SAND2011-7928 C

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Chemically Homogeneous Complex Oxide Thin Films via Improved Substrate Metallization

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Collaborators

Sandia National Labs

- Geoff Brennecka
- Paul Kotula
- Chris T. Shelton
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- Peter Lam

Oregon State University

- Brady Gibbons

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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

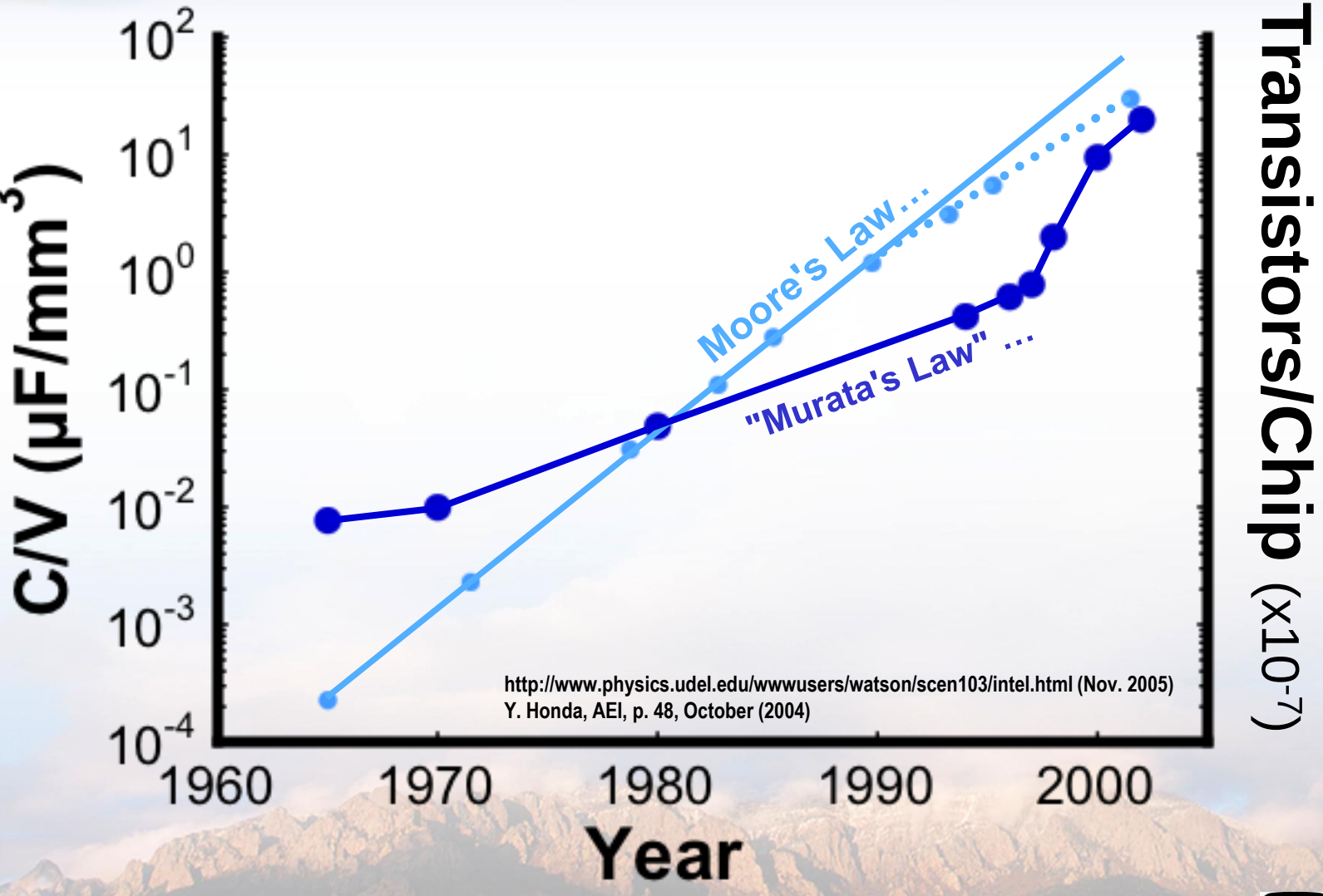
01005: 400 µm X 200 µm
Limited use after 2004

***to-scale* image of salt grain**

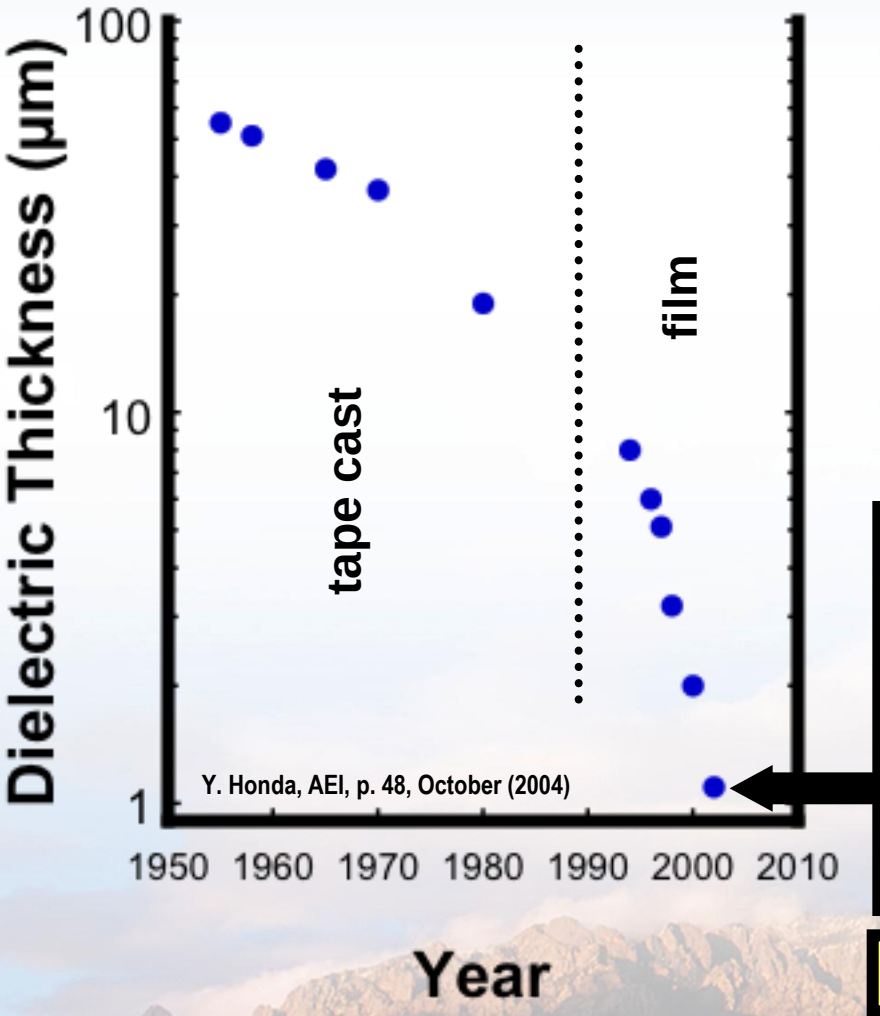
still 10^2 layers!

constant capacitance with increasing technology node

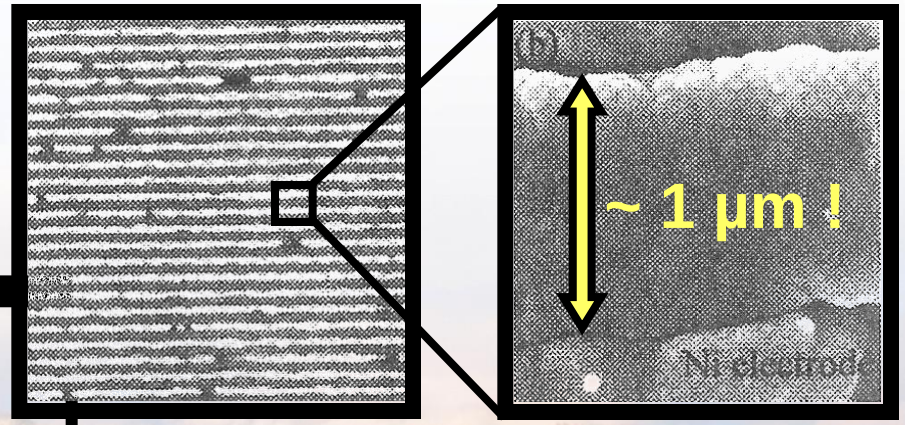
MLC vs. Transistor Scaling



Physically, what's happening?

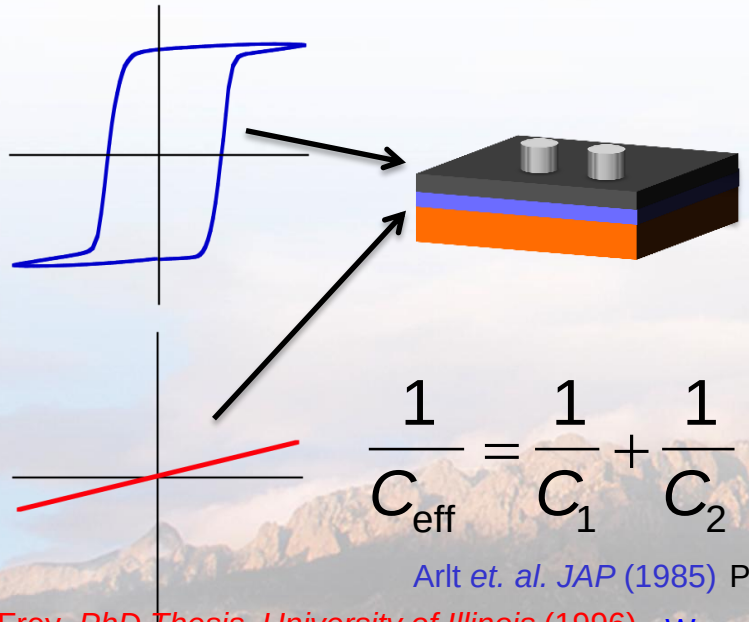


- Incredible scaling demonstration
- Fabricated using powder processing - **mass produced**
- Film / lamination process
- Real *Nano-technology!*

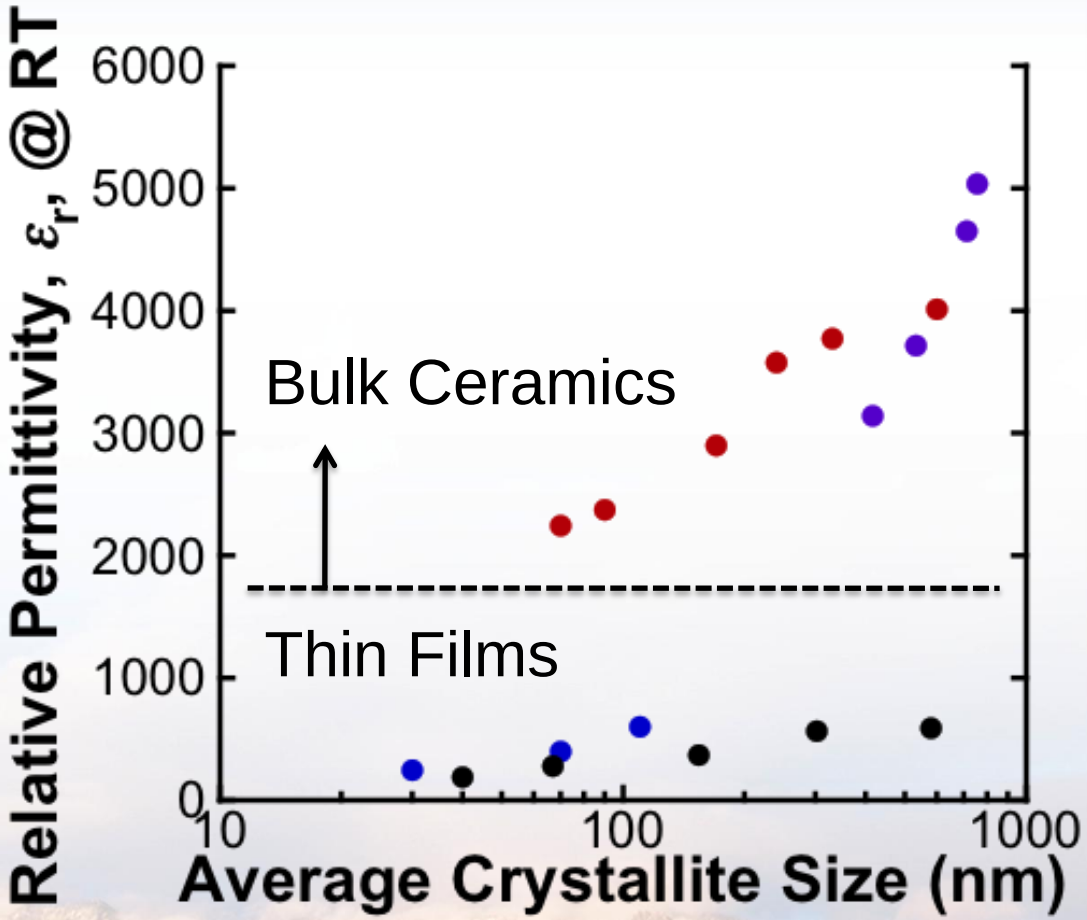


Limits of Scaling

- **Further scaling requires thin film technology**
- **Severely diminished properties in films**
- **Traditionally blamed on 'size effects'**



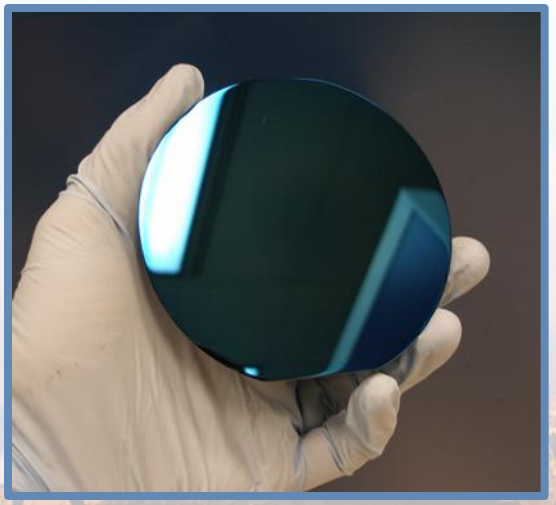
$$\frac{1}{C_{eff}} = \frac{1}{C_1} + \frac{1}{C_2}$$

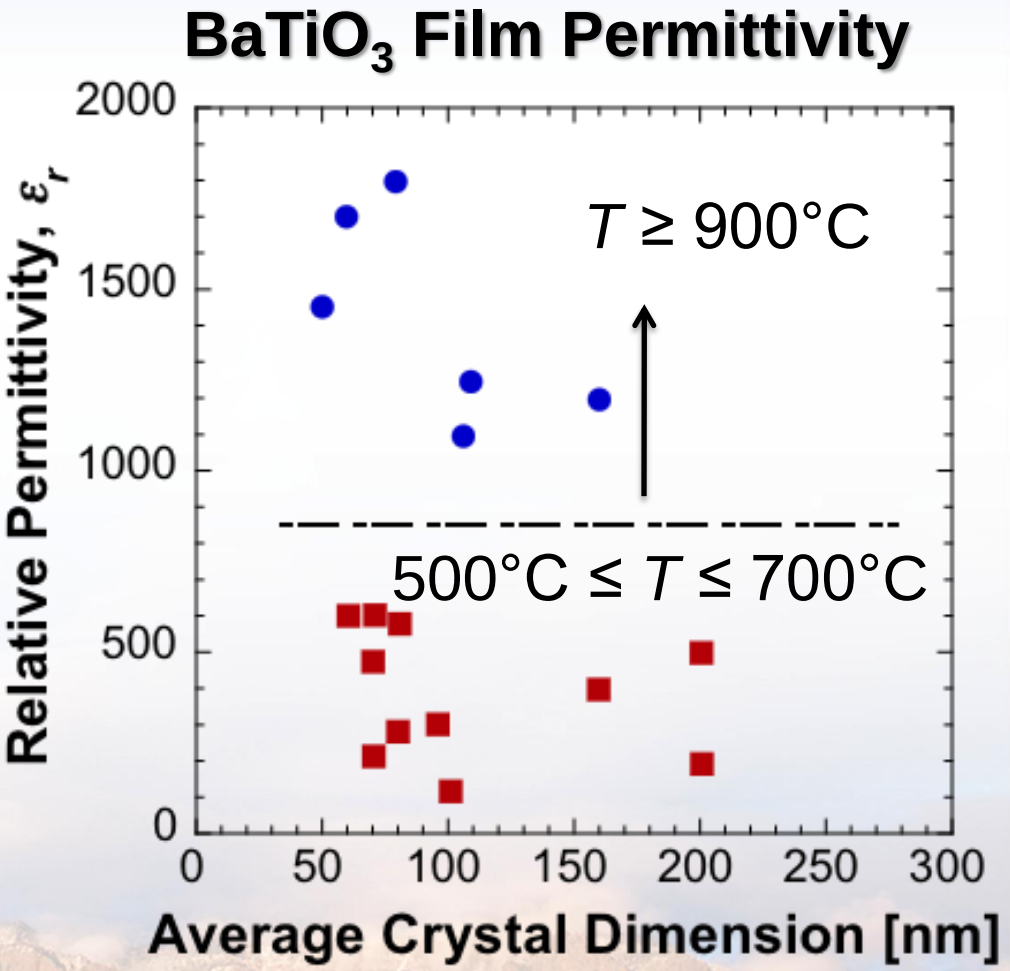


Arlt *et. al. JAP* (1985) Parker *et al., APL* (2002)

Frey, *PhD Thesis, University of Illinois* (1996) Waser *Int. Ferro.* (1997)

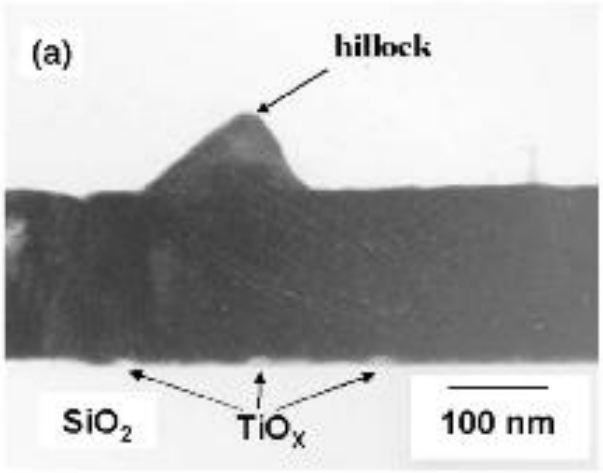
Processing Effects on *K* vs *d*

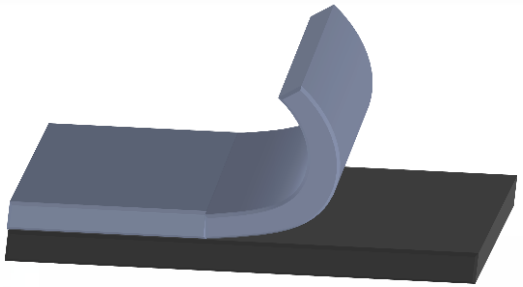




S. Aygün *et al.*, *J. Appl. Phys.*, 2008

Platinized Silicon Substrates



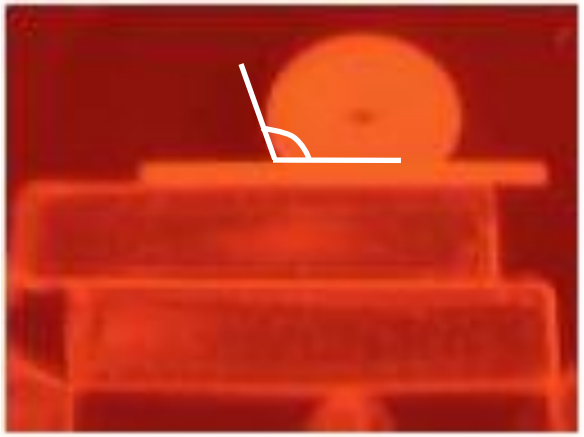


- **Titanium 'adhesion' layers by far the most common**
- **Titanium expands upon oxidation causing hillocks**
- **Adhesion layers fail with large temperature swings (>700˚)**

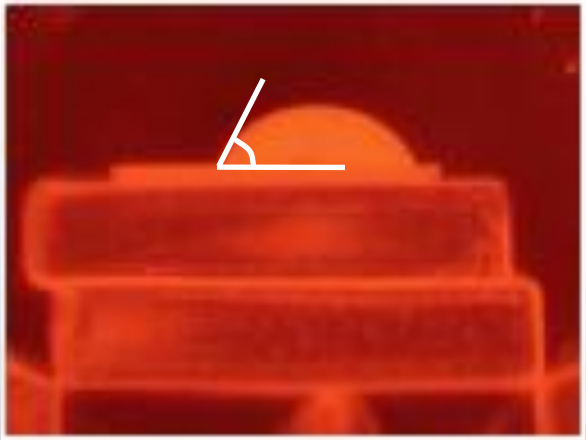
Nam et al., ***Thin Solid Films*** , (2000)

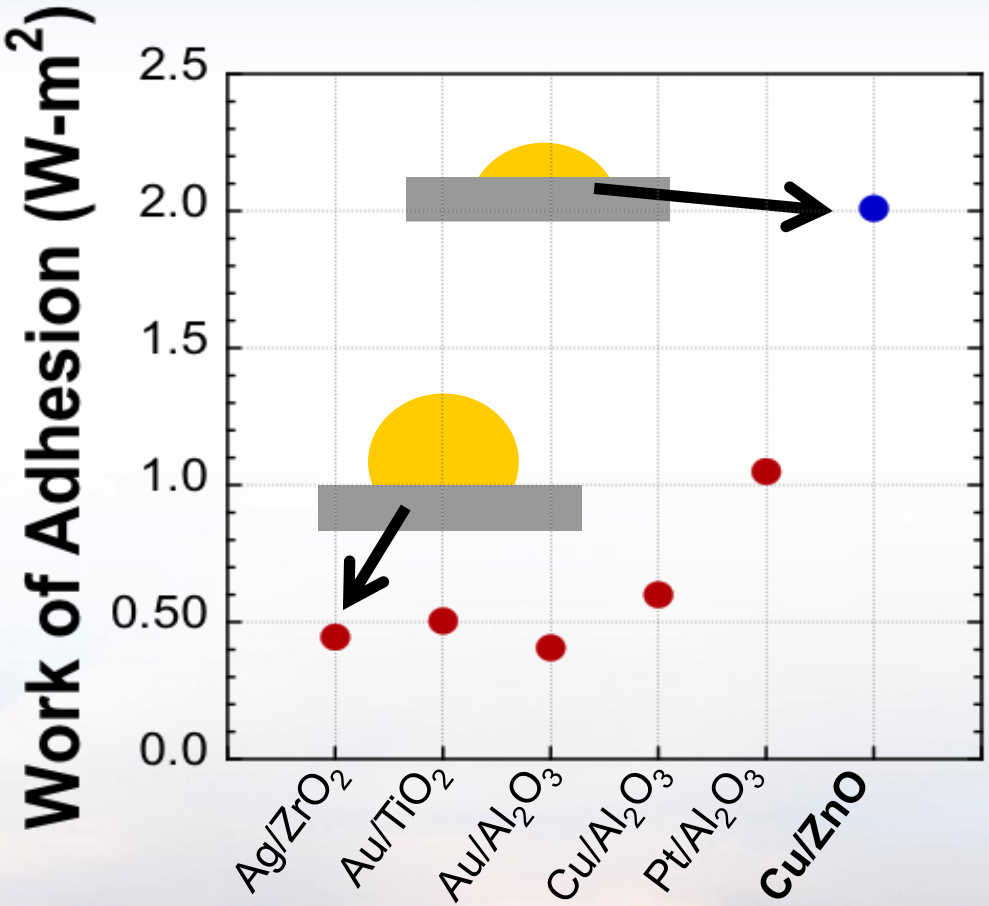
Metal Wetting and Adhesion

Molten Cu on Al_2O_3



Molten Cu on ZnO





Can we use ZnO as an adhesion layer for Pt?

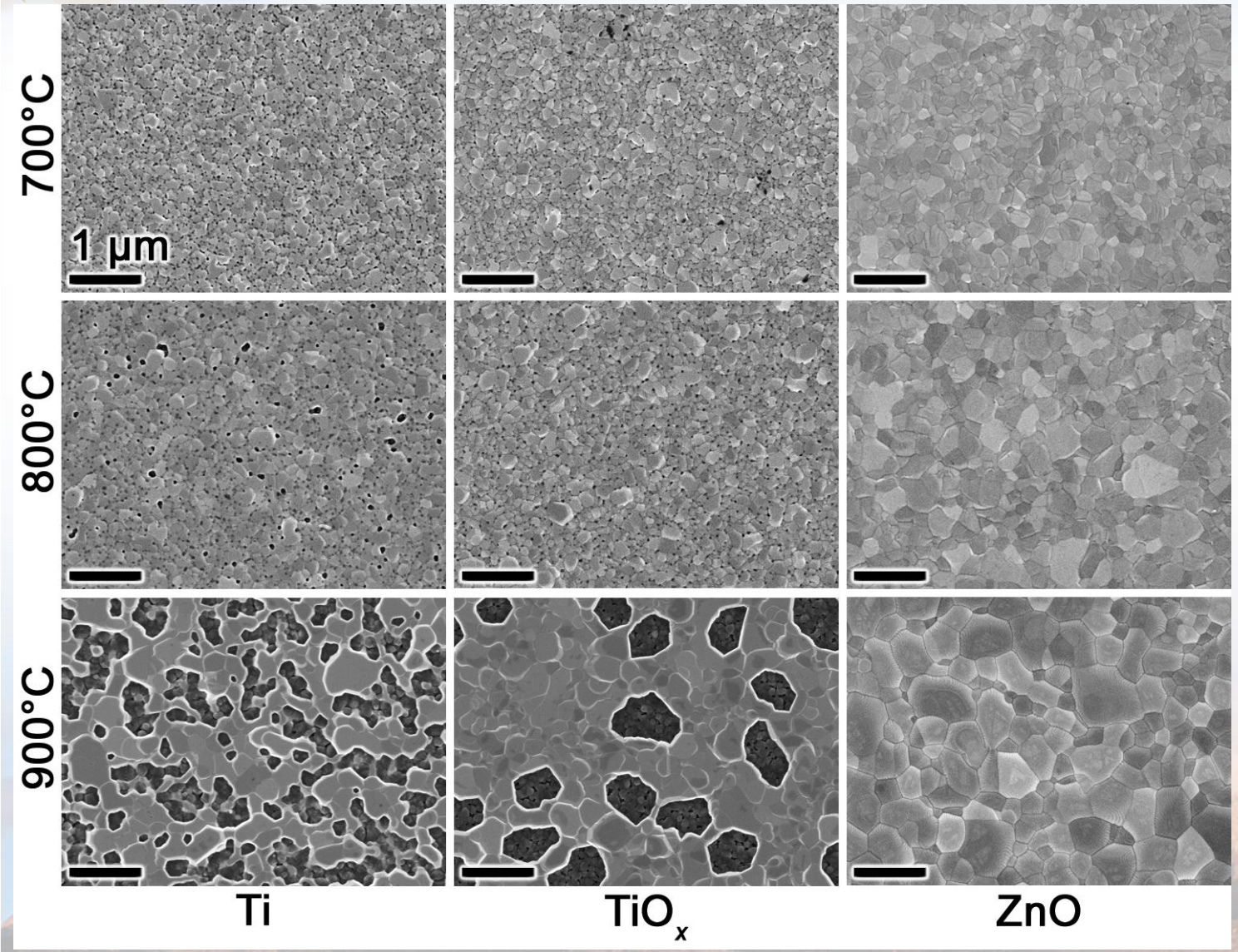
Cu and Pt both *Fm3m* metals

Laughlin, B. Ph.D. thesis, NCSU 2006

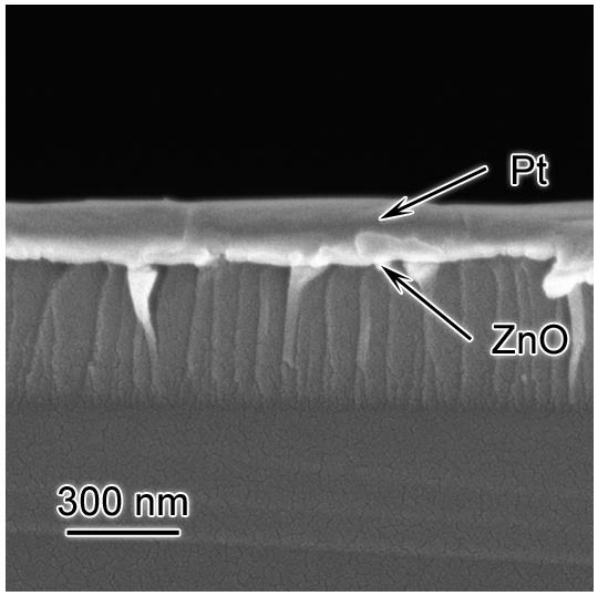
Substrate Preparation

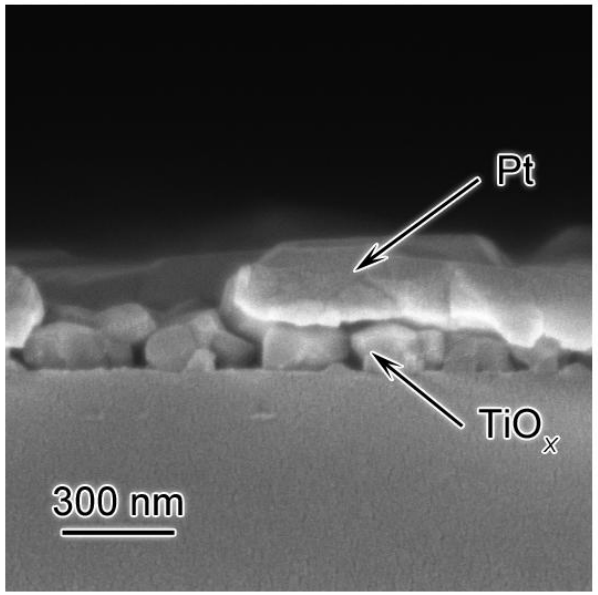
- Ti, TiO_x, ZnO, and Pt prepared via RF magnetron sputtering
  - 30° off-axis geometry
  - Ti: Ar atmosphere
  - TiO_x: Ar sputter, O_2 anneal
  - ZnO: 1:1 Ar:O_2 atmosphere
  - Pt: Ar Atmosphere
- 100 nm Pt/40 nm buffer/40 nm SiO_2/Si

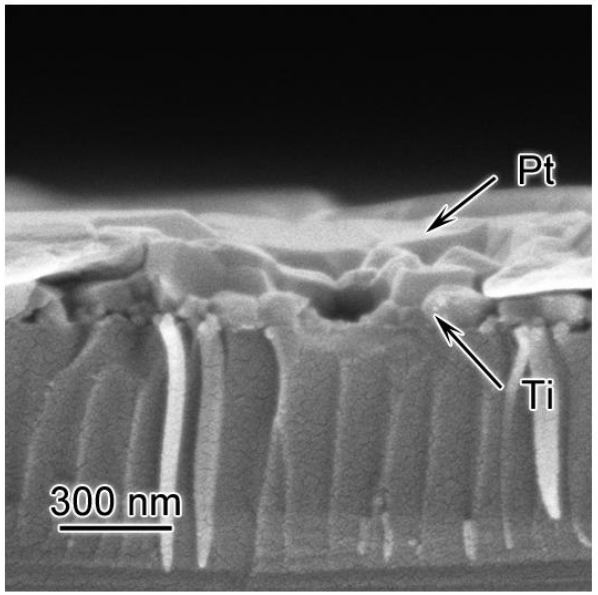
Electrode Temperature Stability



Electrode Temperature Stability







CSD $BaTiO_3$ on Platinized Si

$Ti(OiPr)_4$ + 2,4 pentanedione
1:2 molar ratio

Ba-acetate + propionic acid
Dissolve salt

Combine equimolar amounts Ba and Ti solution

Dilute in MeOH
0.15 M

Spin coat deposition
3000 rpm/30 sec

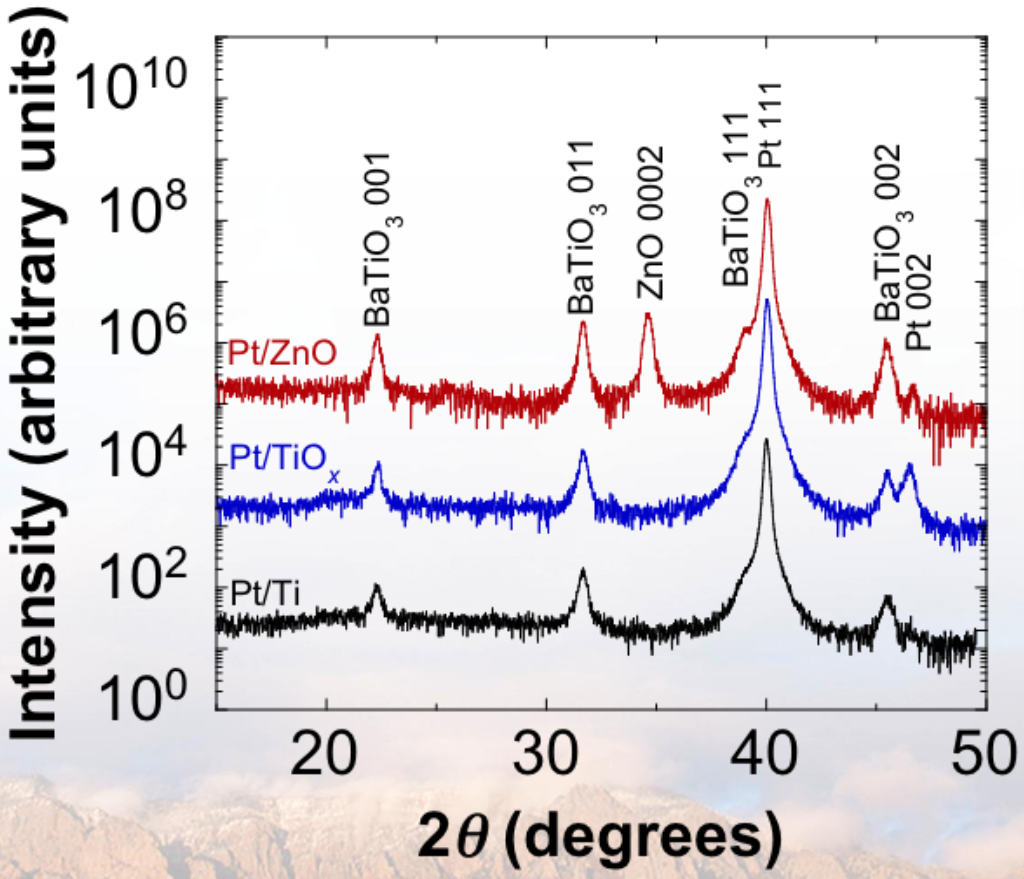
3 layers

Repeat 3x

Dry ~ 250 ºC

Fire 900 ºC

Sputter Pt electrodes



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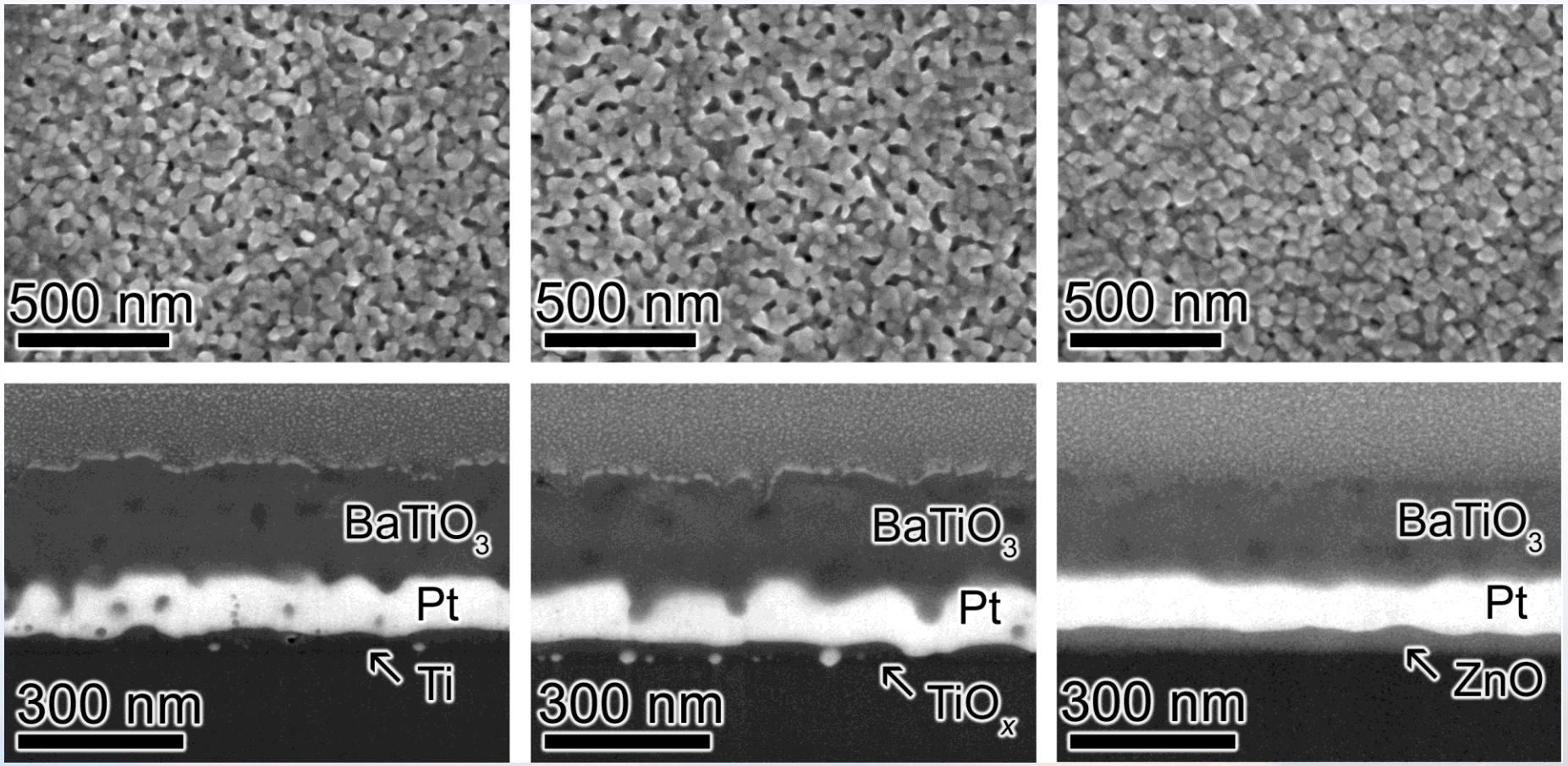
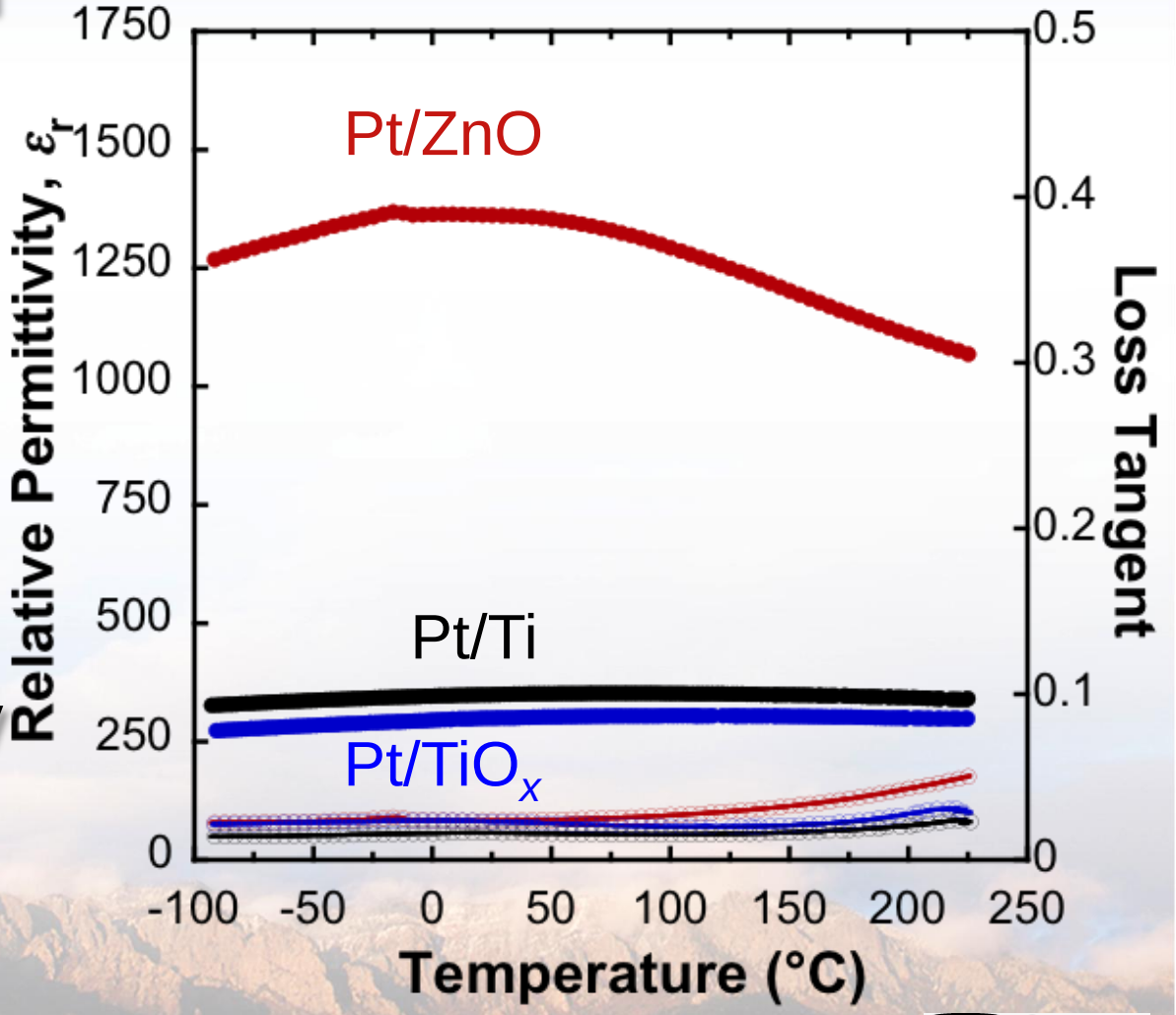
Topography and microstructure



$BaTiO_3$ Dielectric Properties

- **Ti- and TiO_x-buffered films actually survived**
- **$BaTiO_3$ on Pt/ZnO substantially outperforms other substrates**
- **Microstructure nearly identical: Why such a disparity?**
- **What about other Ferroelectrics?**



SNL IMO-based Solution Route

$Zr(Obu)_4 \cdot BuOH + Ti(OiPr)_4$
Blend 5 min

Acetic Acid / Methanol
Chelating agent / Solvent

$Pb(OAc)_4 + La(OAc)_3 \cdot H_2O$
Dissolve at ~90°C

Acetic Acid / Methanol
Adjust Molarity

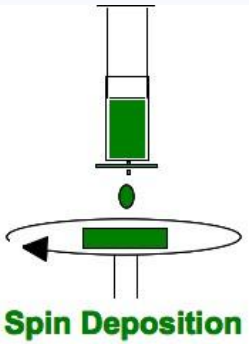
Spin Coat Deposition
4000rpm/30sec

multiple depositions

Pyrolysis

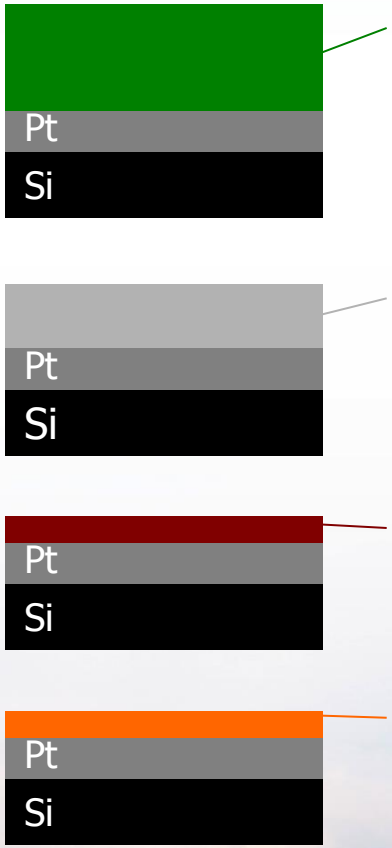
Crystallization

Sputter Pt electrodes



Spin Deposition

heating



Deposited solution

Amorphous gel ~100-300 °C

Intermediate flourite ~400-500 °C

Perovskite ~500-700 °C

R.A. Assink and R.W. Schwartz; ***Chem. Mater.*** *(1993) G. Yi and M. Sayer.* ***J. Appl. Phys.*** *(1988)*

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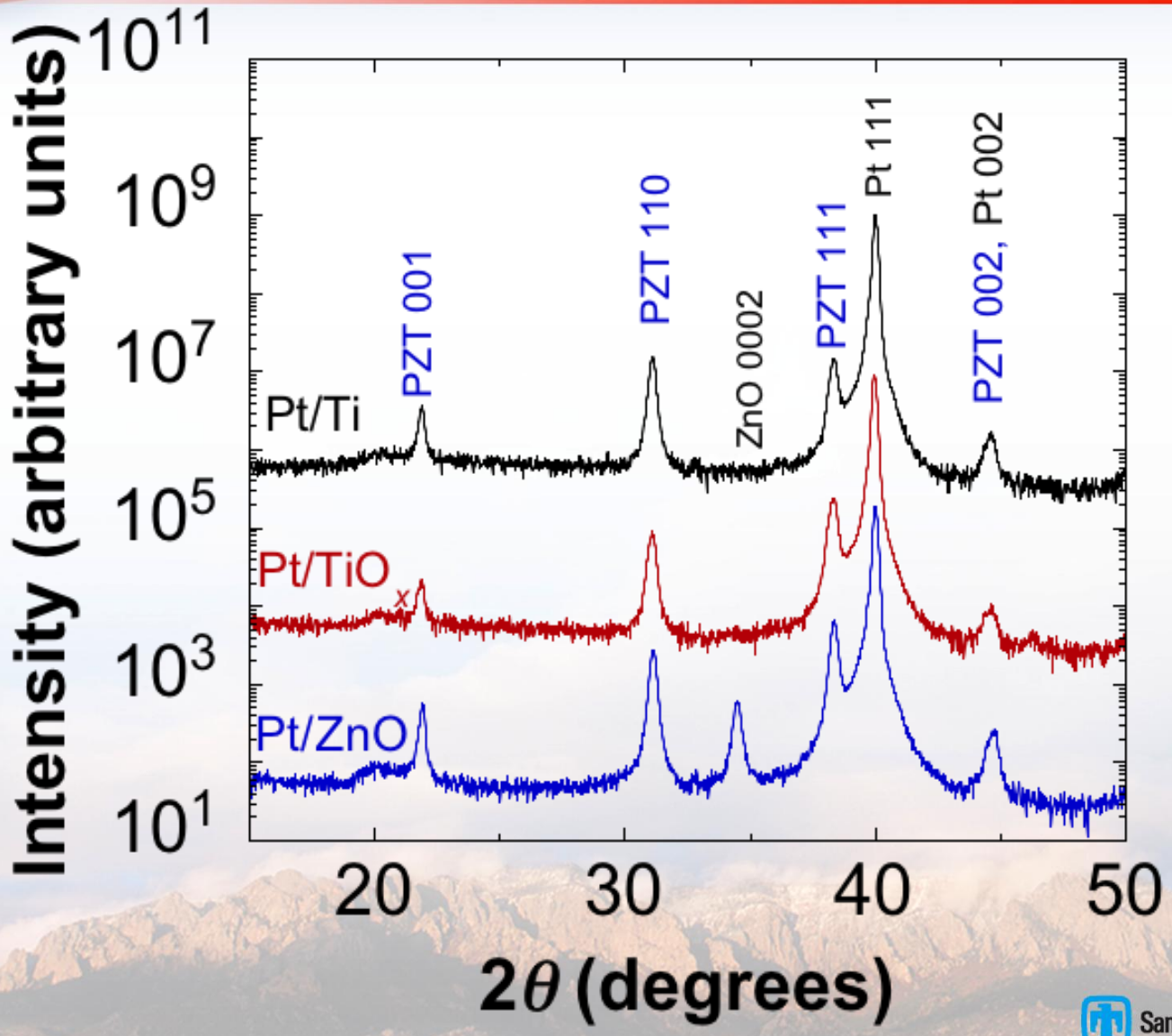
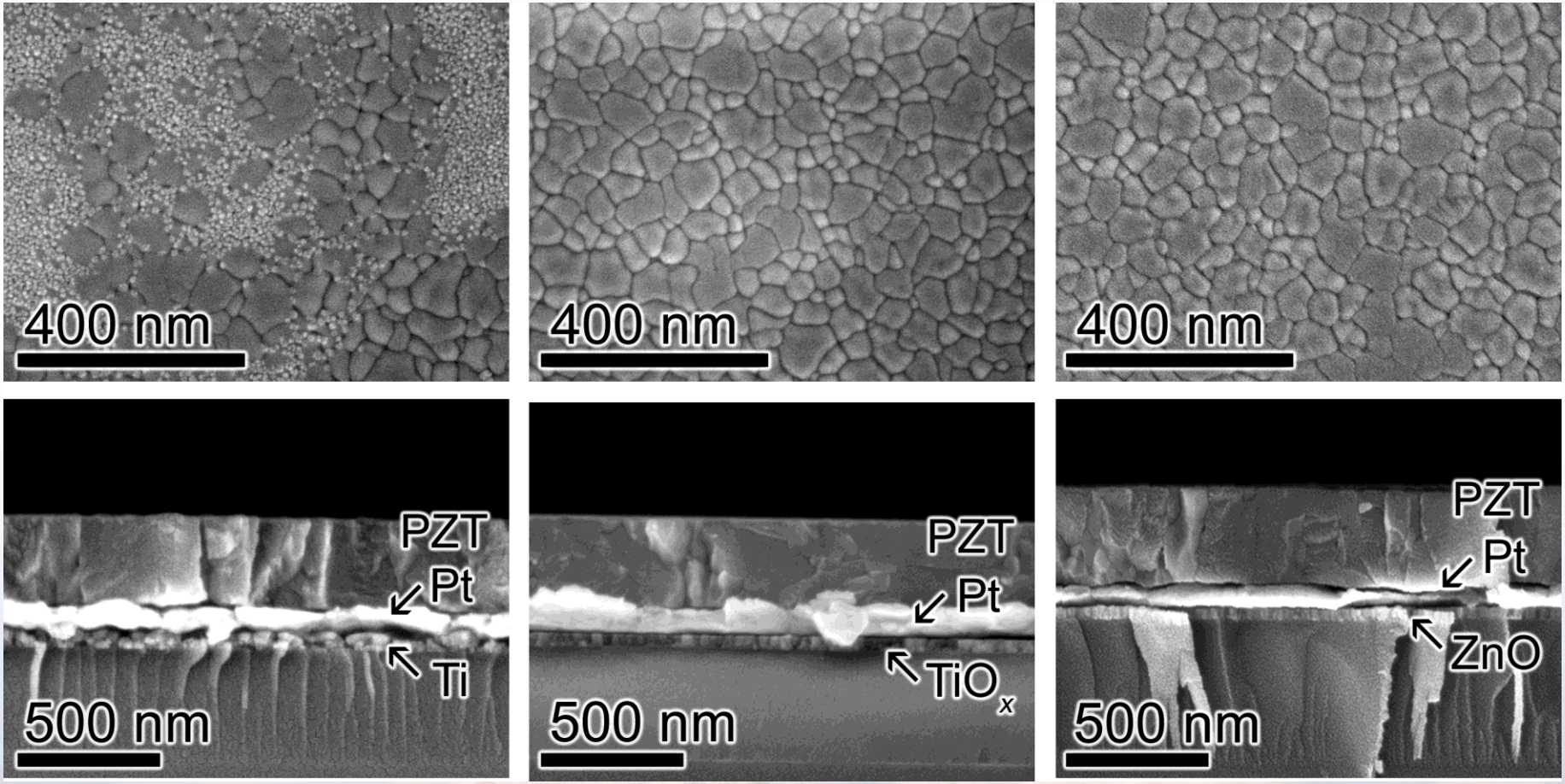
Film Crystallographic Properties

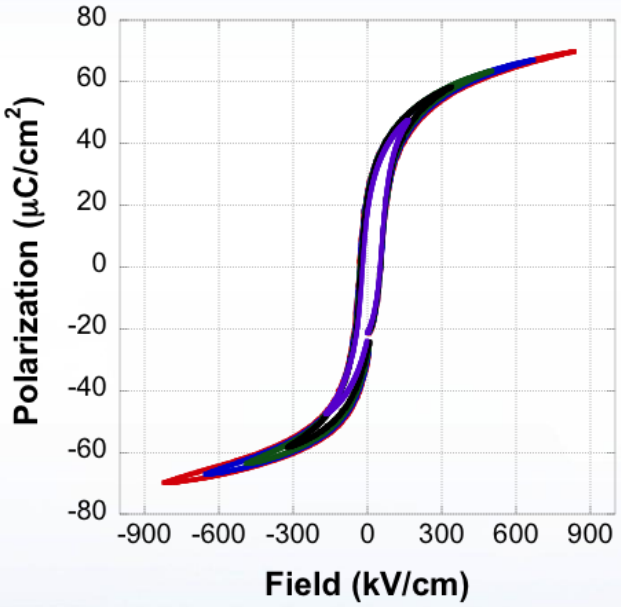


PZT Film Microstructure

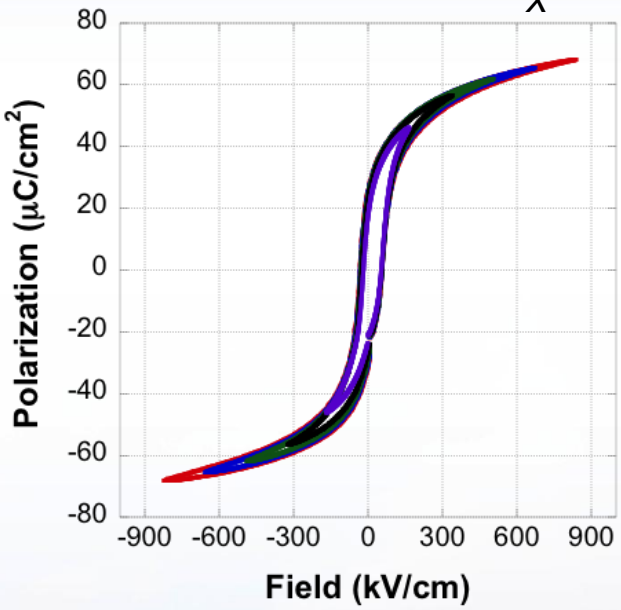


Dielectric and Ferroelectric properties

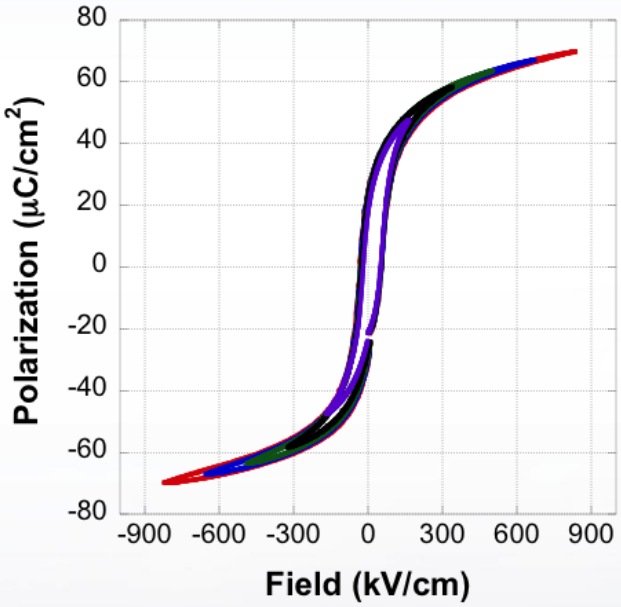
PZT/Pt/Ti



PZT/Pt/TiO_x



PZT/Pt/ZnO

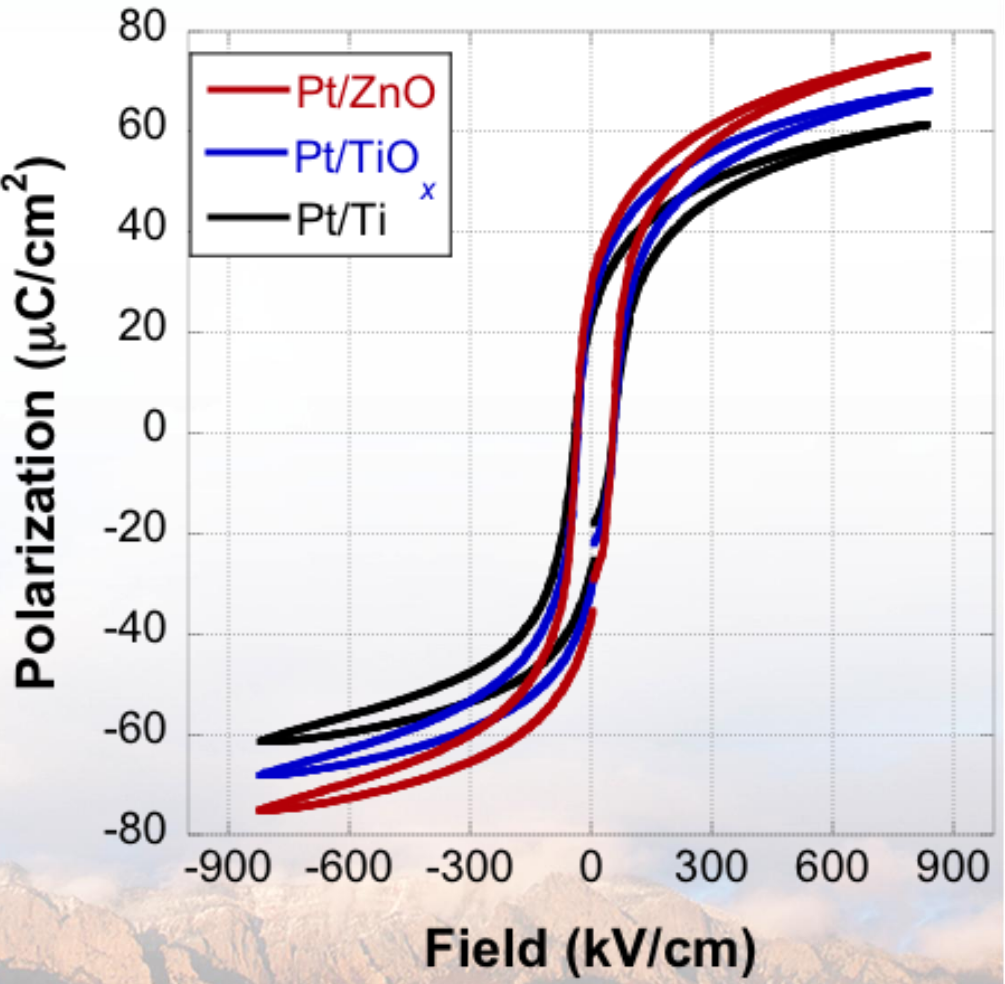


- Measurements conducted at 10 Hz
- All films saturate well
- Low leakage

Ferroelectric properties

	P_{max} (μC/cm²)	P_r (μC/cm²)	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**



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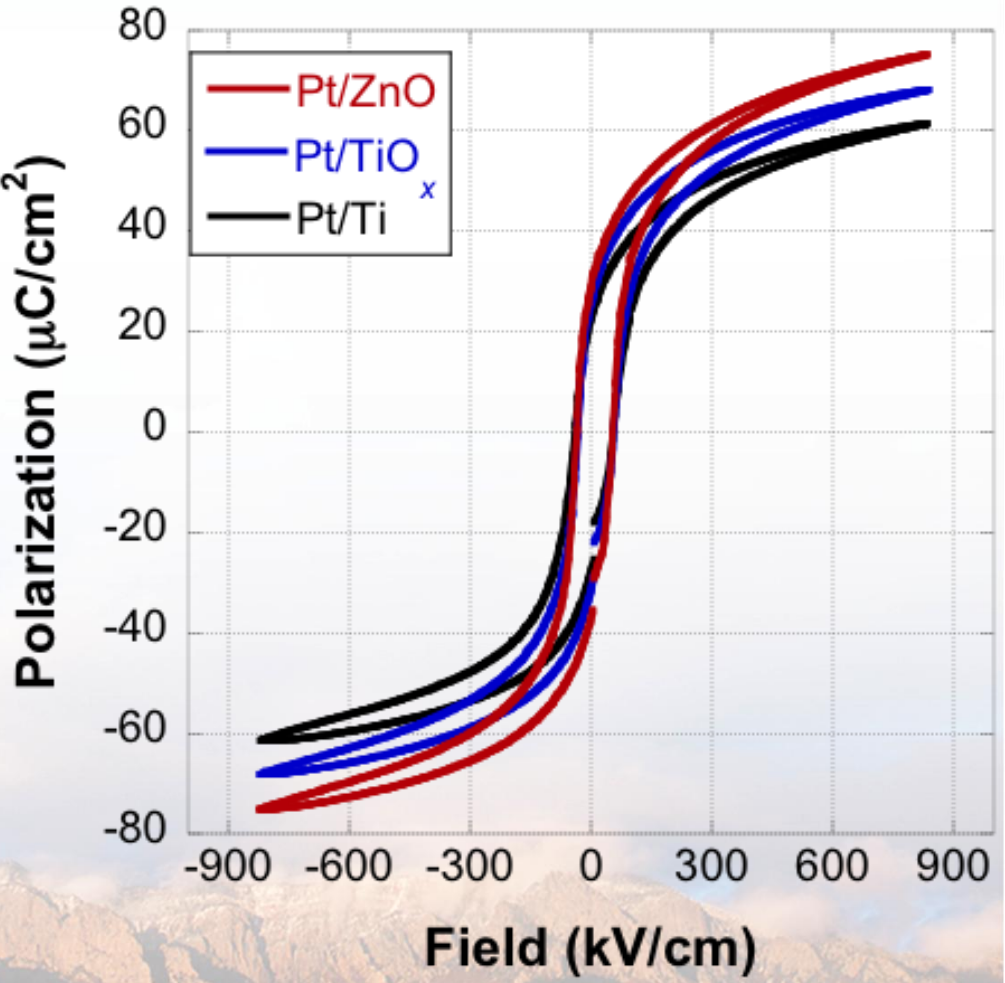
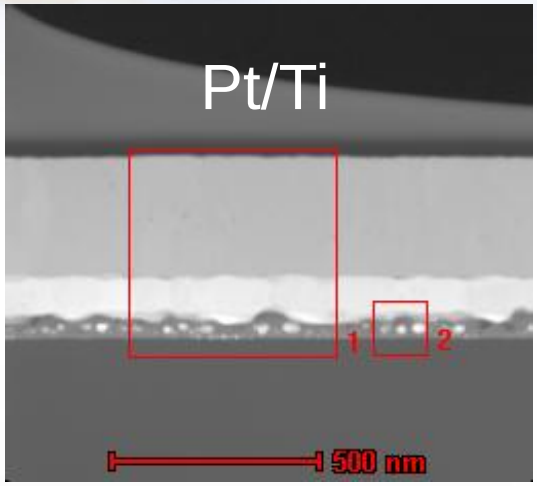
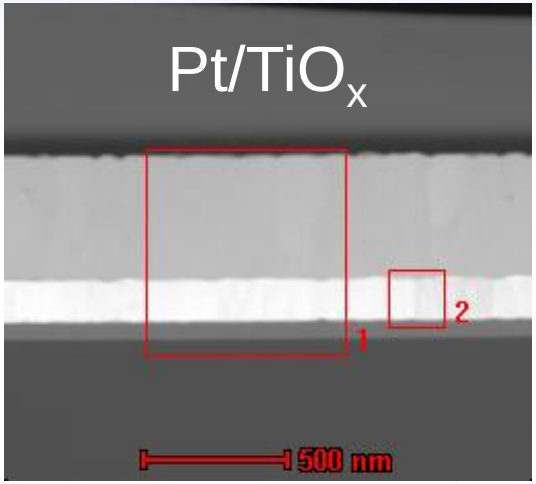
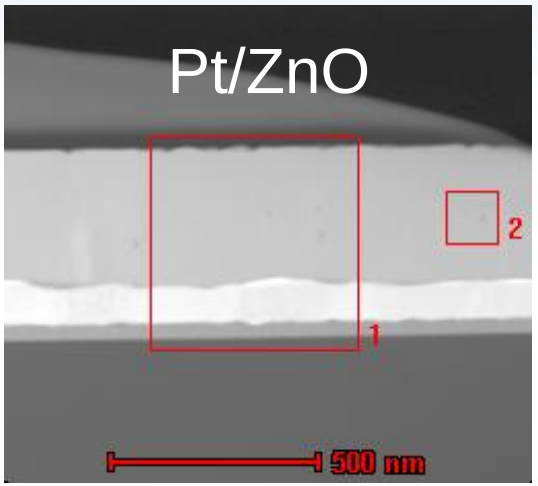
- **Two film systems**
- **Performance improvements identified in both on ZnO-buffered substrates**
- **Mechanism?**



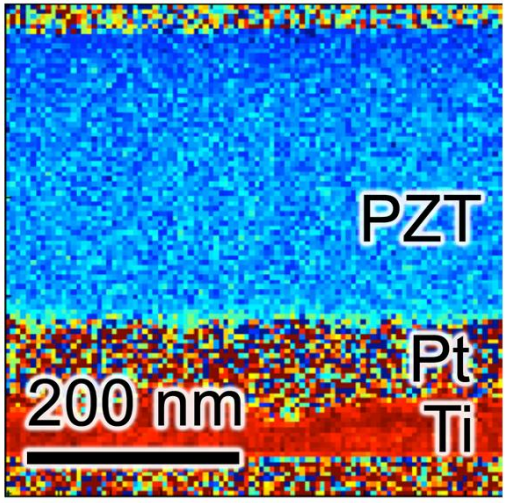
PZT Composition Analysis

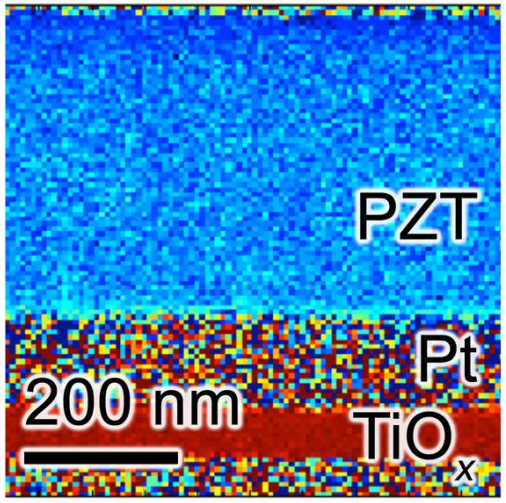


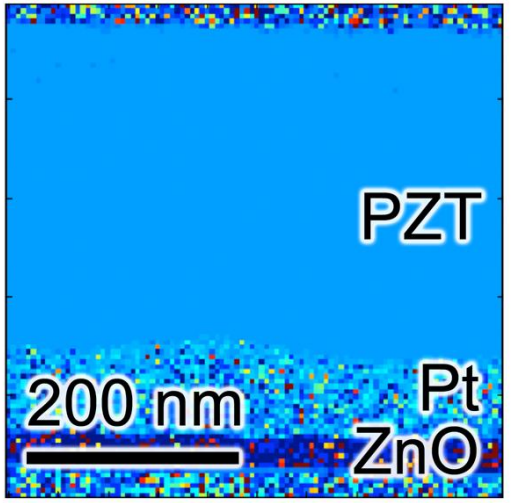


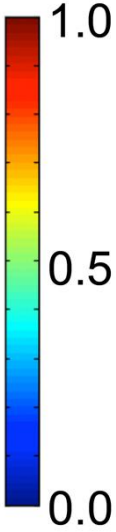


Titanium Distribution

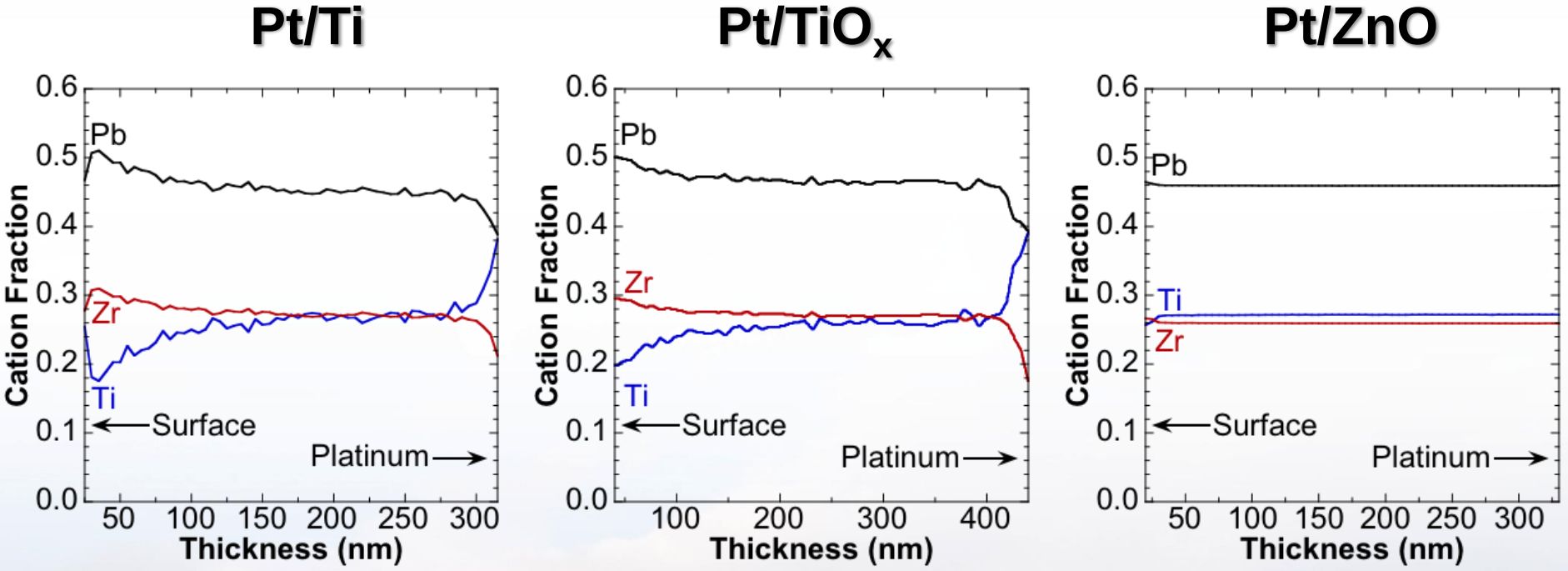








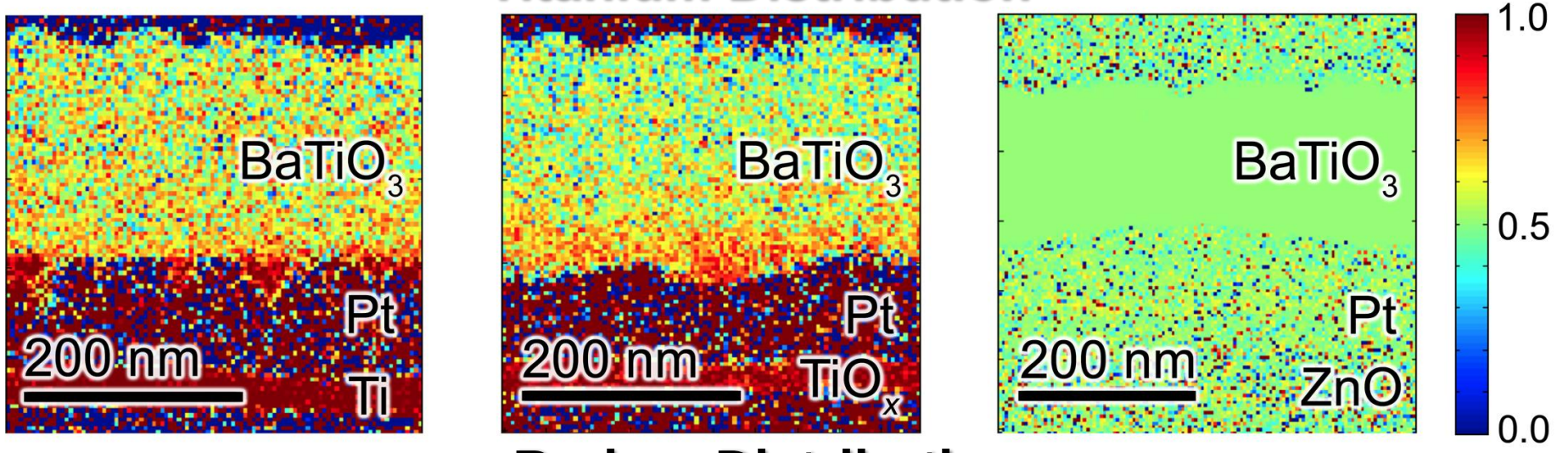
PZT Composition Analysis



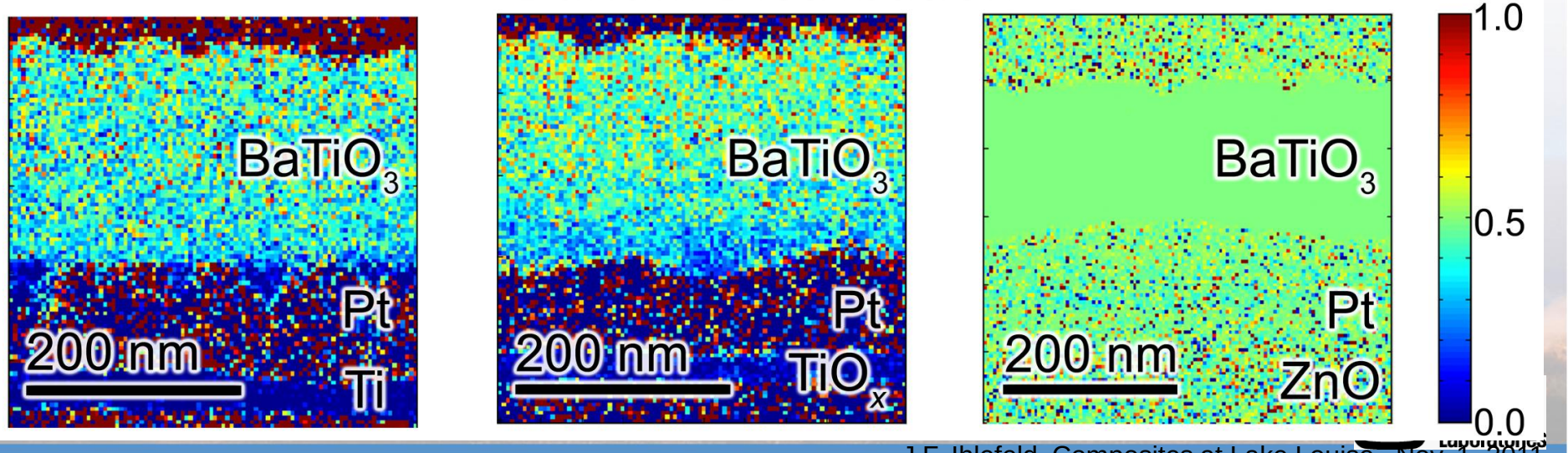
Substantially improved chemical homogeneity in films on Pt/ZnO substrates

$BaTiO_3$ Compositional Analysis

Titanium Distribution

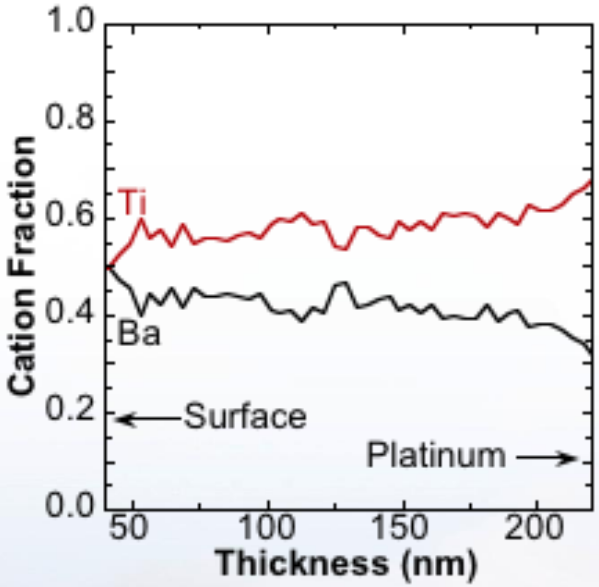


Barium Distribution

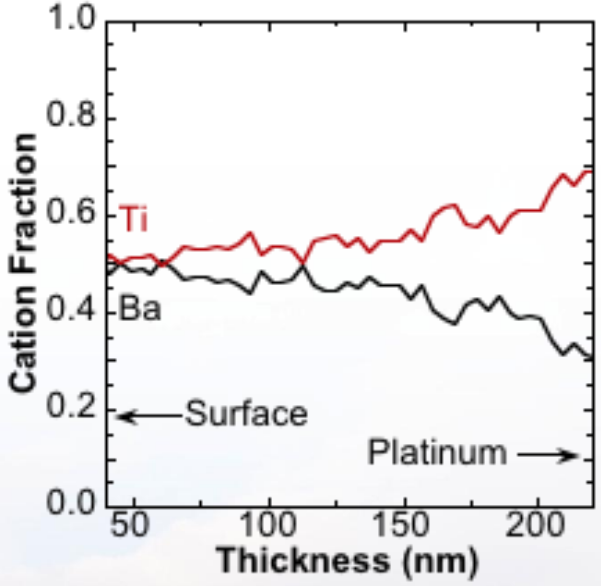


$BaTiO_3$ Compositional Analysis

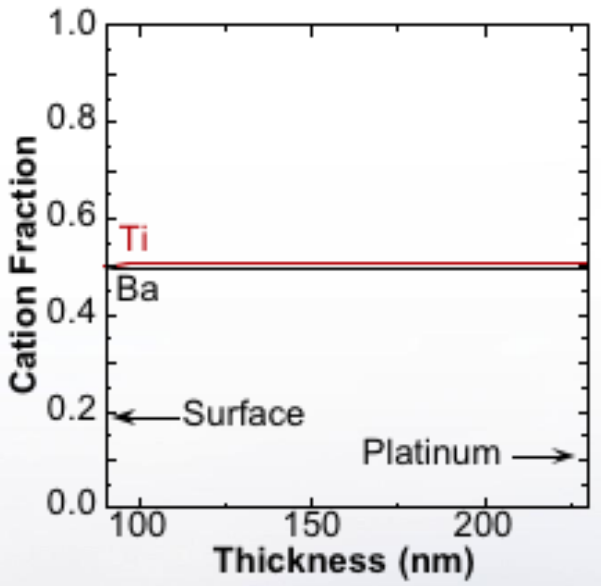
Pt/Ti



Pt/TiO_x



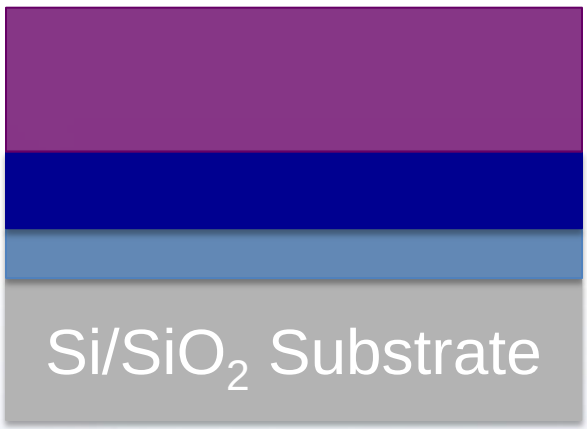
Pt/ZnO

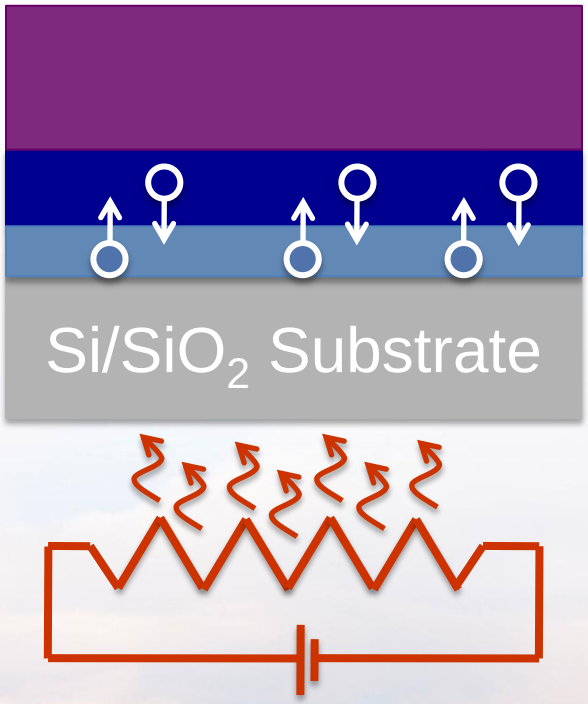


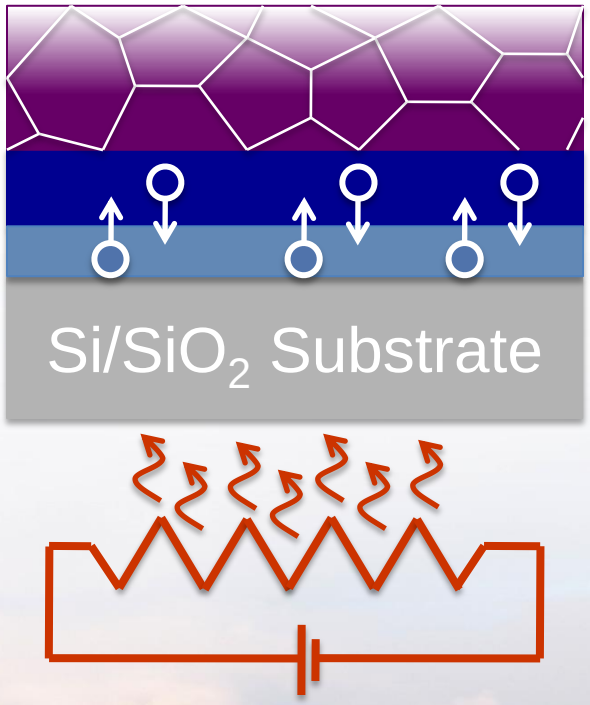
Substantially improved chemical homogeneity in films on Pt/ZnO substrates

Mechanism?

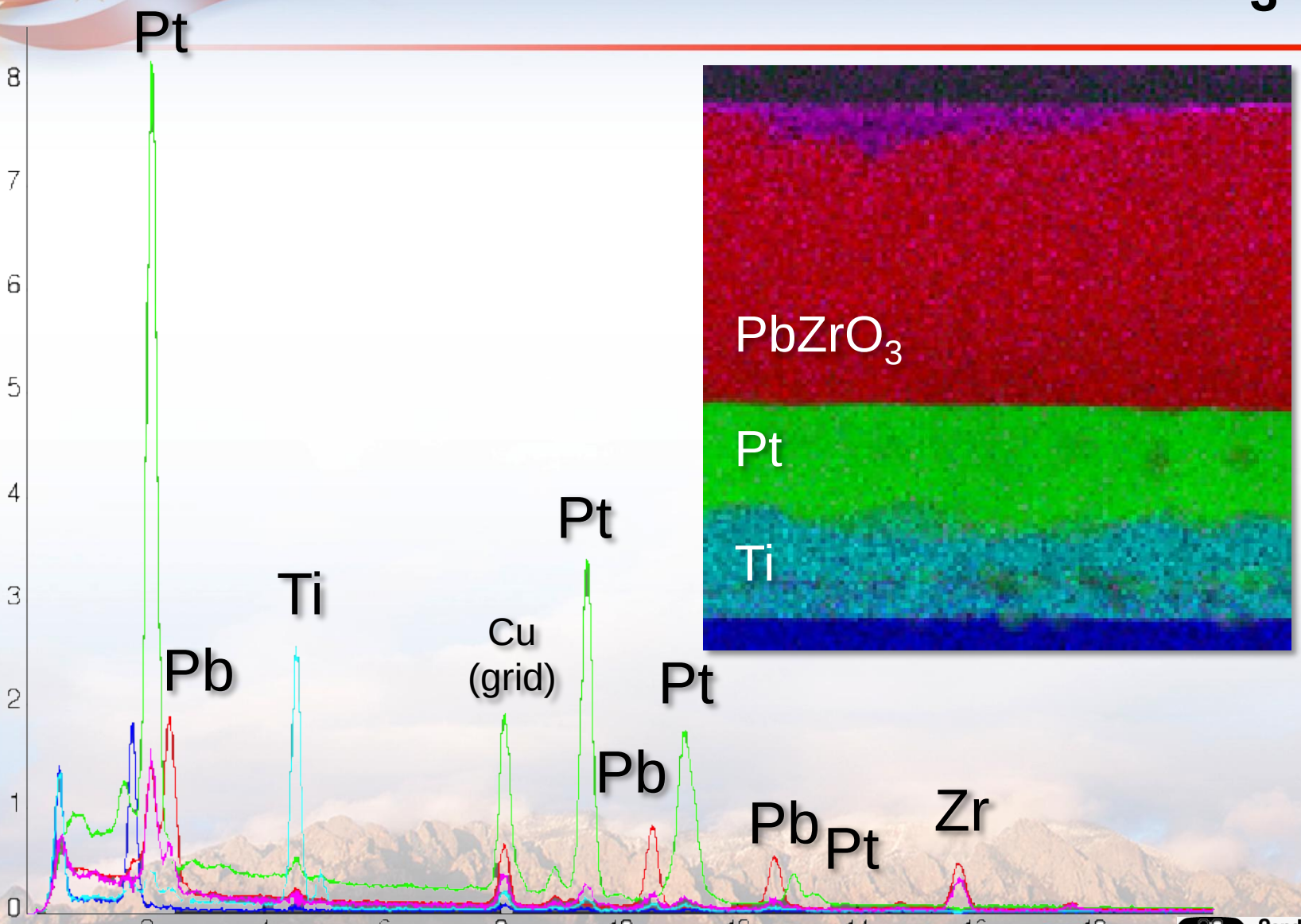
Our Model







Test for Gradient Mechanism: $PbZrO_3$



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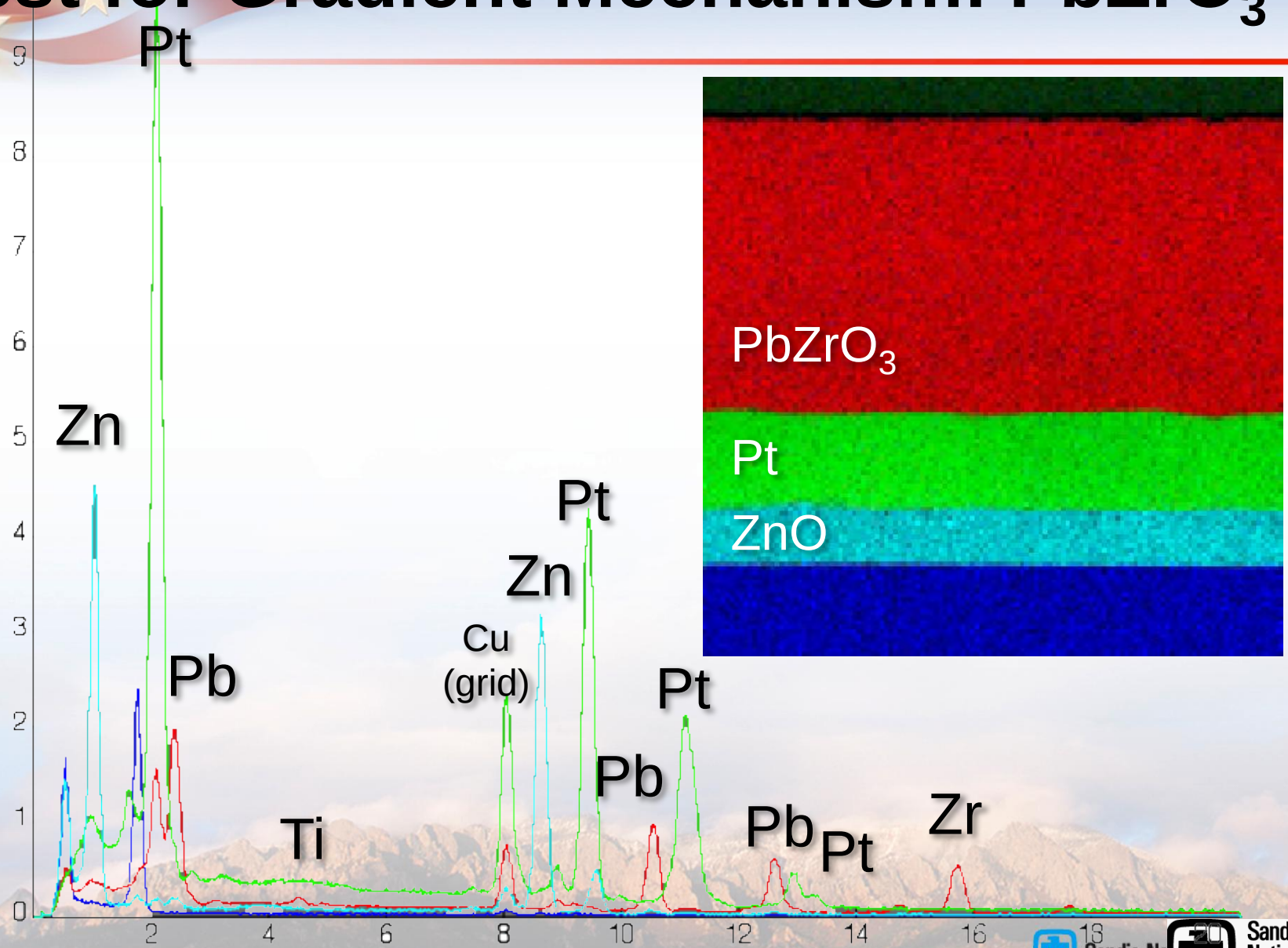

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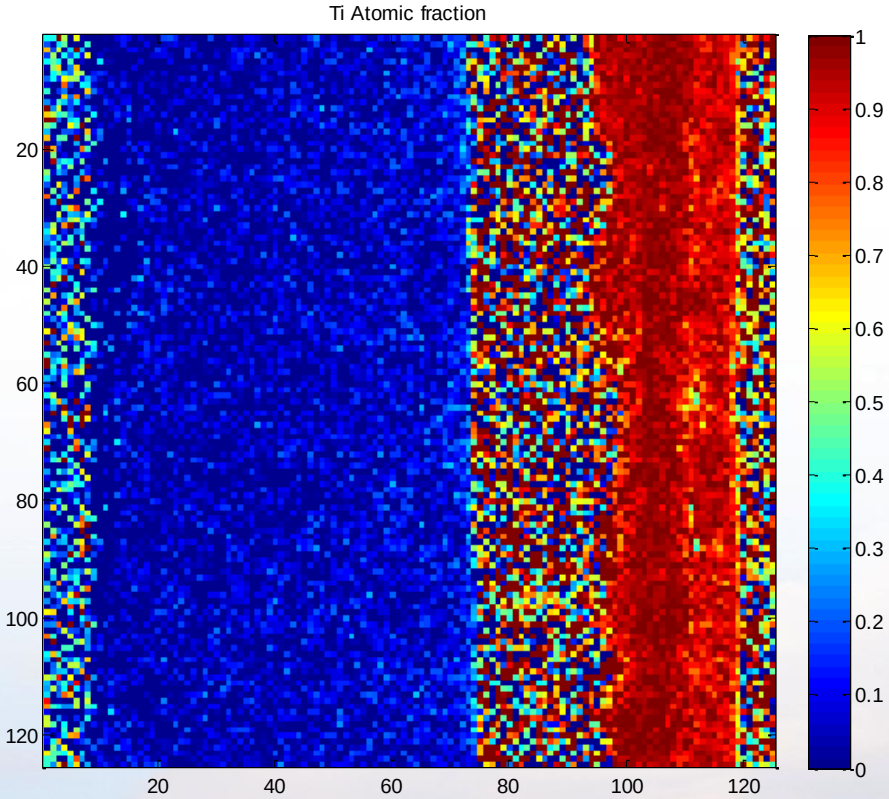
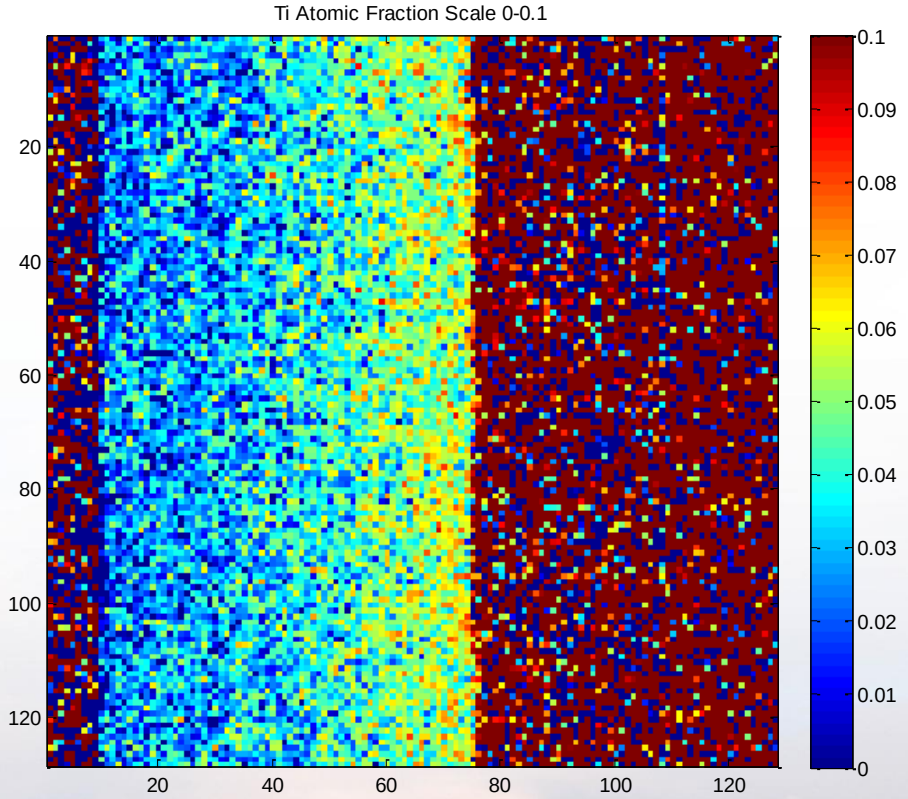
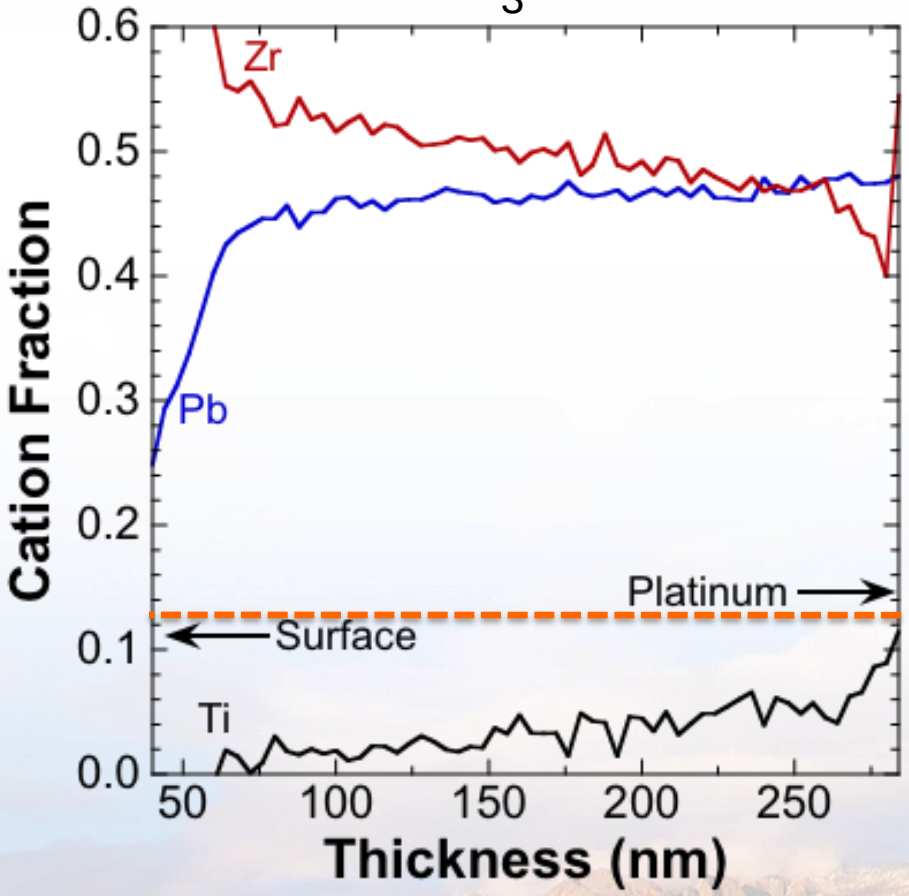


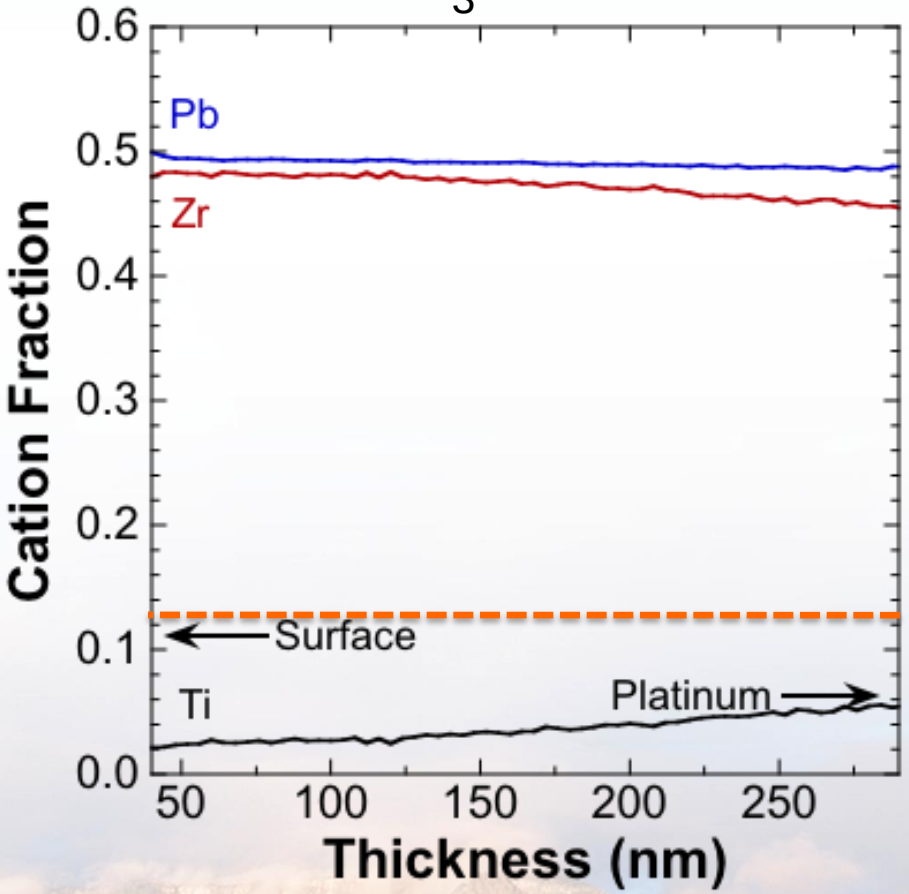


Test for Gradient Mechanism: $PbZrO_3$

$PbZrO_3$/Pt/Ti/Si



$PbZrO_3$/Pt/ZnO/Si



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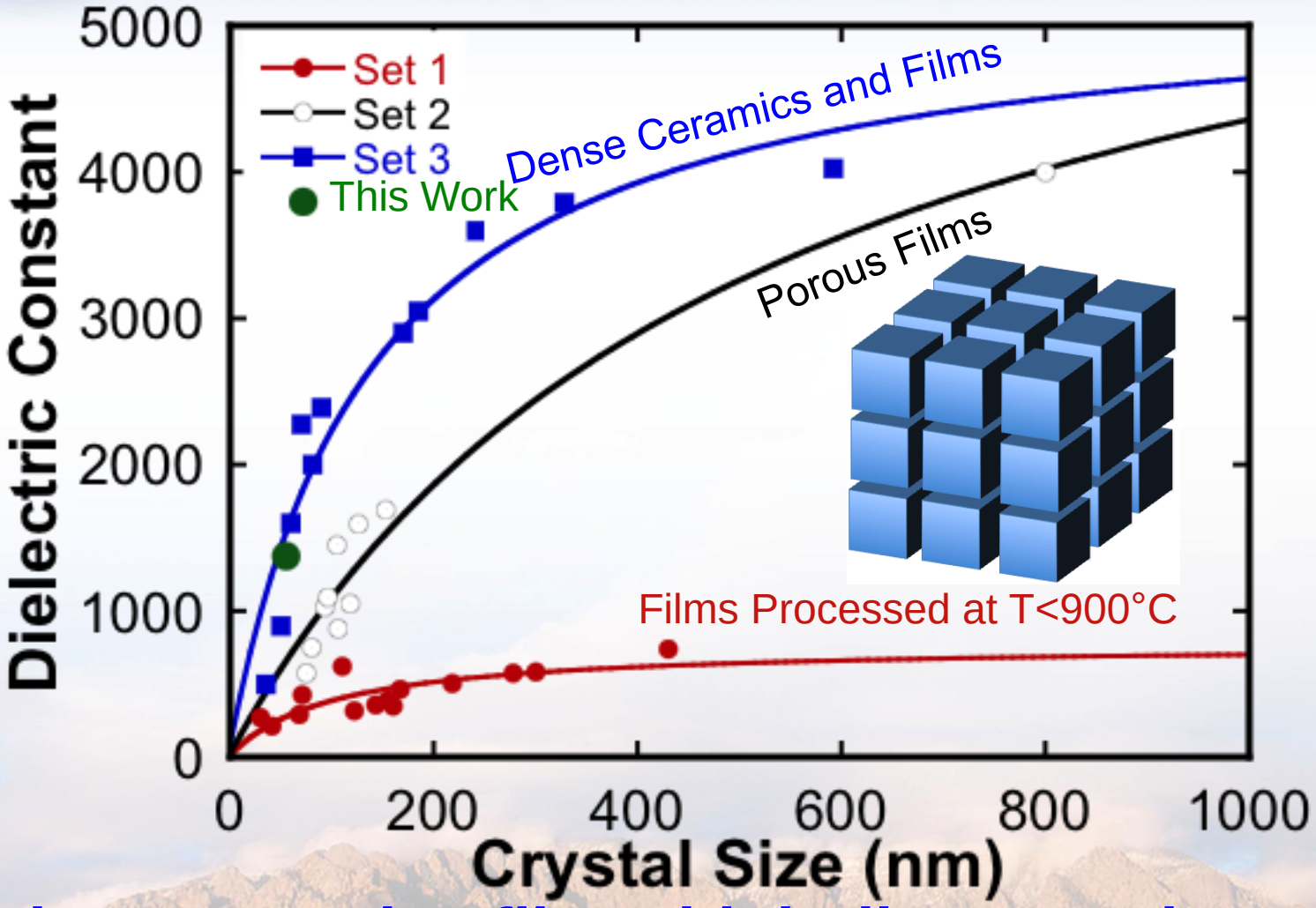
Summary

- Eliminating titanium from the electrode stack minimizes chemical gradients
- Extrinsic integration and processing conditions ultimately prevent study of intrinsic material properties

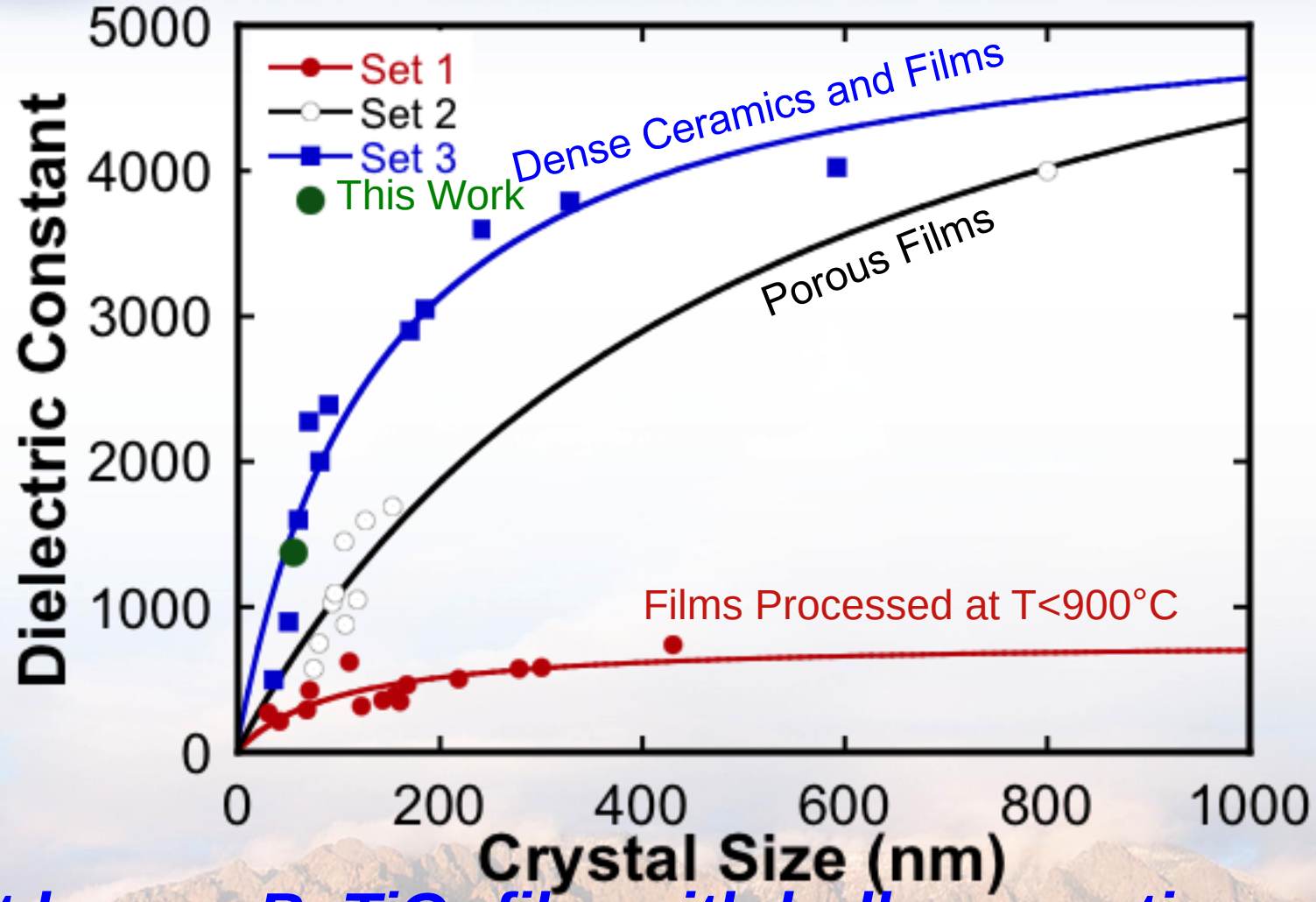
$BaTiO_3$ Scaling Effects



First known $BaTiO_3$ film with bulk properties on Si

Plot adapted from Aygün *et. al. JAP* (2011)

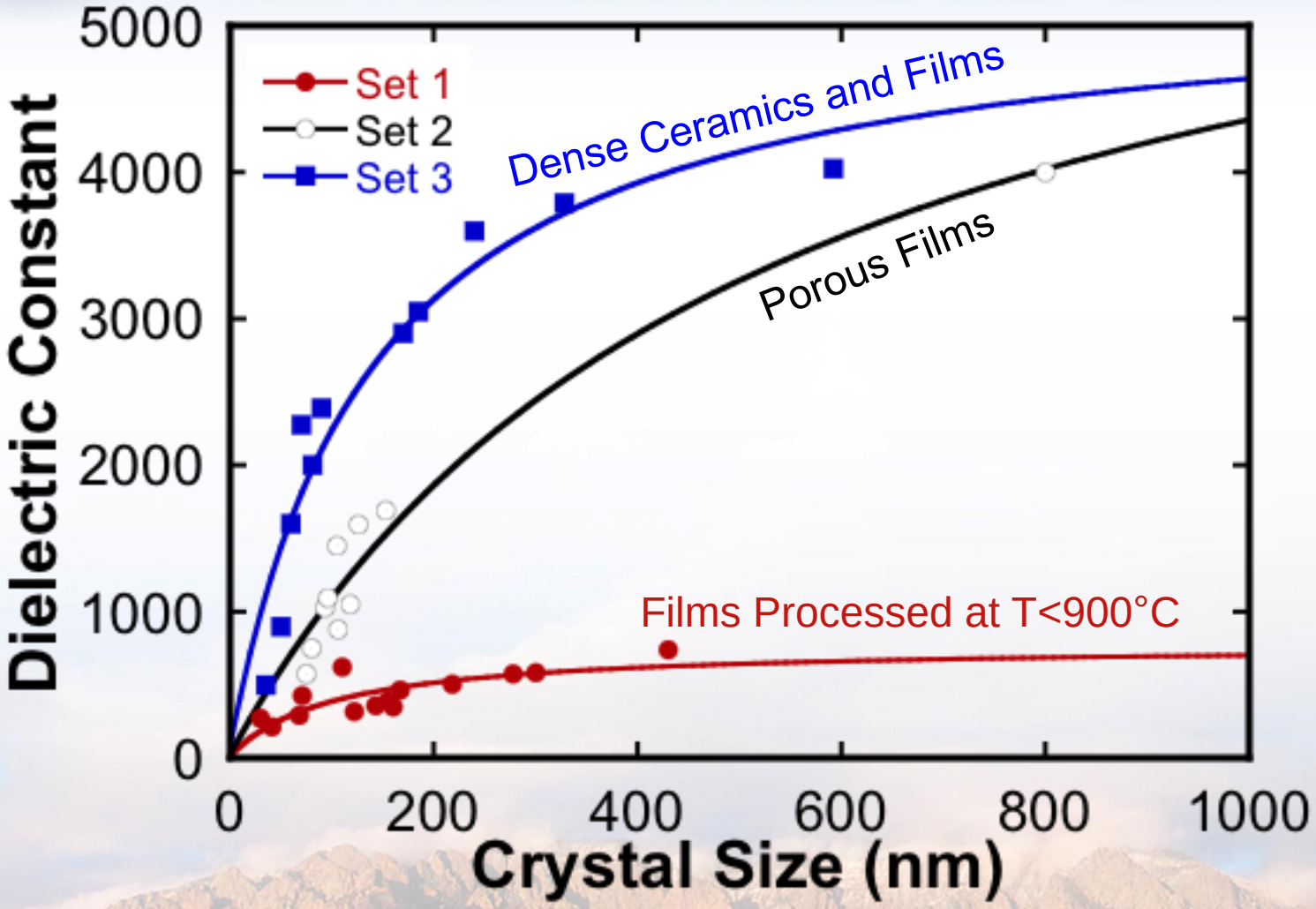
$BaTiO_3$ Scaling Effects



First known $BaTiO_3$ film with bulk properties on Si

Aygün *et. al. JAP* (2011)

$BaTiO_3$ Scaling Effects



Crystallite vs. Grain Size

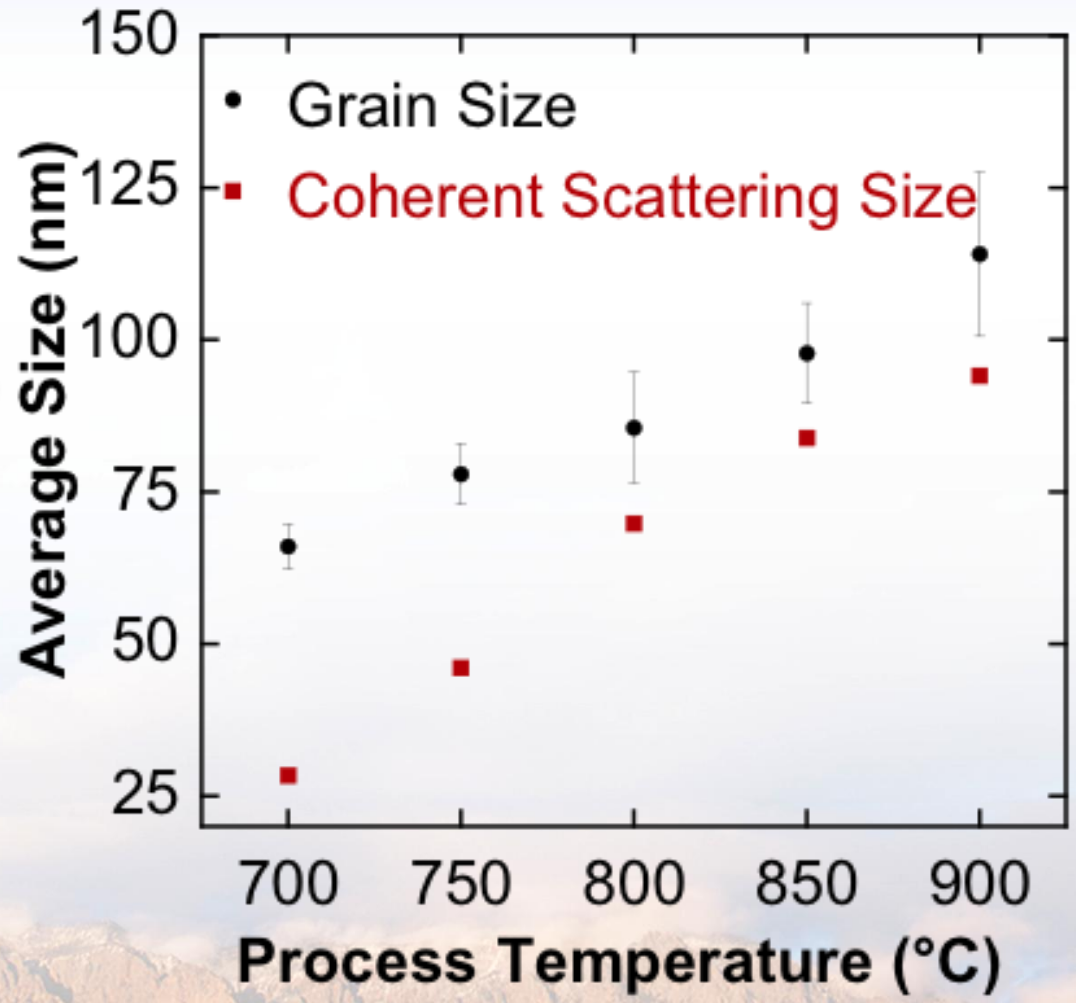
Grain Size

- AFM and FE-SEM
- 95% confidence interval

Coherent Scattering Size

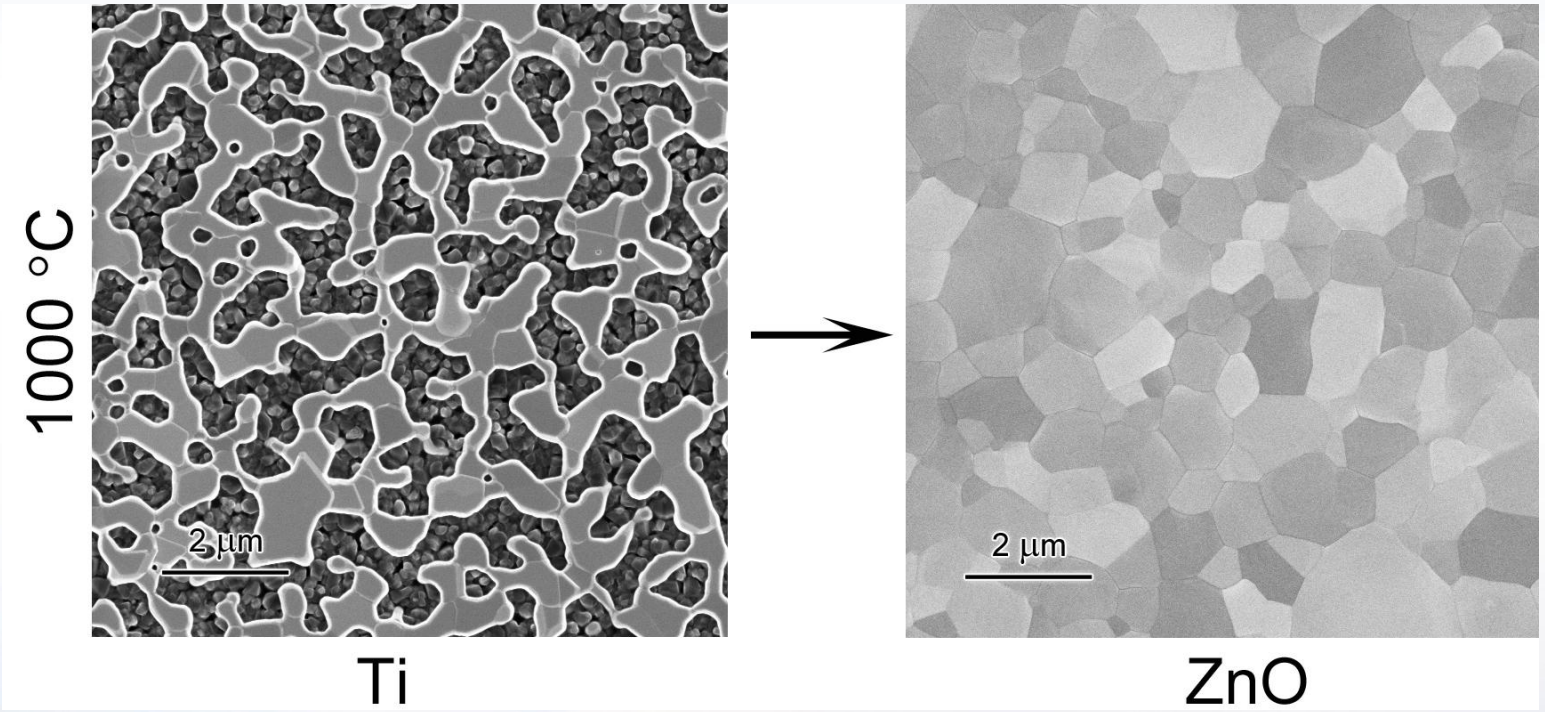
- CHESS
- Scherrer's Formula on 111 reflections

Sub-grain structure dominates dielectric response



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

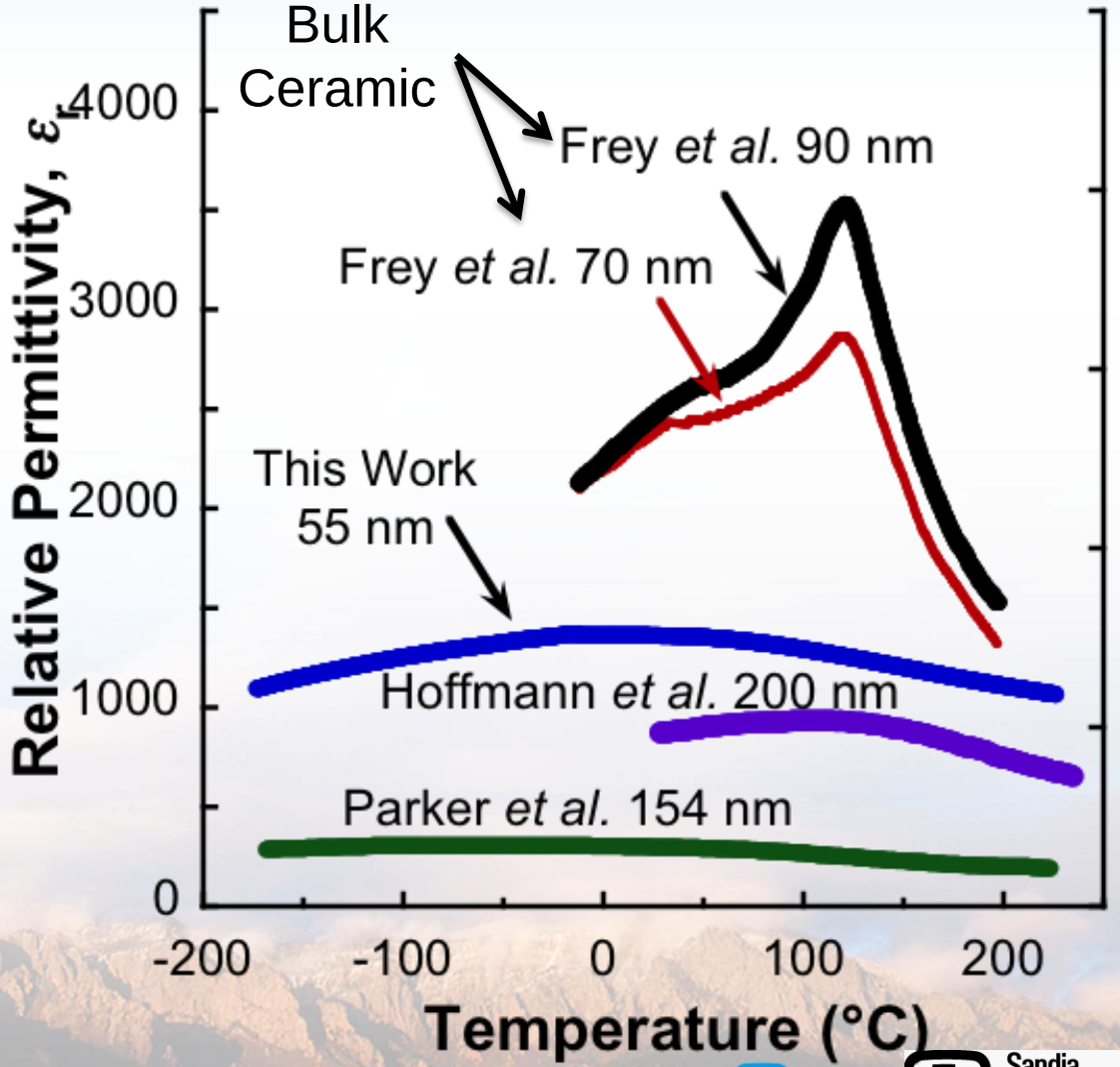
Pt/ZnO as a high temperature substrate



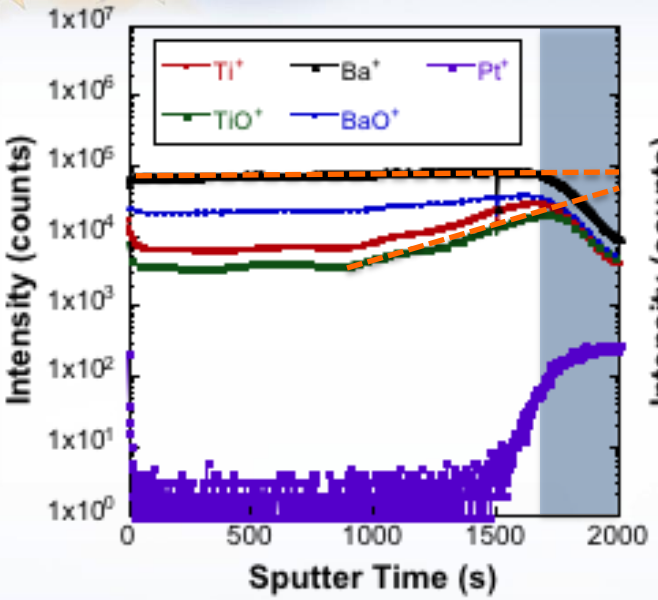
- ZnO buffered Pt/Si is robust enough to withstand process temps in excess of 1000 ºC
- Ideal candidate for materials previously best grown on single crystals:
  - $BaTiO_3$
  - $(Ba,Sr)TiO_3$

$BaTiO_3$ Comparison

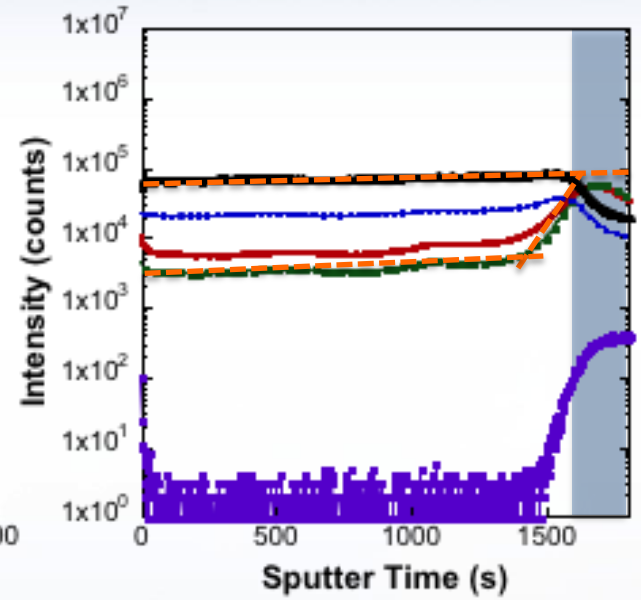
- **Current films compare favorably with bulk ceramics**
- **Much higher *K* than similar thickness and grain size films**
- **Microstructure nearly identical: Why such a disparity?**
- **What about other Ferroelectrics?**



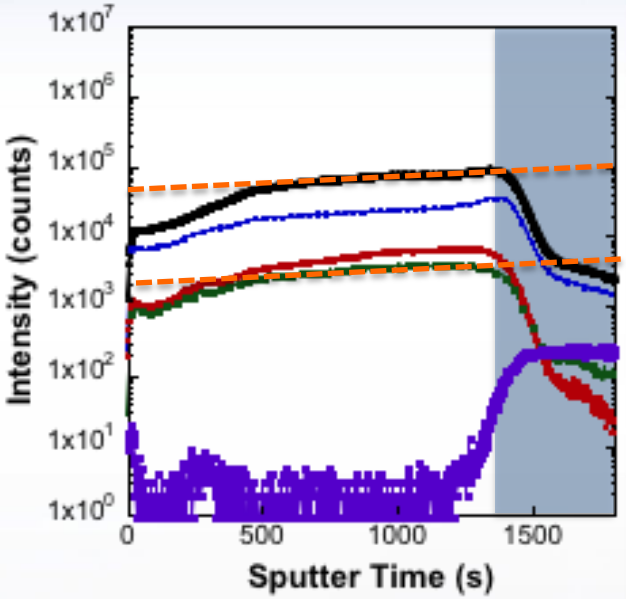
Chemical Distribution in $BaTiO_3$



$BaTiO_3$/Pt/Ti



$BaTiO_3$/Pt/TiO_x



$BaTiO_3$/Pt/ZnO

- **Clear composition gradient in film on Pt/Ti**
- **Bimodal gradient in film on Pt/TiO_x**
- **No obvious gradient in film on Pt/ZnO**
- **Mechanism?**