SAND2012-5443C

Chemically Homogeneous Complex Oxide Thin Films via Improved Substrate Metallization

Jon Ihlefeld

Sandia National Laboratories

Albuquerque, NM, USA

This work is supported, in part, by the Laboratory Directed Research and Development Program at Sandia.
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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

MLC Scaling History

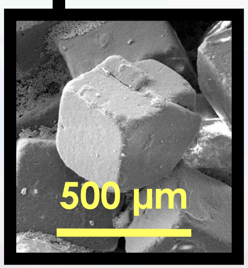
0603: 1600 µm X 800 µm
Most popular pre-2002 size

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

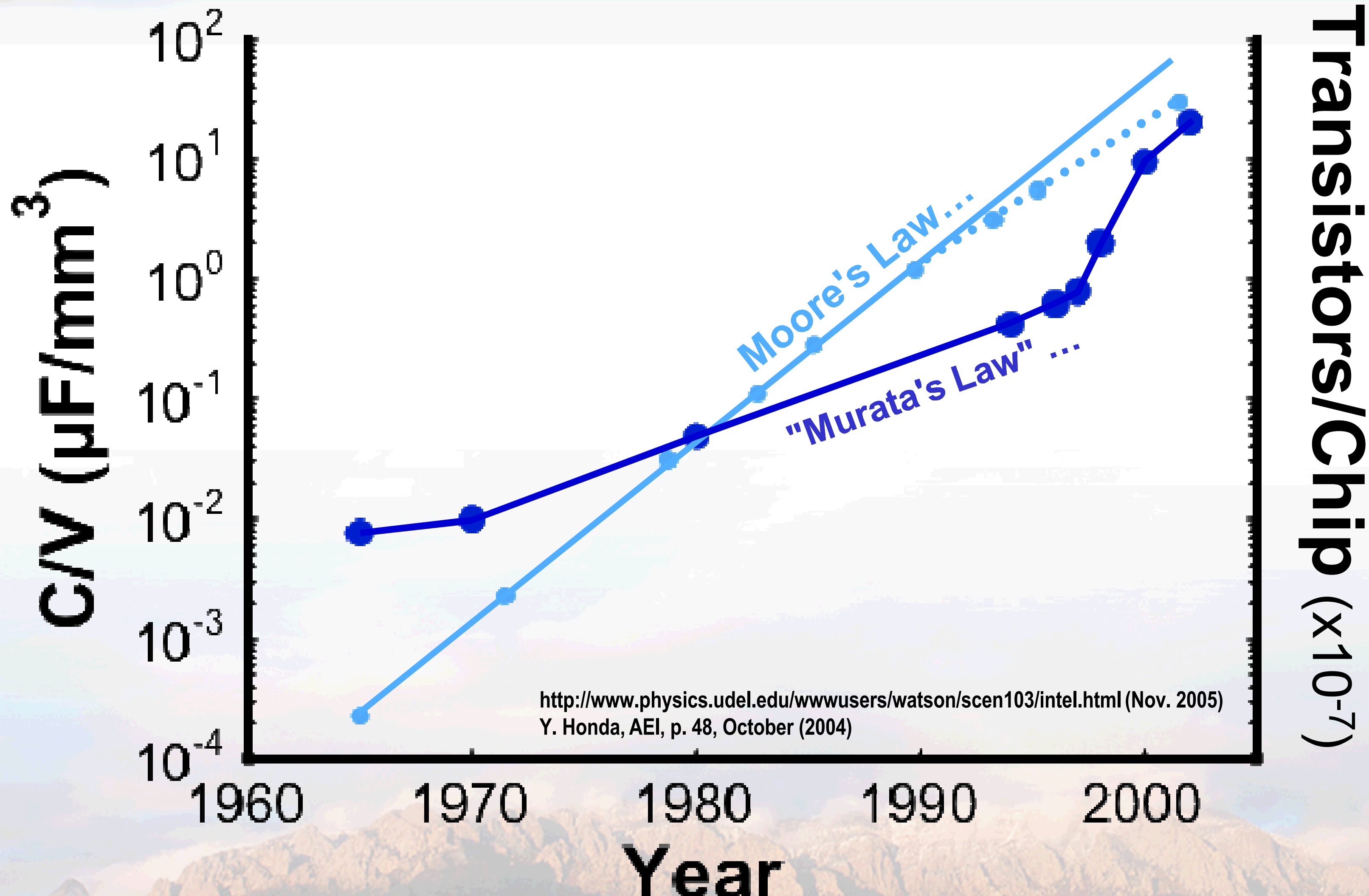
to-scale image of salt grain



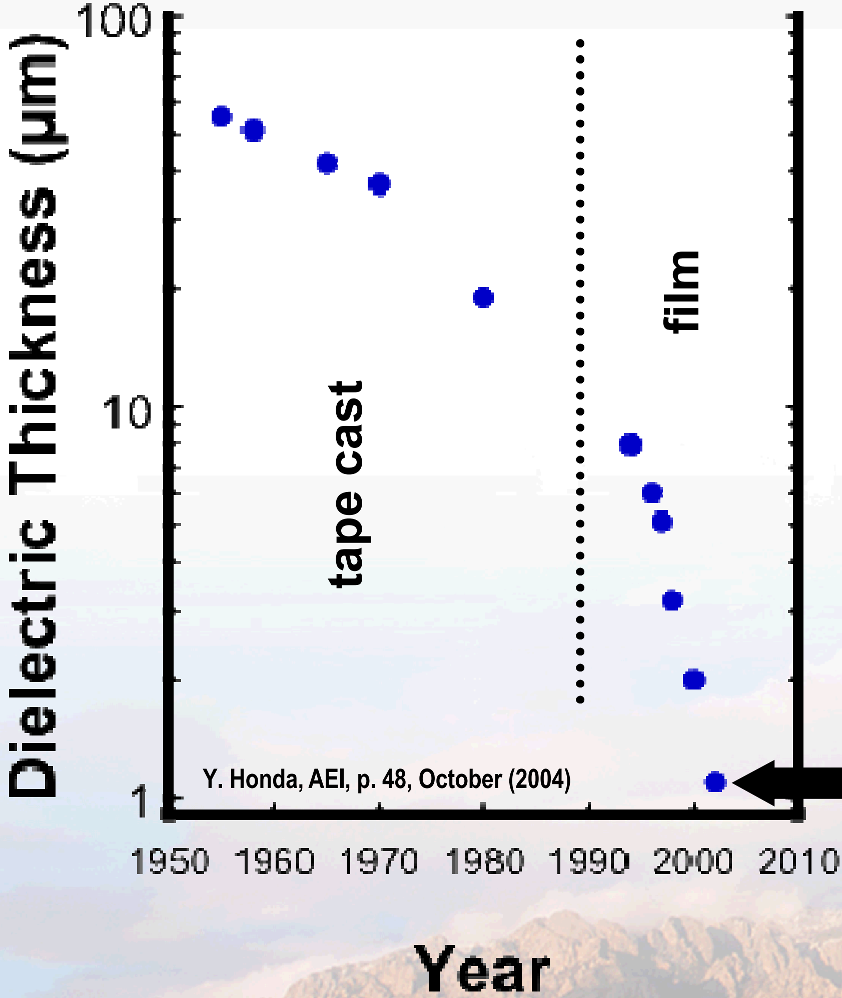
still 10^2 layers!

constant capacitance with increasing technology node

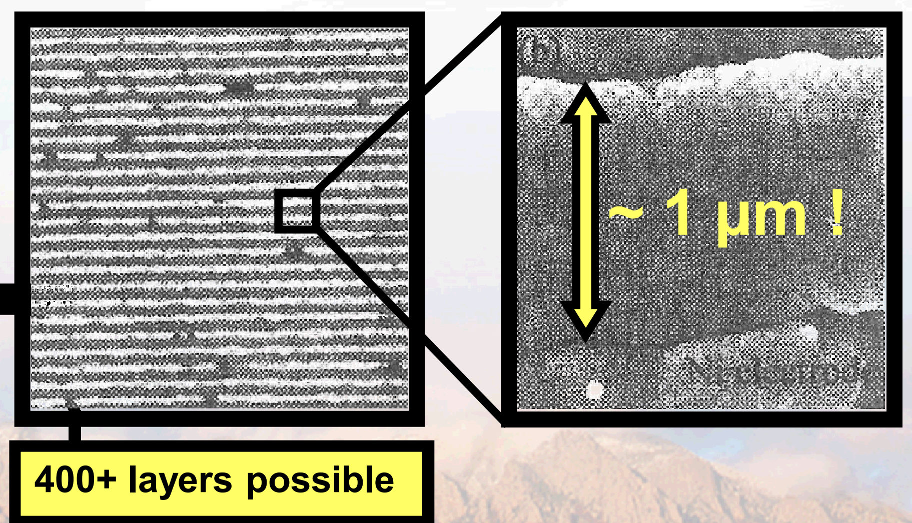
MLC vs. Transistor Scaling



Physically, what's happening?

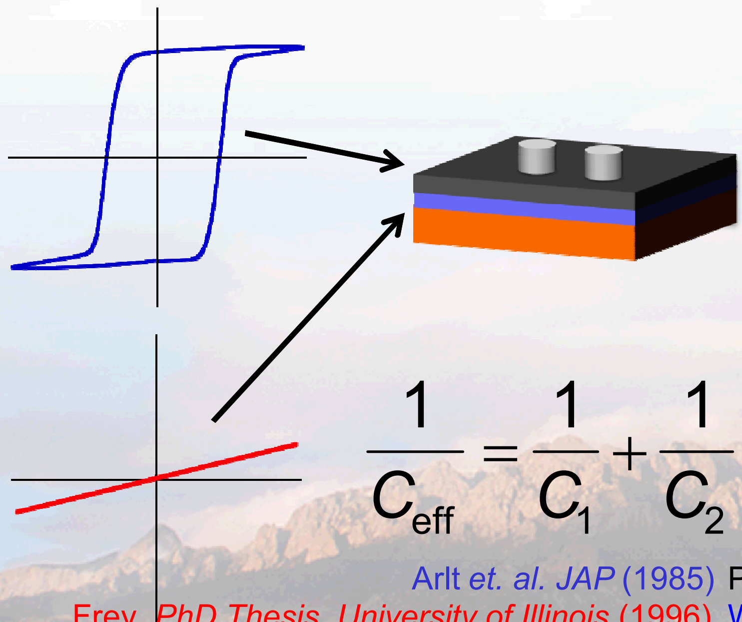


- Incredible scaling demonstration
- Fabricated using powder processing - **mass produced**
- Film / lamination process
- Real *Nano-technology!*

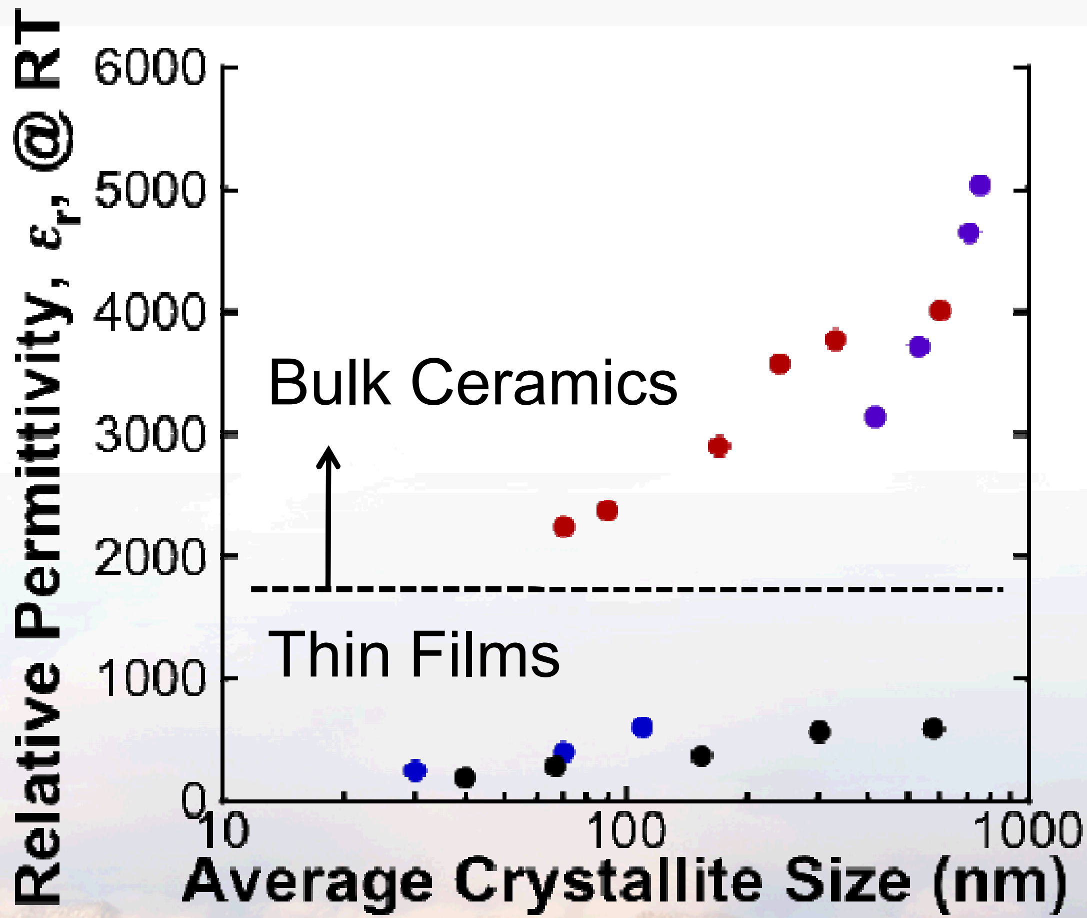


Limits of Scaling

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

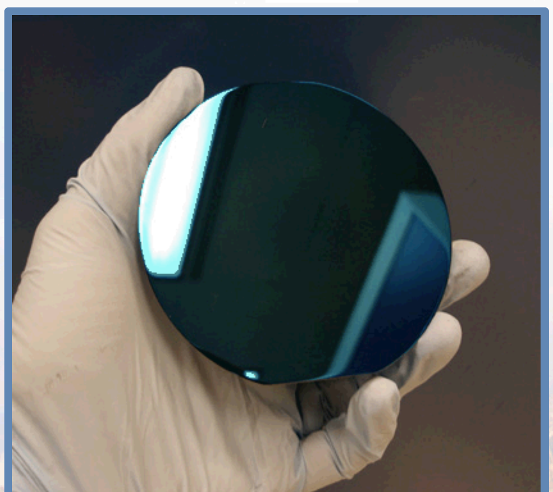


$$\frac{1}{C_{eff}} = \frac{1}{C_1} + \frac{1}{C_2}$$

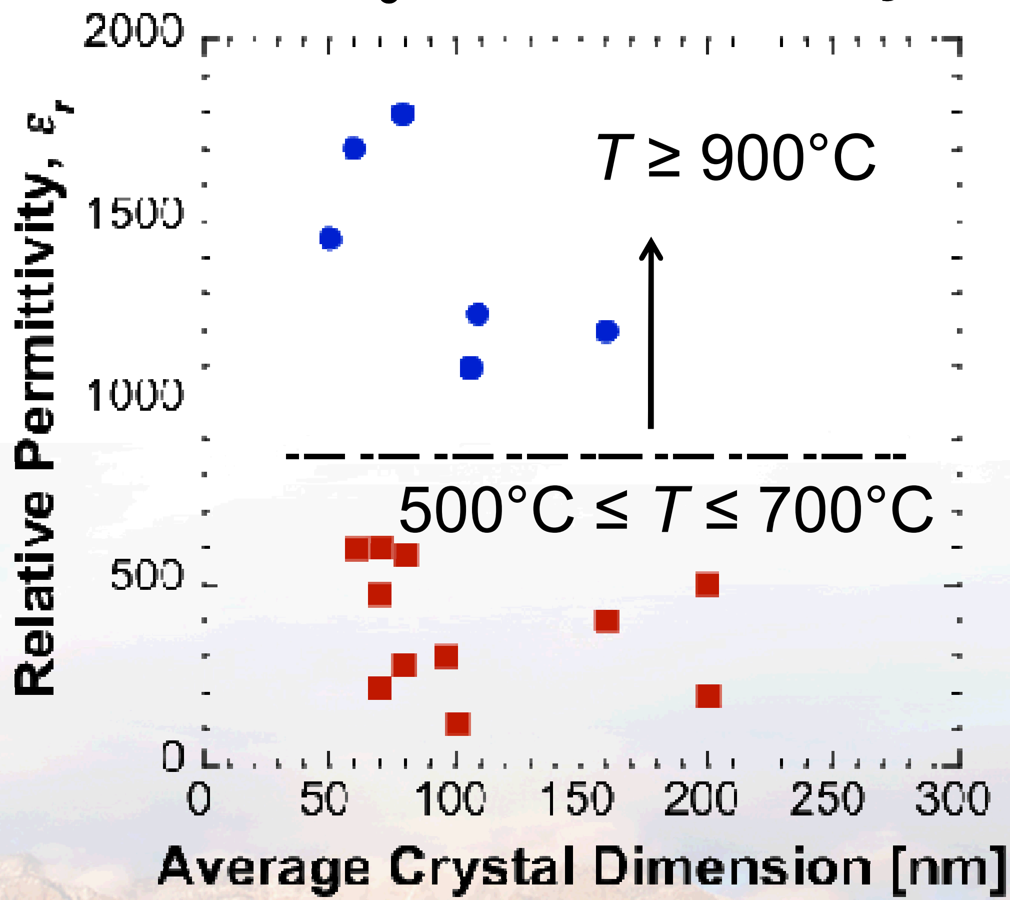


Arlt *et. al.* *JAP* (1985) Parker *et al.*, *APL* (2002)
Frey, *PhD Thesis, University of Illinois* (1996) Waser *Int. Ferro.* (1997)

Processing Effects on *K* vs *d*

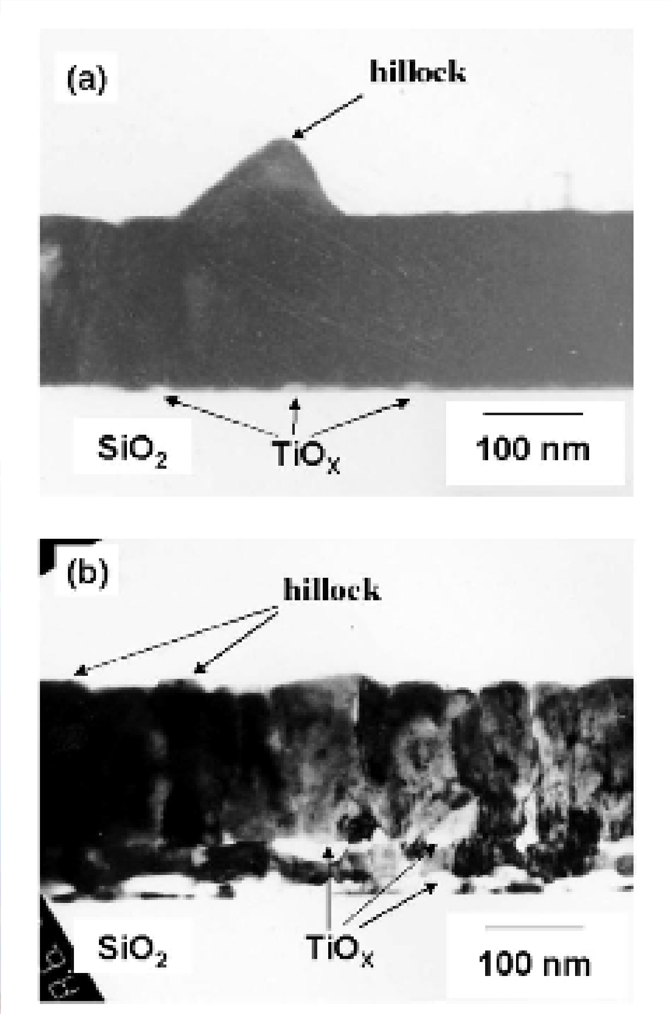


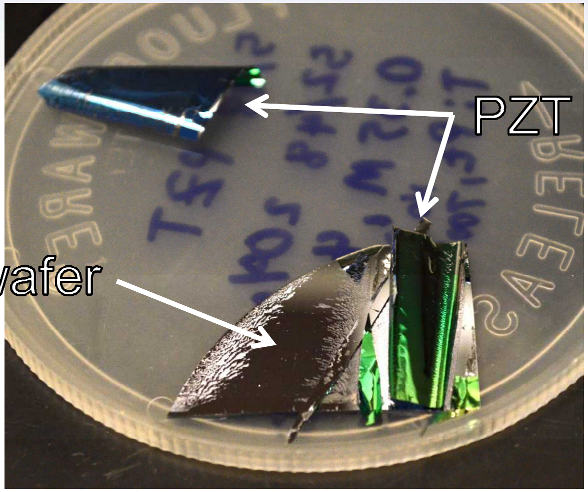
$BaTiO_3$ Film Permittivity



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

Platinized Silicon Substrates



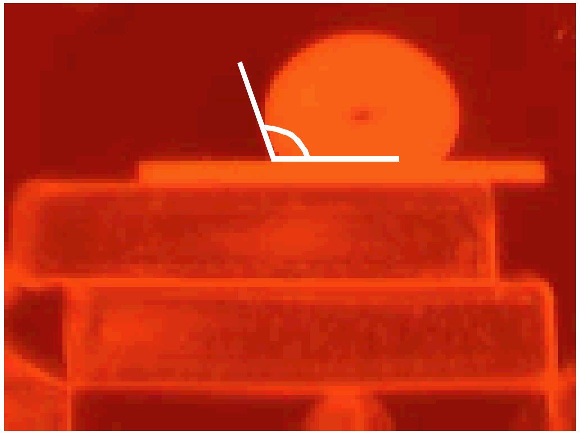


- **Titanium 'adhesion' layers by far the most common**
- **Titanium expands upon oxidation causing hillocks**
- **Adhesion layers fail with large temperature swings (>700°)**

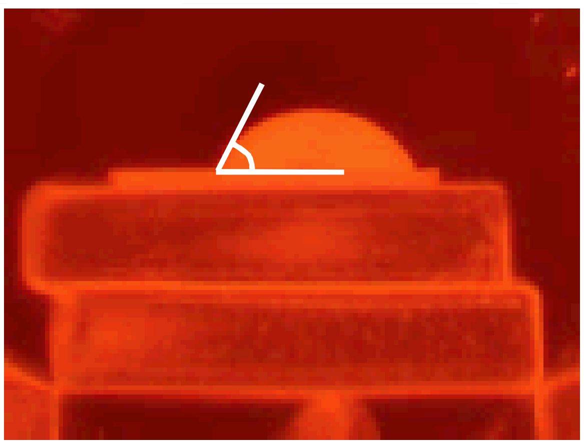
Nam et al., ***Thin Solid Films*** , (2000)

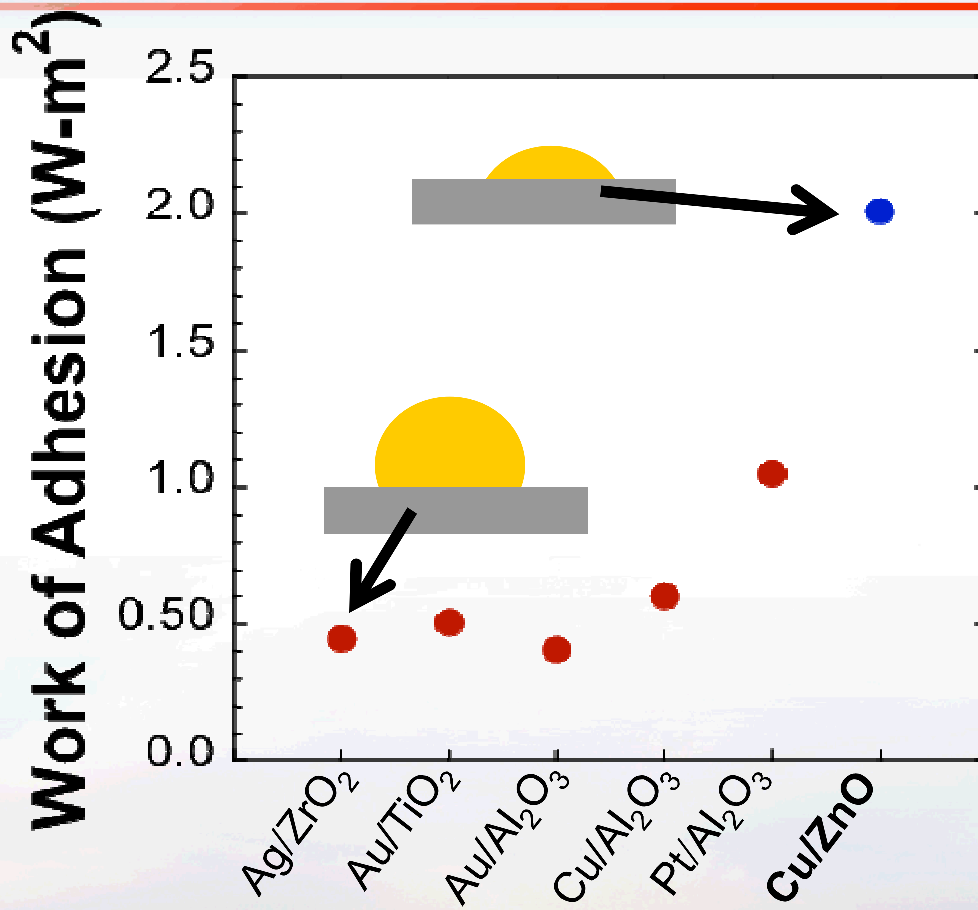
Metal Wetting and Adhesion

Molten Cu on Al_2O_3



Molten Cu on ZnO





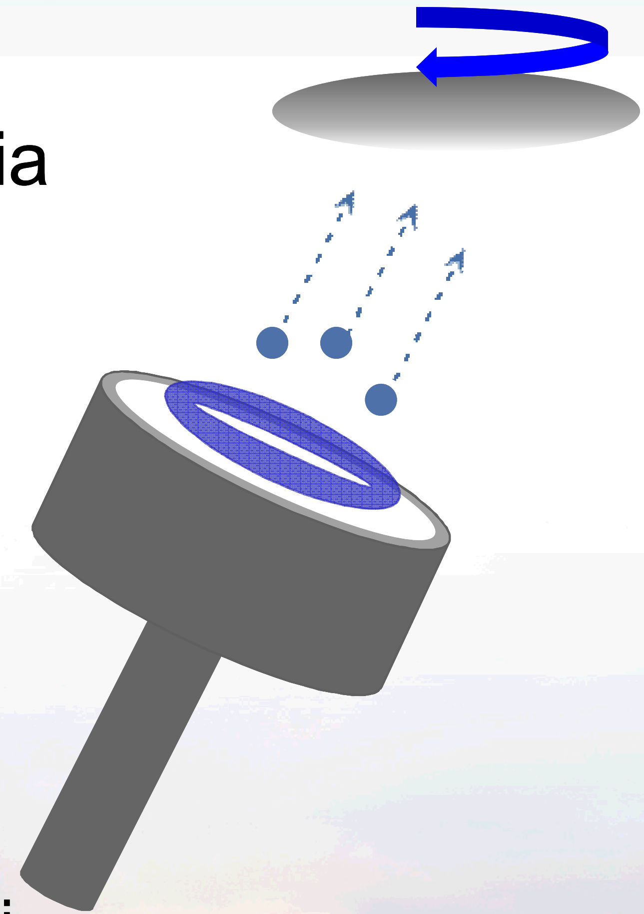
Can we use ZnO as an adhesion layer for Pt?

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

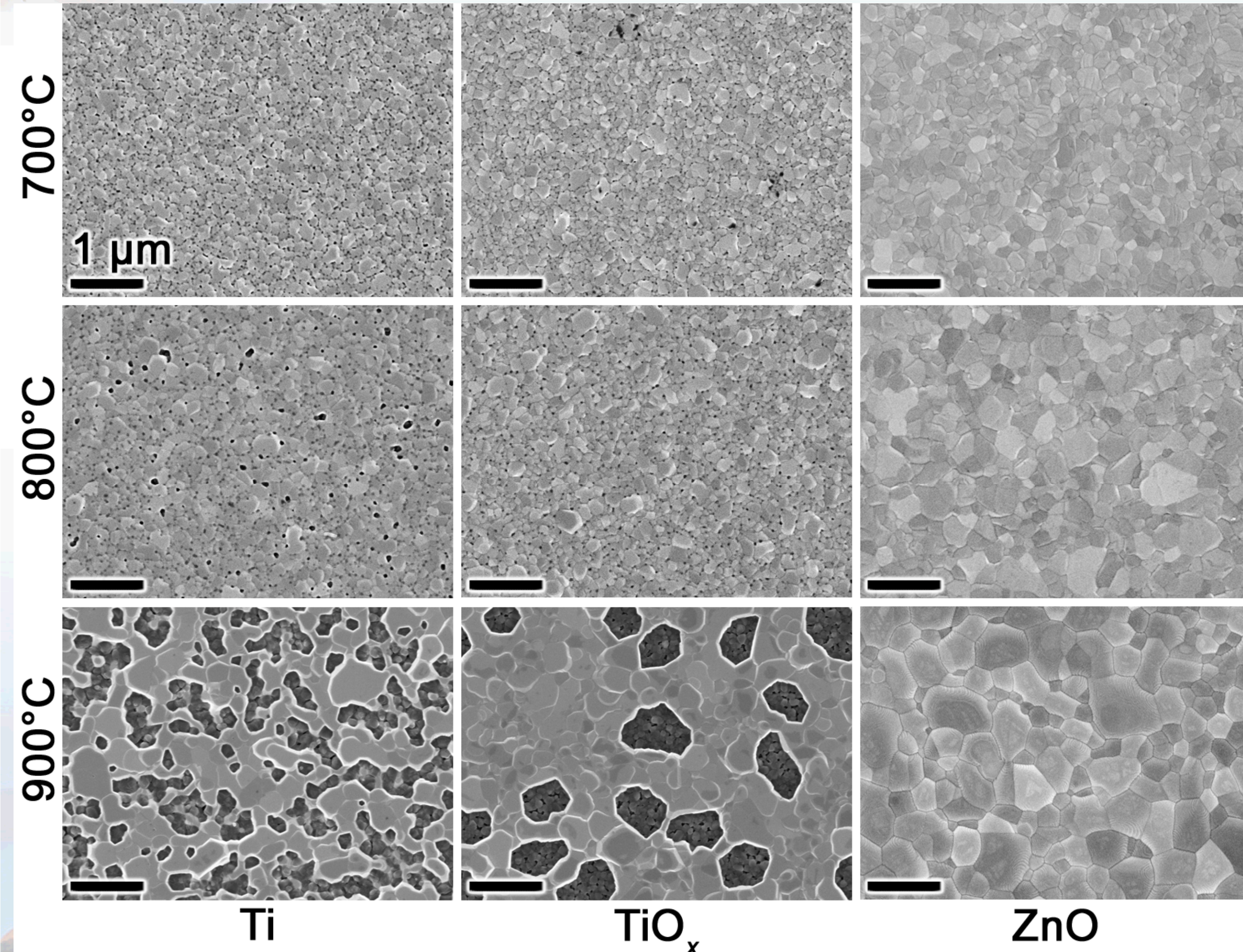
Laughlin, B. Ph.D. thesis, NCSU 2006

Substrate Preparation

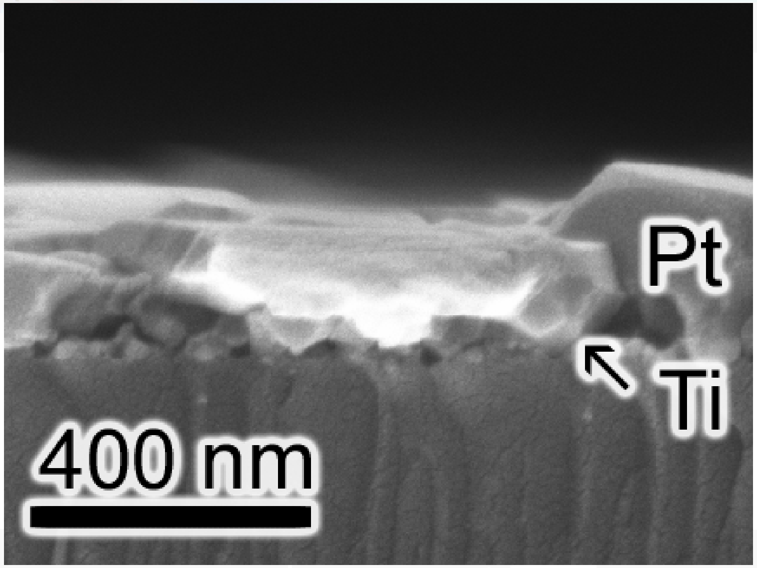
- Ti, TiO_x, ZnO, and Pt prepared via RF magnetron sputtering
  - 30° off-axis geometry
  - Ti: Ar atmosphere
  - TiO_x: Ar sputter, O_2 anneal
  - ZnO: 1:1 Ar:O_2 atmosphere
  - Pt: Ar Atmosphere
- 100 nm Pt/40 nm buffer/40 nm SiO_2/Si

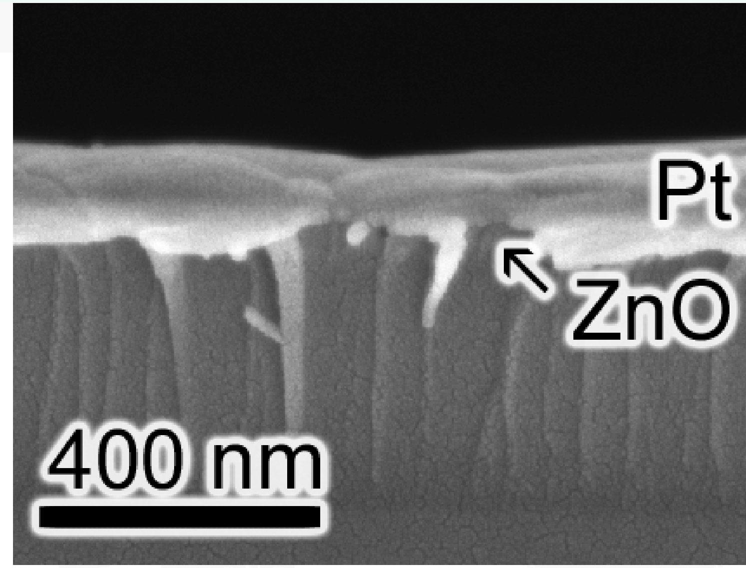


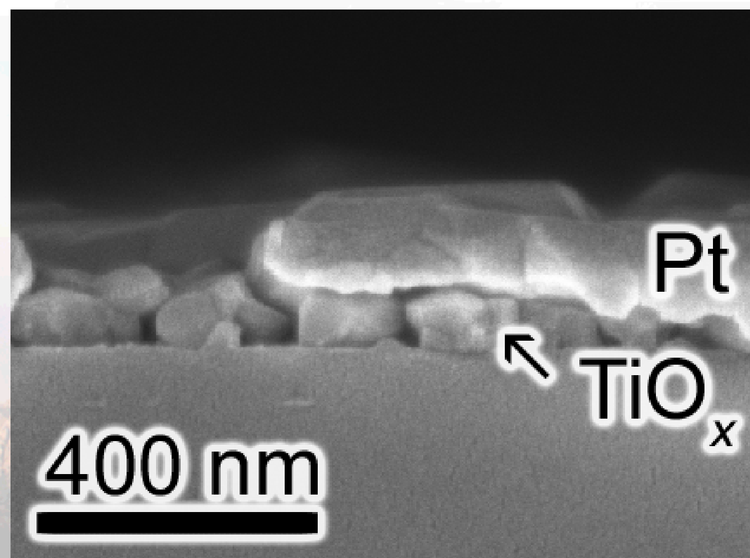
Electrode Temperature Stability



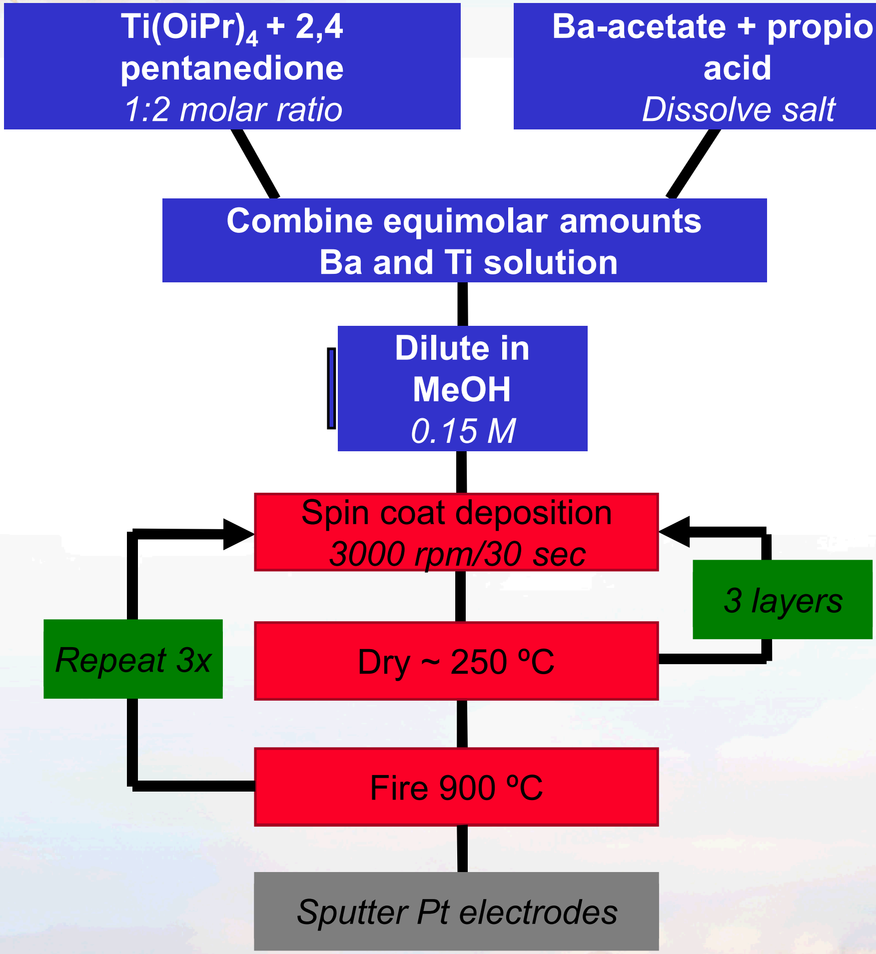
Electrode Stability: 900°C

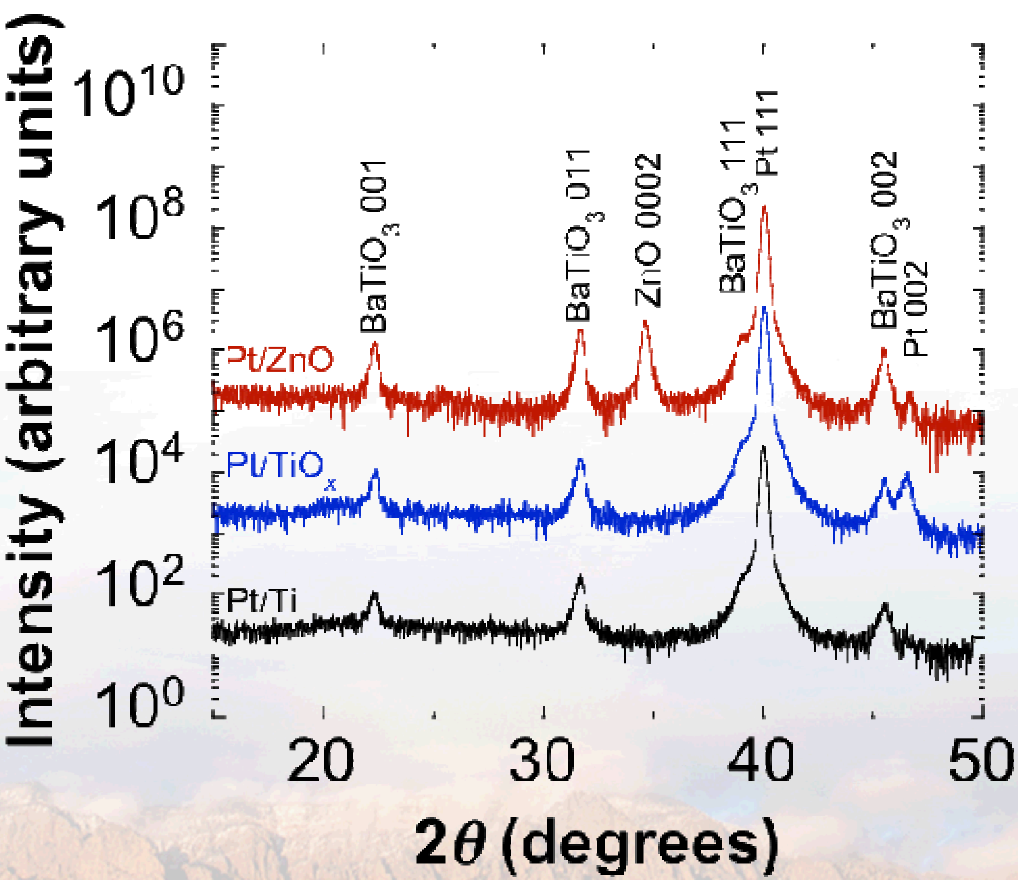




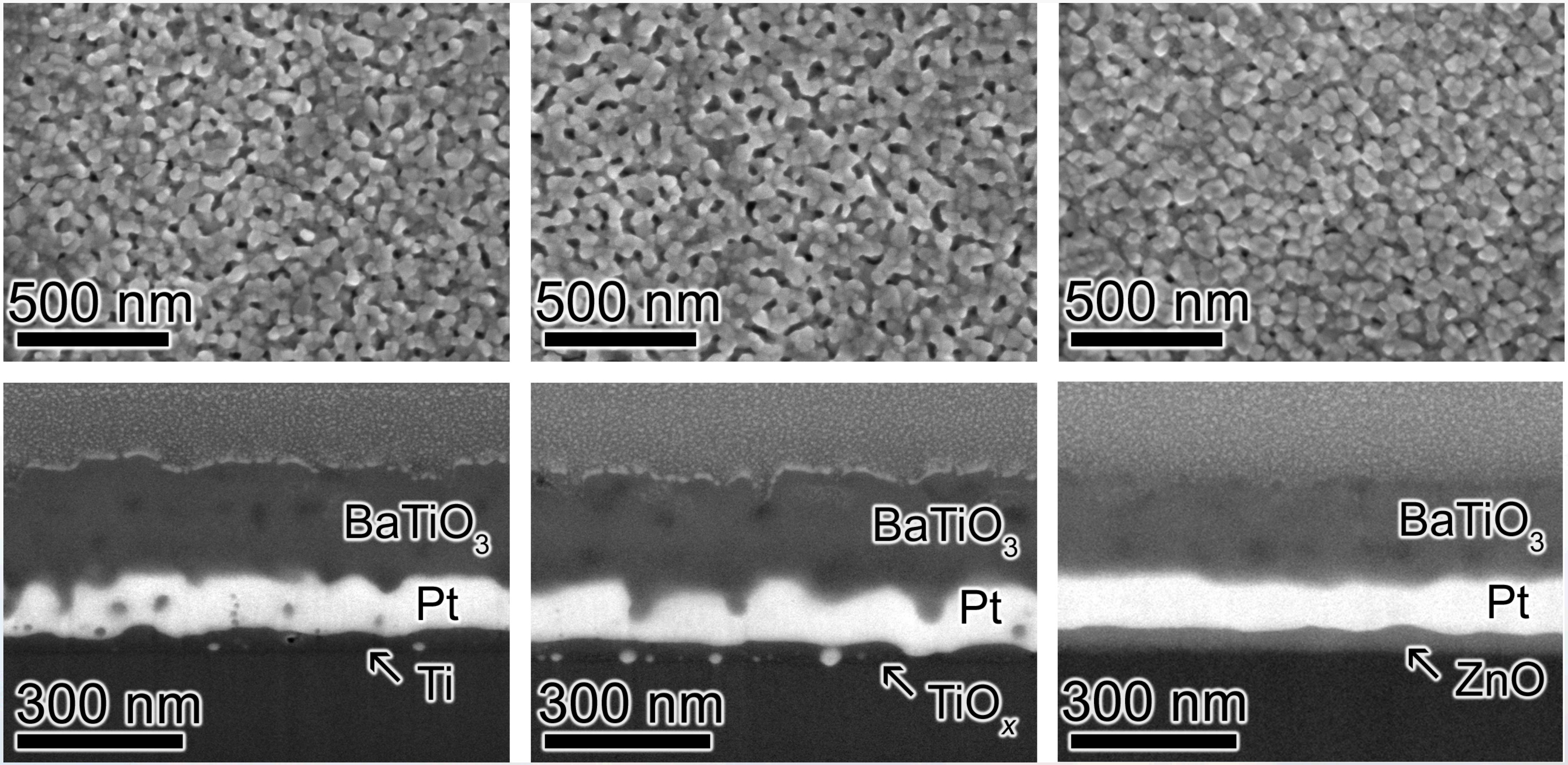


CSD $BaTiO_3$ on Platinized Si



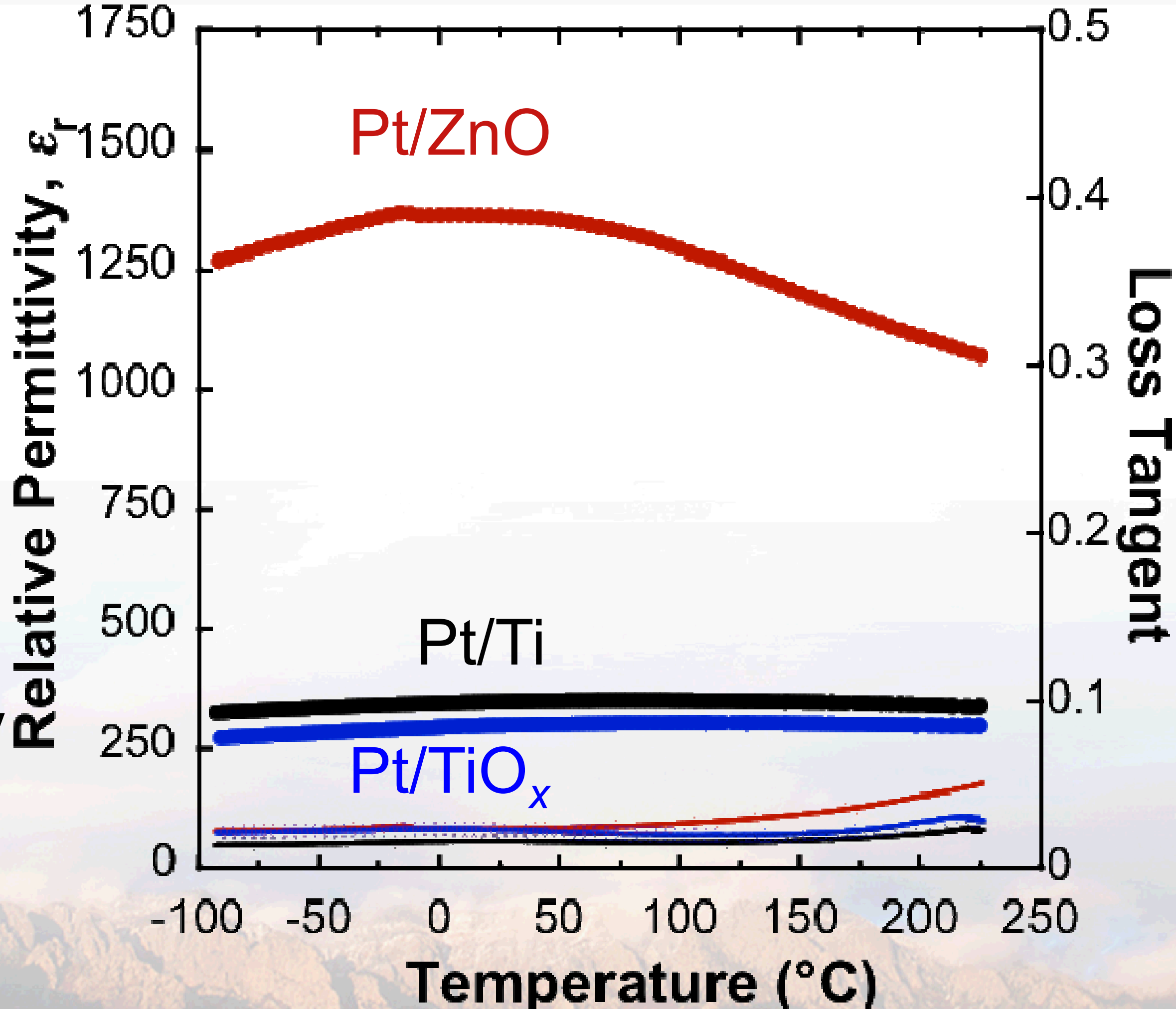


Topography and microstructure



$BaTiO_3$ 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

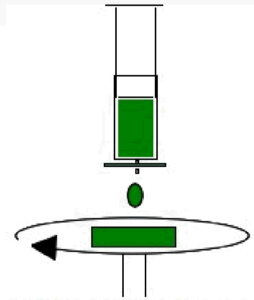
Spin Coat Deposition
4000rpm/30sec

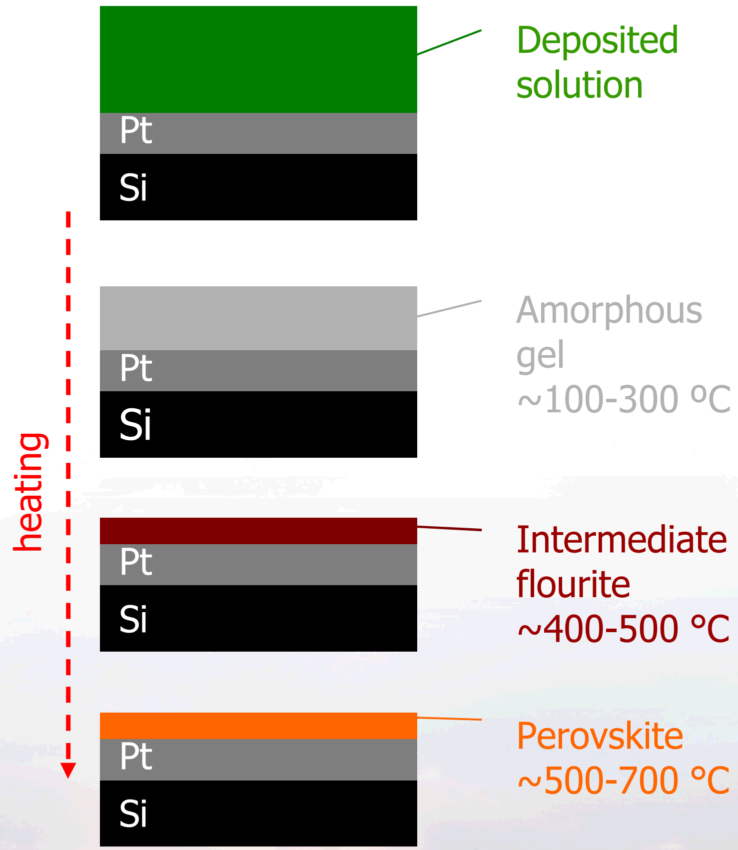
multiple depositions

Pyrolysis

Crystallization

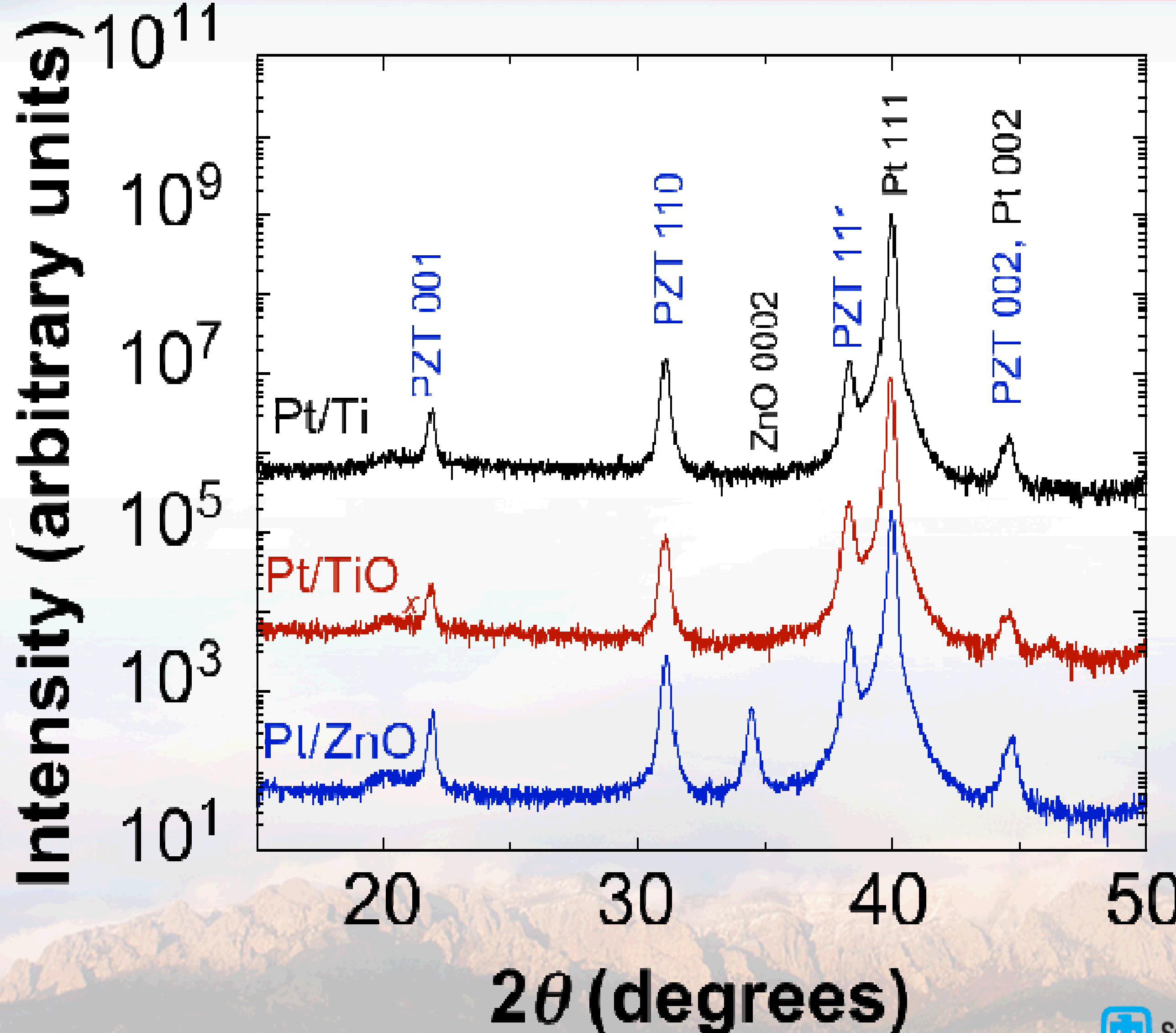
Sputter Pt electrodes



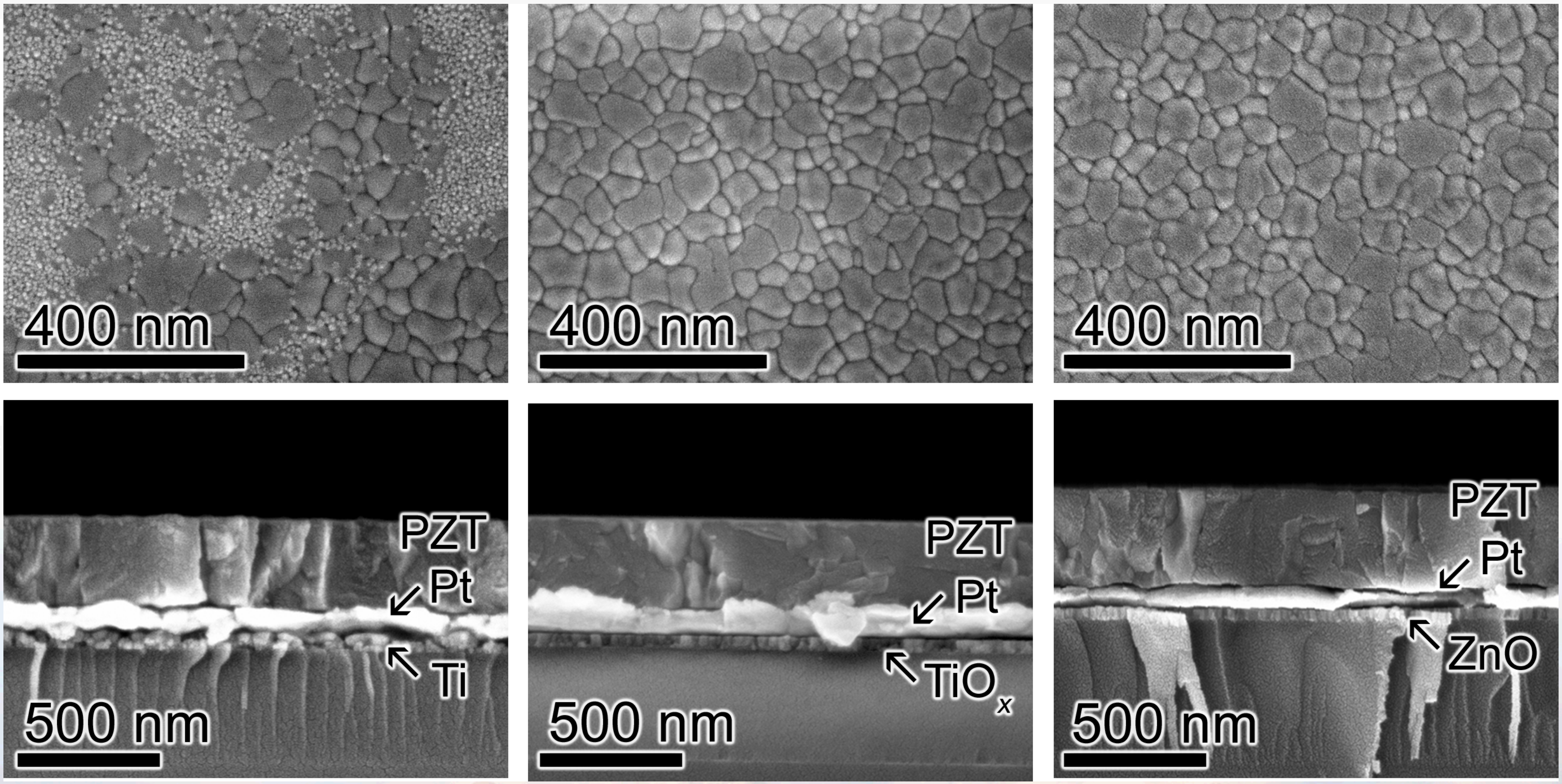


R.A. Assink and R.W. Schwartz; **Chem. Mater.** (1993) G. Yi and M. Sayer.**J. Appl. Phys.** (1988)

Film Crystallographic Properties

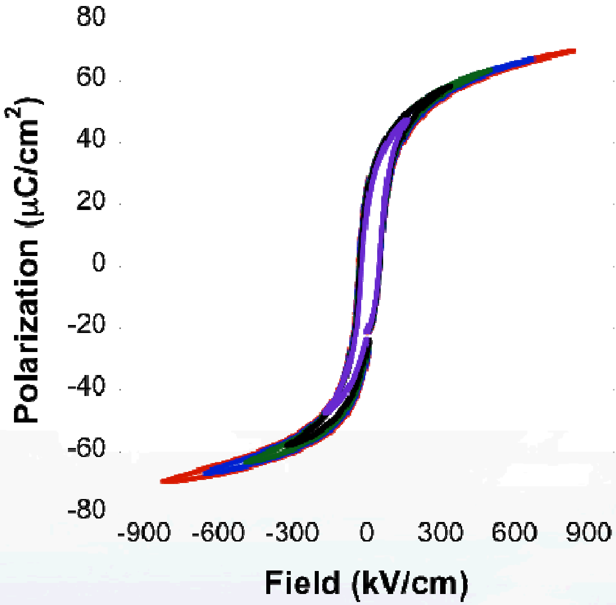


PZT Film Microstructure

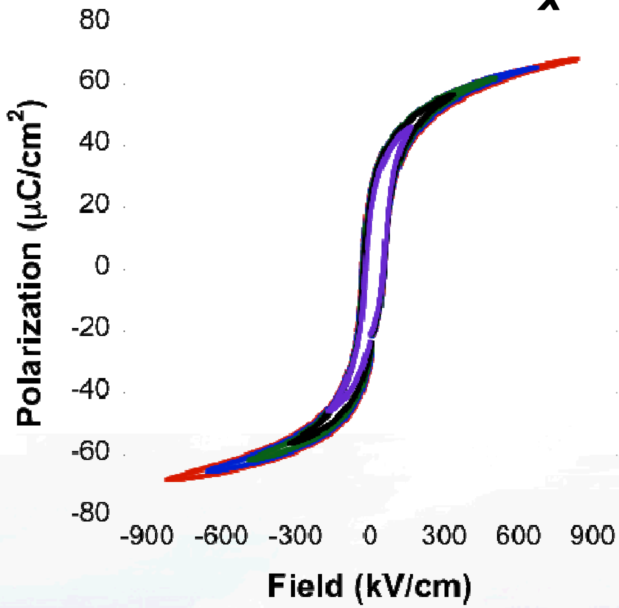


Dielectric and Ferroelectric properties

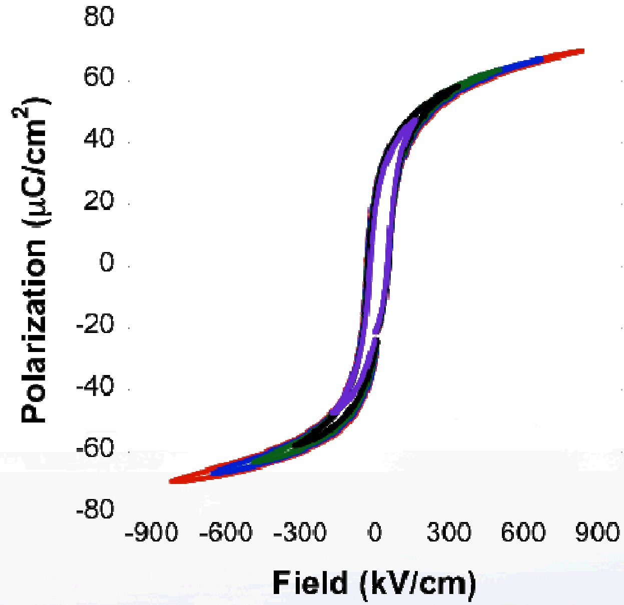
PZT/Pt/Ti



PZT/Pt/TiO_x



PZT/Pt/ZnO

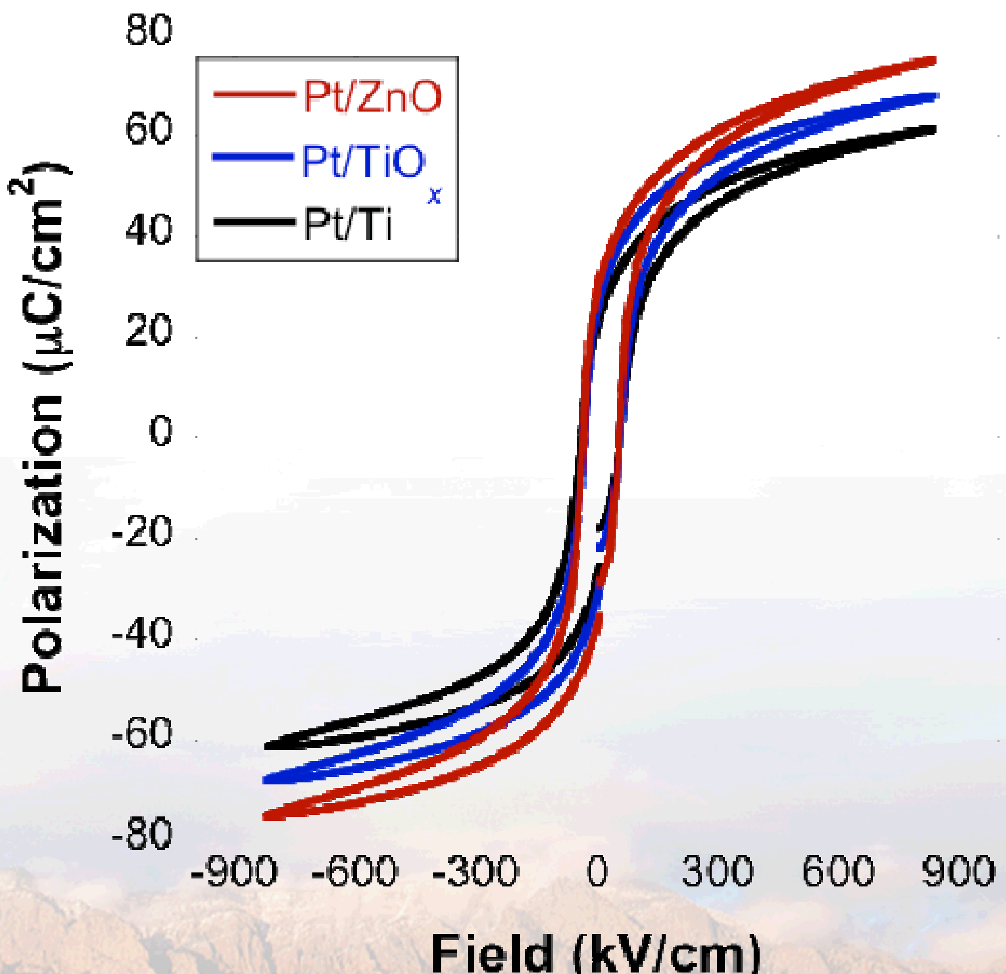


- Measurements conducted at 10 Hz
- All films saturate well
- Low leakage

Ferroelectric properties

	P_{max} ($\mu C/cm^2$)	P_r ($\mu C/cm^2$)	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

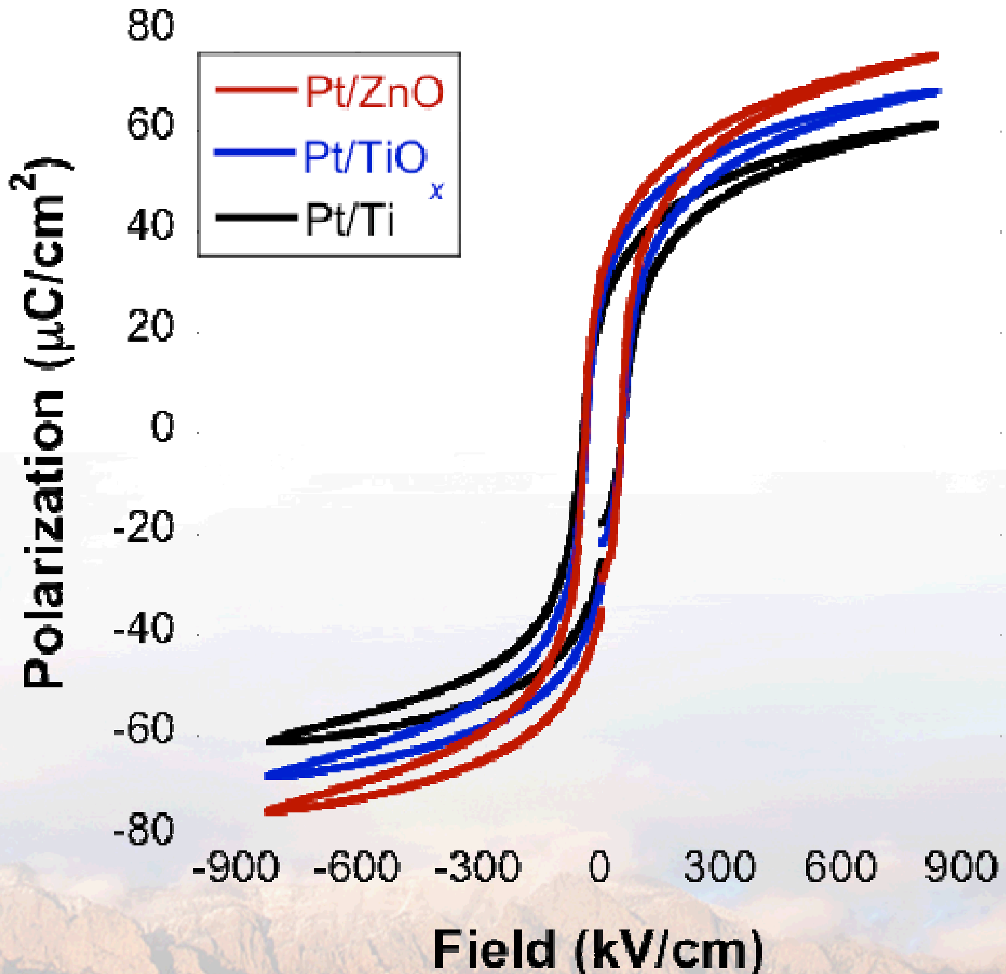
- **Both P_r and K increase on ZnO-buffered substrates**
- **Coercive field decreases slightly for PZT on ZnO-buffered substrates**



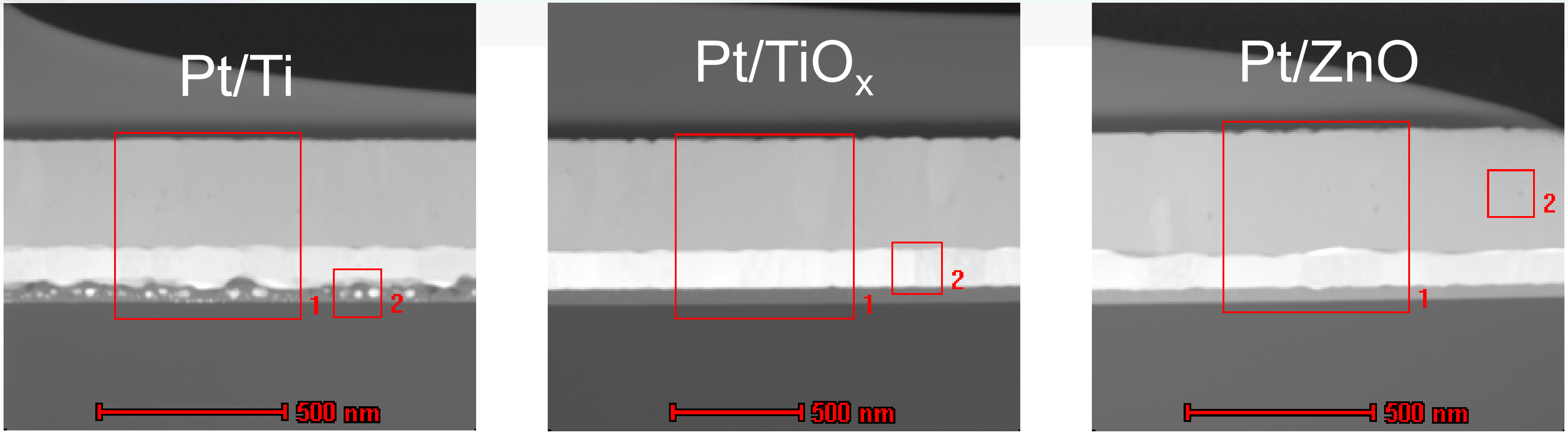
Ferroelectric properties

	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

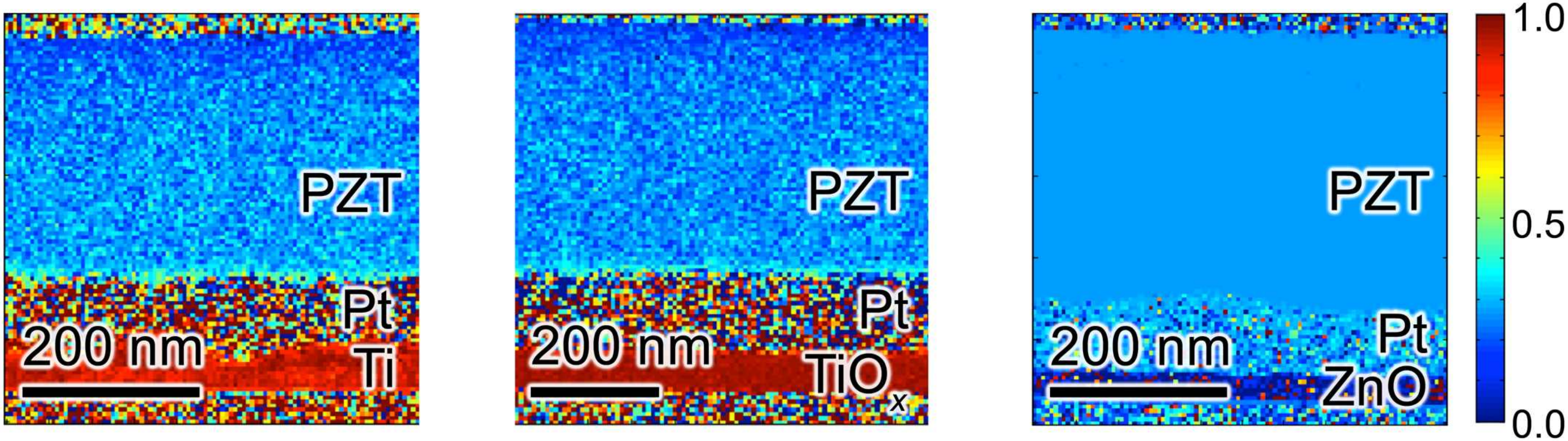
- **Two film systems**
- **Performance improvements identified in both on ZnO-buffered substrates**
- **Mechanism?**



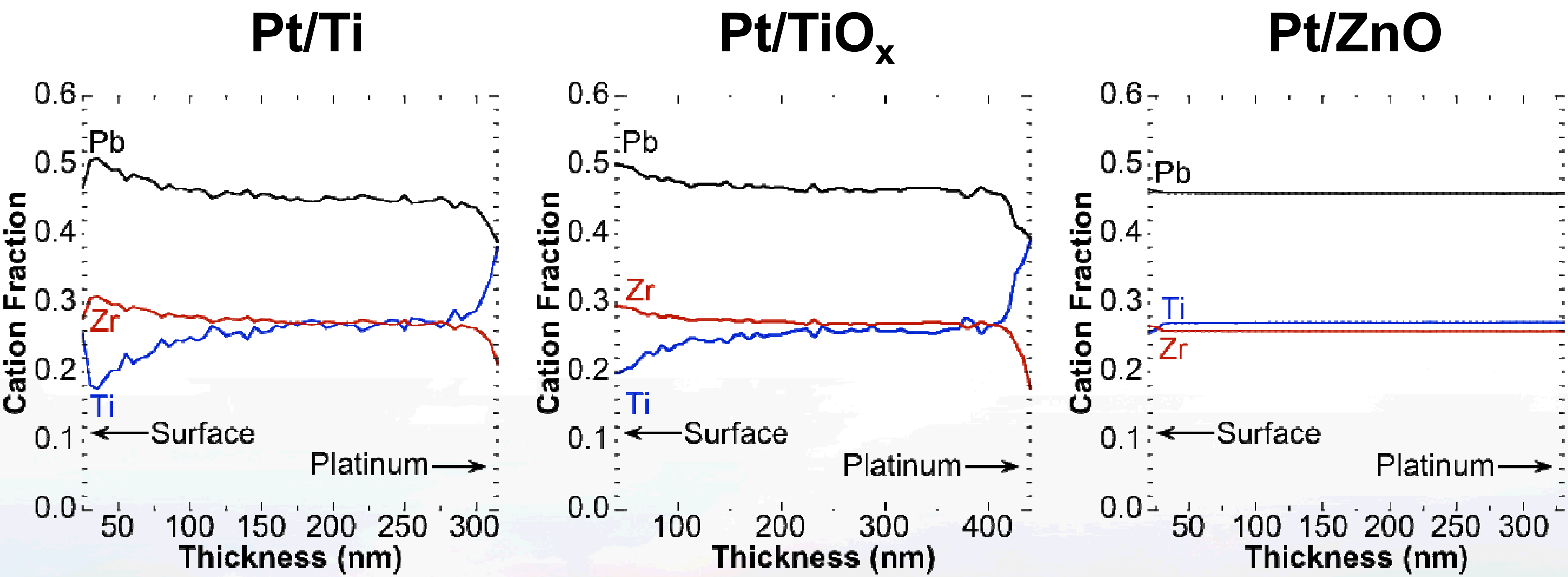
PZT Composition Analysis



Titanium Distribution



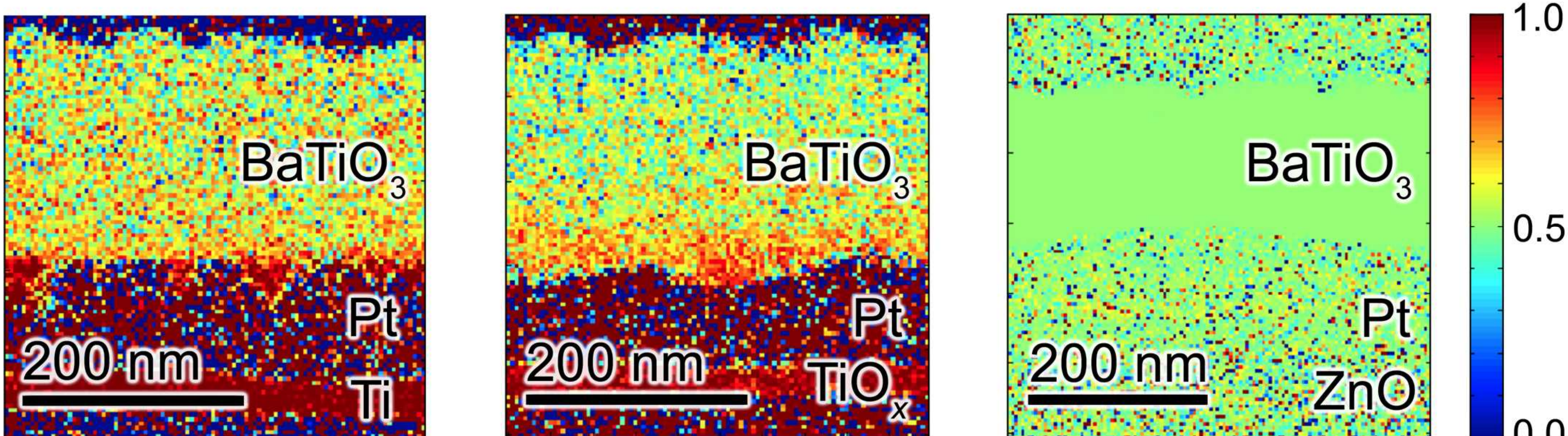
PZT Composition Analysis



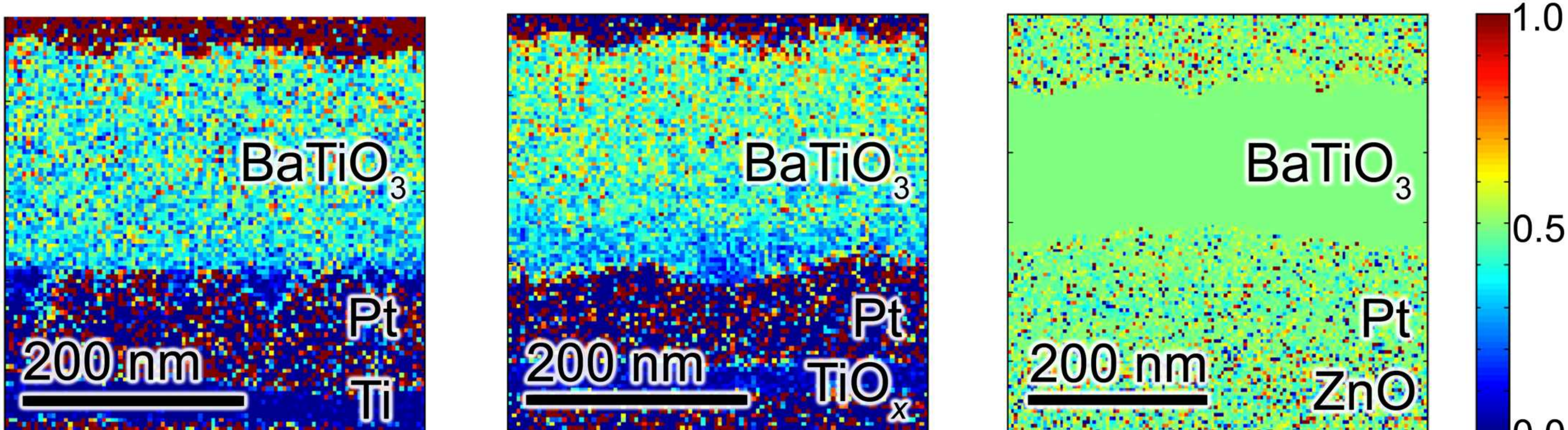
Substantially improved chemical homogeneity in films on Pt/ZnO substrates

$BaTiO_3$ Compositional Analysis

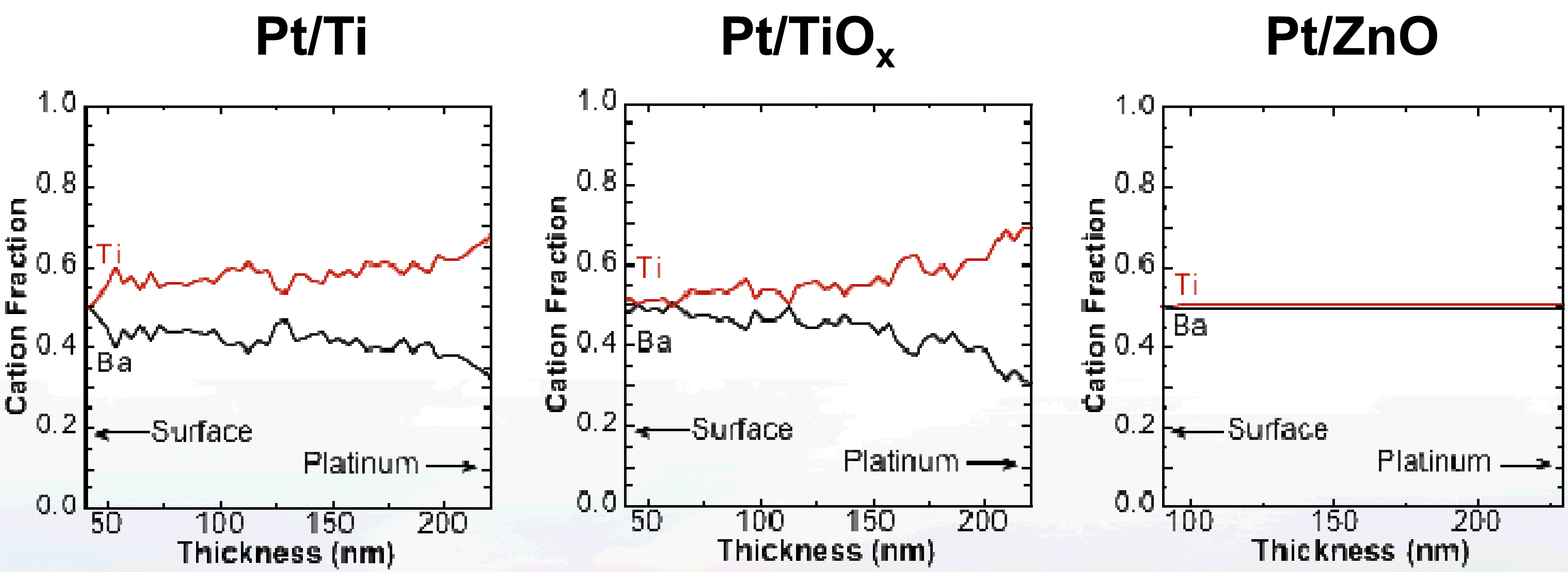
Titanium Distribution



Barium Distribution



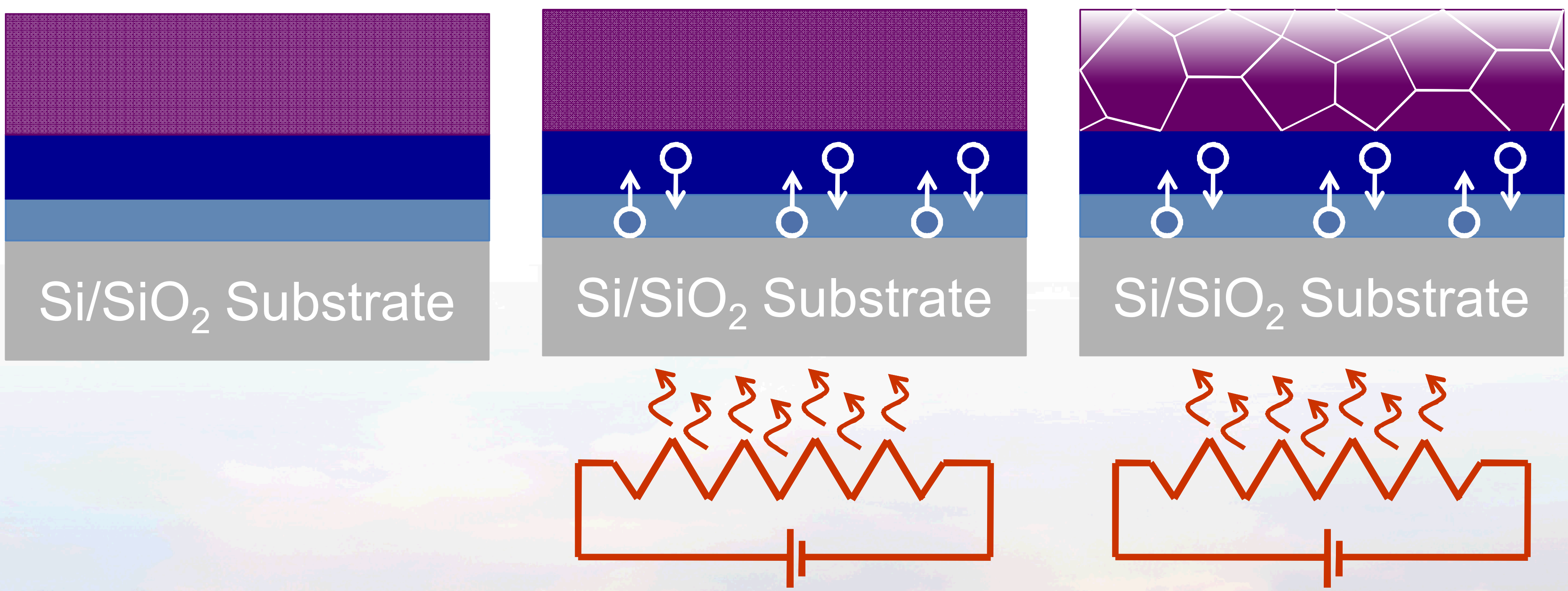
$BaTiO_3$ Compositional Analysis



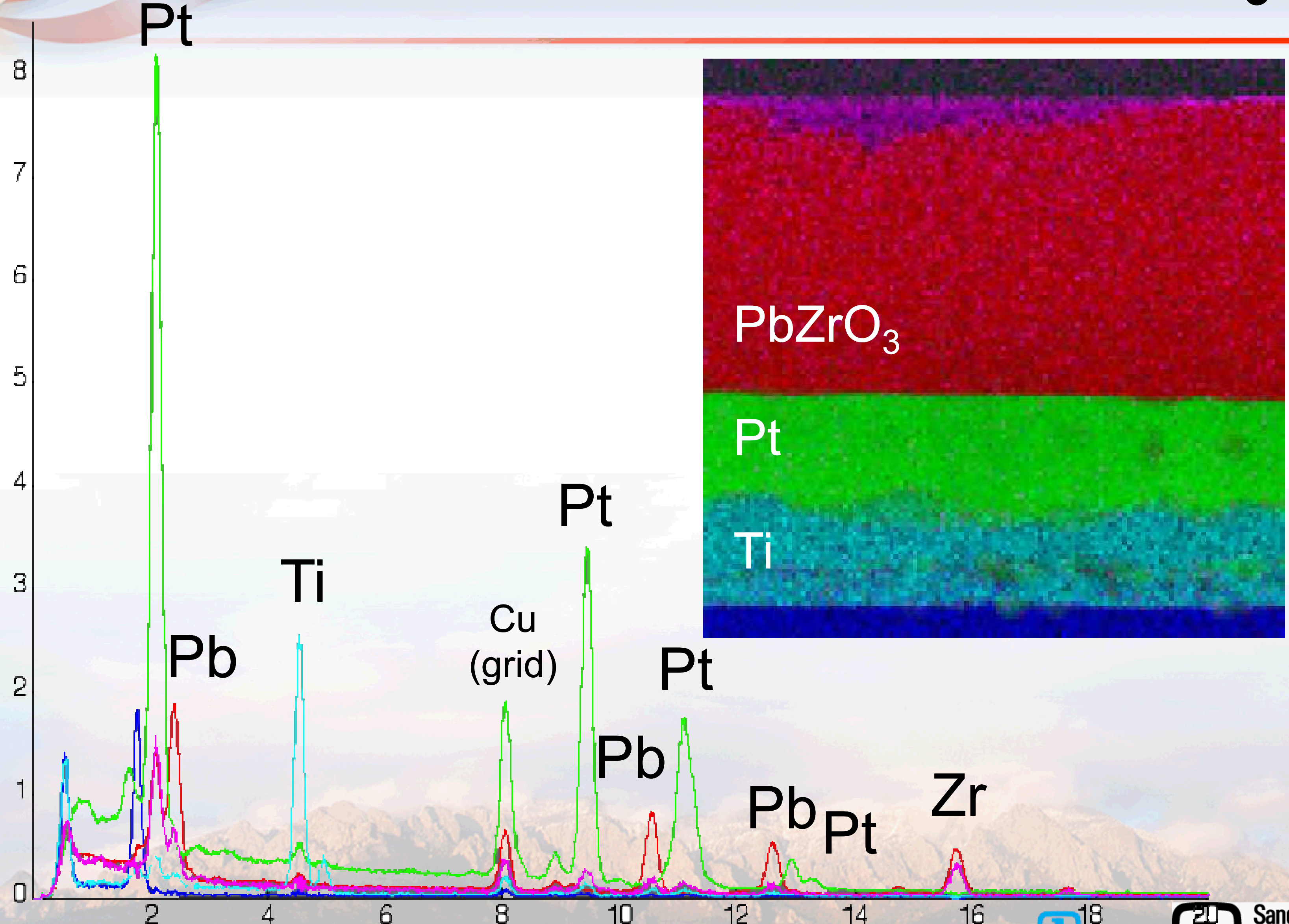
Substantially improved chemical homogeneity in films on Pt/ZnO substrates

Mechanism?

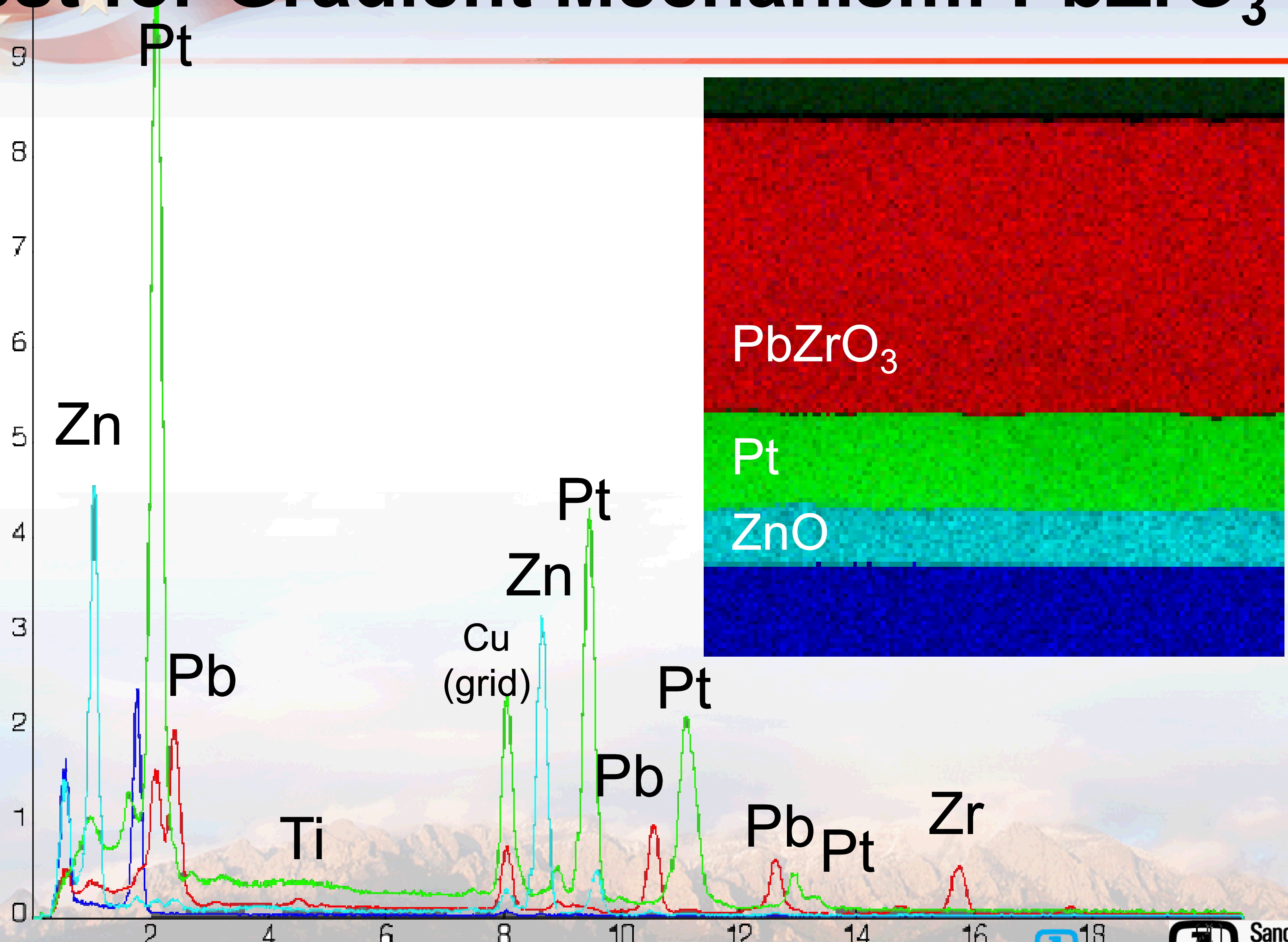
Our Model



Test for Gradient Mechanism: $PbZrO_3$

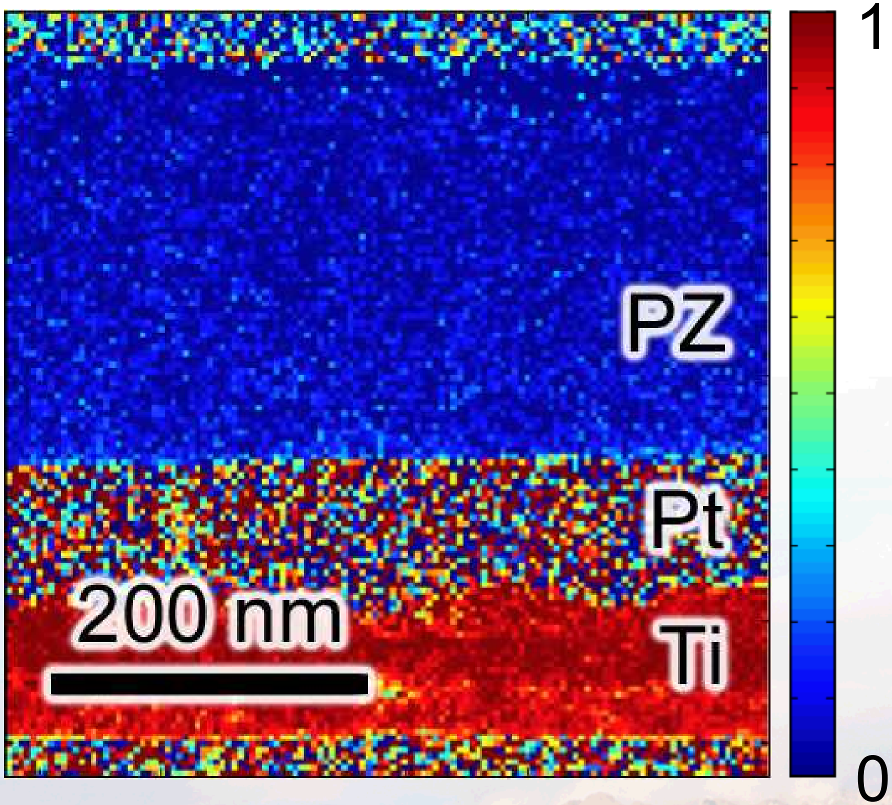


Test for Gradient Mechanism: $PbZrO_3$

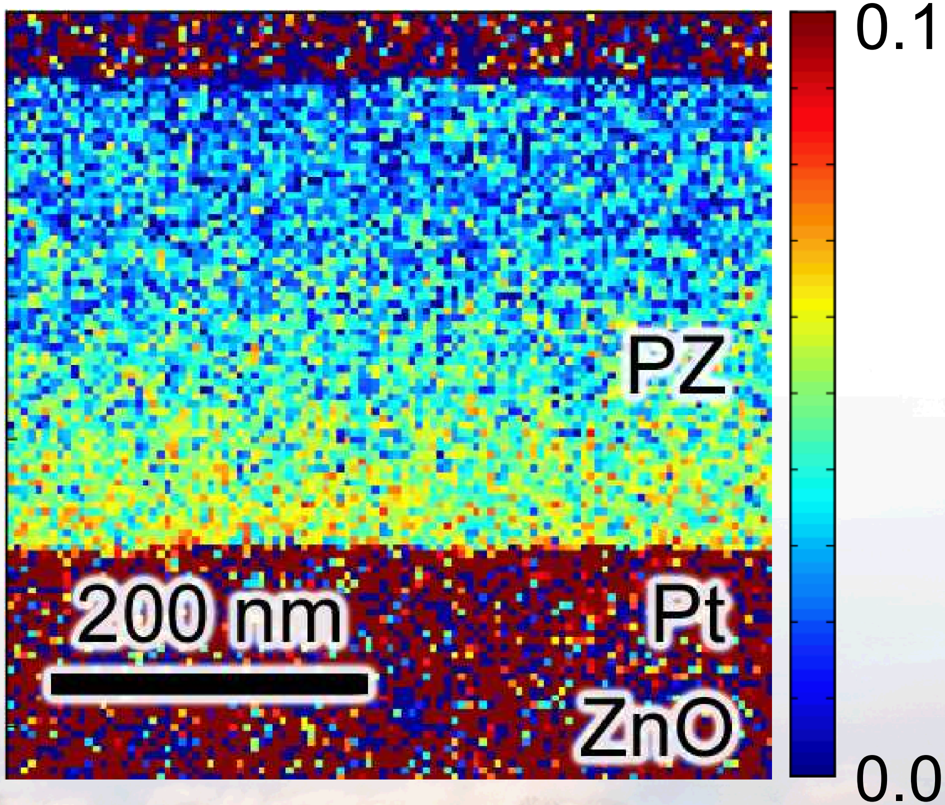


Test for Gradient Mechanism: $PbZrO_3$

PZ/Pt/Ti

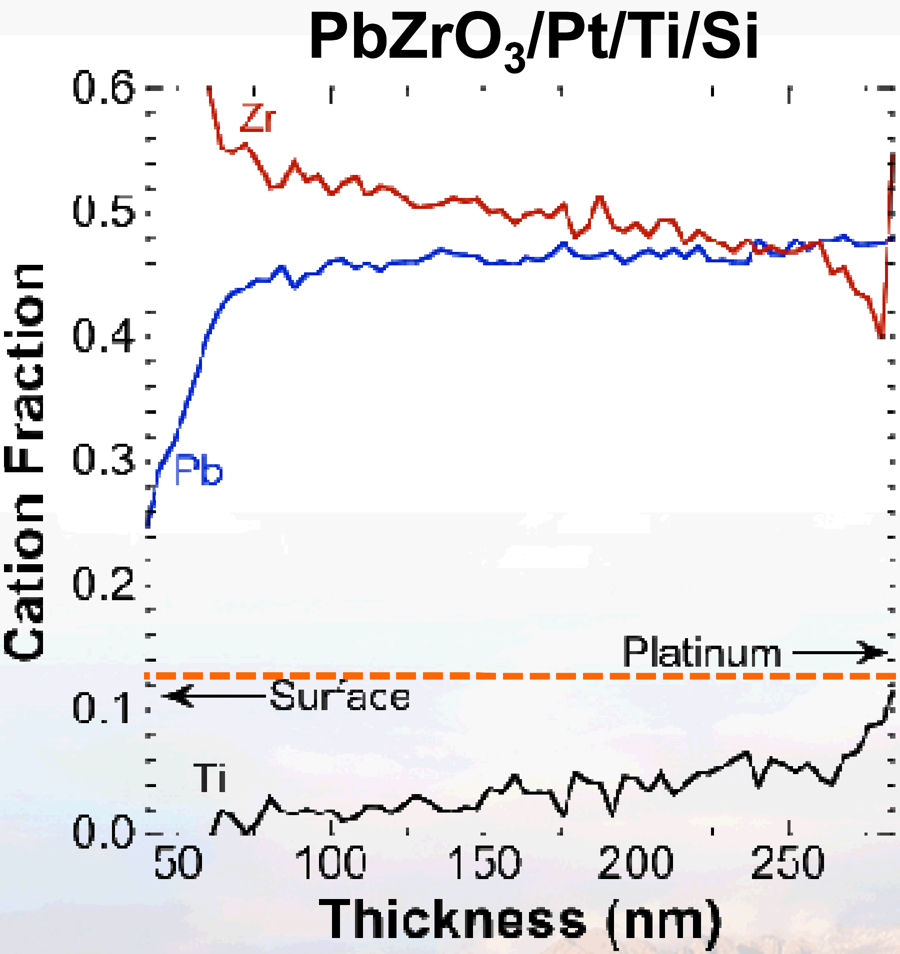


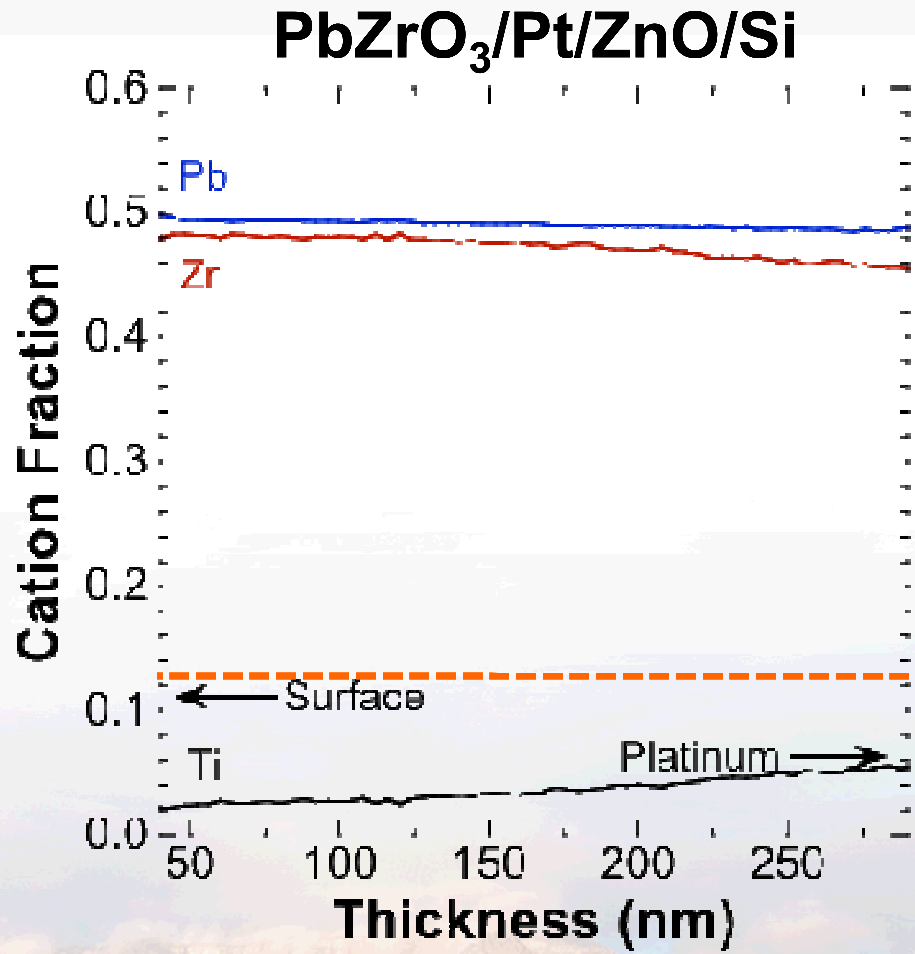
PZ/Pt/ZnO



Note Scale Difference

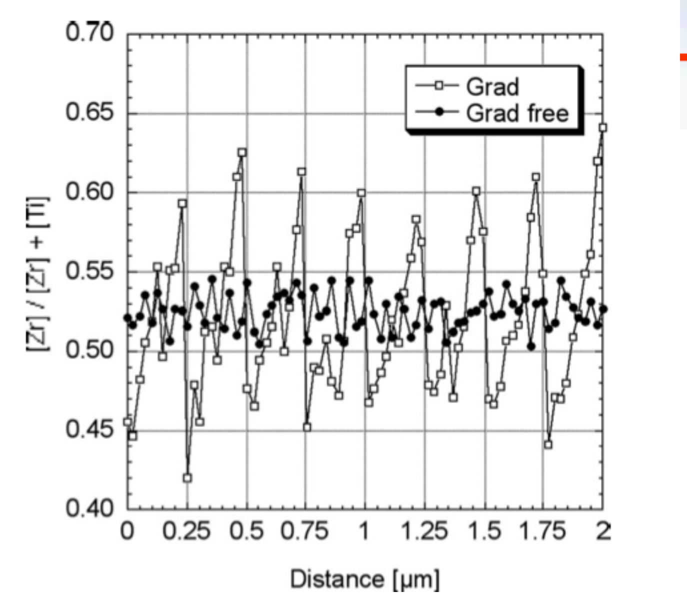
Test for Gradient Mechanism: $PbZrO_3$





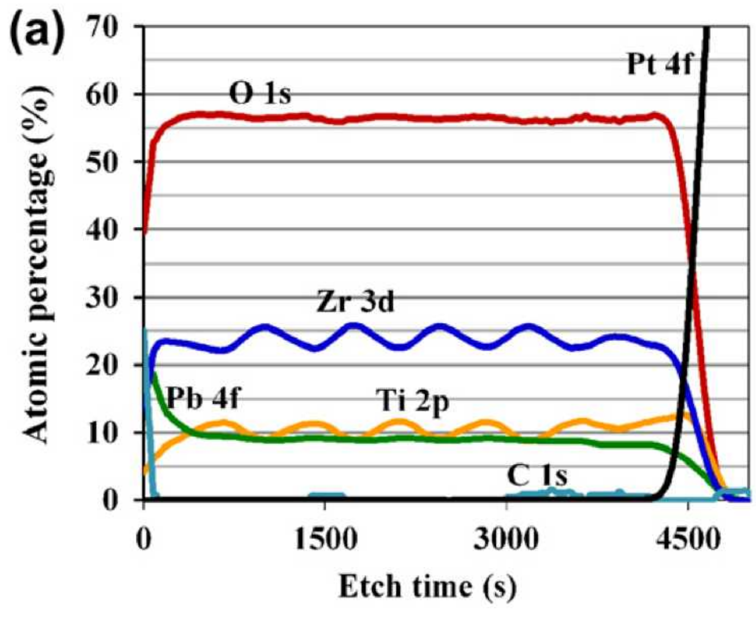
Less Ti and smaller gradient on Pt/ZnO

Solution Chemistry Effects?



Open Issues:

- **This model cannot explain 'saw-tooth' profiles observed by other groups***
- **What role do solution chemistry and processing conditions play in gradient formation?**
- **More experiments necessary to isolate controlling variables**



*Calame and Muralt, *Appl. Phys. Lett*. **90**, 062907 (2007)
Bastani and Bassiri-Gharb, *Acta. Mater*. **60**, 1346 (2012)

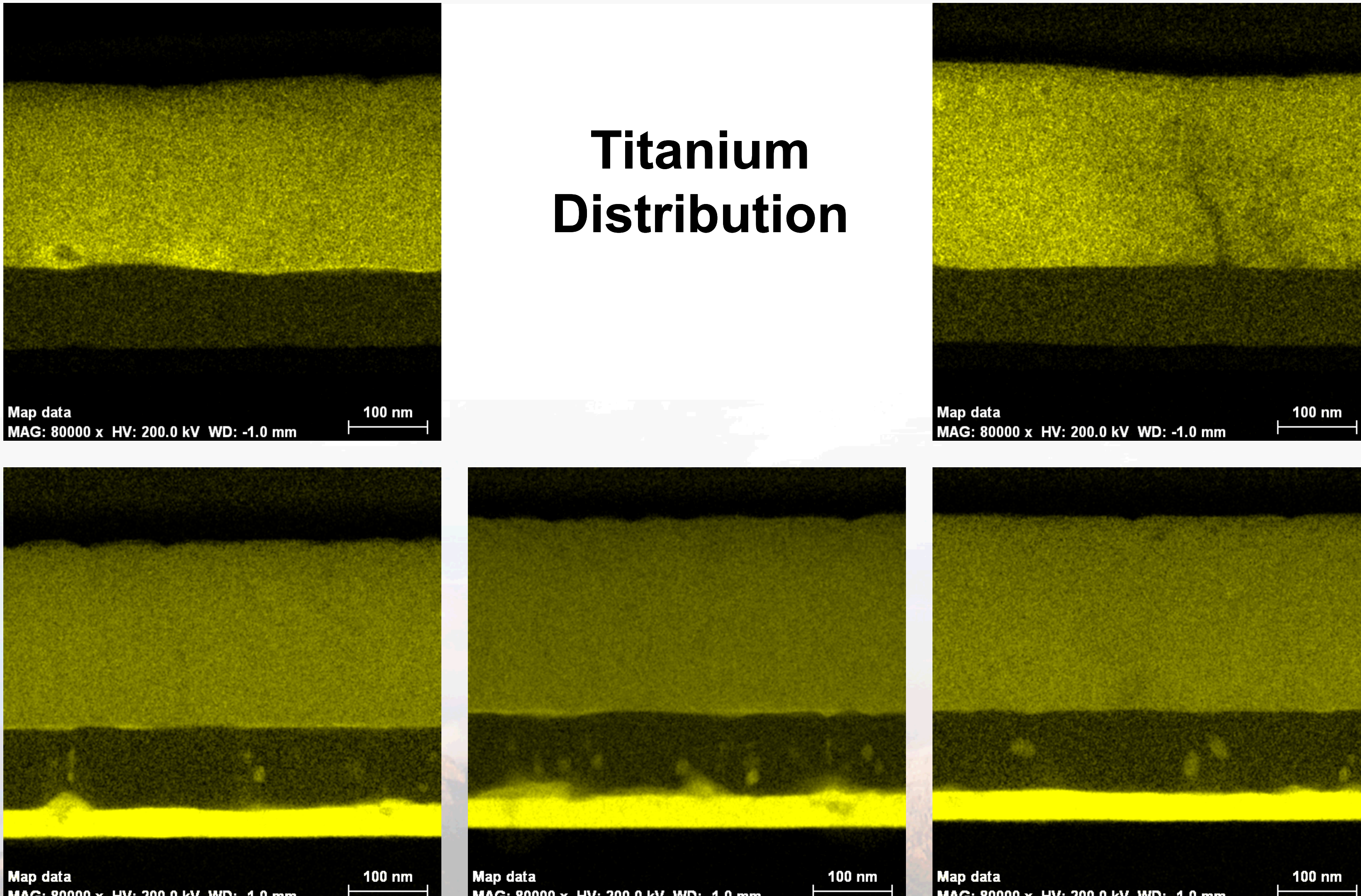
Solution Chemistry Effect: Sol-gel films

300°C | 350°C | 400°C

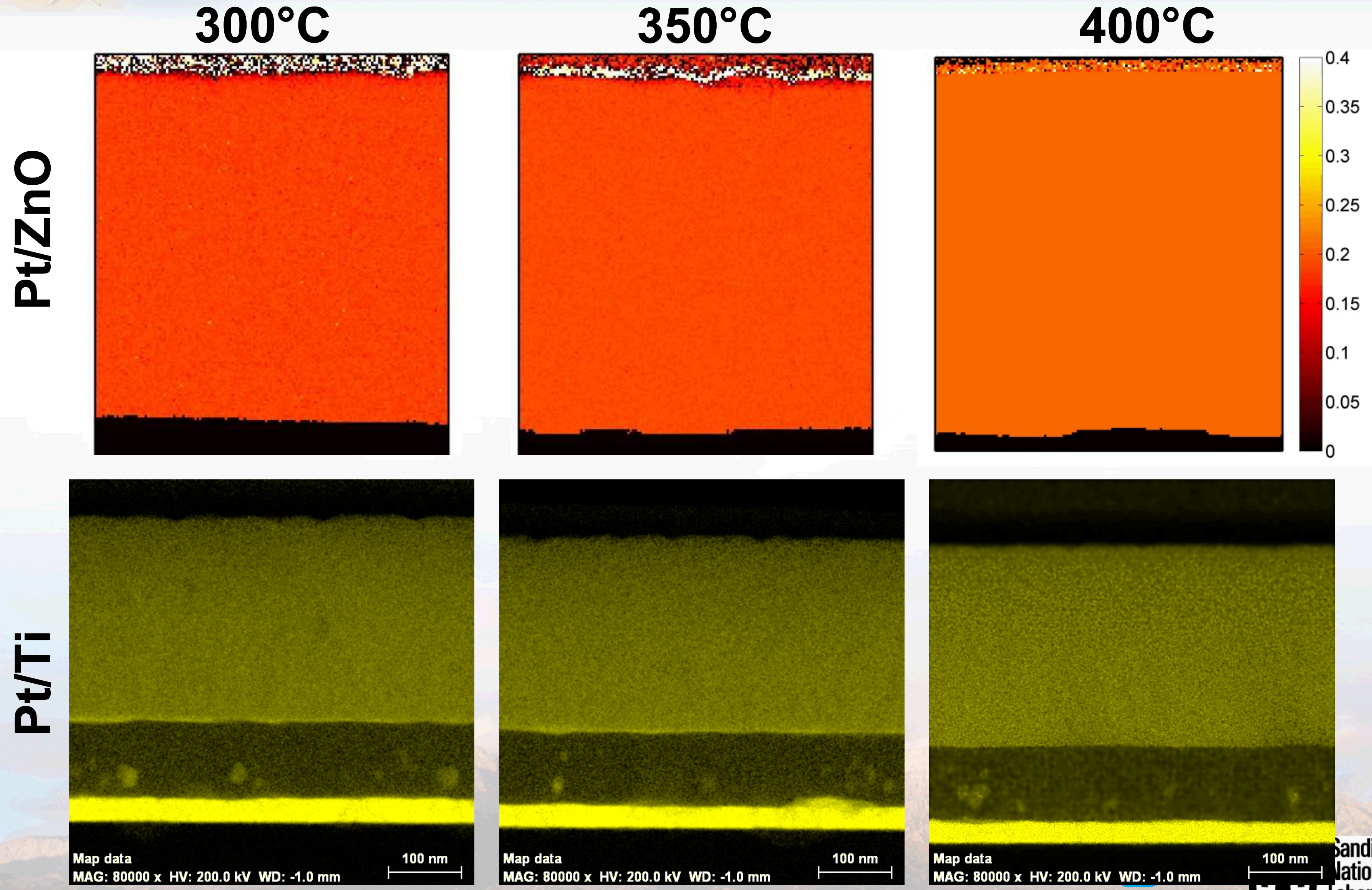
Pt/ZnO

Titanium Distribution

Pt/Ti



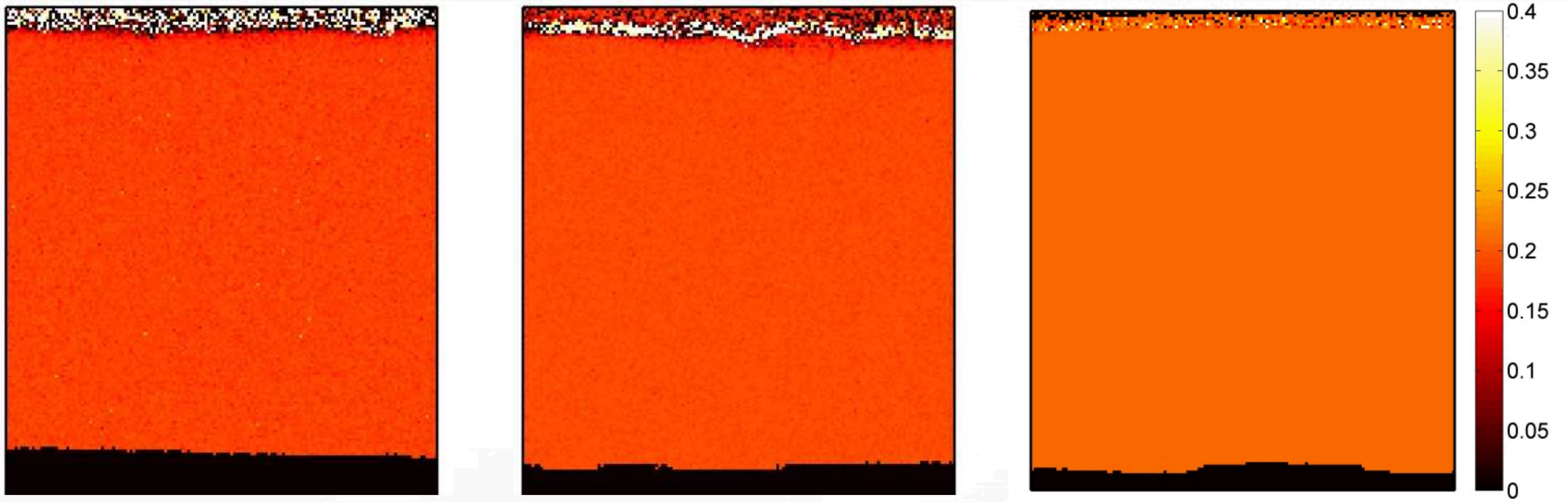
Solution Chemistry Effect: IMO Films

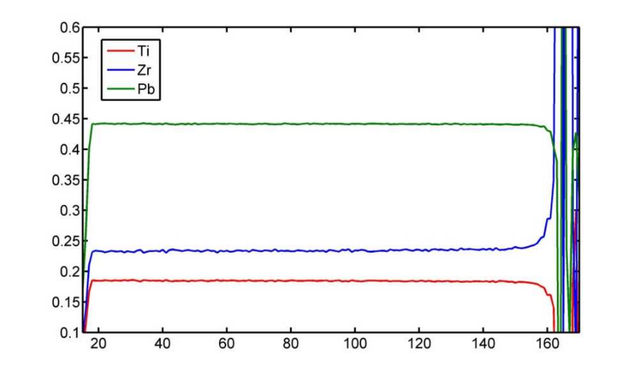


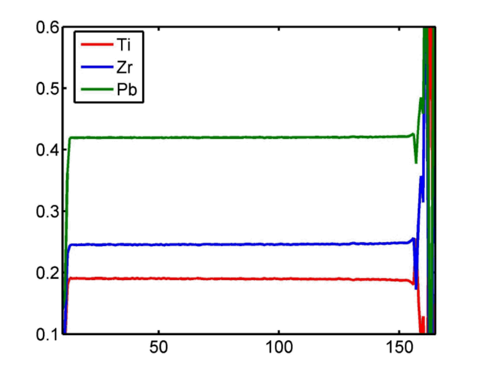
Solution Chemistry Effect: IMO Films

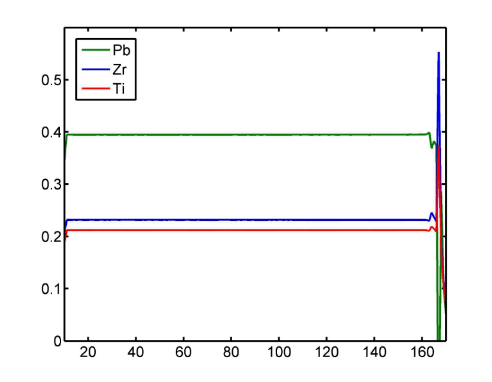
300°C **350°C** **400°C**

Pt/ZnO





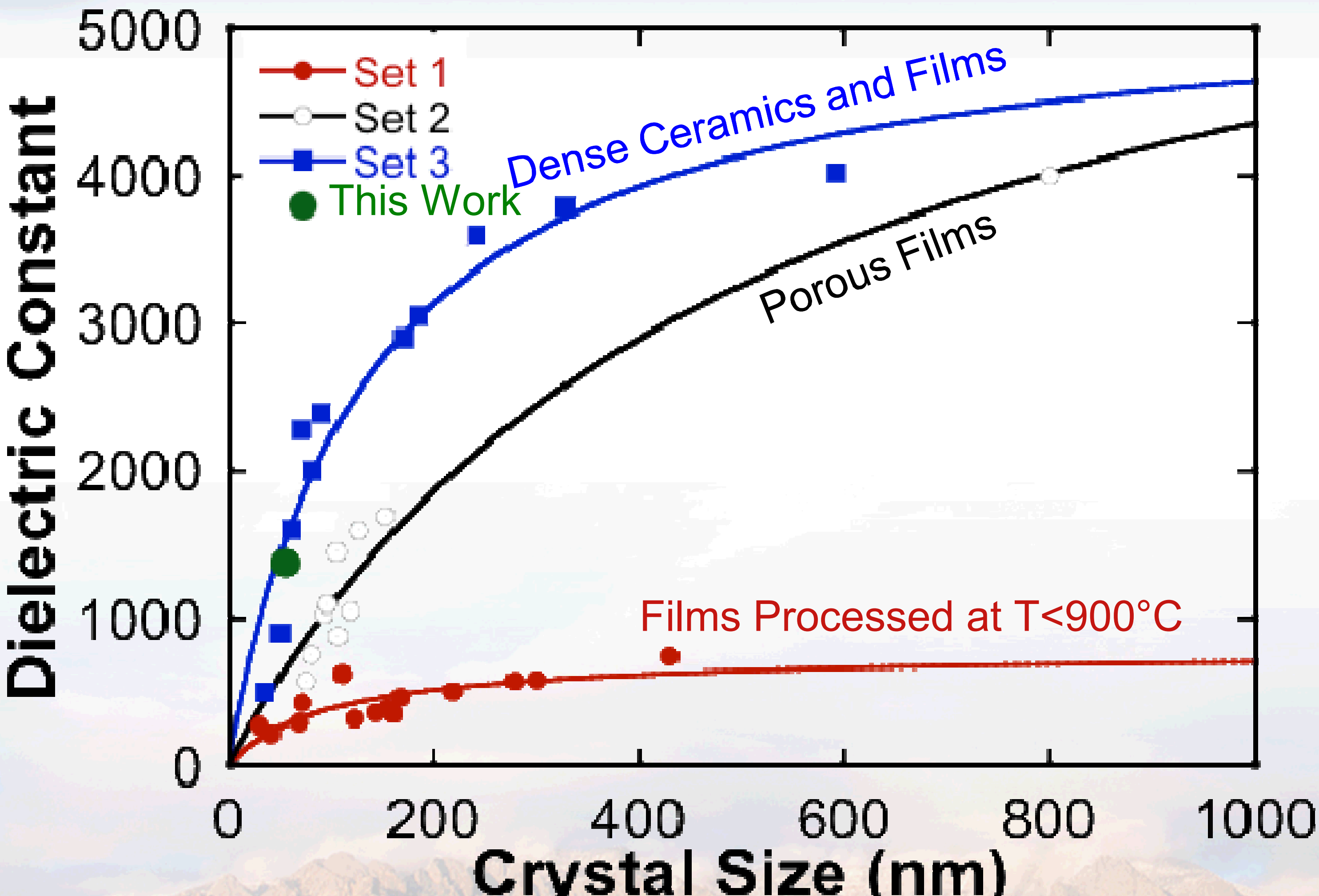




Summary

- **Work of Adhesion is an effective means in selecting adhesion layers**
- **ZnO is a superior adhesion layer**
- **$BaTiO_3$ and IMO PZT films prepared on Pt/ZnO substrates possess improved electronic properties compared to traditional substrates**
- **Traditional sol-gel films still appear to possess composition gradients: thermodynamic effect?**
- **Improved electronic properties can be correlated with improved chemical homogeneity**

$BaTiO_3$ Scaling Effects



First known $BaTiO_3$ film with bulk properties on Si

Aygün *et. al. JAP* (2011)