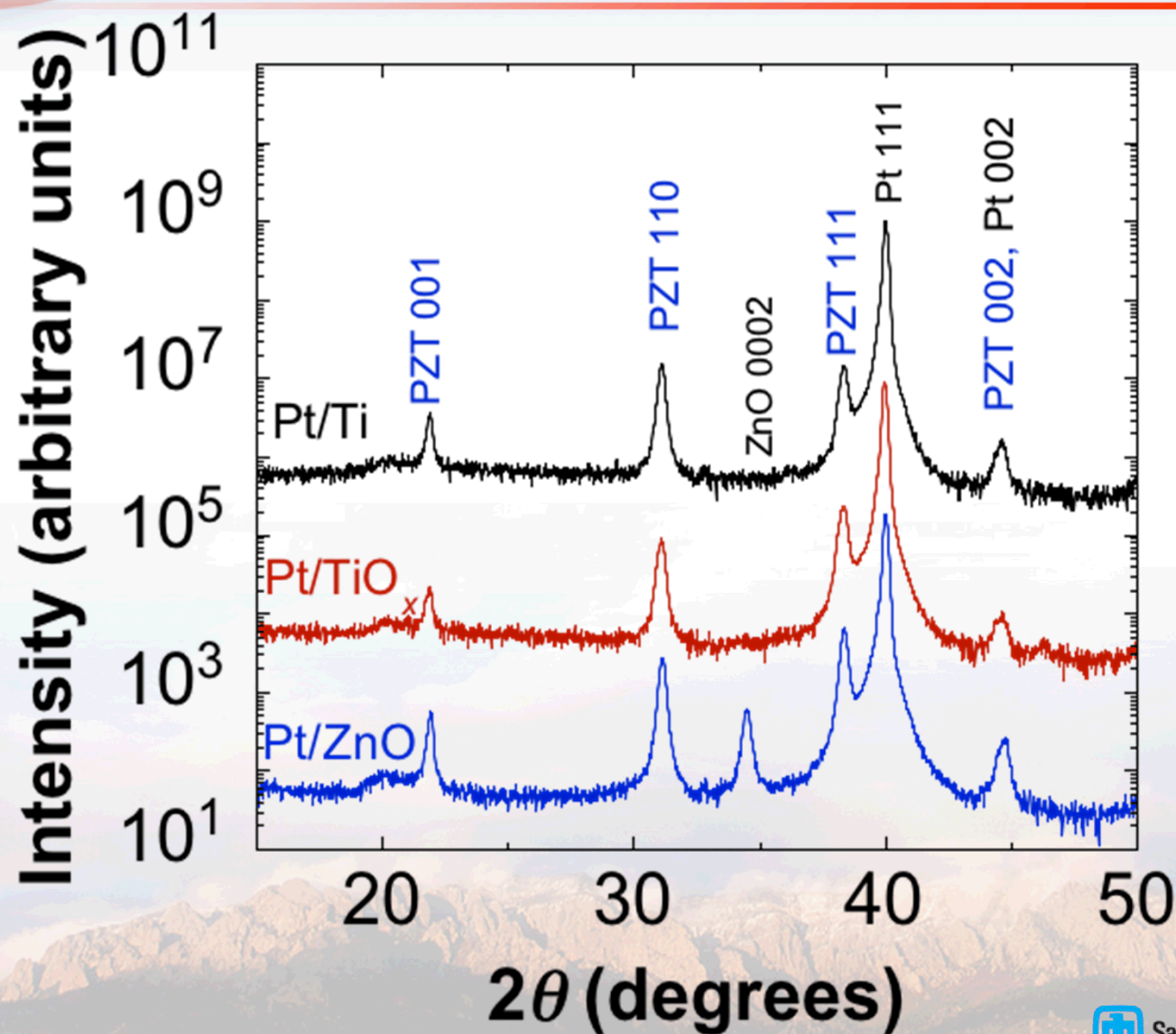
- Ti- and TiO_x-buffered films actually survived
- BaTiO₃ on Pt/ZnO substantially outperforms other substrates
- Microstructure nearly identical: Why such a disparity?
- What about other Ferroelectrics?



SNL IMO PZT CSD Film Preparation

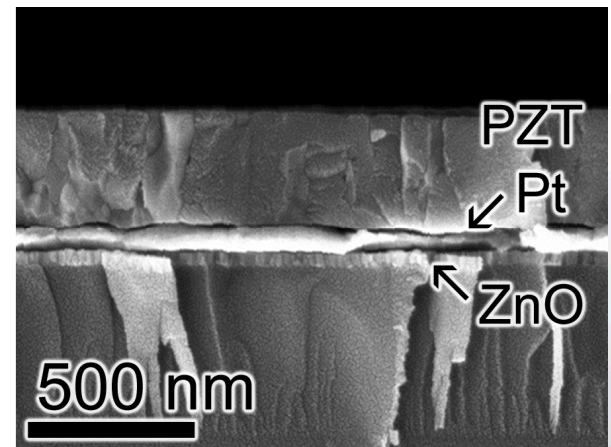
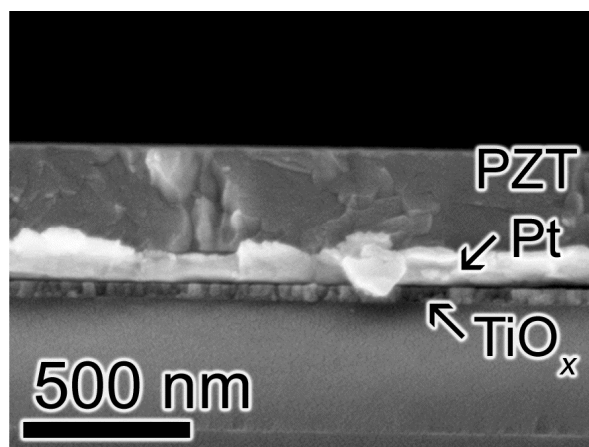
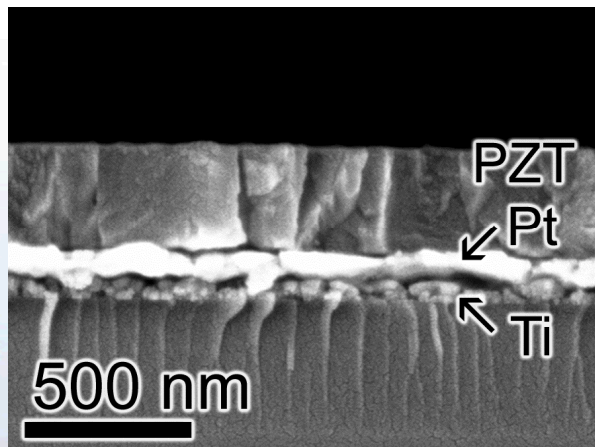
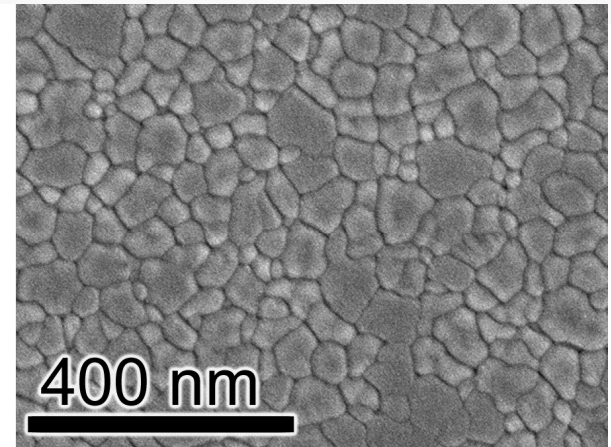
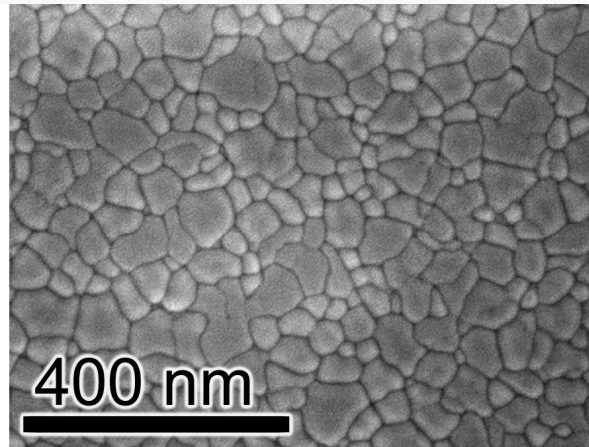
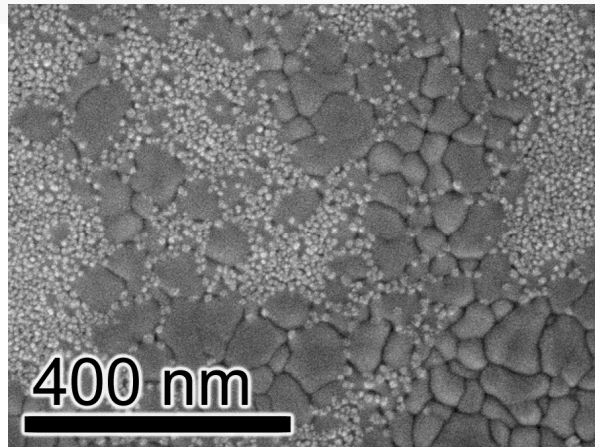


Film Phase/Crystallographic Properties



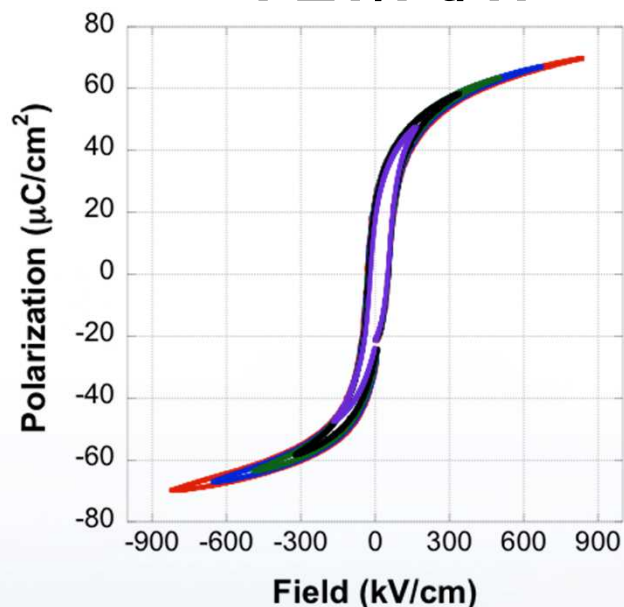
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PZT Film Microstructure

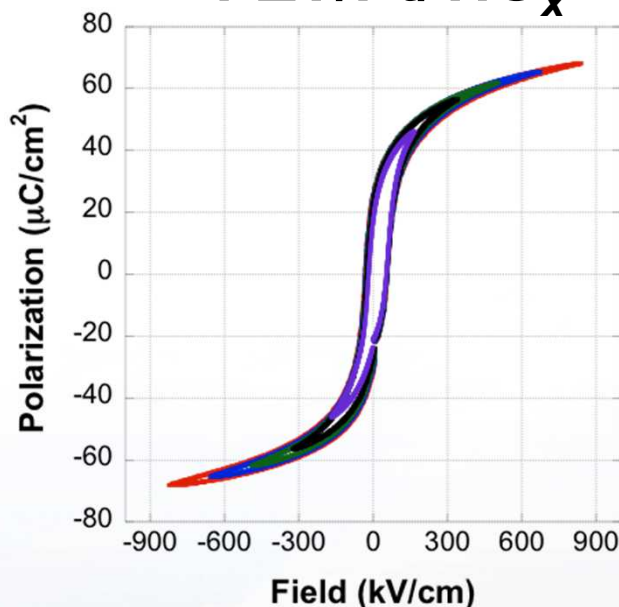


Dielectric and Ferroelectric properties

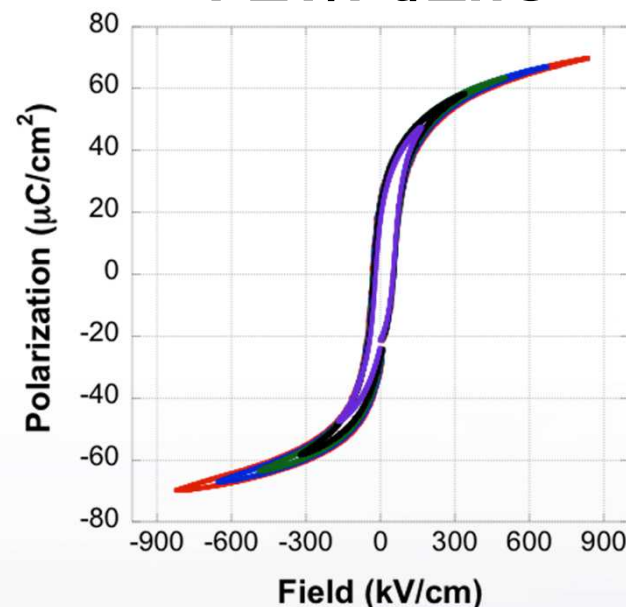
PZT/Pt/Ti



PZT/Pt/TiO_x



PZT/Pt/ZnO



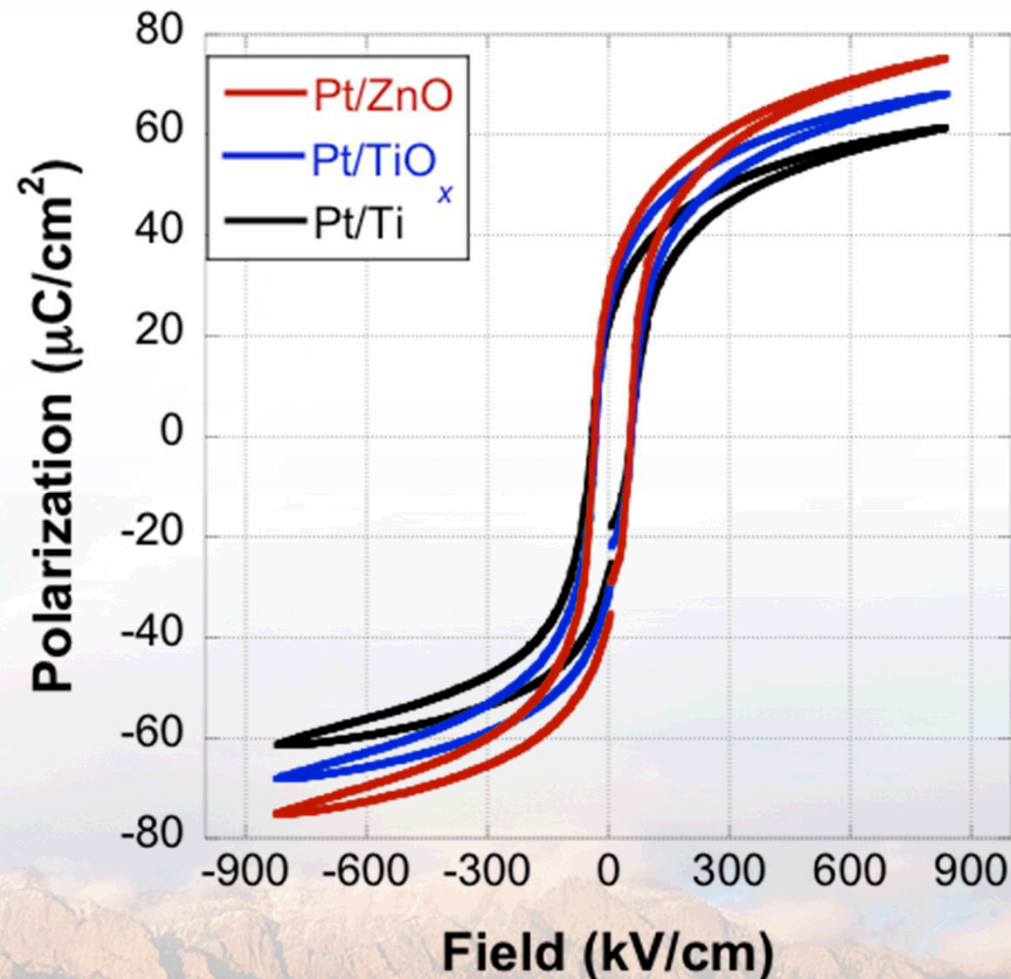
- Measurements conducted at 10 Hz
- All films saturate well
- Low leakage



PZT Films Ferroelectric Properties: Pt/ZnO Substrates Superior

	$P_{\max}$ ($\mu\text{C}/\text{cm}^2$)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kV/cm)	K
Pt/Ti	61.5	23.8	47.0	1440
Pt/TiO _x	68.2	27.0	44.1	1620
Pt/ZnO	75.3	32.2	43.8	1740

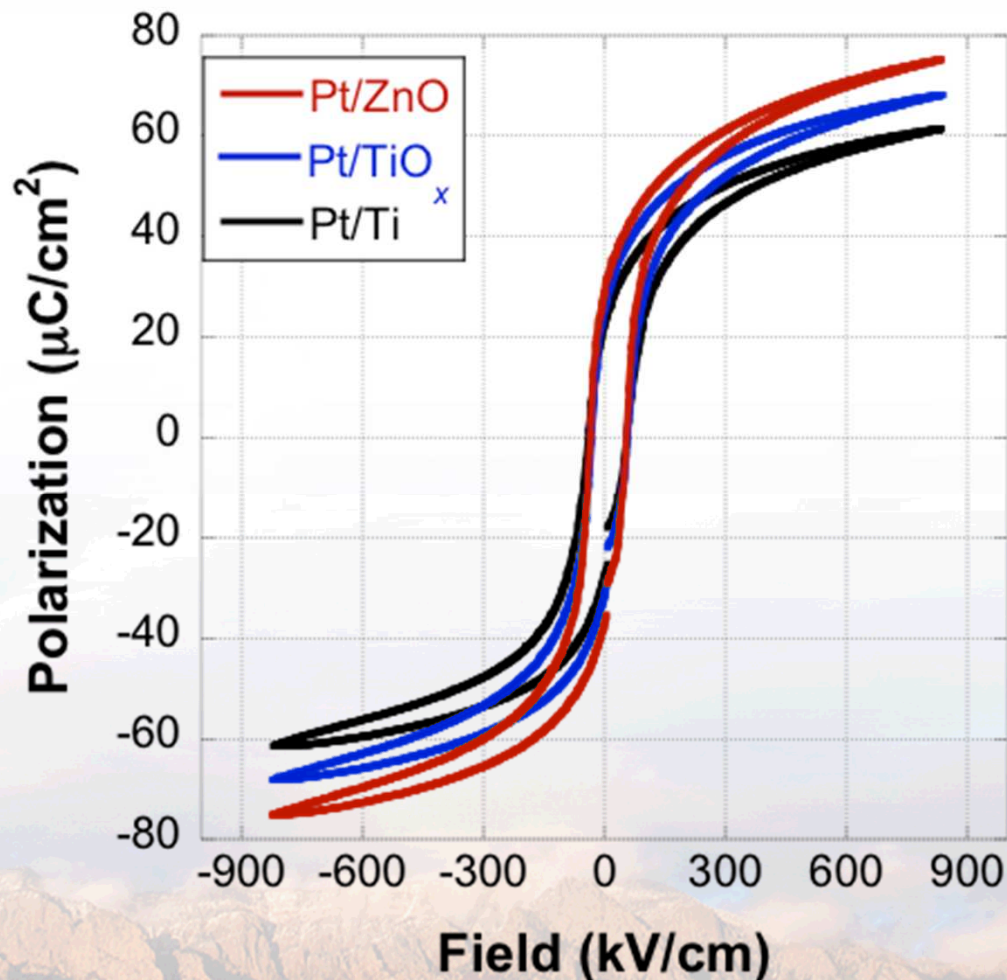
- Both P_r and K increase on ZnO-buffered substrates
- Coercive field decreases slightly for PZT on ZnO-buffered substrates



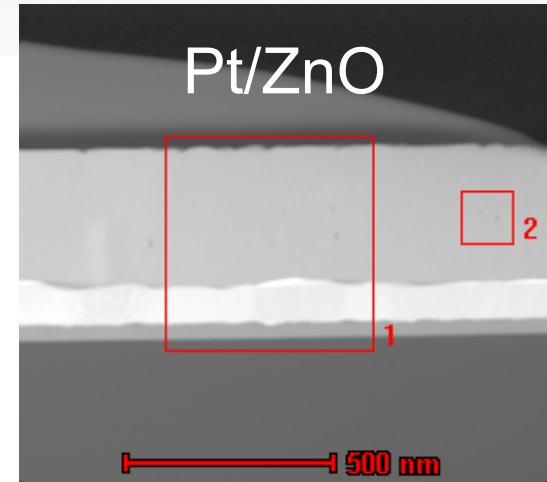
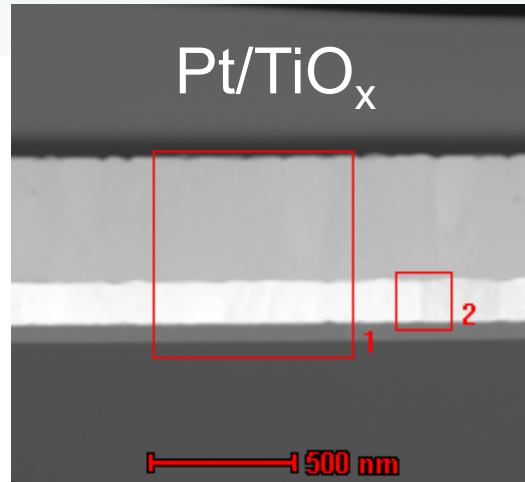
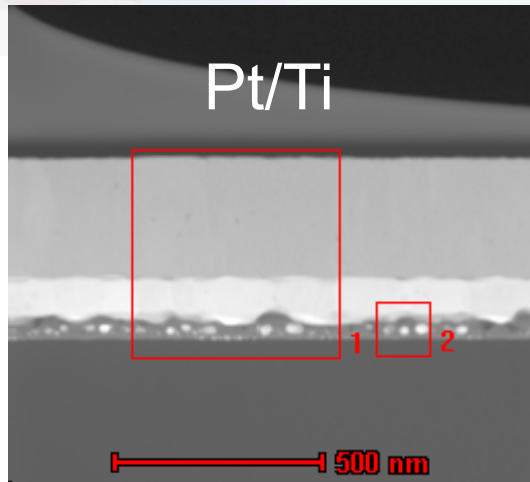
PZT Films Ferroelectric Properties: Pt/ZnO Substrates Superior

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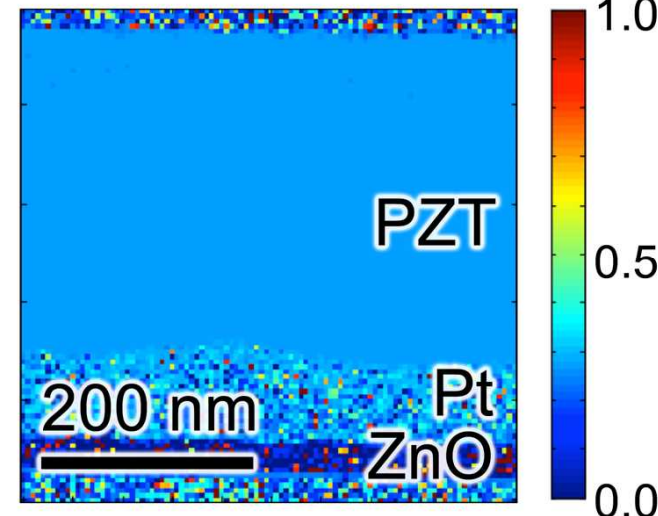
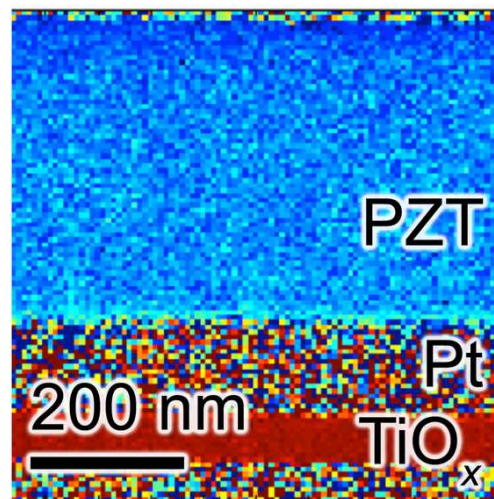
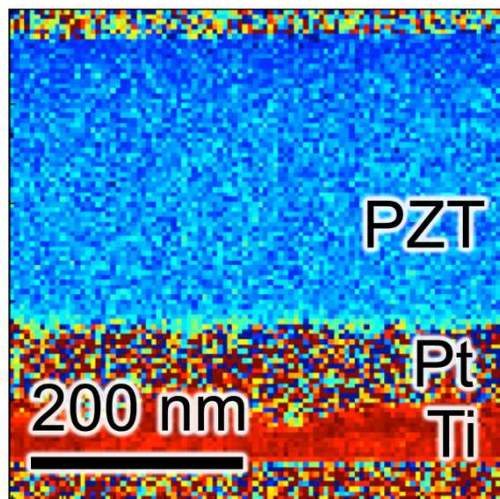
- Two film systems
- Performance improvements identified in both on ZnO-buffered substrates
- Mechanism?



PZT Composition Analysis: No Composition Gradient on Pt/ZnO

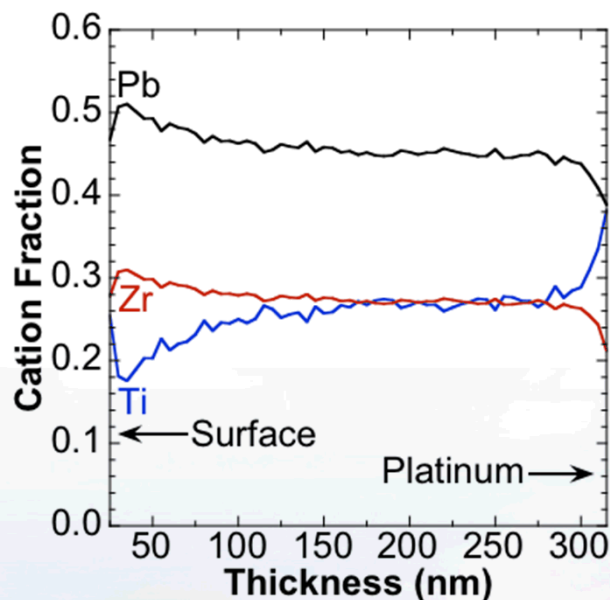


Titanium Distribution

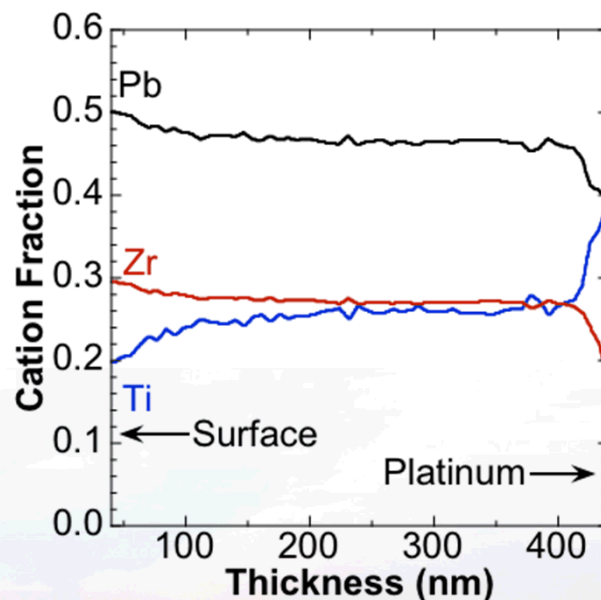


PZT Composition Analysis: No Composition Gradient on Pt/ZnO

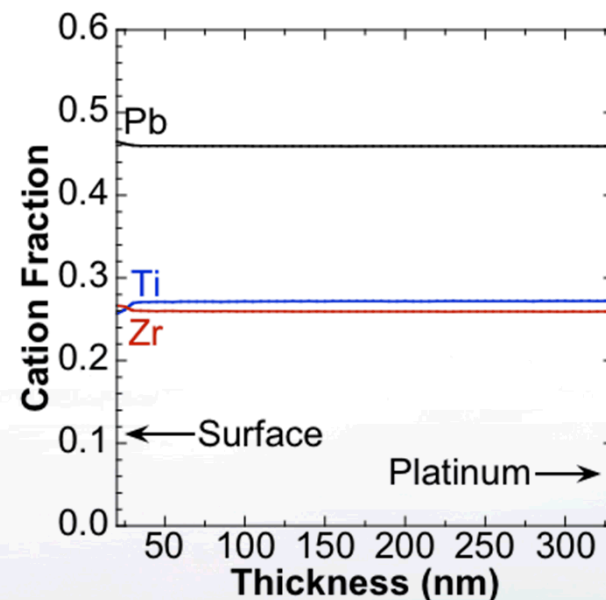
Pt/Ti



Pt/TiO_x



Pt/ZnO



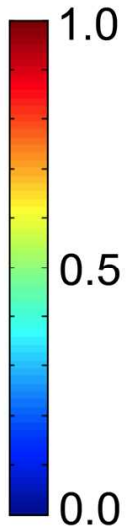
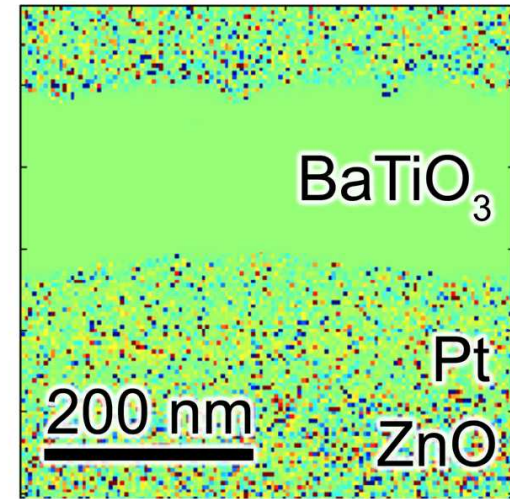
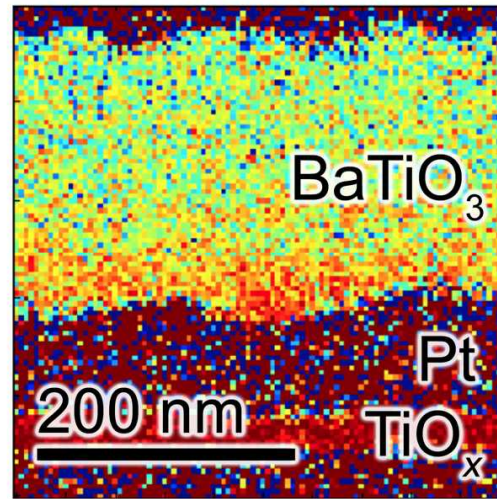
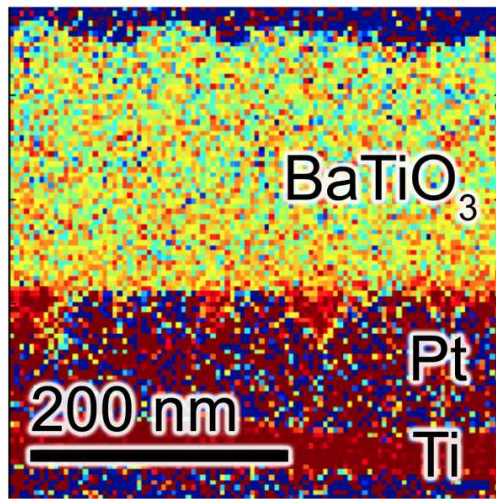
***Substantially improved chemical
homogeneity in films on Pt/ZnO substrates***



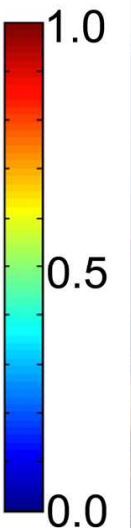
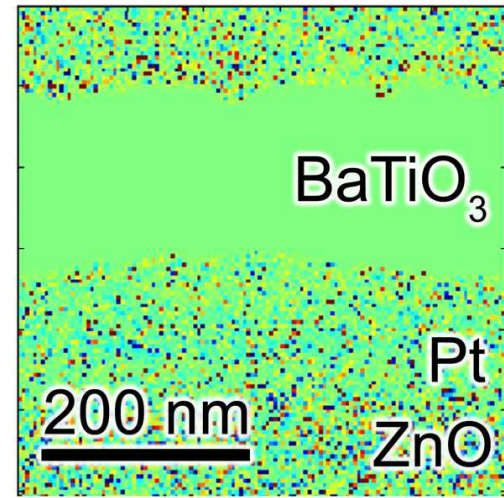
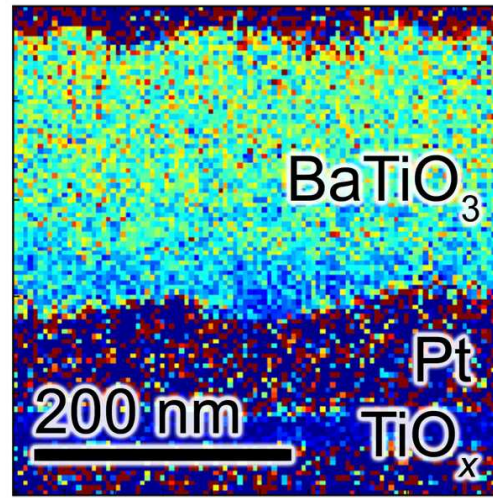
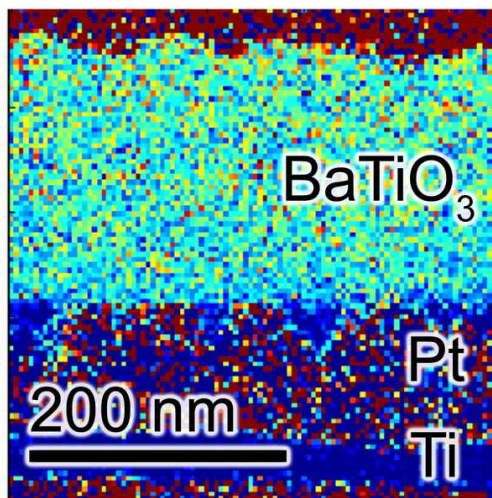
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BaTiO₃ Compositional Analysis: No Composition Gradient on Pt/ZnO

Titanium Distribution

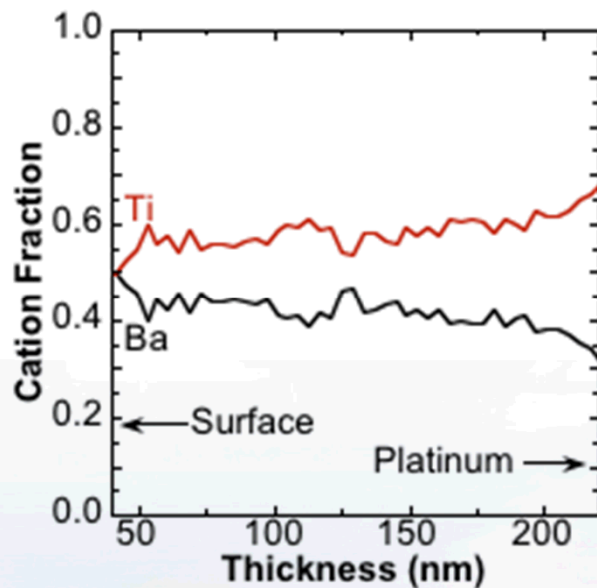


Barium Distribution

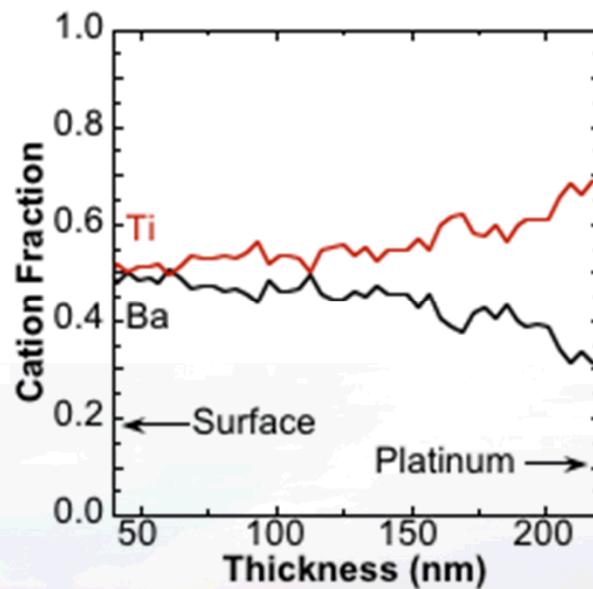


BaTiO₃ Compositional Analysis: No Composition Gradient on Pt/ZnO

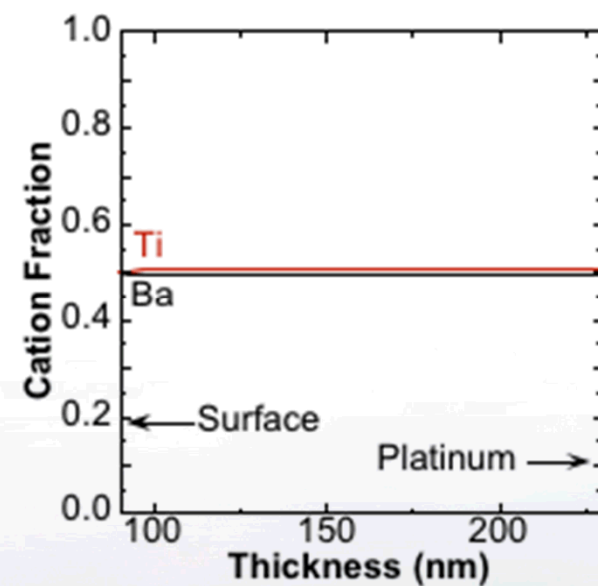
Pt/Ti



Pt/TiO_x



Pt/ZnO



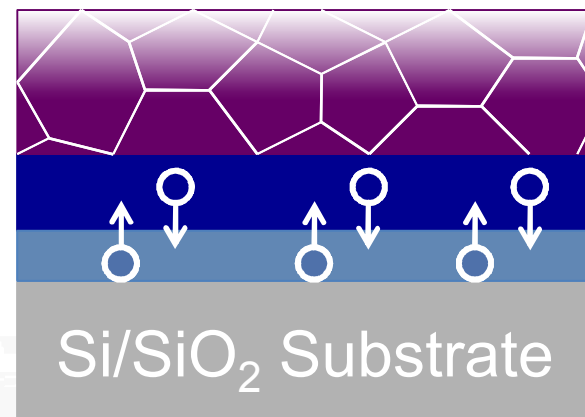
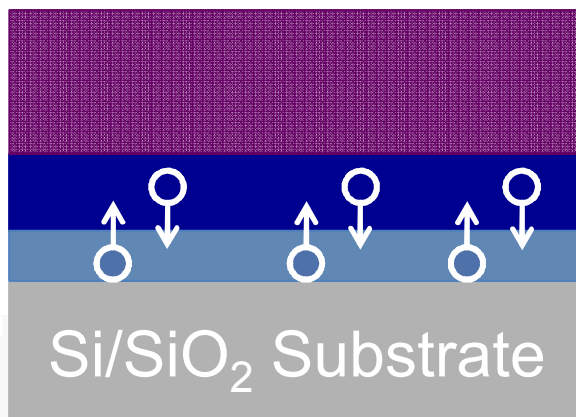
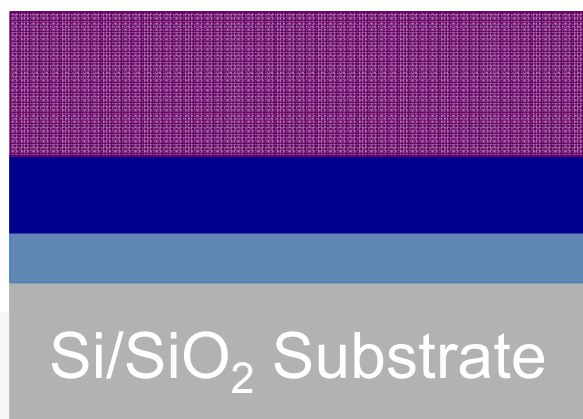
***Substantially improved chemical
homogeneity in films on Pt/ZnO substrates***

Mechanism?



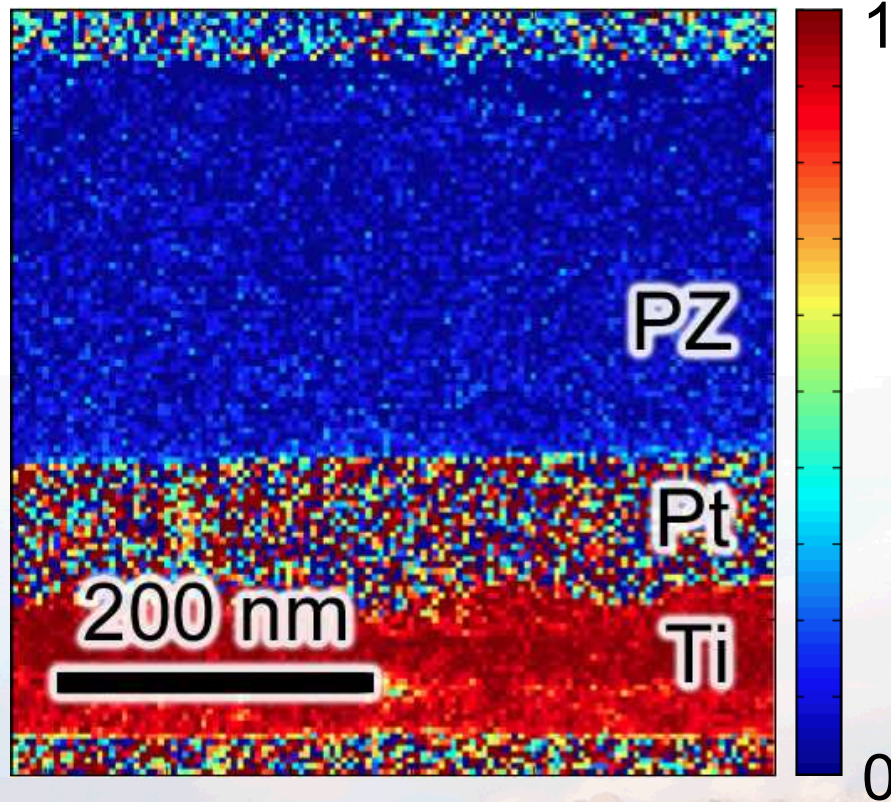
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Our Model

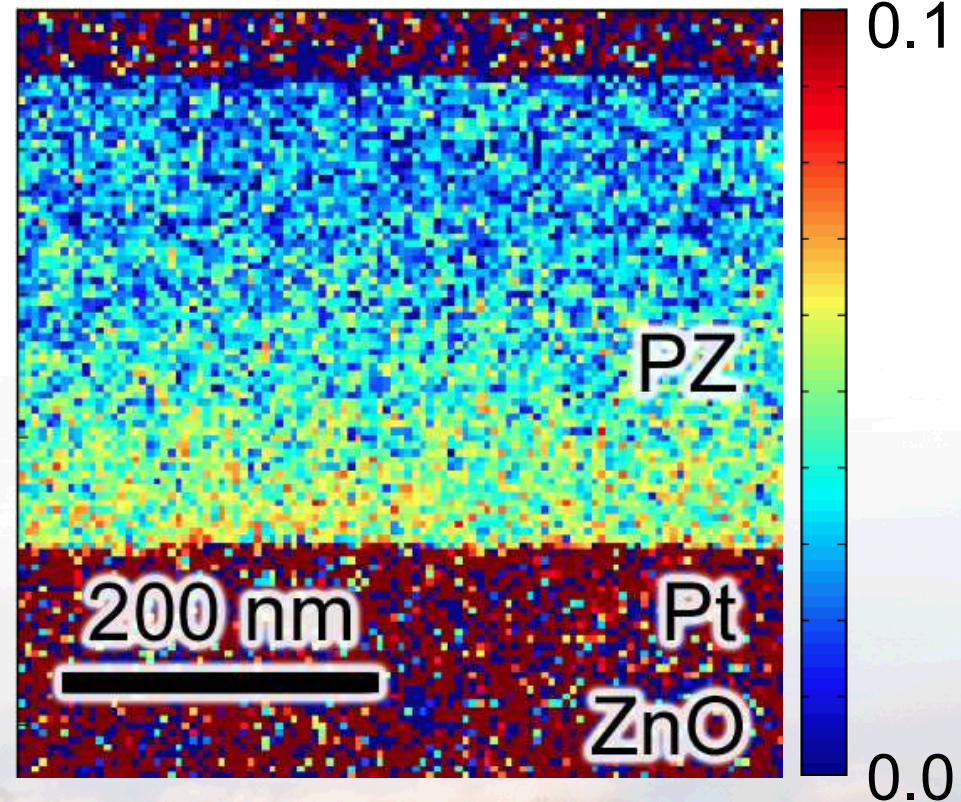


Test for Gradient Mechanism: PbZrO_3

PZ/Pt/Ti



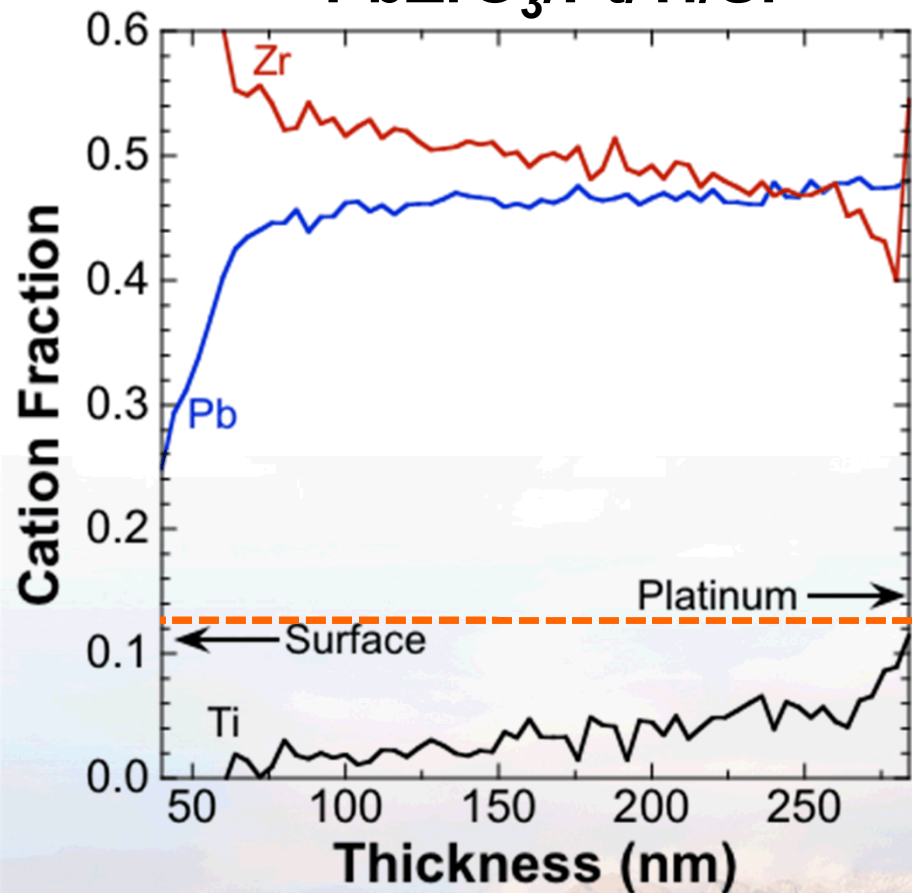
PZ/Pt/ZnO



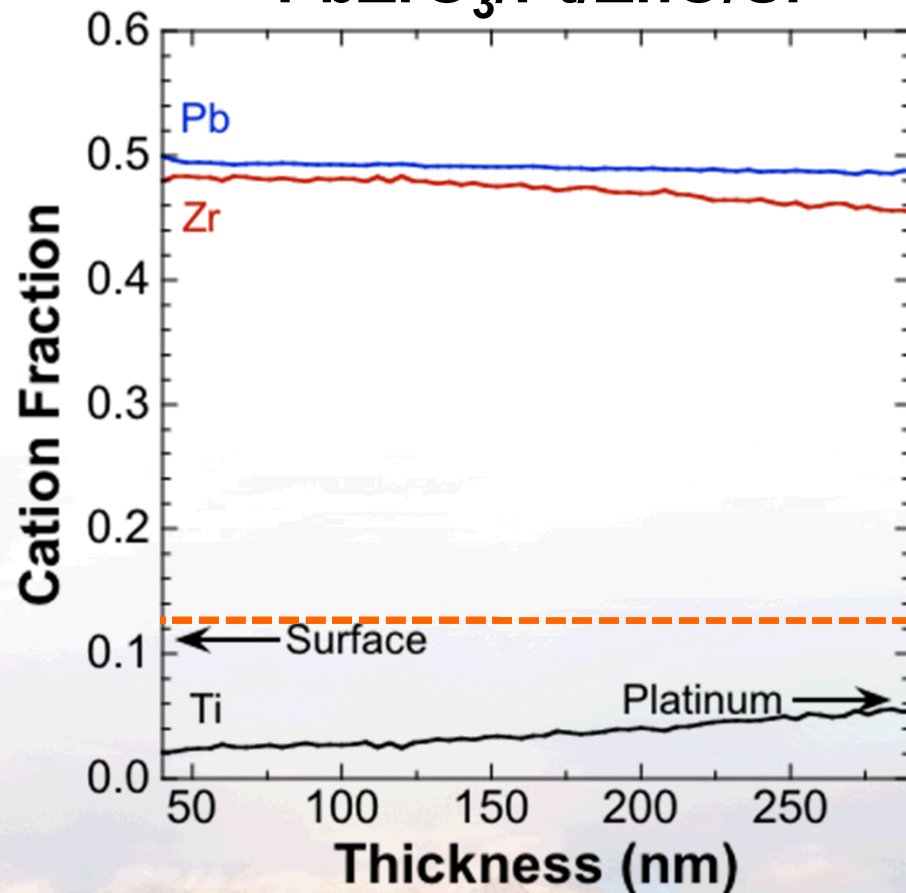
Note Scale Difference

Mechanism: Ti Diffusion from Adhesion Layer: Test with PbZrO_3

$\text{PbZrO}_3/\text{Pt}/\text{Ti}/\text{Si}$



$\text{PbZrO}_3/\text{Pt}/\text{ZnO}/\text{Si}$



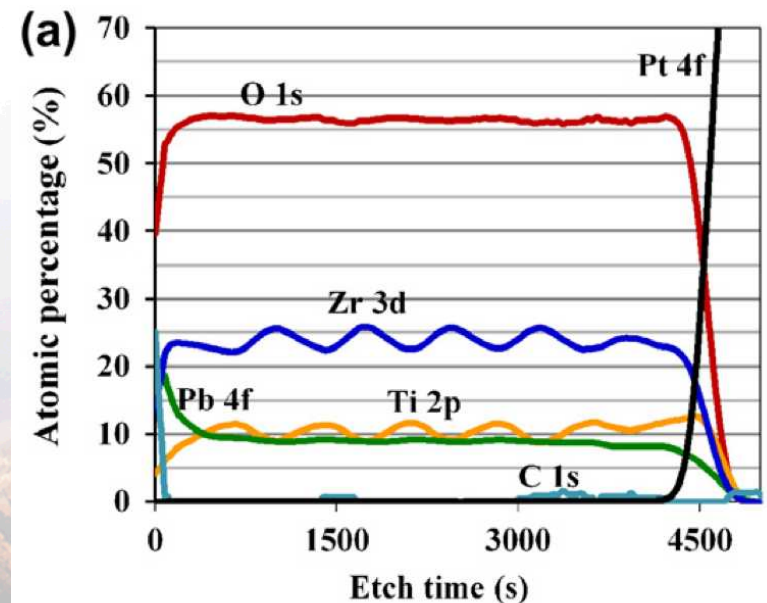
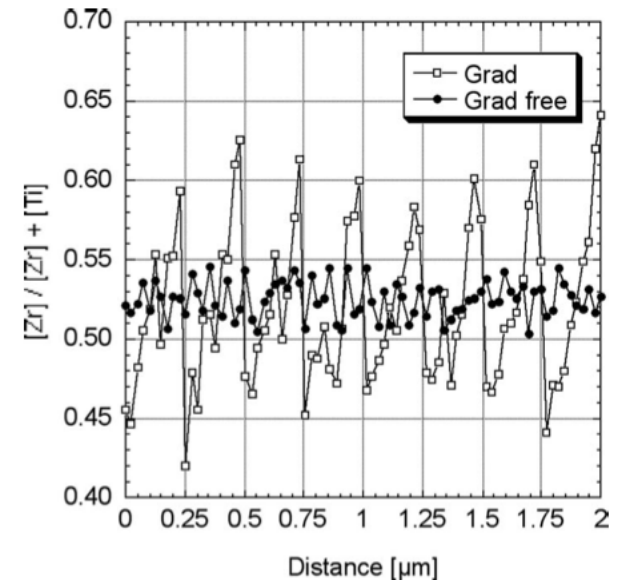
Less Ti and smaller gradient on Pt/ZnO



Solution Chemistry Effects?

Open Issues:

- This model cannot explain 'saw-tooth' profiles observed by other groups*
- What roles do solution chemistry and processing conditions play in gradient formation?
- More experiments necessary to isolate controlling variables
 - Substrate: Pt/Ti vs Pt/ZnO
 - Chemistry: IMO vs 2-MOE
 - Pyrolysis: 300, 350, 400° C



*Amanuma, *et al.*, *Appl. Phys. Lett.* **65**, 3140 (1994)
Calame and Muralt, *Appl. Phys. Lett.* **90**, 062907 (2007)
Bastani and Bassiri-Gharb, *Acta. Mater.* **60**, 1346 (2012)

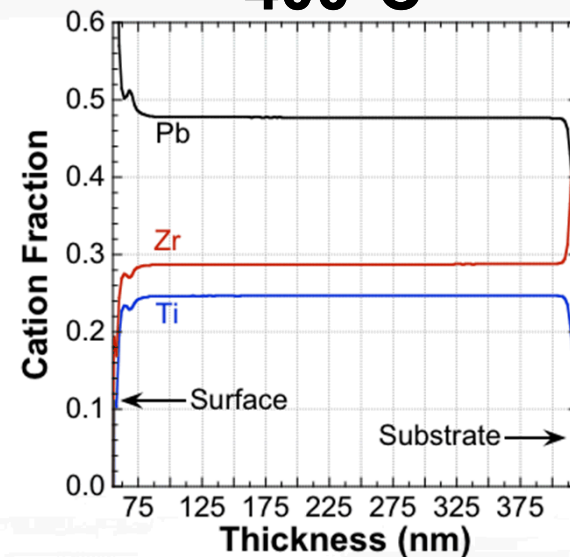
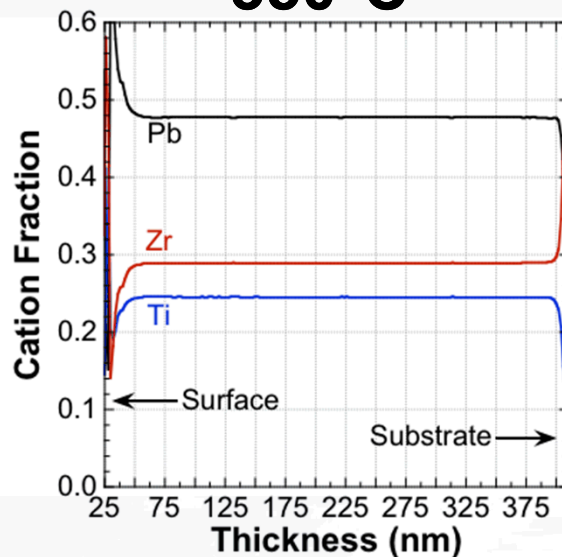
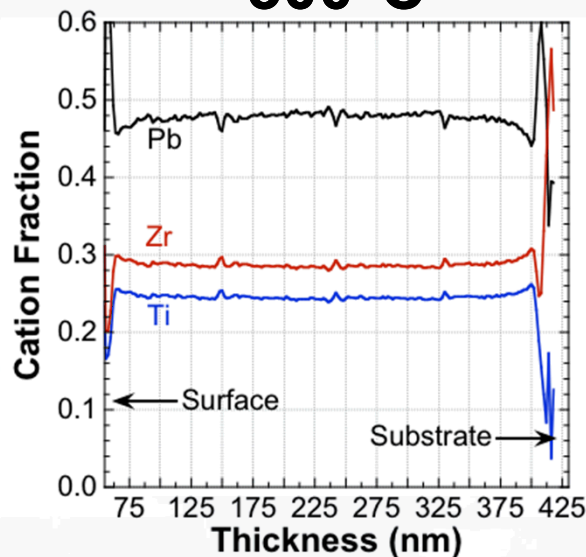
Unfired Chemical Distribution: 2-MOE Films

300°C

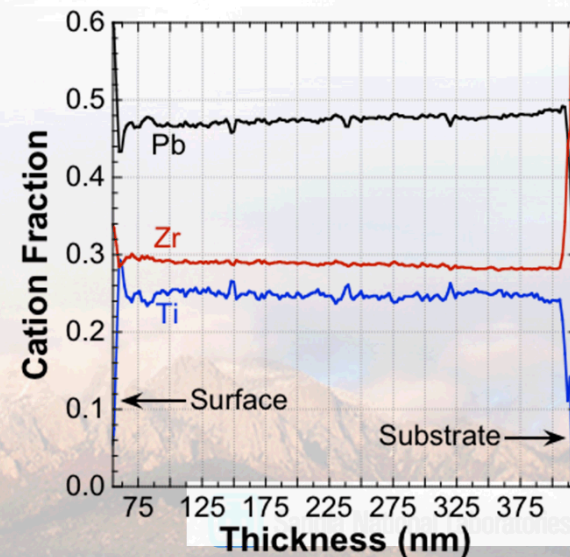
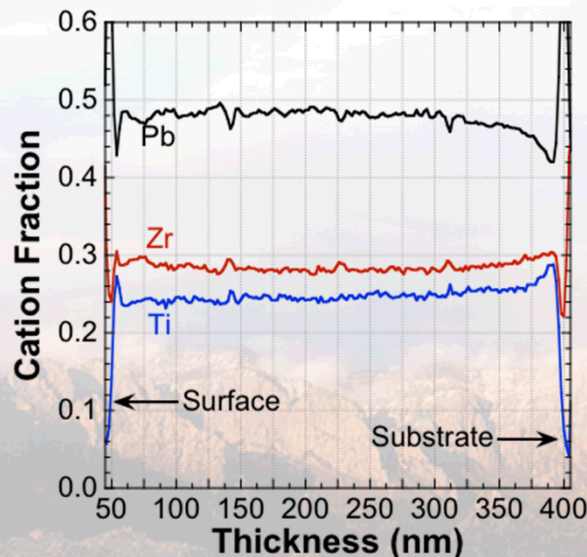
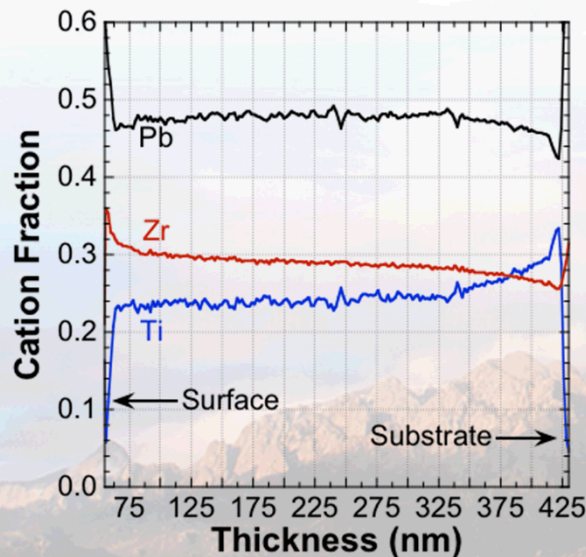
350°C

400°C

Pt/ZnO



Pt/Ti



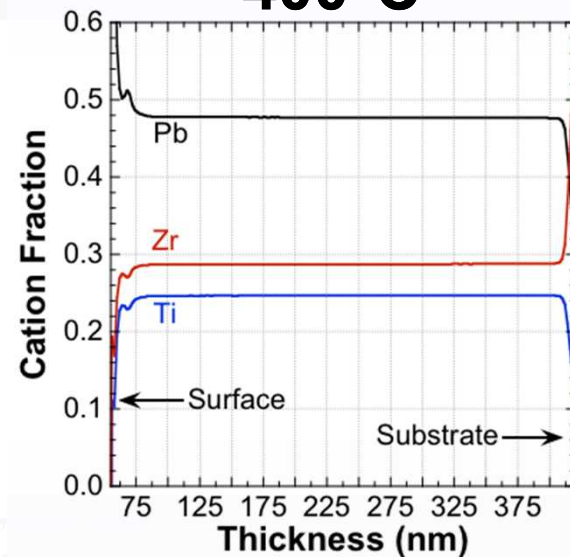
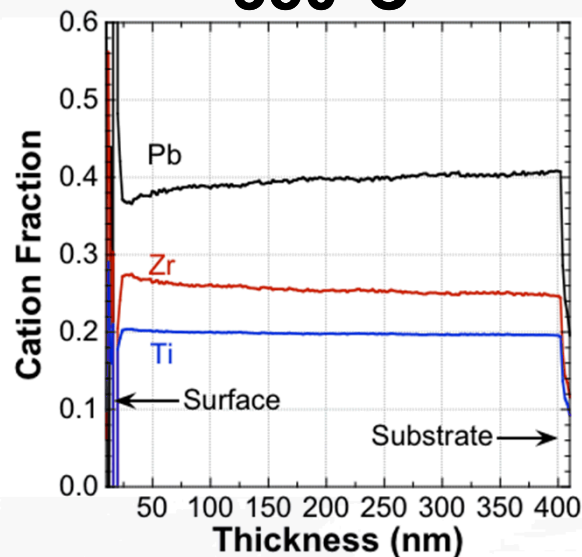
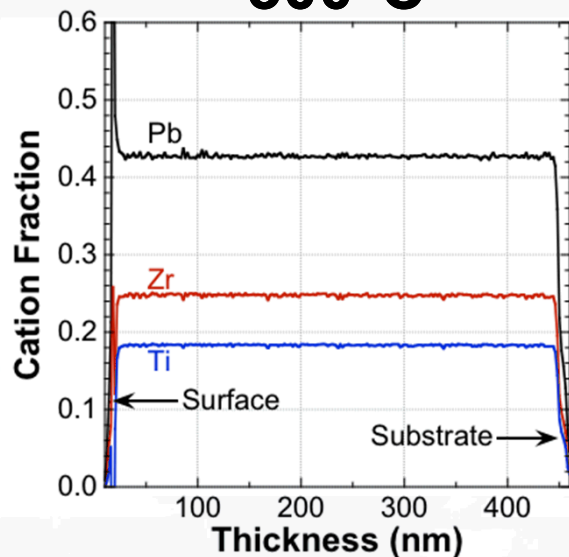
Unfired Chemical Distribution: IMO Films

300°C

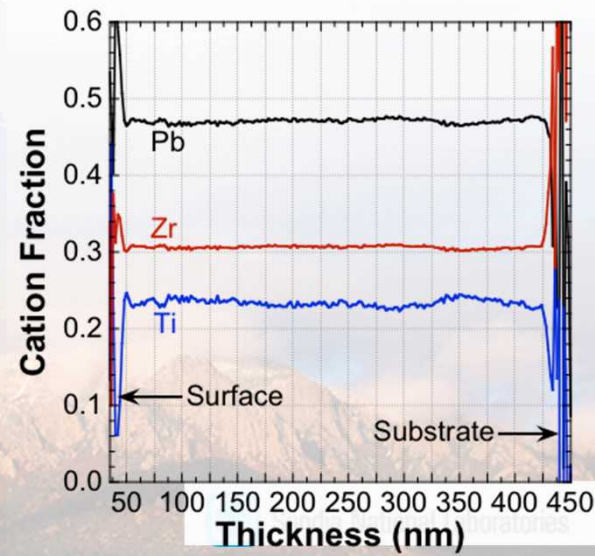
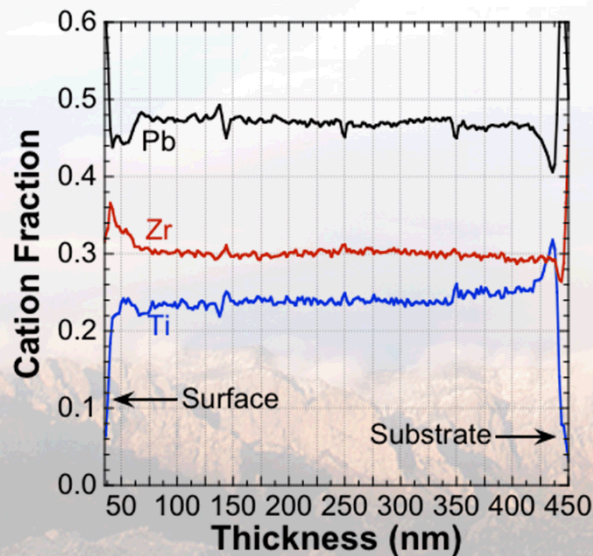
350°C

400°C

Pt/ZnO

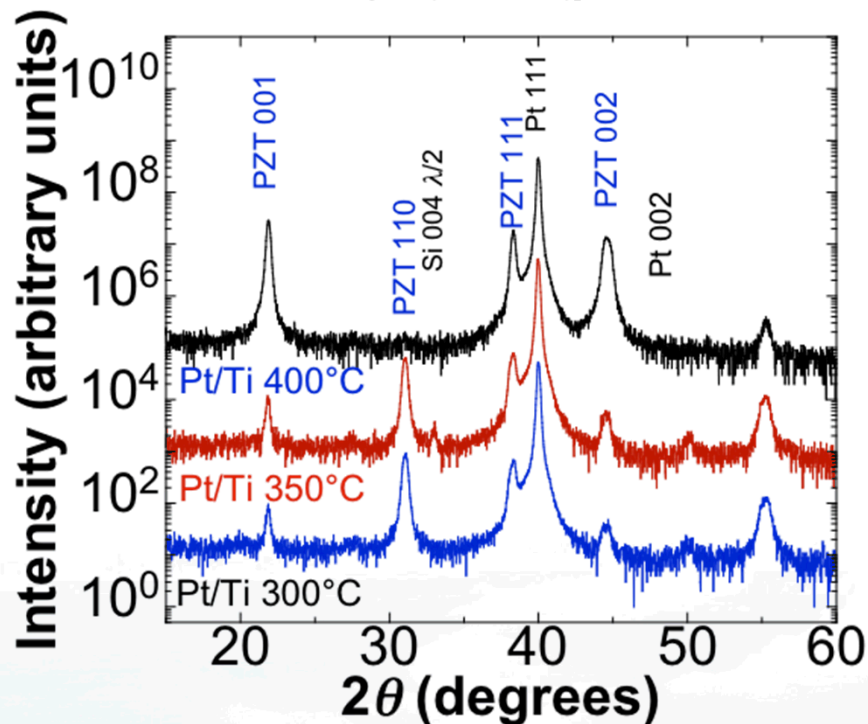


Pt/Ti

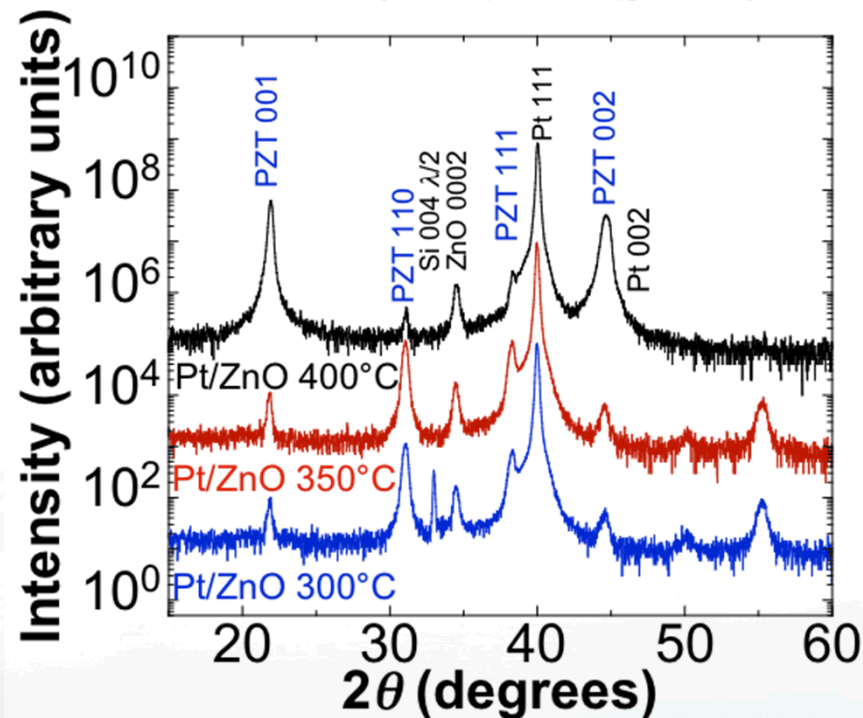


Pyrolysis Effects: Texture

IMO on Pt/Ti



2-MOE on Pt/ZnO



- ***Pyrolysis temperature effects texture***
- ***No apparent difference with substrate or chemistry***
- ***Consistent with previous work****

*Chen and Chen, *JACerS*, **81** (1) 97-105 (1998)

*Brennecka, et al., *Proc. 14th US-Japan*, 136 (2009)

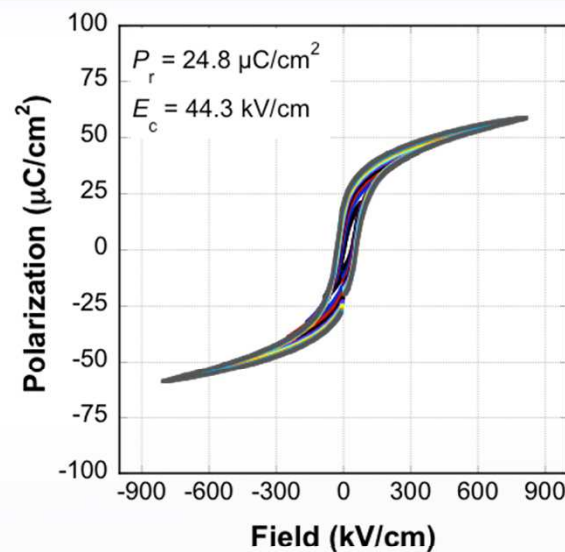
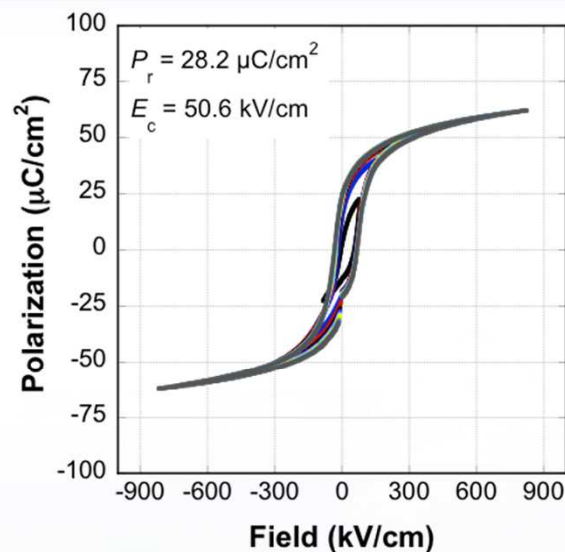
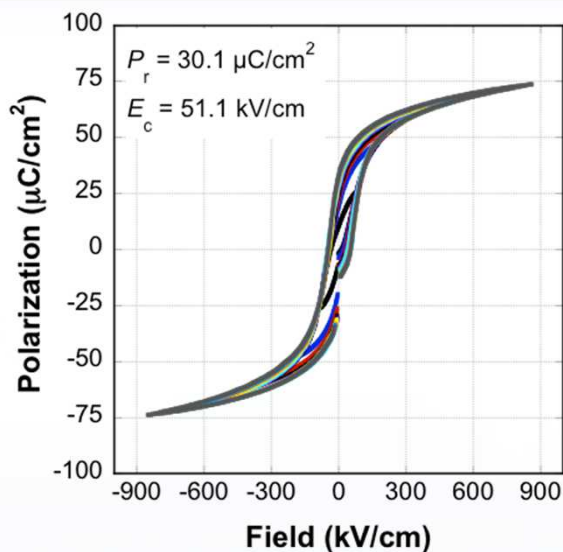
Ferroelectric Properties: IMO Films

300°C

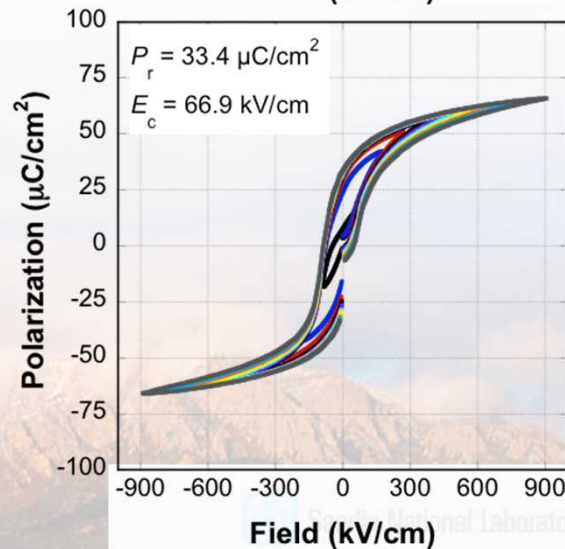
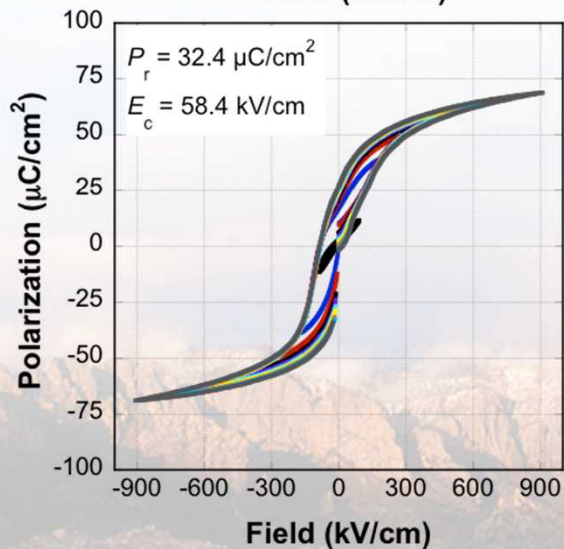
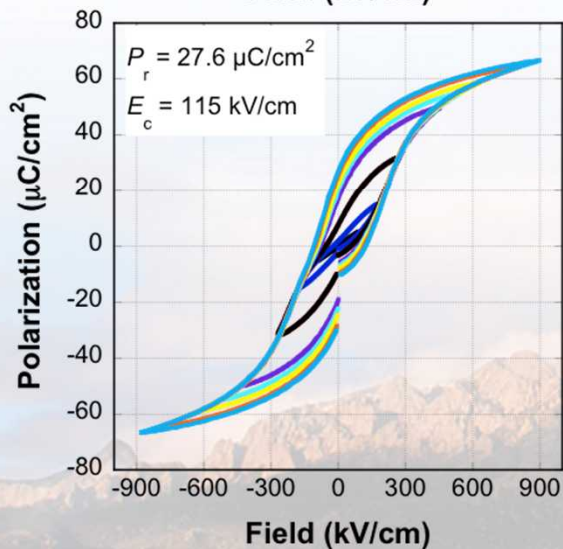
350°C

400°C

Pt/ZnO



Pt/Ti



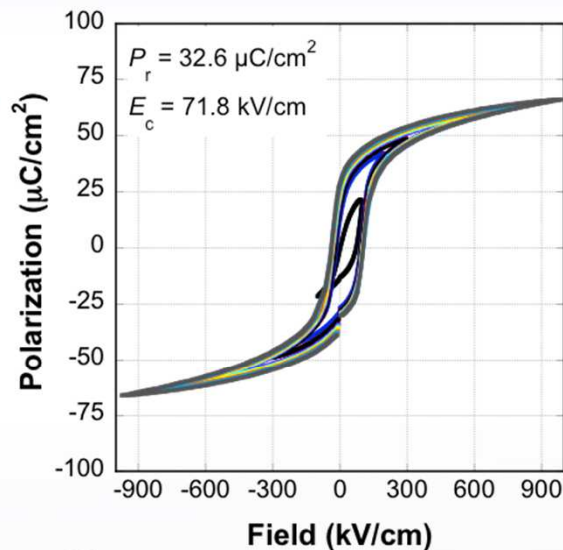
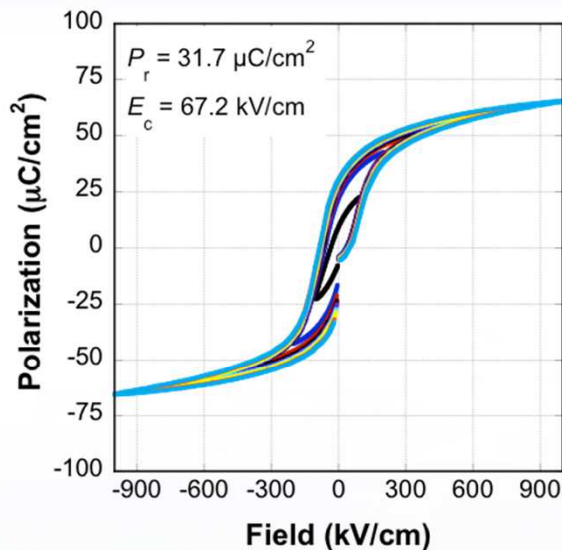
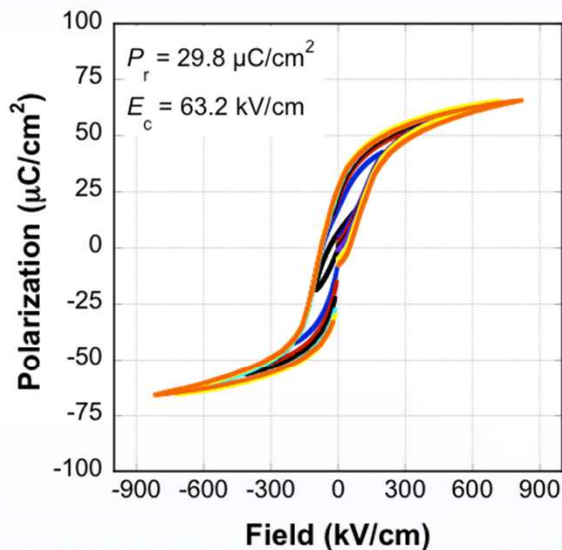
Ferroelectric Properties: 2MOE Films

300°C

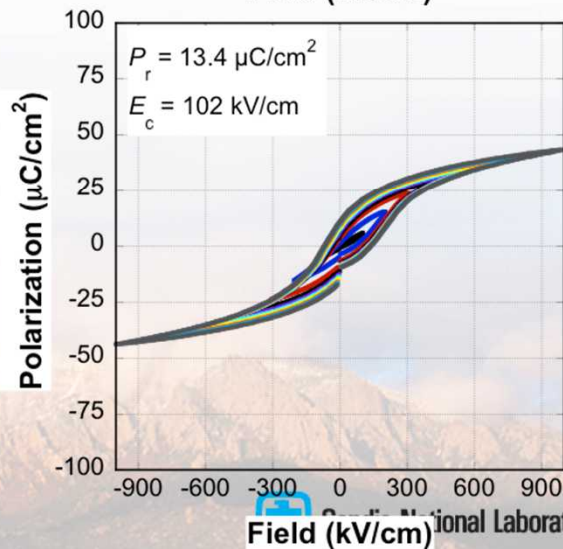
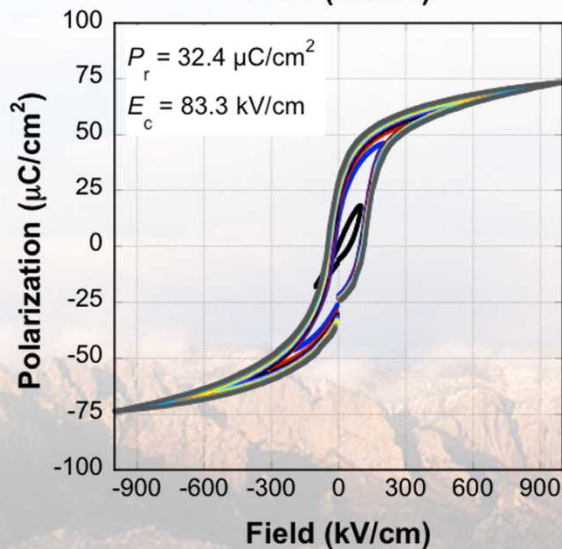
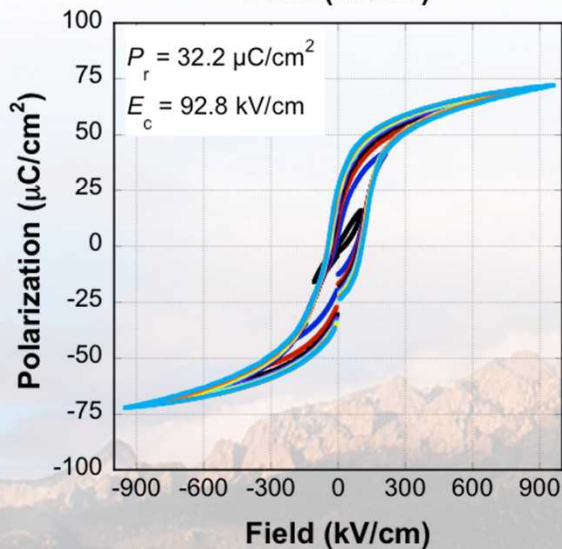
350°C

400°C

Pt/ZnO



Pt/Ti



Field (kV/cm) National Laboratories

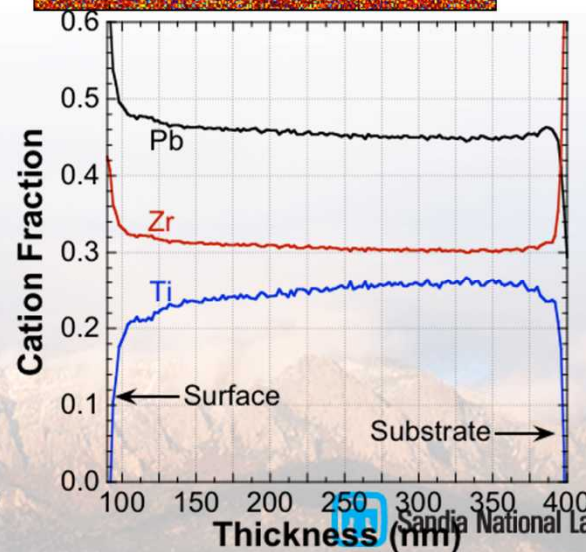
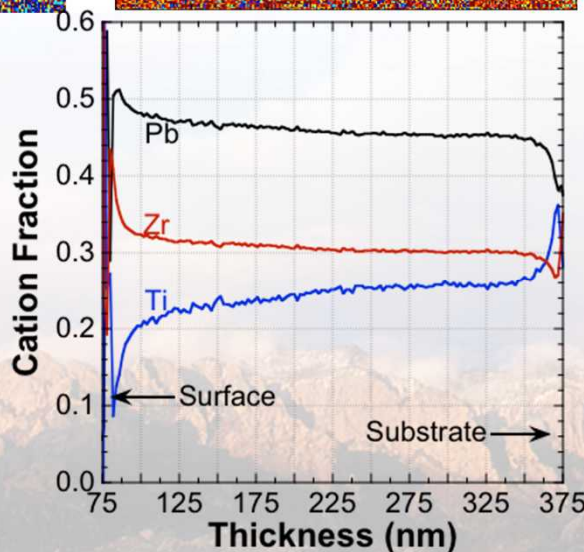
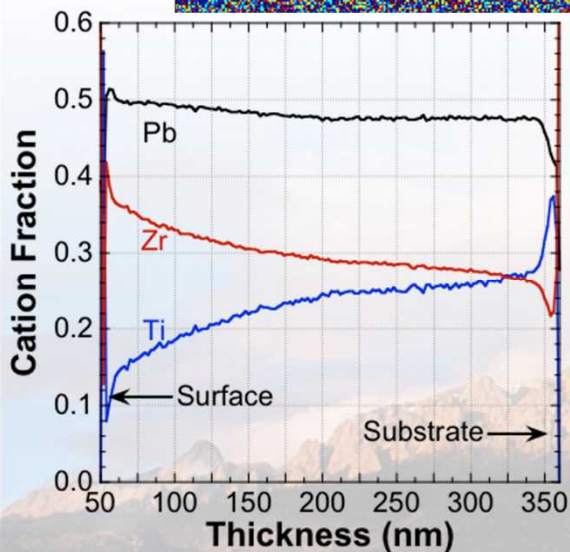
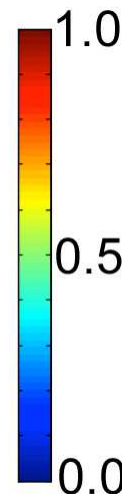
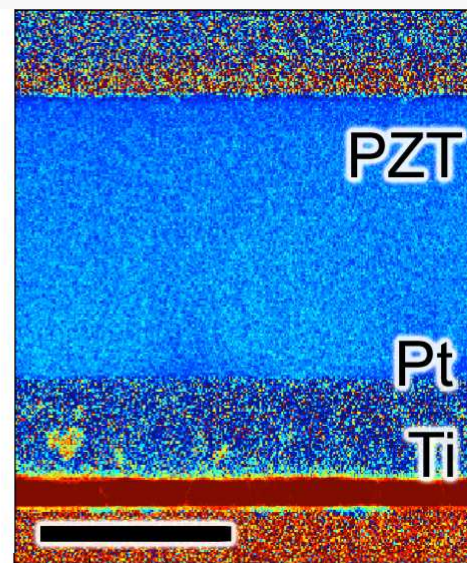
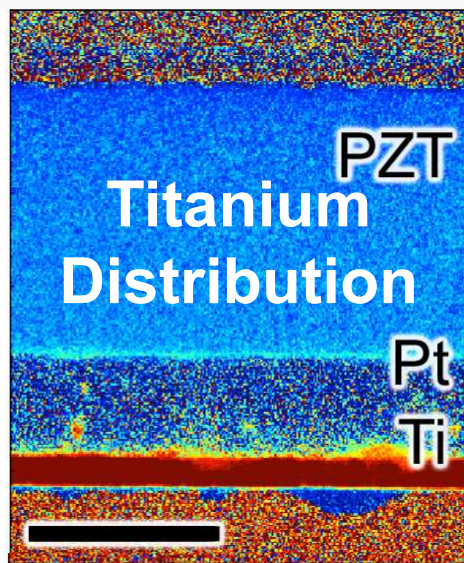
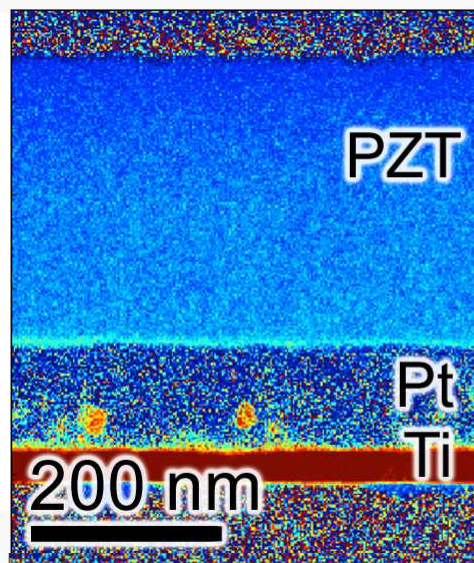
Solution Chemistry Effect: IMO films

300°C

350°C

400°C

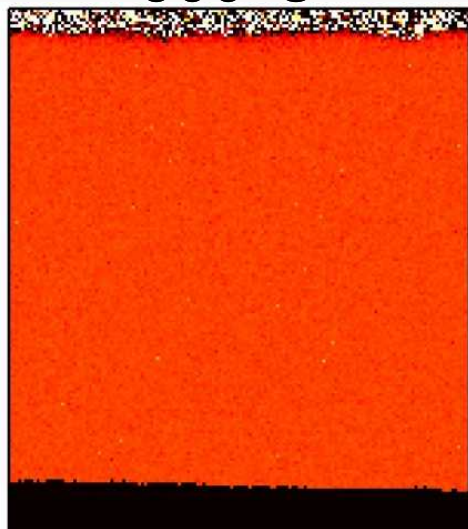
Pt/Ti



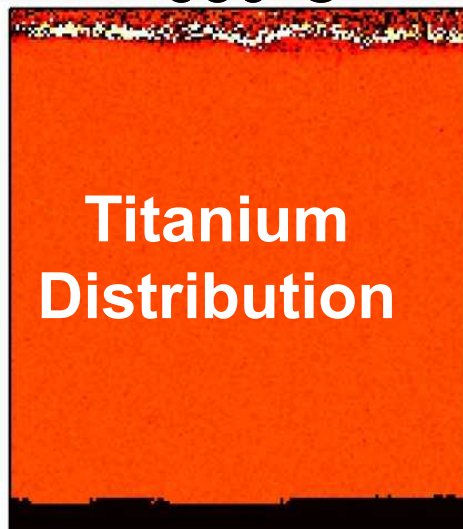
Solution Chemistry Effect: IMO Films

Pt/ZnO

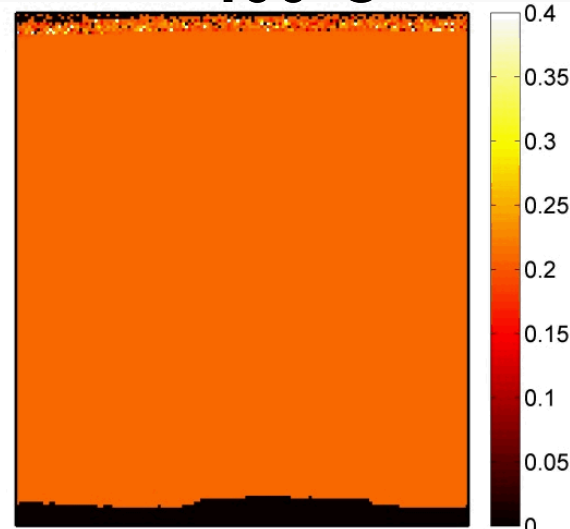
300°C



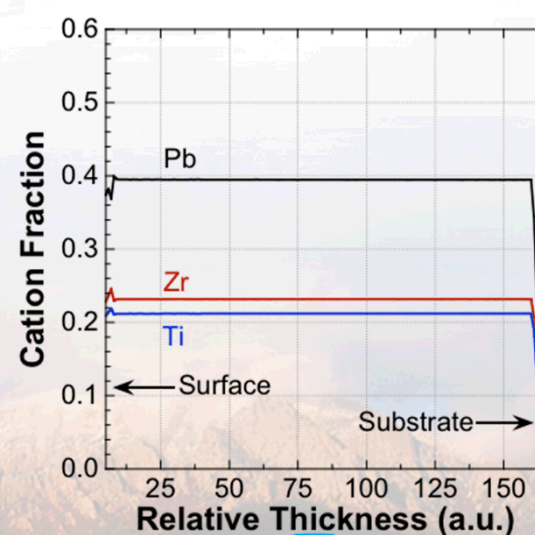
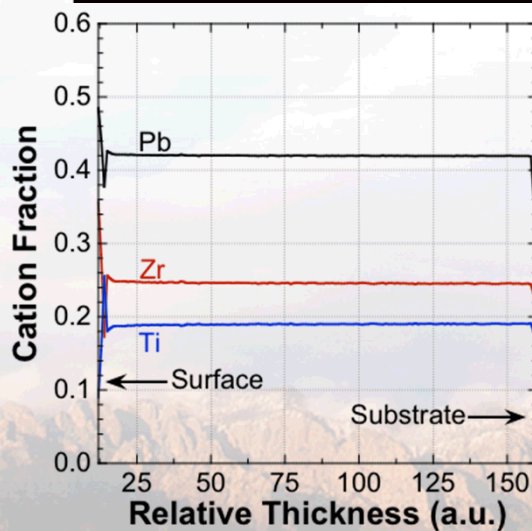
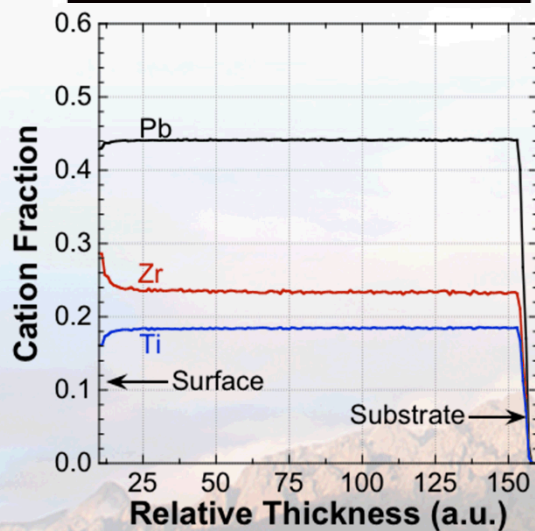
350°C



400°C



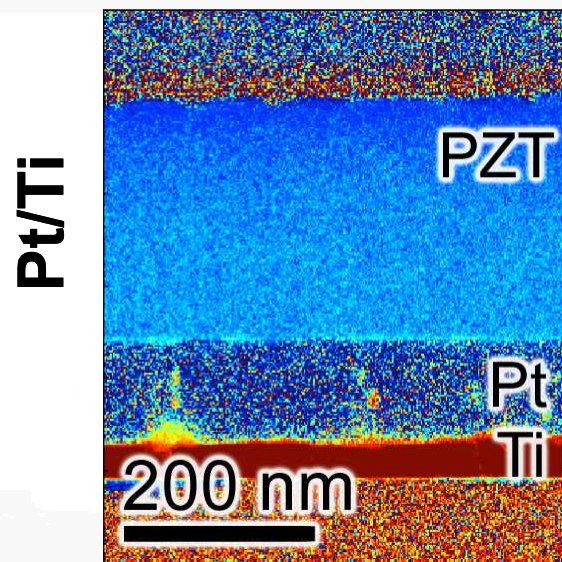
Titanium
Distribution



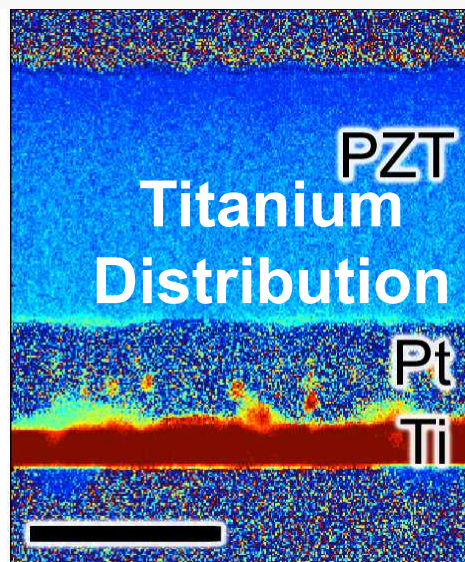
Sandia National Laboratories

Solution Chemistry Effect: 2-MOE films

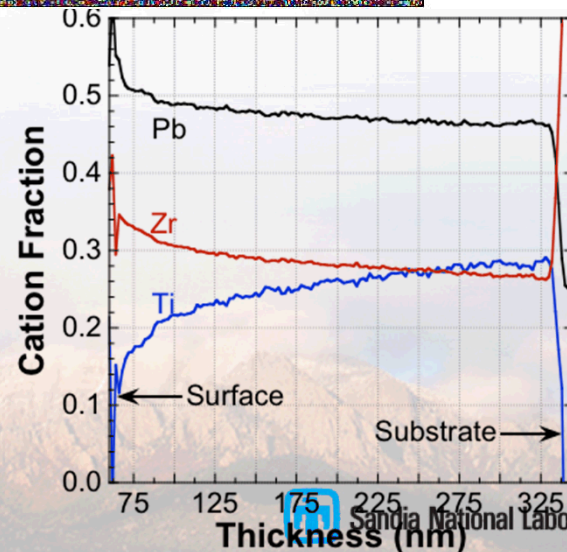
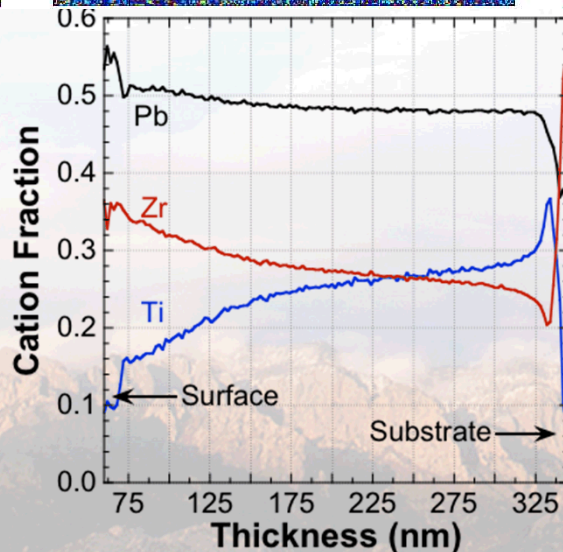
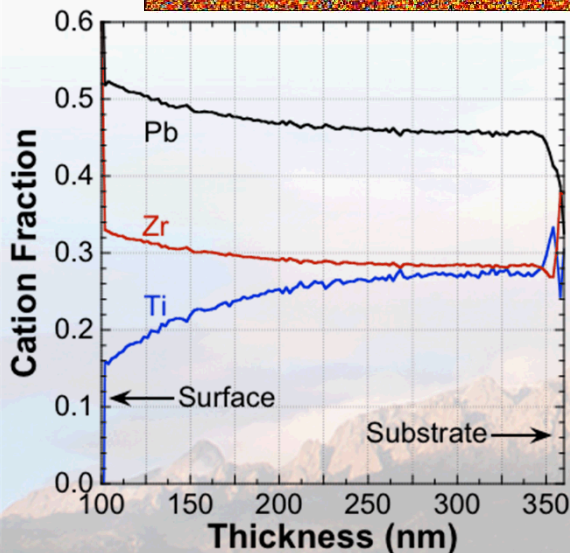
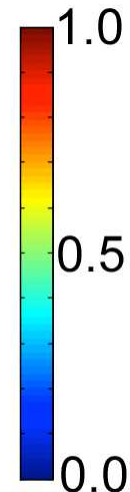
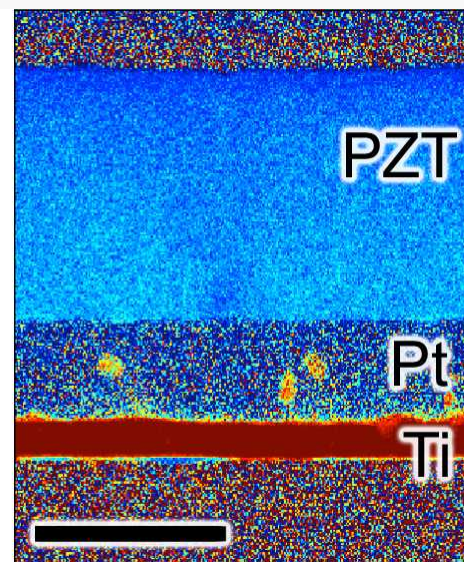
300°C



350°C



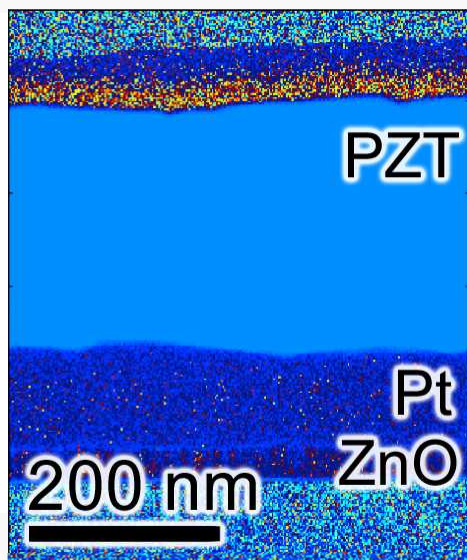
400°C



Solution Chemistry Effect: 2-MOE films

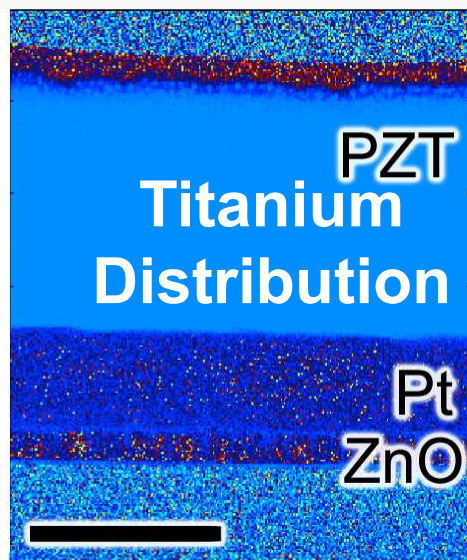
300°C

Pt/ZnO

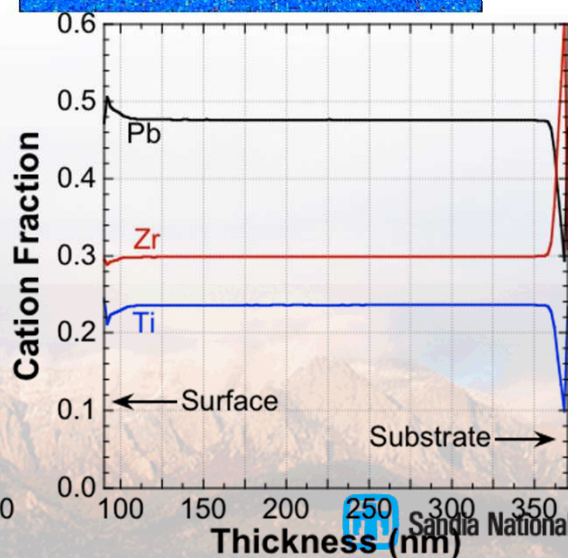
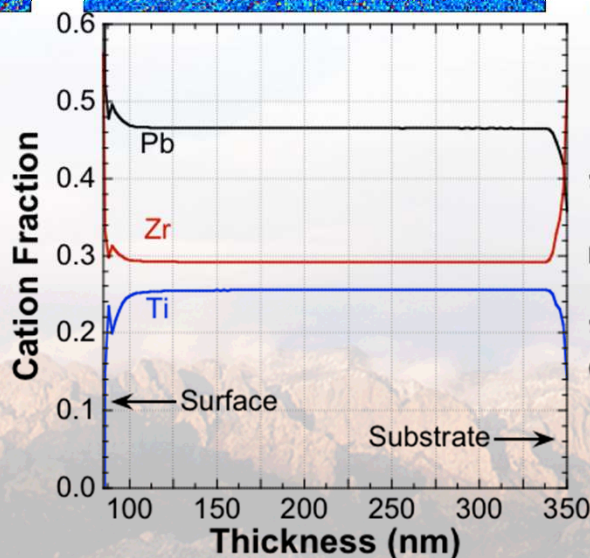
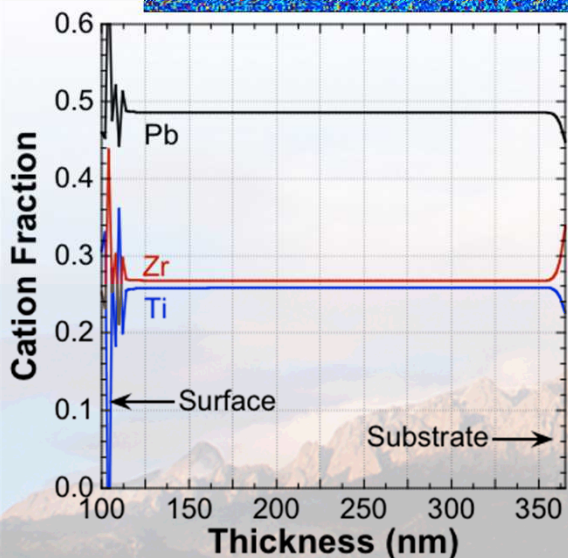
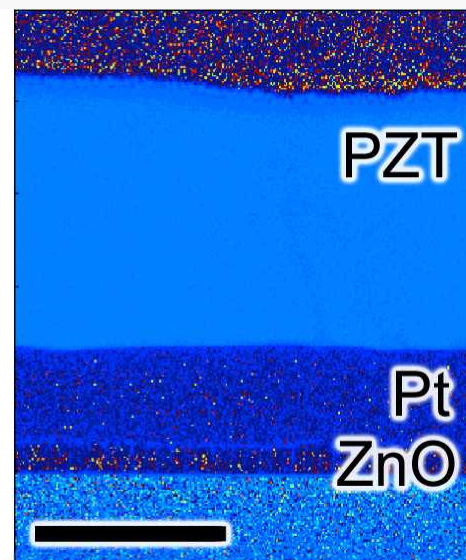


350°C

PZT
Titanium
Distribution



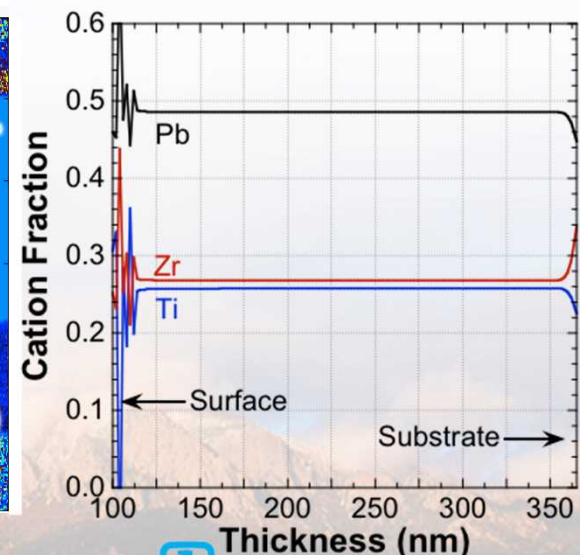
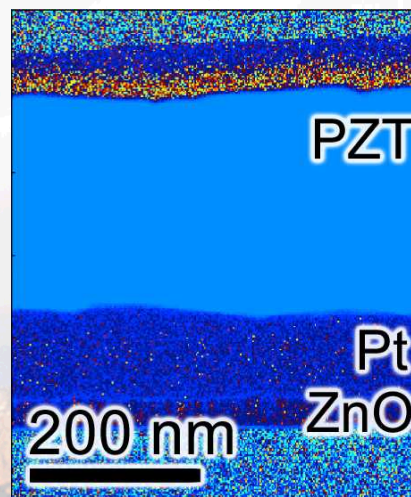
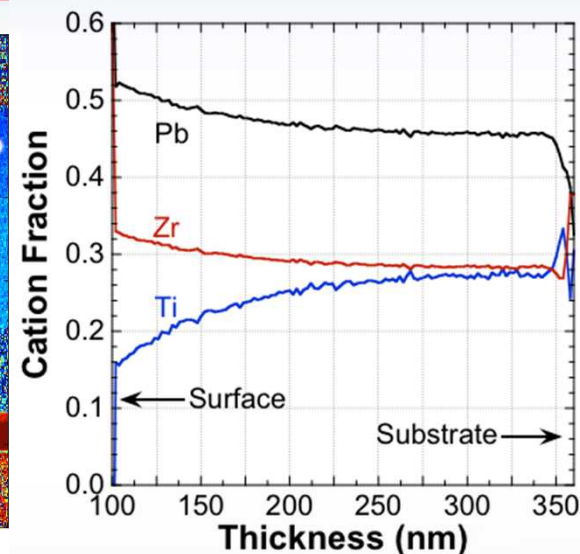
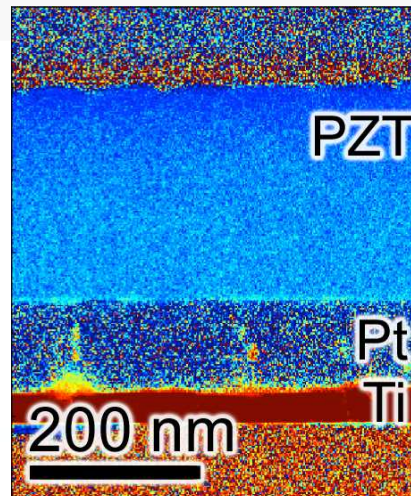
400°C



Open Questions? Still Open!

Open Issues:

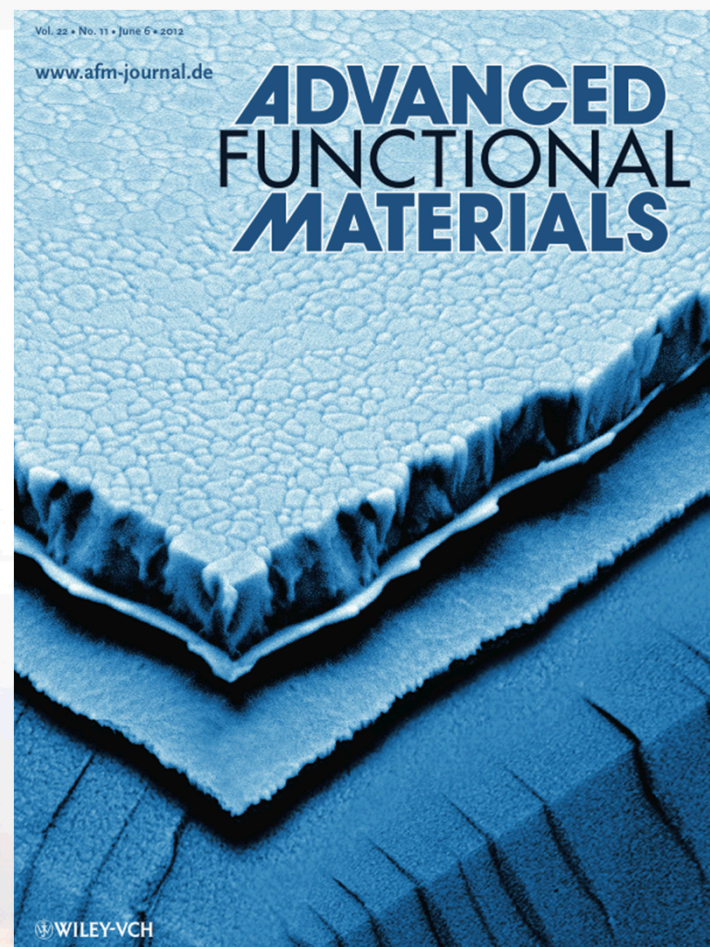
- Pyrolysis temperature does not seem to effect gradient formation
- On substrates devoid of a titanium adhesion layer, no gradients form – even for sol-gel chemistries
- What is the origin of the chemical gradient observed by other groups?
 - Heating rate?



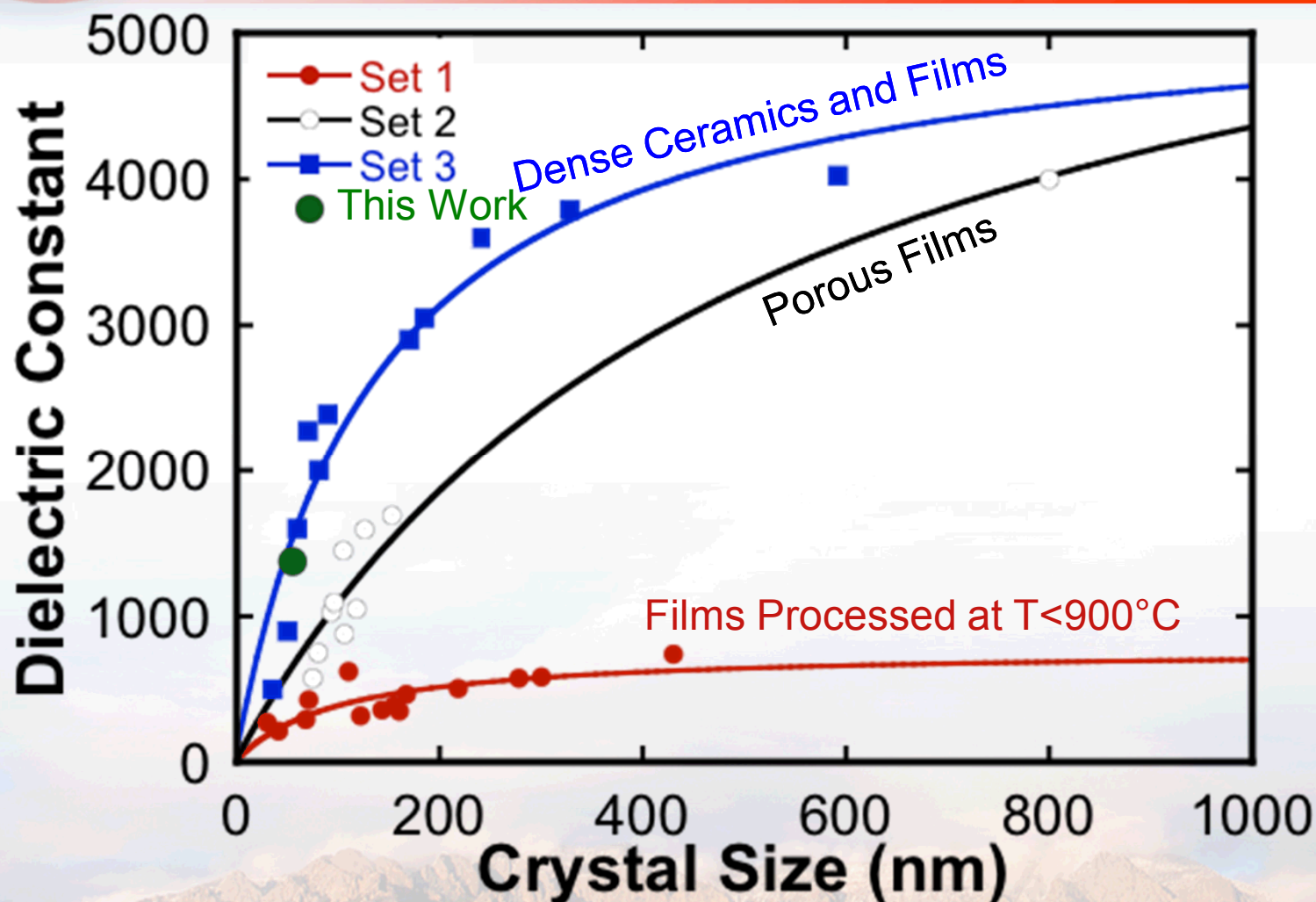
Thickness (nm)
Sandia National Laboratories

Summary

- Work of Adhesion is an effective means in selecting adhesion layers
- ZnO is a superior adhesion layer
- BaTiO₃ and IMO PZT films prepared on Pt/ZnO substrates possess improved electronic properties compared to traditional substrates
- Even traditional sol-gel PZT films did not possess composition gradients: heating rate effect?
- Improved electronic properties can be correlated with improved chemical homogeneity



BaTiO₃ Scaling Effects



First known BaTiO₃ film with bulk properties on Si

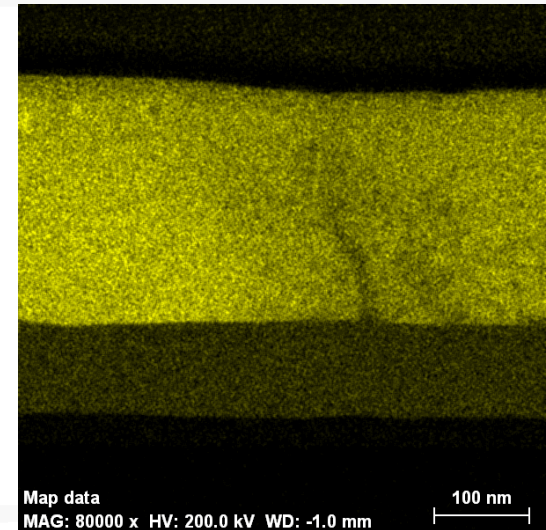
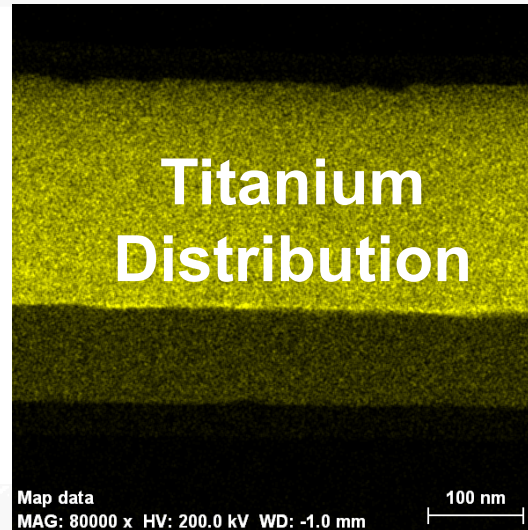
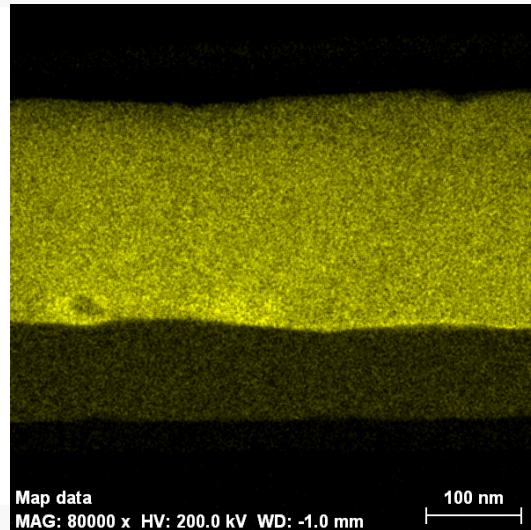
Solution Chemistry Effect: 2-MOE films

300°C

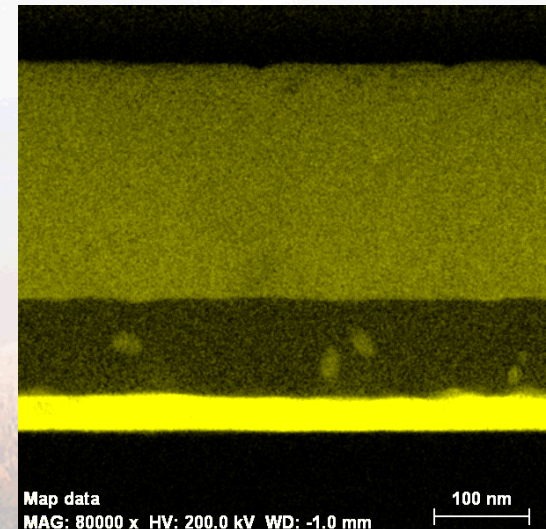
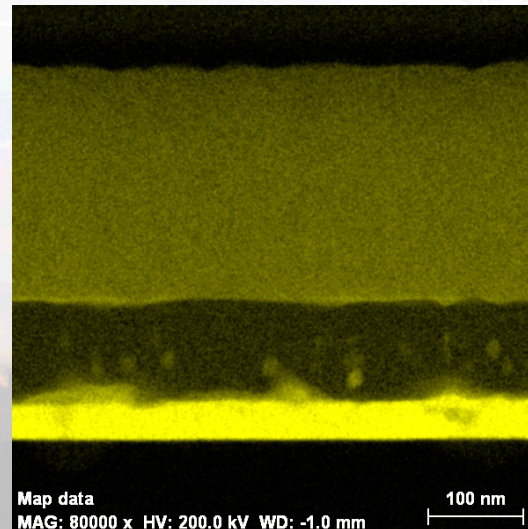
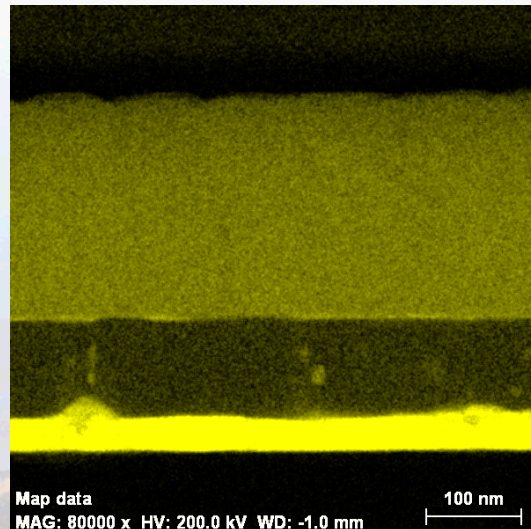
350°C

400°C

Pt/ZnO



Pt/Ti



atories

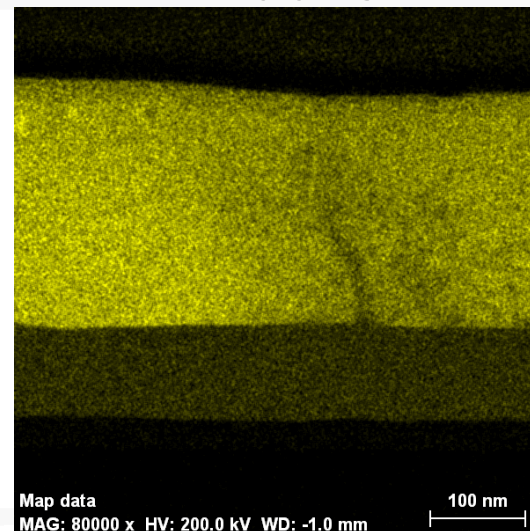
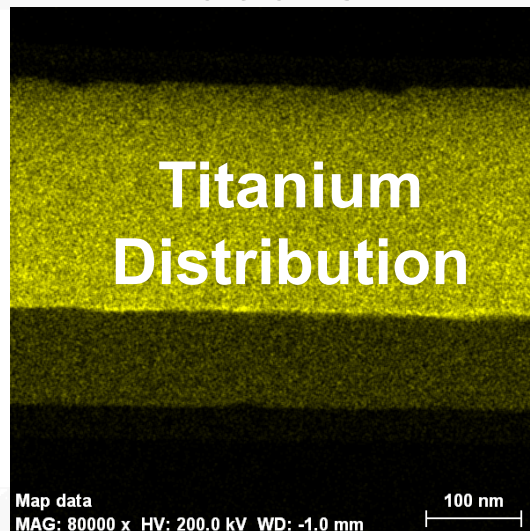
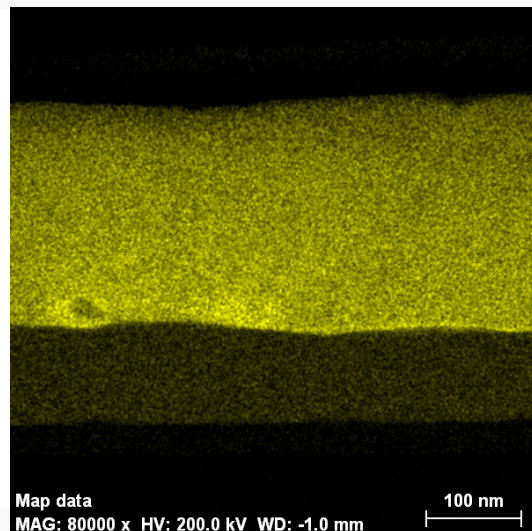
Solution Chemistry Effect: 2-MOE films

300°C

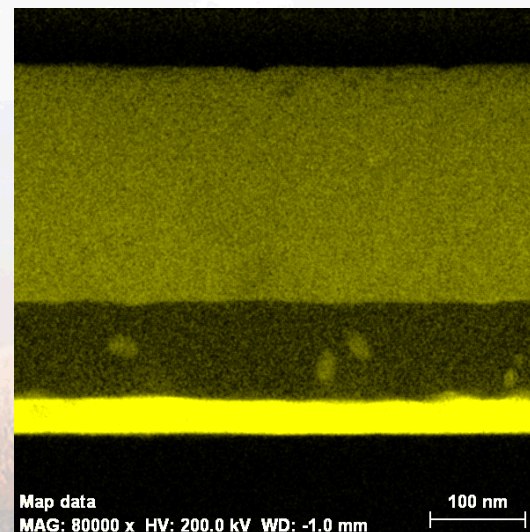
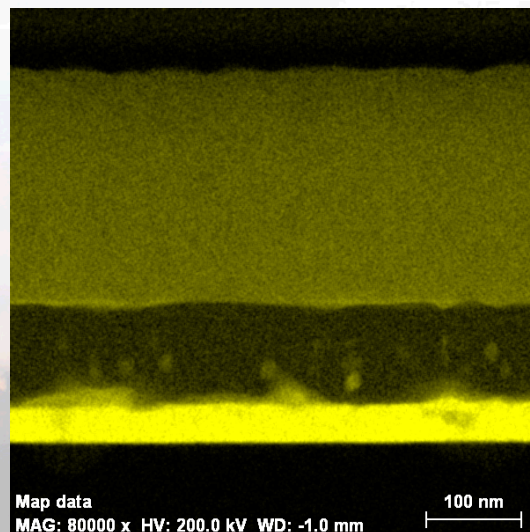
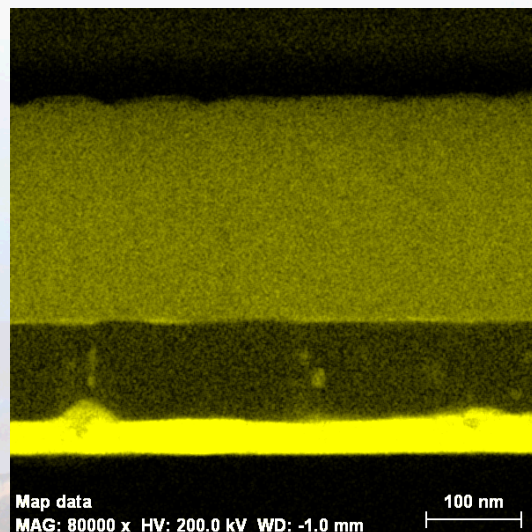
350°C

400°C

Pt/ZnO



Pt/Ti



atories

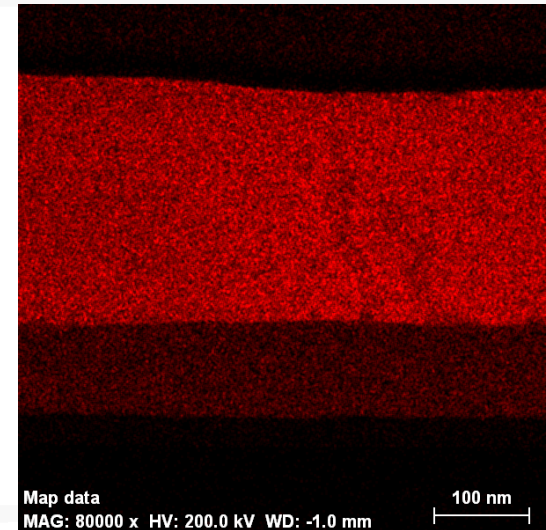
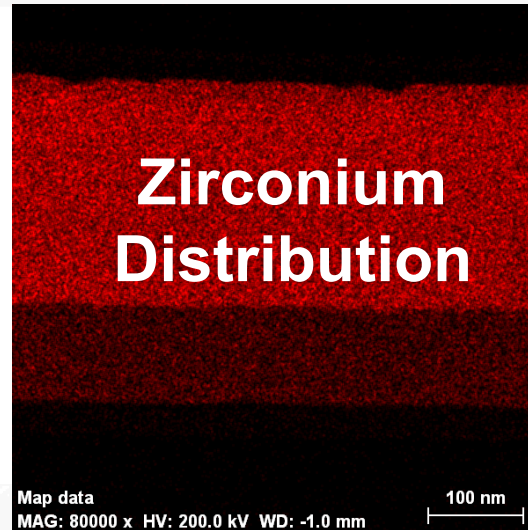
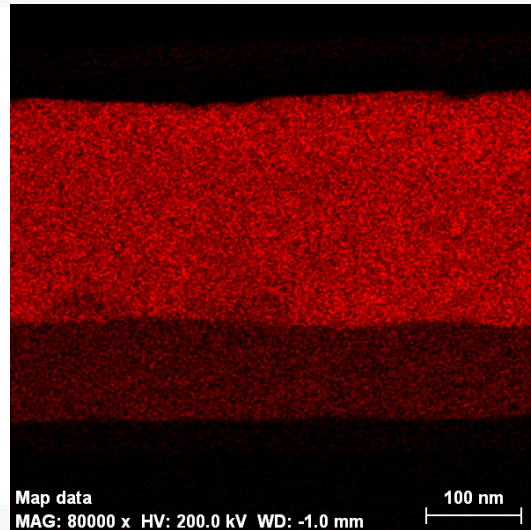
Solution Chemistry Effect: 2-MOE films

300°C

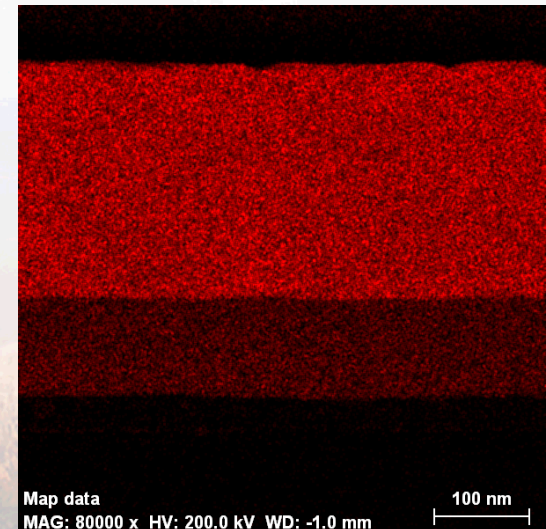
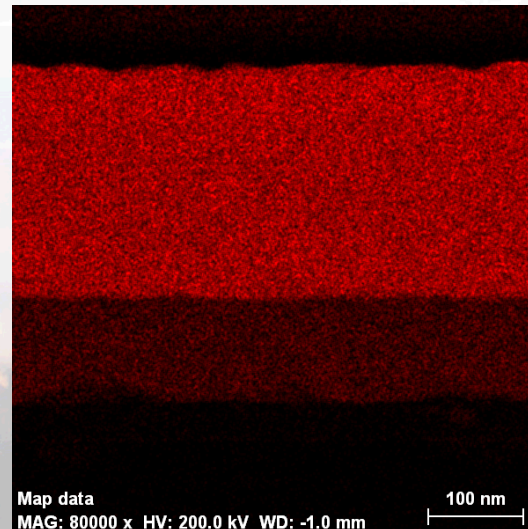
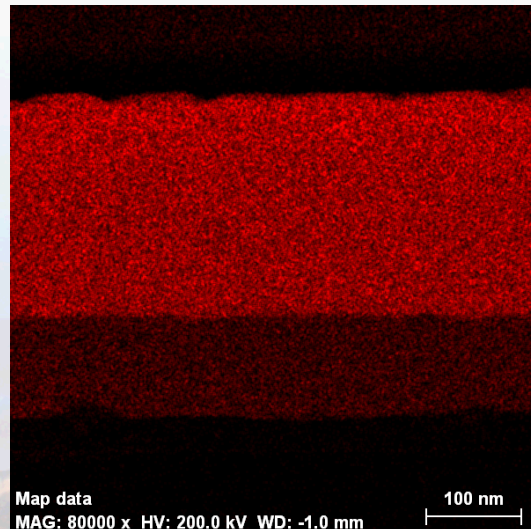
350°C

400°C

Pt/ZnO



Pt/Ti



ratories

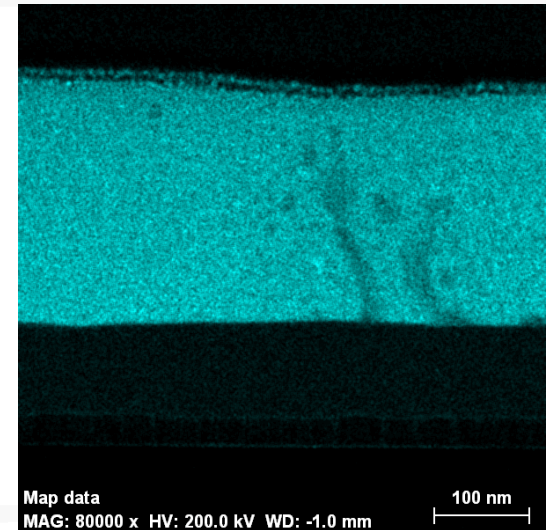
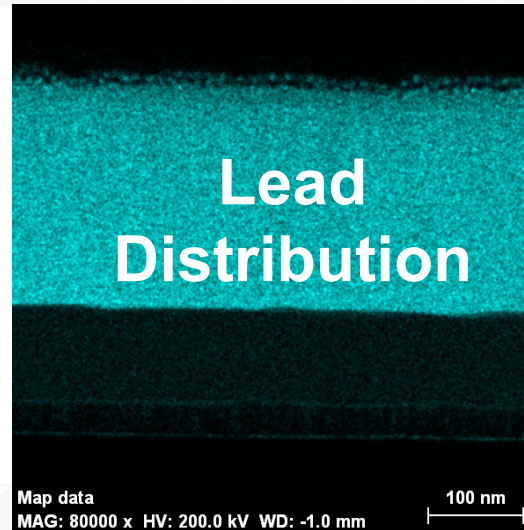
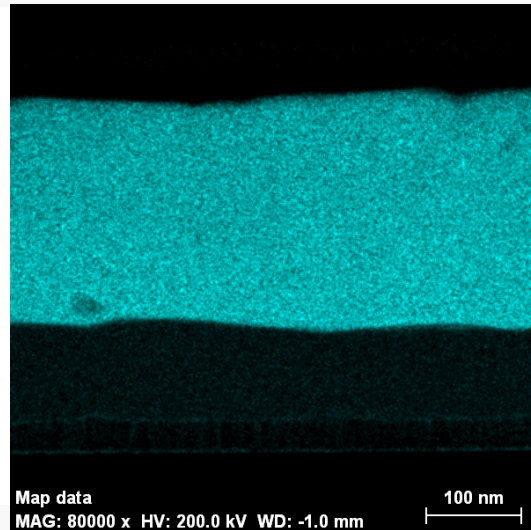
Solution Chemistry Effect: 2-MOE films

300°C

350°C

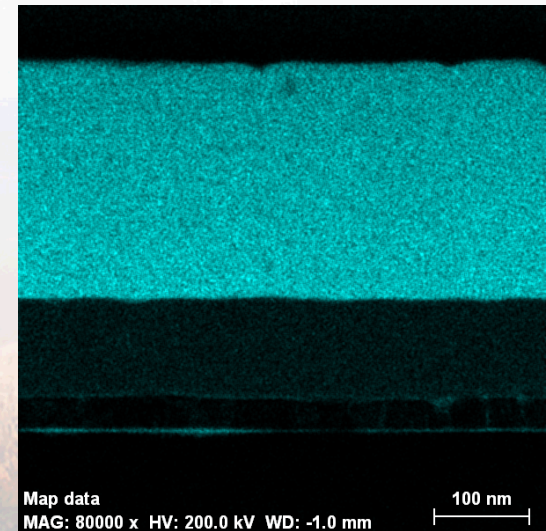
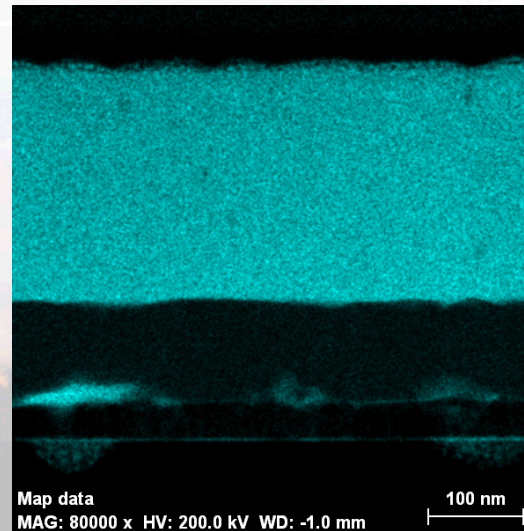
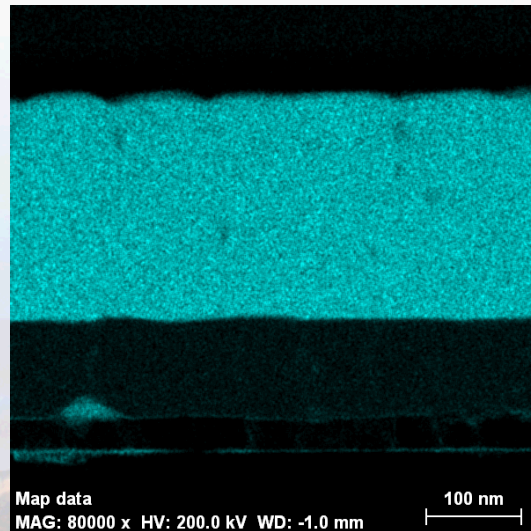
400°C

Pt/ZnO



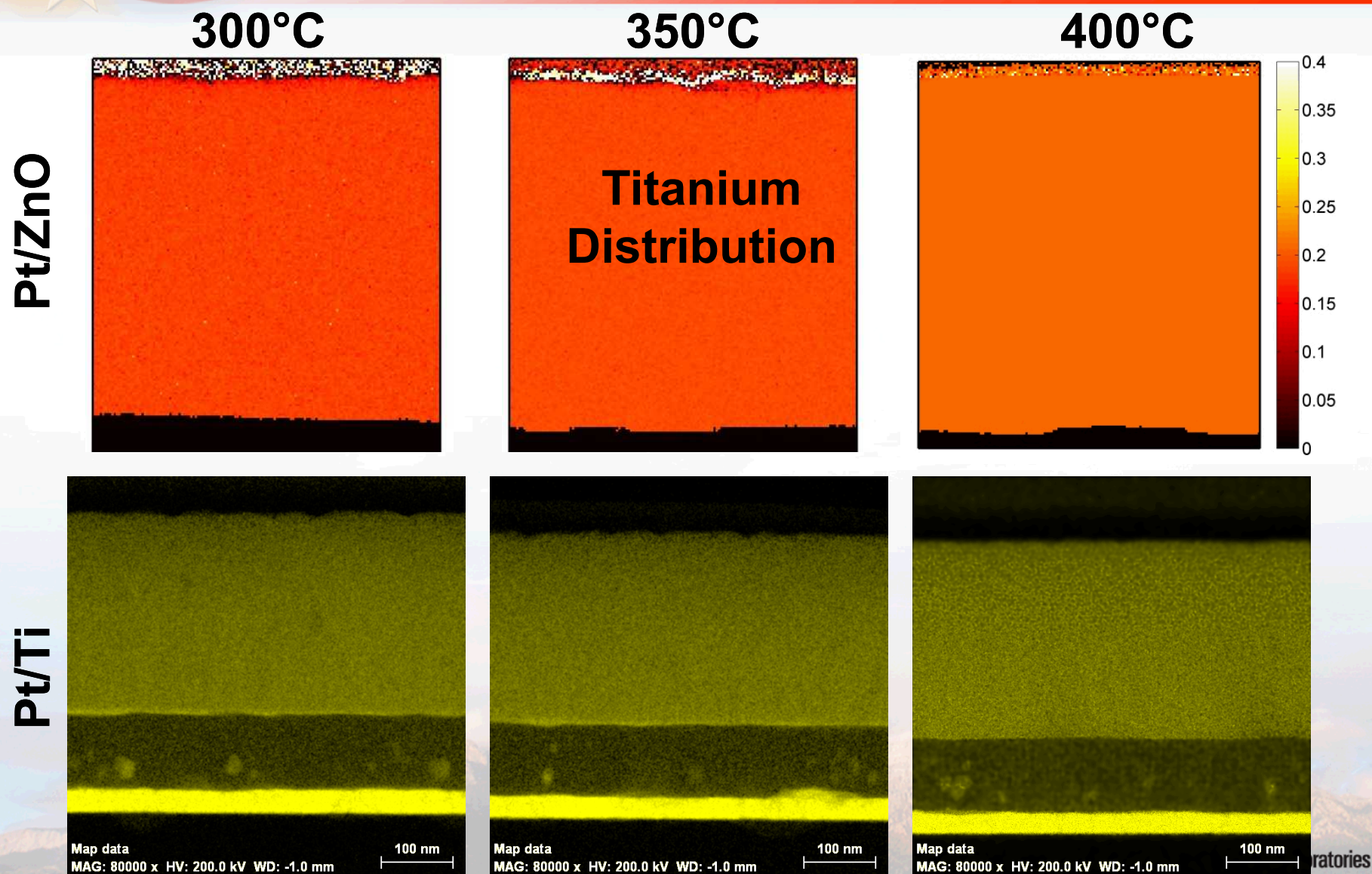
Lead
Distribution

Pt/Ti



ratories

Solution Chemistry Effect: IMO Films



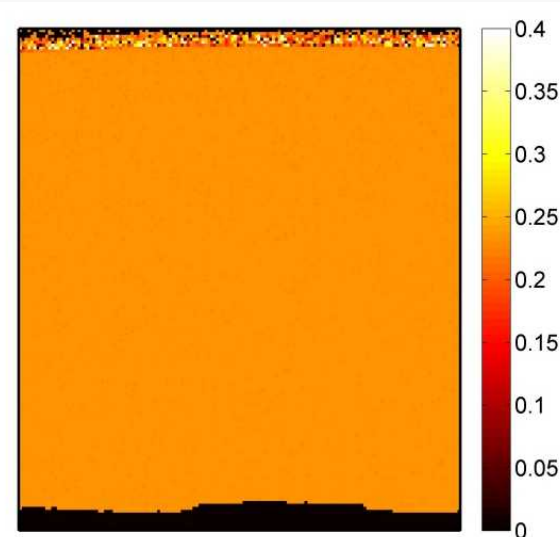
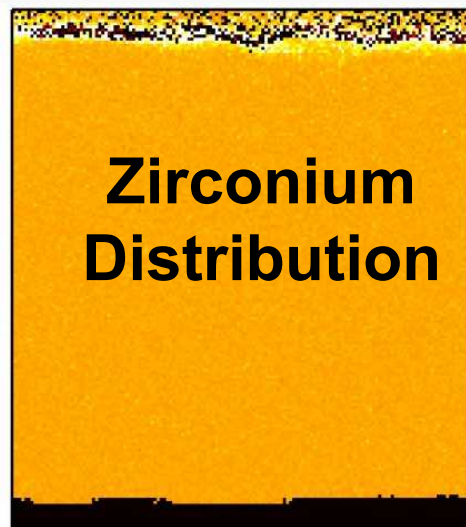
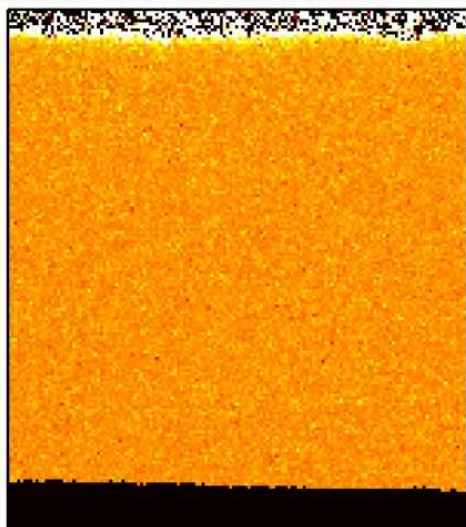
Solution Chemistry Effect: IMO Films

300°C

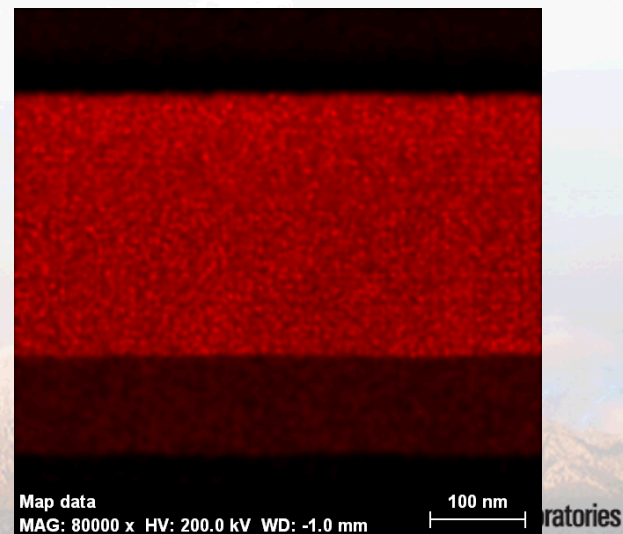
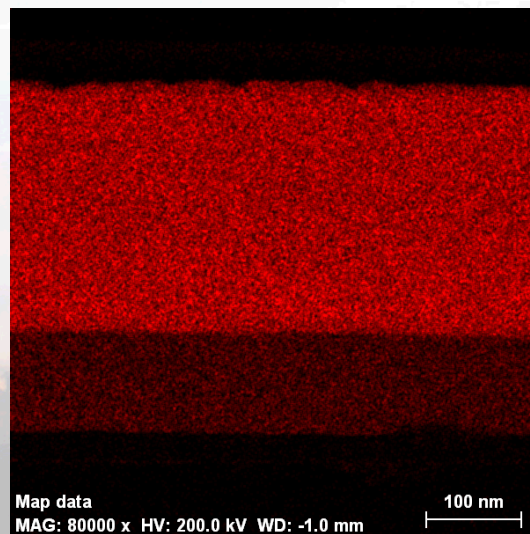
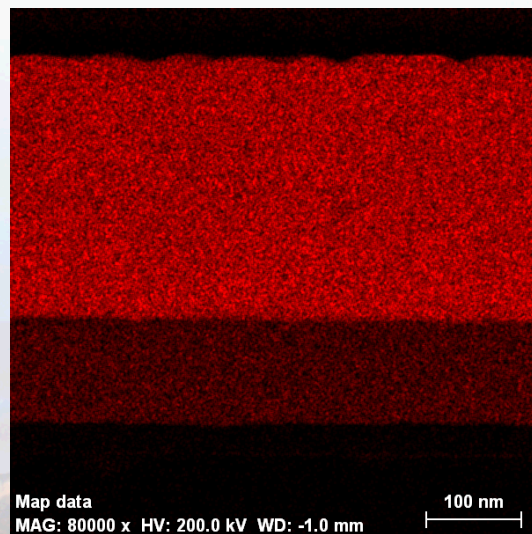
350°C

400°C

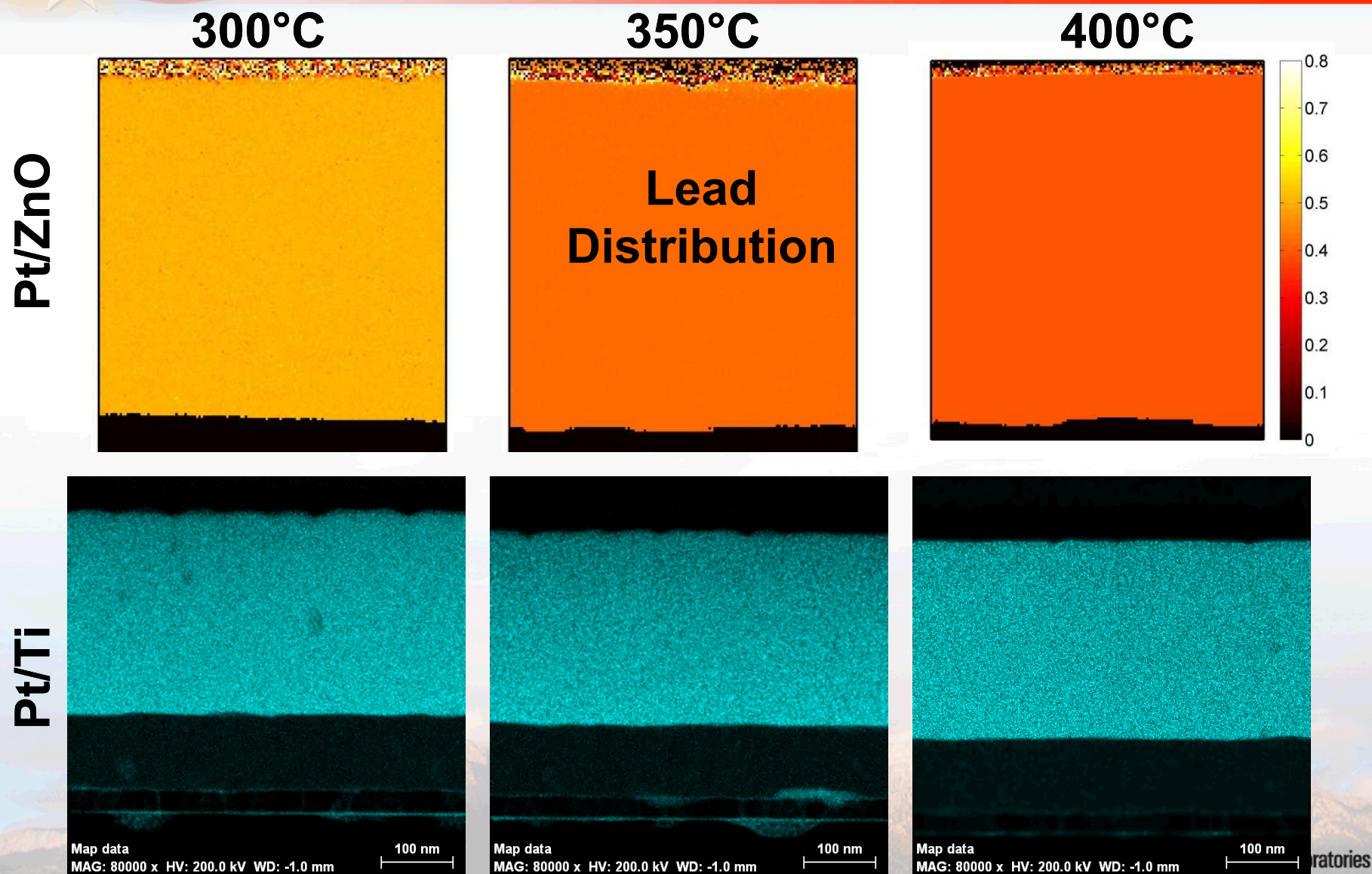
Pt/ZnO

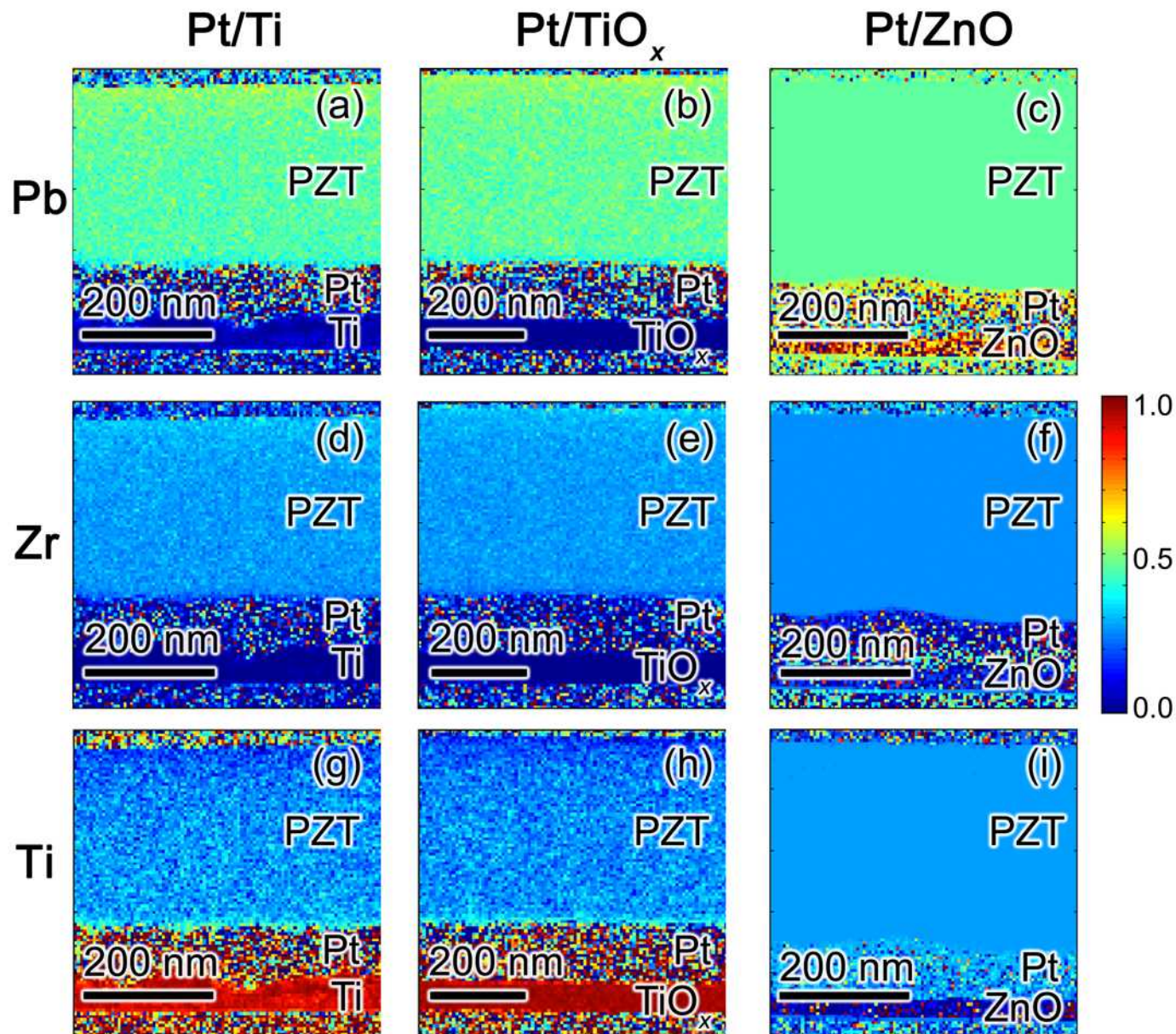


Pt/Ti



Solution Chemistry Effect: IMO Films





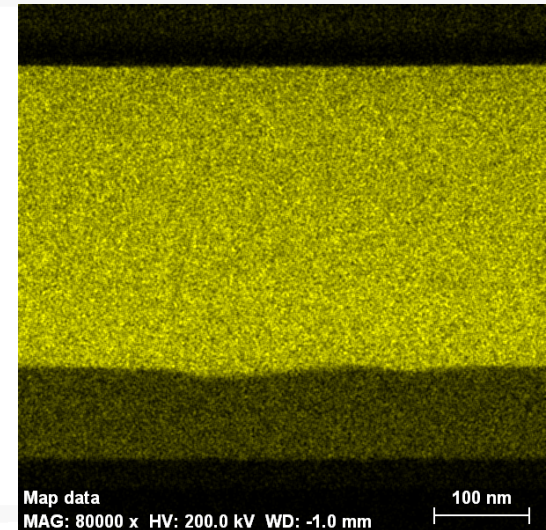
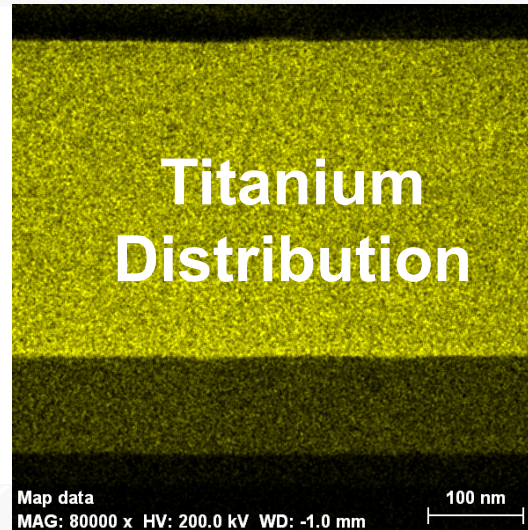
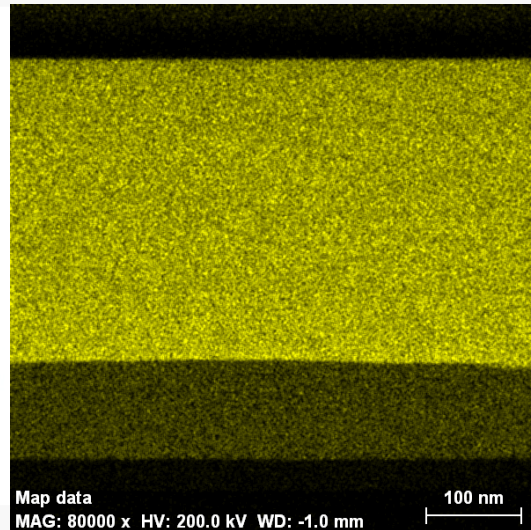
Solution Chemistry Effect: 2-MOE films Prior to Crystallization

300°C

350°C

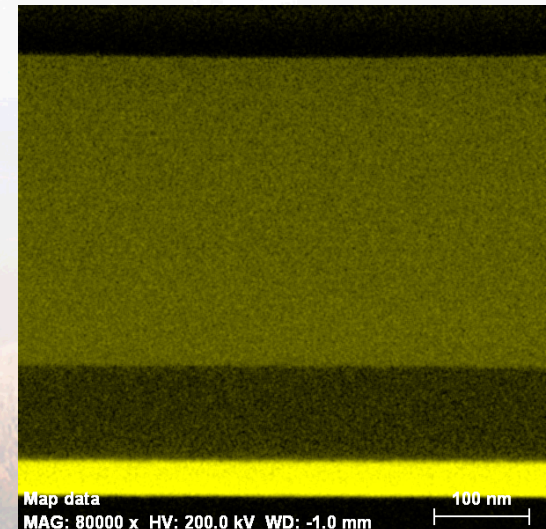
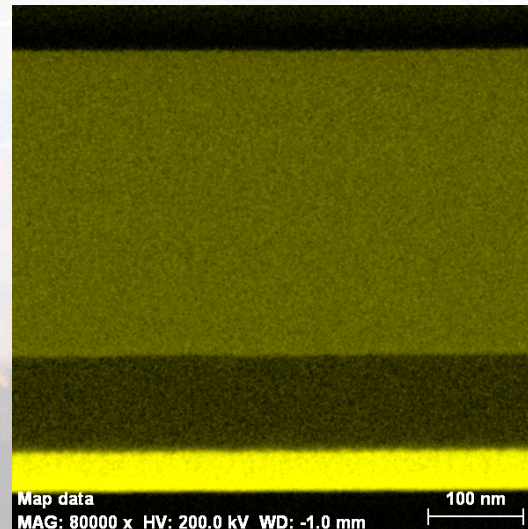
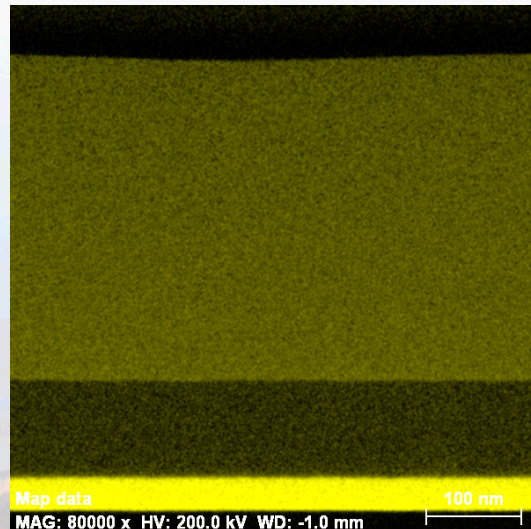
400°C

Pt/ZnO



Titanium
Distribution

Pt/Ti



Solution Chemistry Effect: 2-MOE films

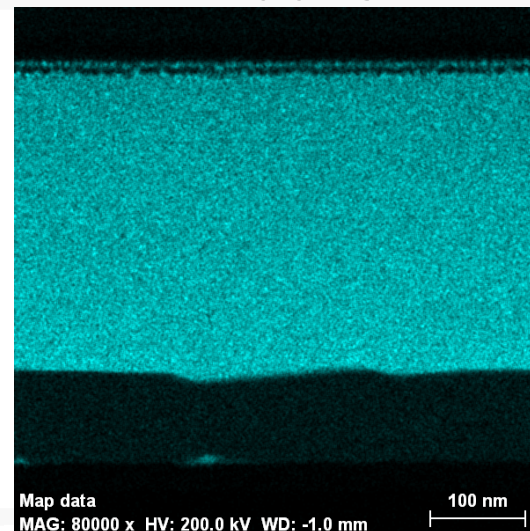
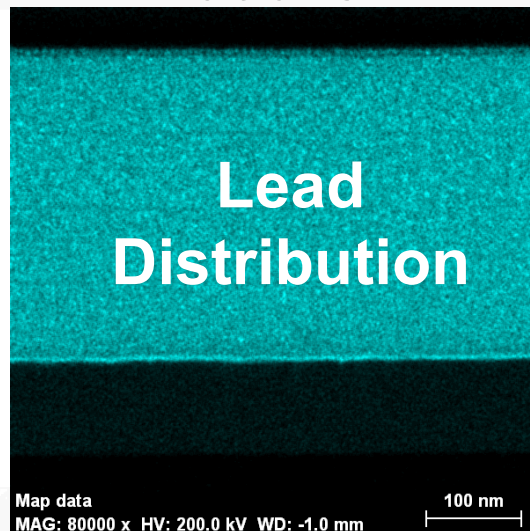
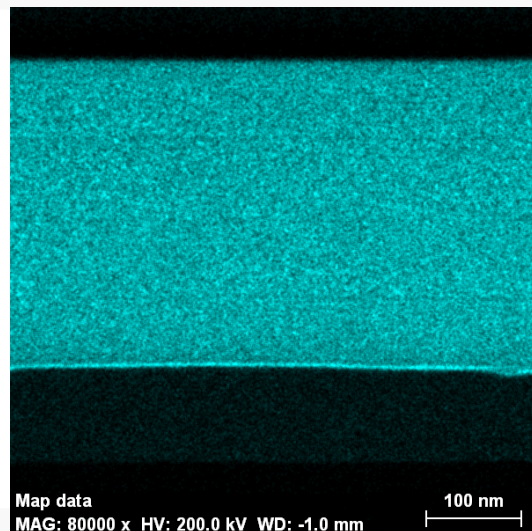
Prior to crystallization

300°C

350°C

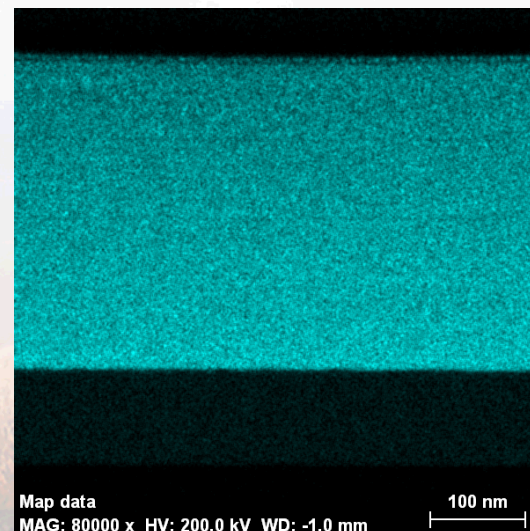
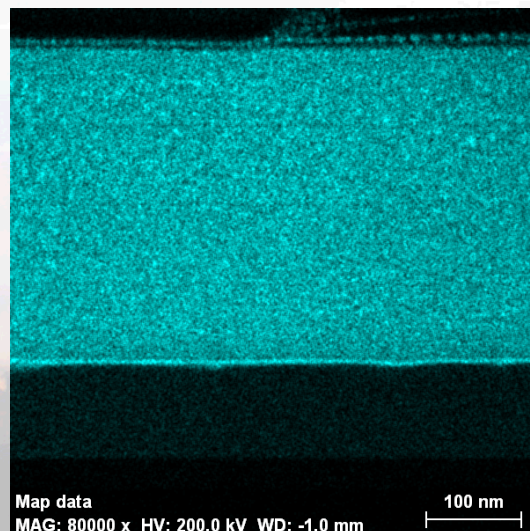
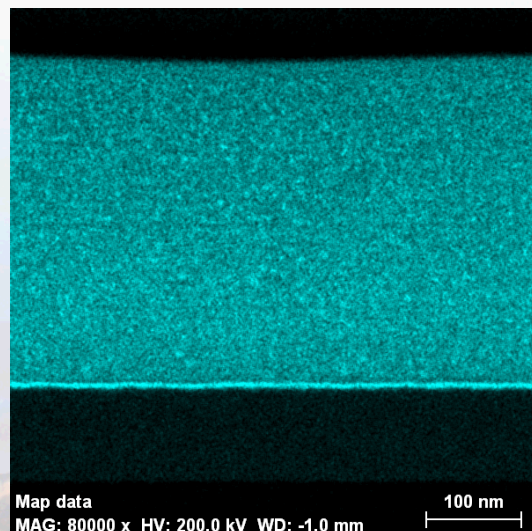
400°C

Pt/ZnO

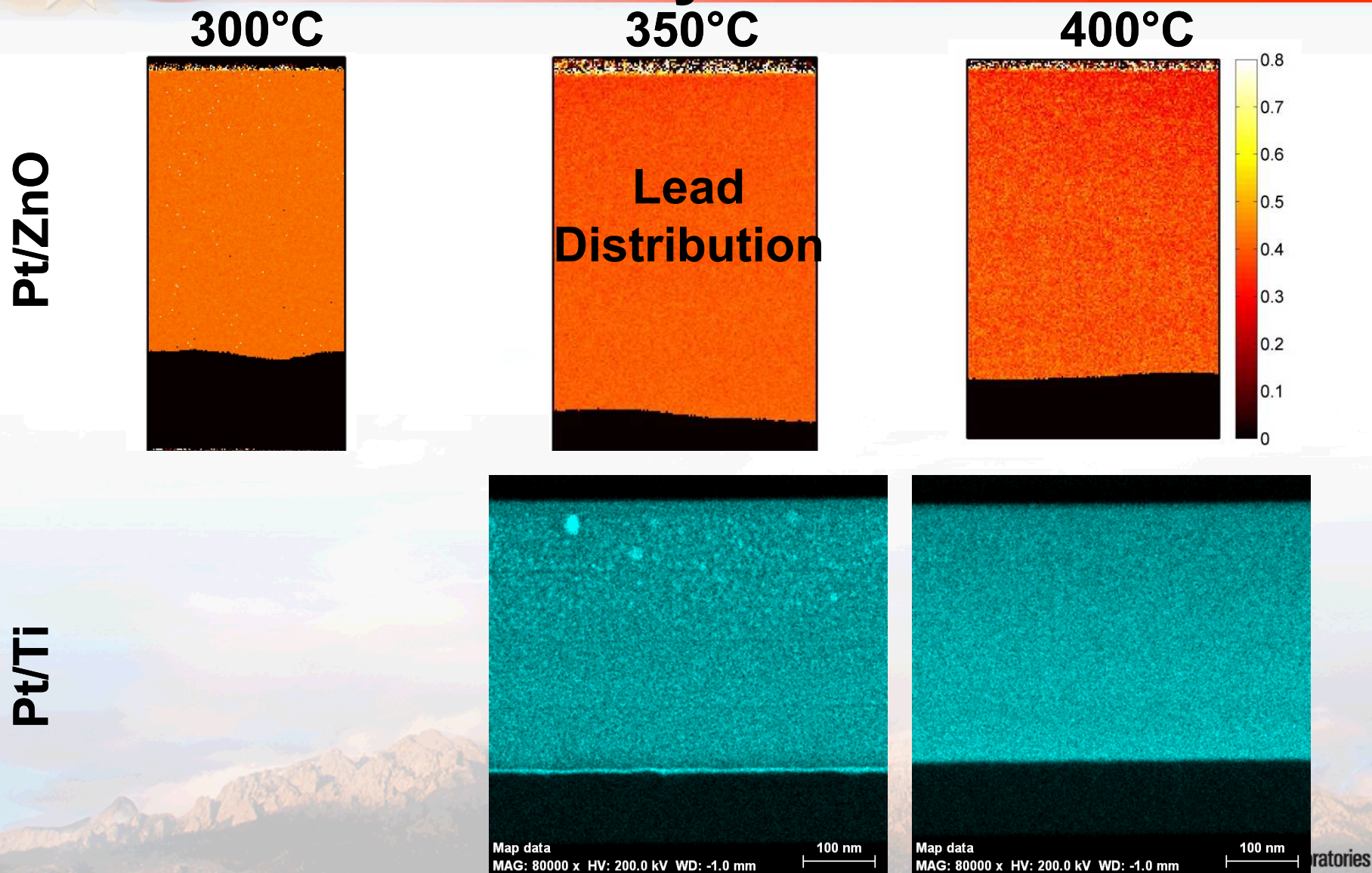


Lead
Distribution

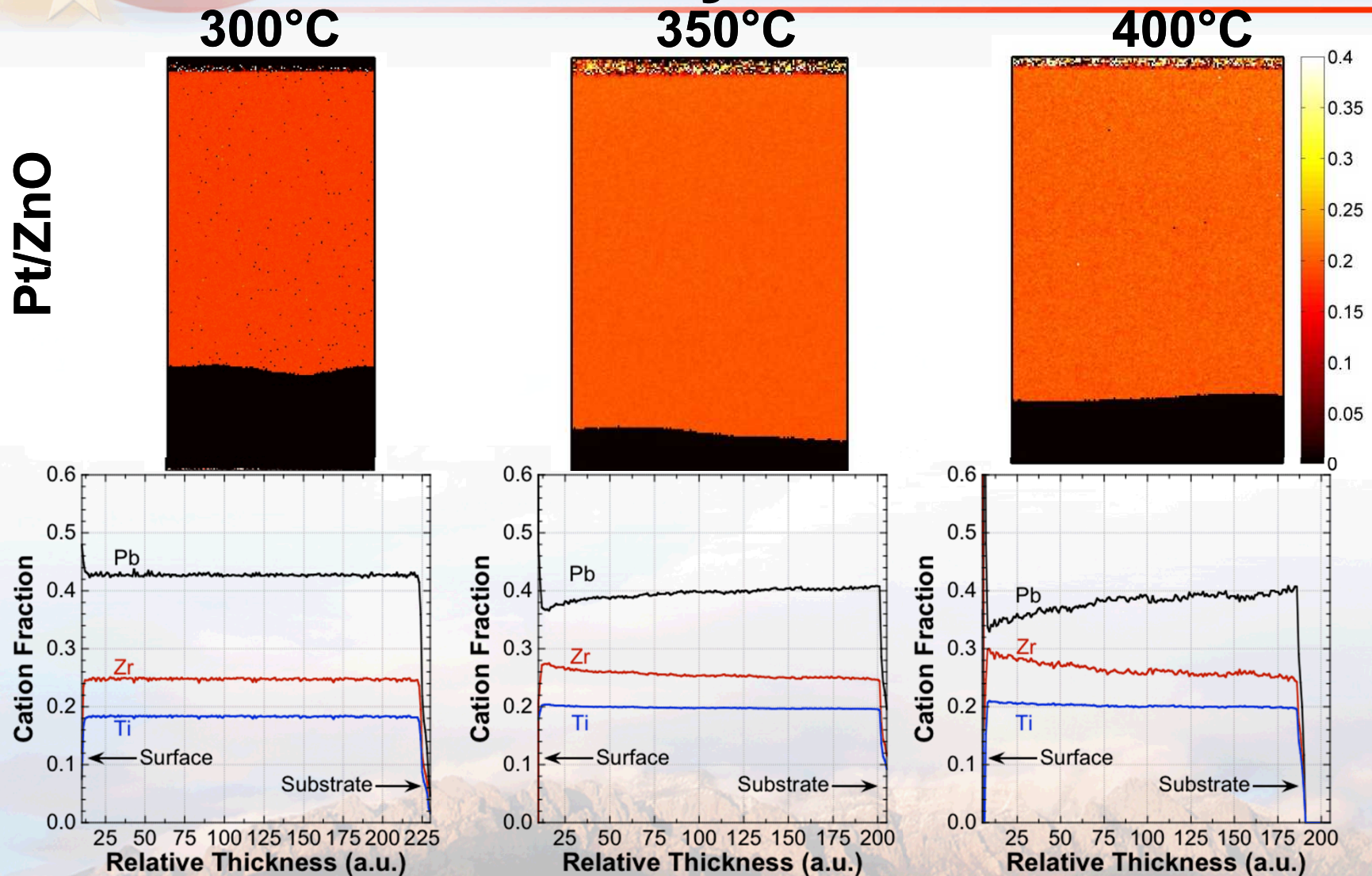
Pt/Ti



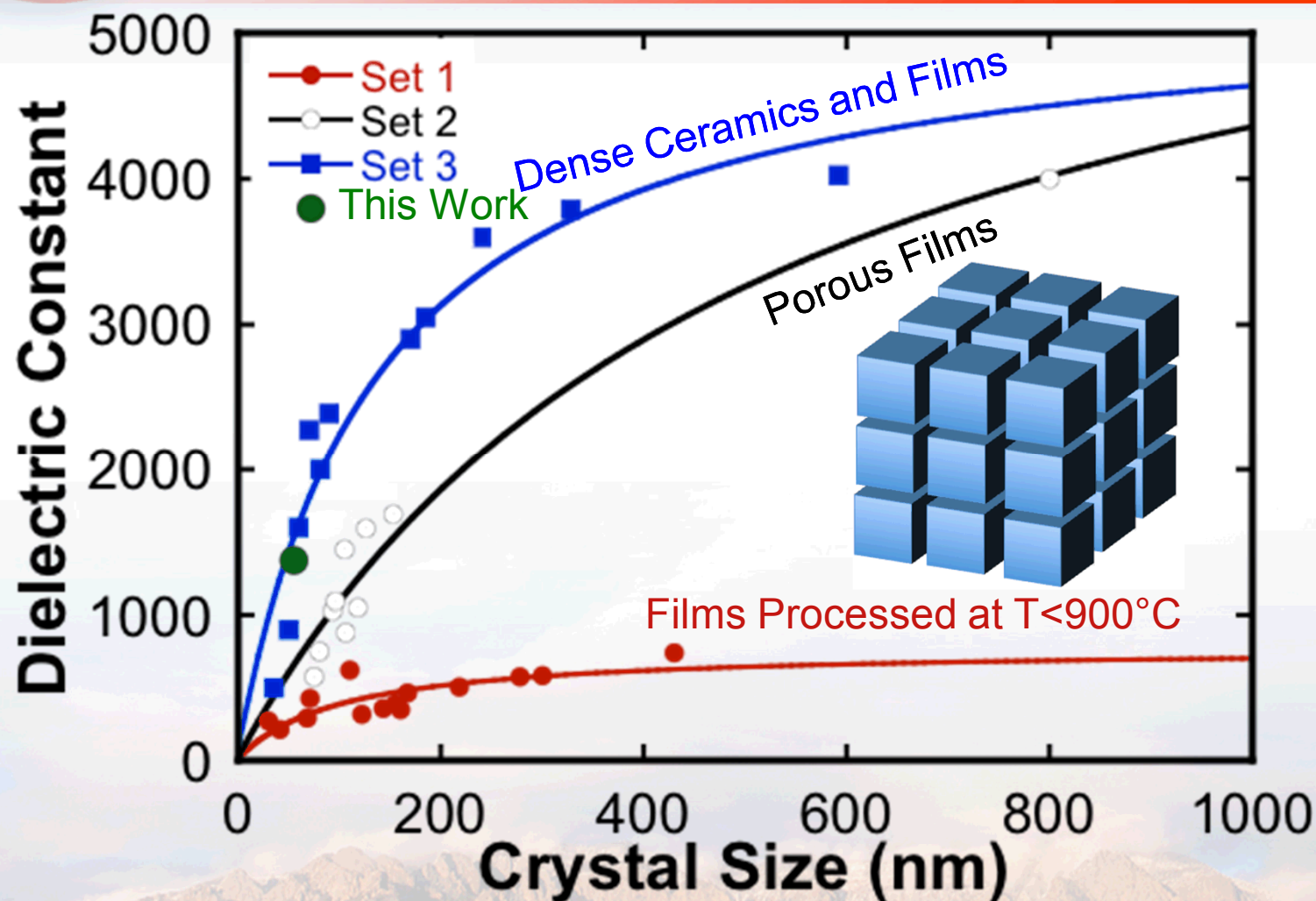
Solution Chemistry Effect: IMO Films Prior to Crystallization



Solution Chemistry Effect: IMO Films Prior to crystallization

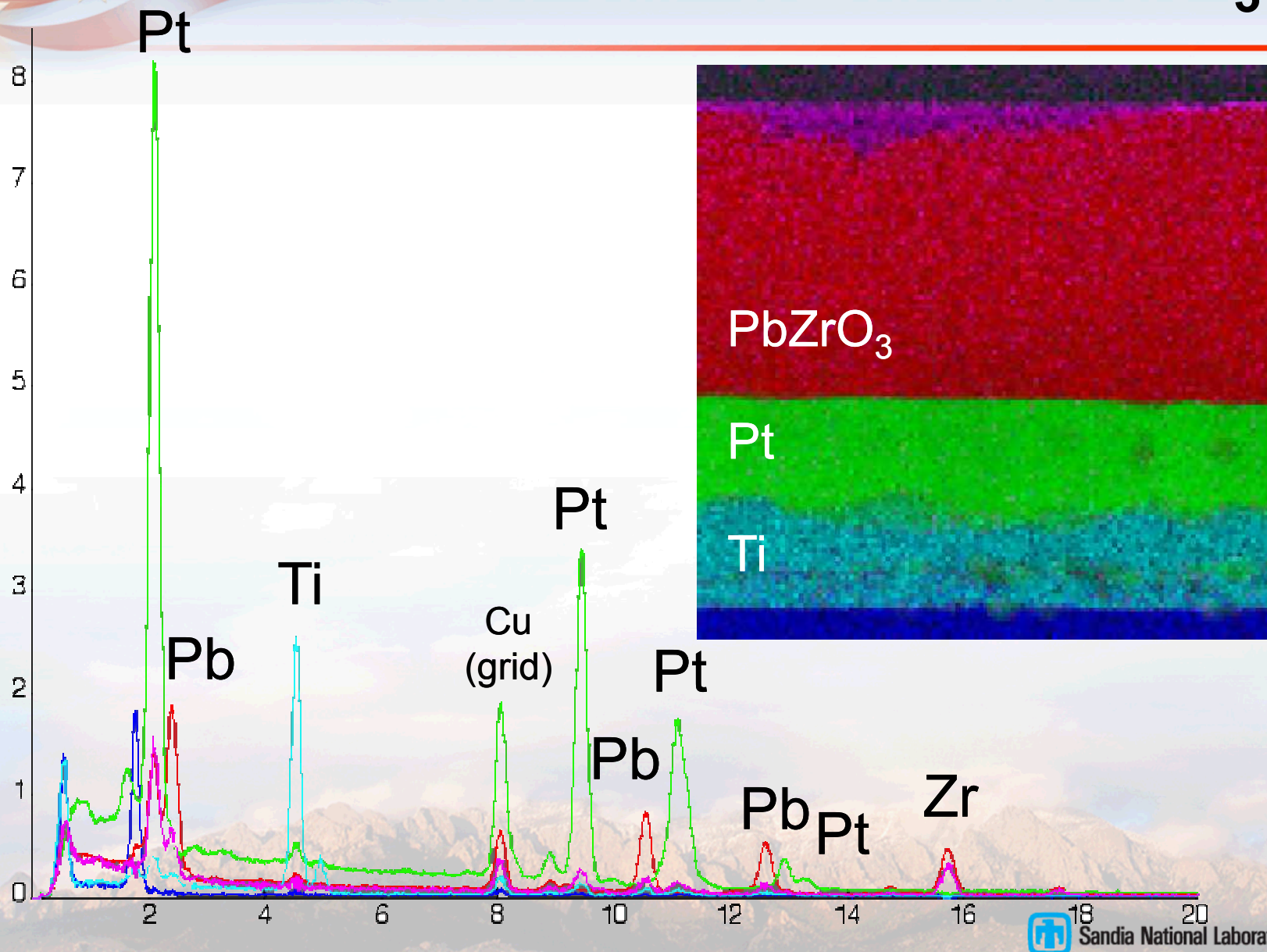


BaTiO₃ Scaling Effects

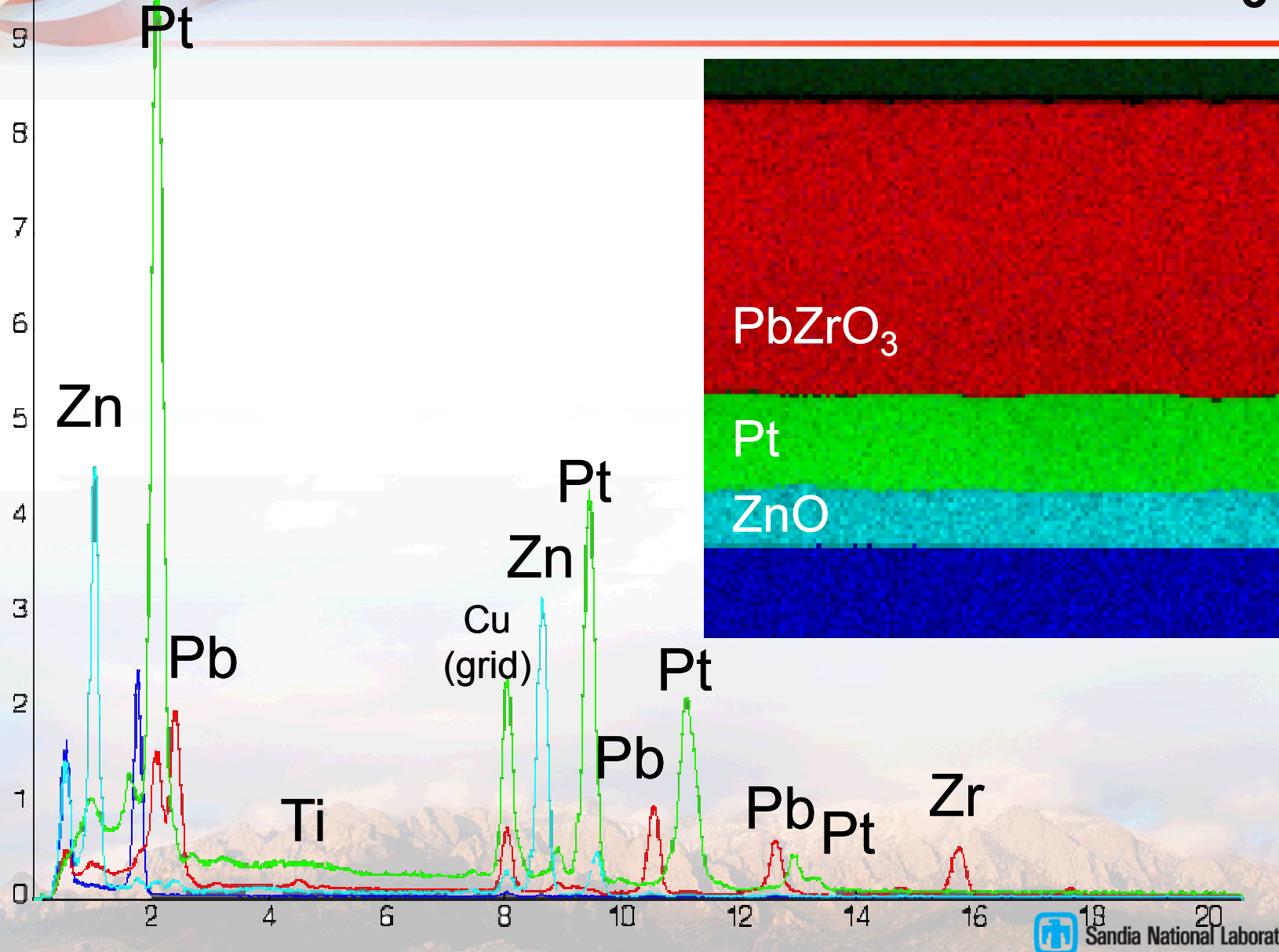


First known BaTiO₃ film with bulk properties on Si

Test for Gradient Mechanism: PbZrO_3



Test for Gradient Mechanism: PbZrO_3



Crystallite vs. Grain Size

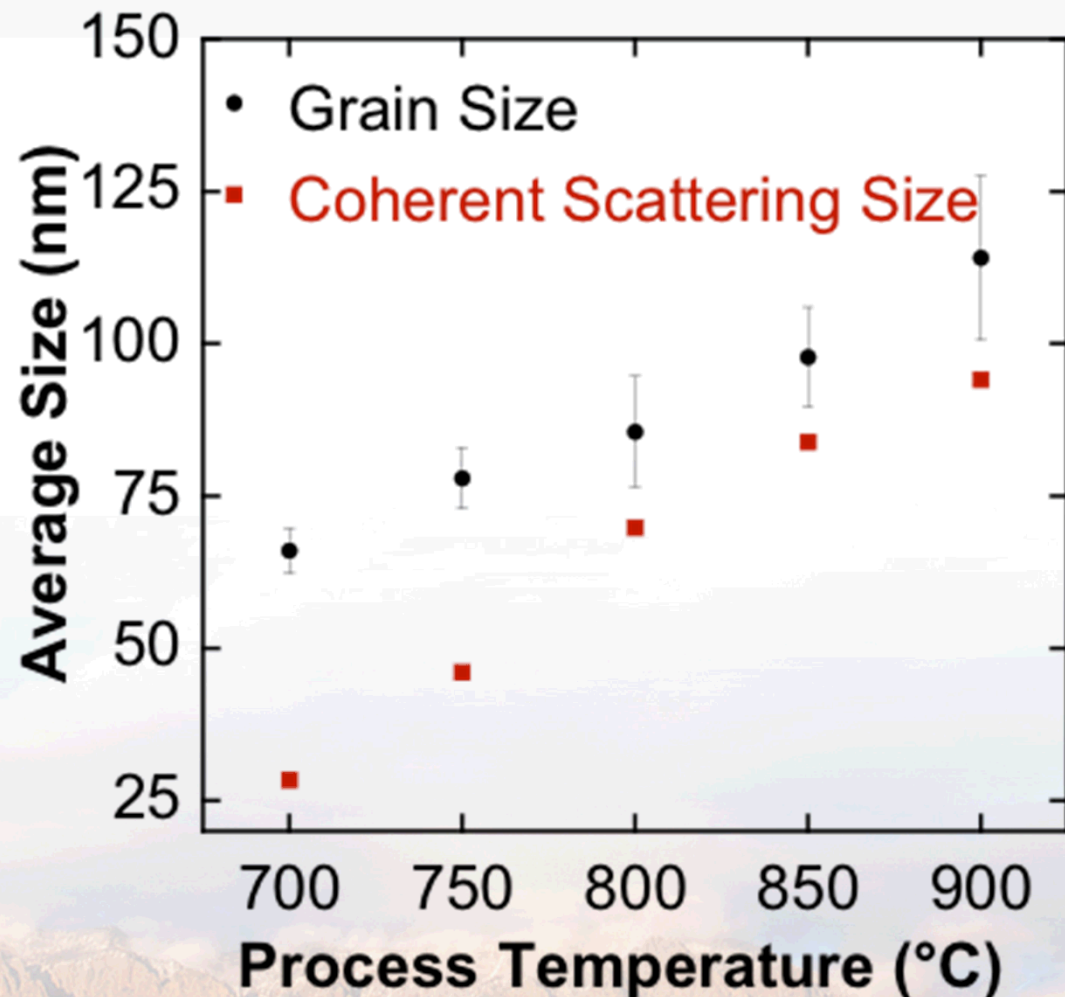
Grain Size

- AFM and FE-SEM
- 95% confidence interval

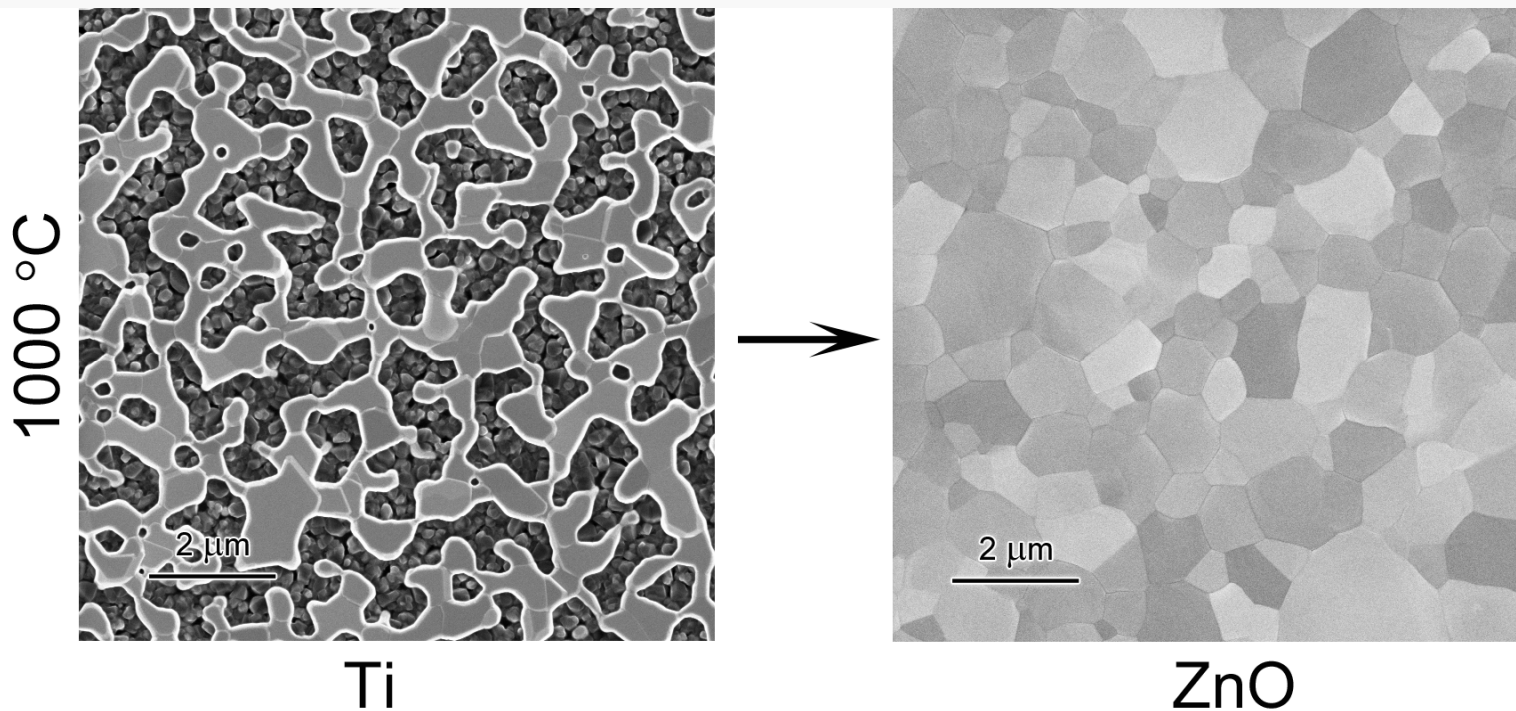
Coherent Scattering Size

- CHES
- Scherrer's Formula on 111 reflections

Sub-grain structure dominates dielectric response



Pt/ZnO as a high temperature substrate



- ZnO buffered Pt/Si is robust enough to withstand process temps in excess of 1000 °C
- Ideal candidate for materials previously best grown on single crystals:
 - BaTiO_3
 - $(\text{Ba,Sr})\text{TiO}_3$



MLC Scaling History



0603: 1600 μm X 800 μm
Most popular pre-2002 size



0402: 1000 μm X 500 μm
Most widely used size



0201: 600 μm X 300 μm
1 μF in X5R rating



01005: 400 μm X 200 μm
Limited use after 2004

to-scale image
of salt grain



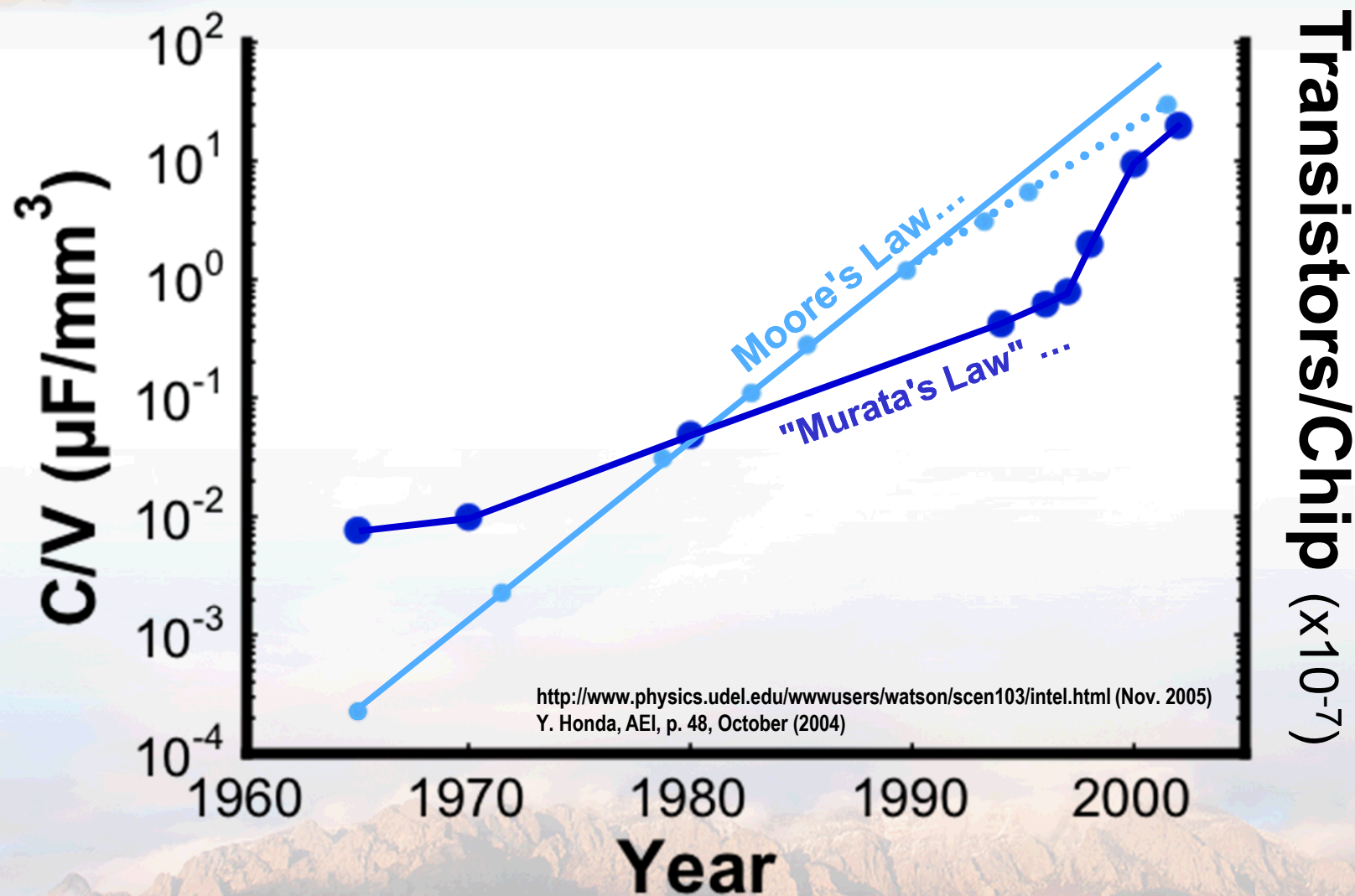
still 10^2 layers!

constant capacitance with
increasing technology node

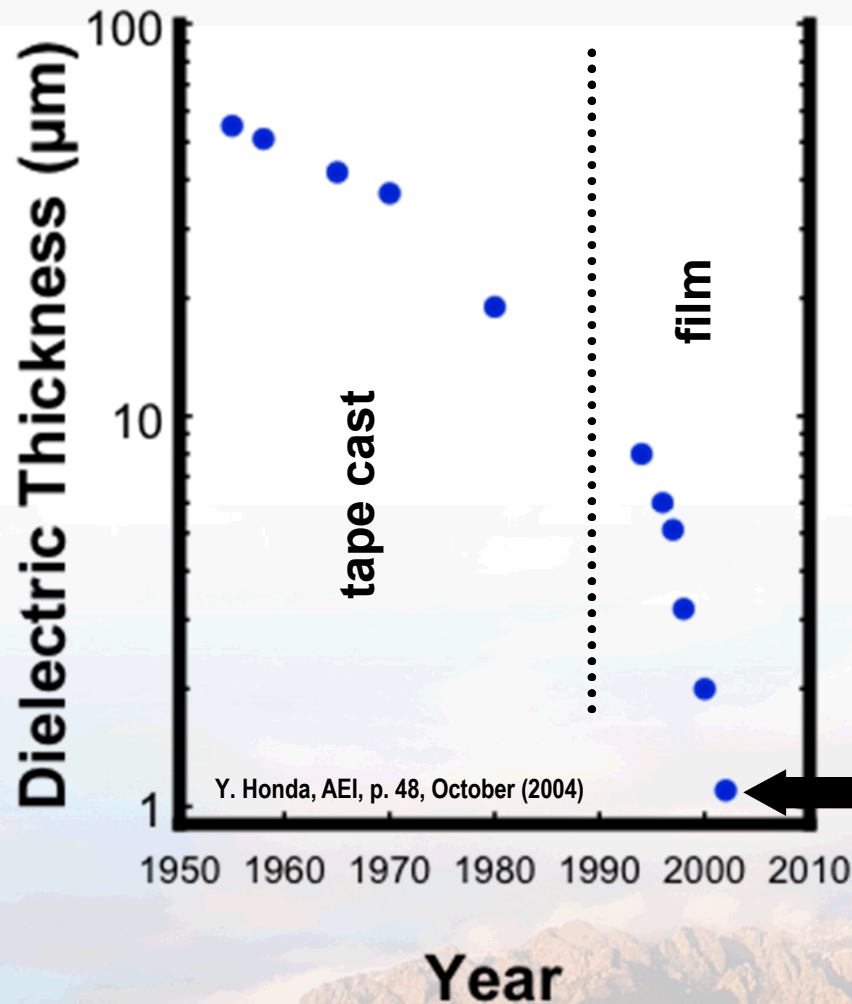


Sandia National Laboratories

MLC vs. Transistor Scaling



Physically, what's happening?



- Incredible scaling demonstration
- Fabricated using powder processing - **mass produced**
- Film / lamination process
- Real *Nano-technology*!

