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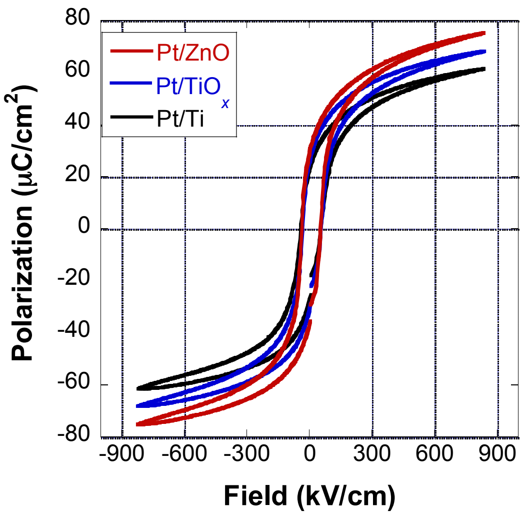

Solution Chemistry, Substrate, and Processing Effects on the Chemical Heterogeneity in PZT Films

Jon Ihlefeld

Sandia National Laboratories

Albuquerque, NM, USA

jihlefe@sandia.gov

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NNSA National Nuclear Security Administration

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Collaborators

Sandia National Labs

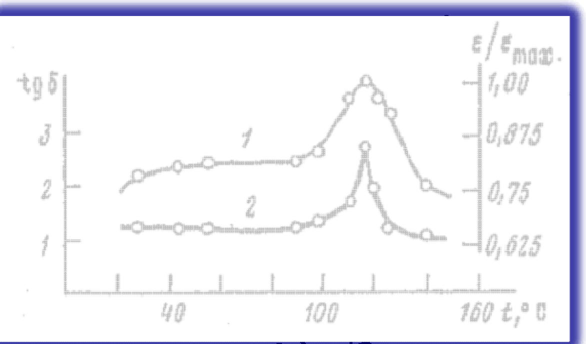
Microscopy

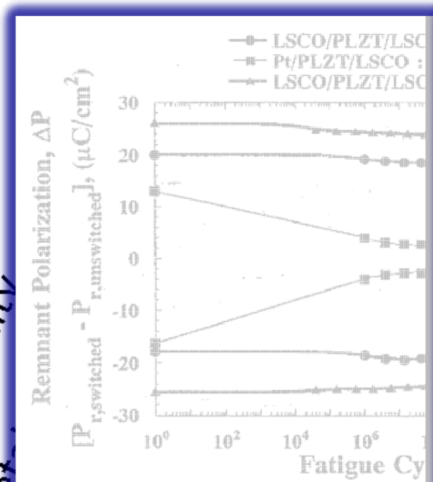
- Paul Kotula
- Bryan Gauntt
- Ping Lu
- Bonnie McKenzie
- Amy Allen
- Michael Rye

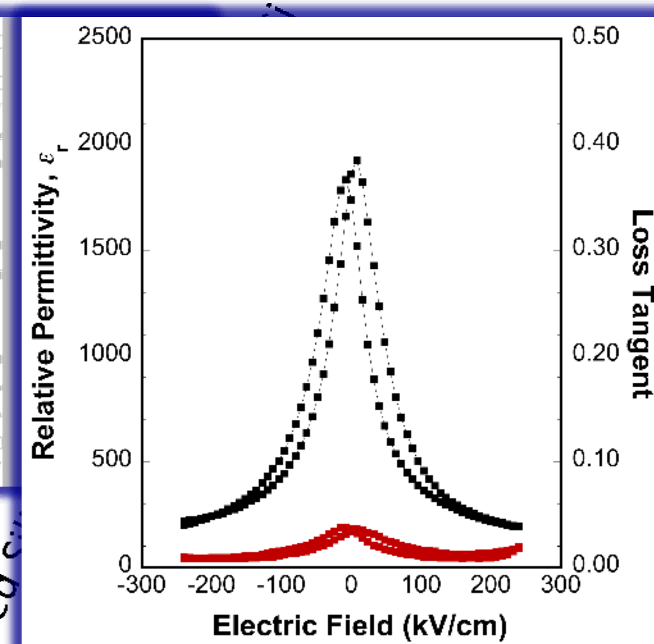
Solution/Film Preparation

- Chris T. Shelton
- Geoff Brennecka
- Dara V. Gough
- Erik Spoerke
- Kelsey Meyer
- Harlan Brown-Shaklee

A brief history of ferroelectric thin film substrates*







Platinum … Pratt & Fires… others — 1955-1981

Platinized Silicon: $Pt/SiO_2/Si$ Virtually Entire Community — 1988?-1991

Non-Noble Met… Sayer, Newnham… — 1988-1992

Platinized Silic… Virtually Entire… — 1990-Present

Conductive Ox… Kingon and Ram… — 1992

Platinized … Dimos… — 1996

Base … Kingon… — 1997-2002

Base … Clem… — 2003-2011

?? — 2013-Present

* Not a comprehensive history – apologies to those not included

Lessons Learned (and forgotten?)

Tani and Payne 1992

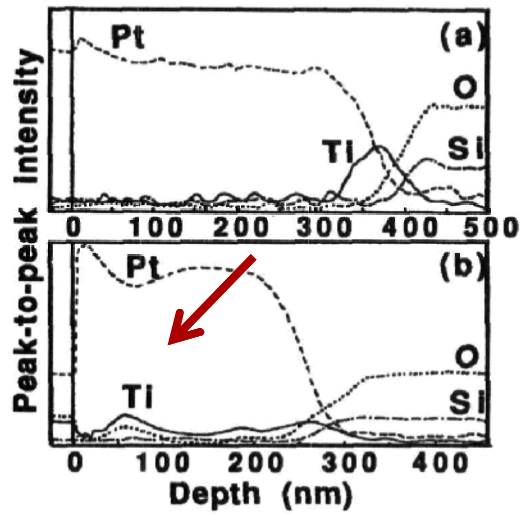
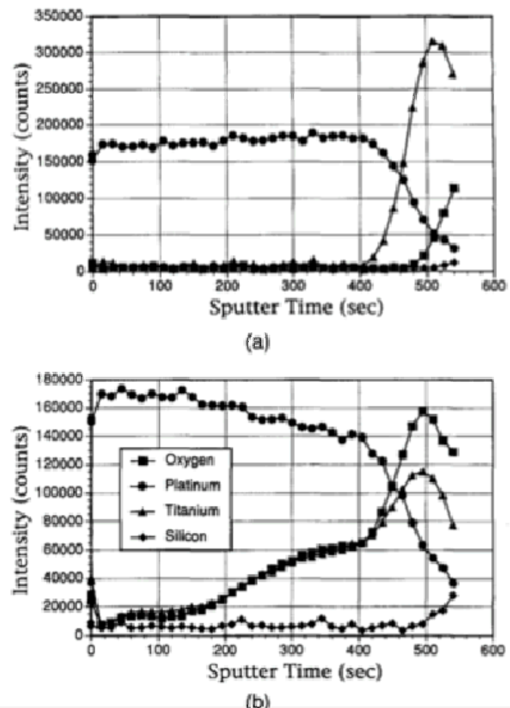


Fig.2 AES of A substrates (a) before and (b) after annealing at 650 °C for 30 min.

Fox, *et al.* 1994



Kim, *et al.* 2000

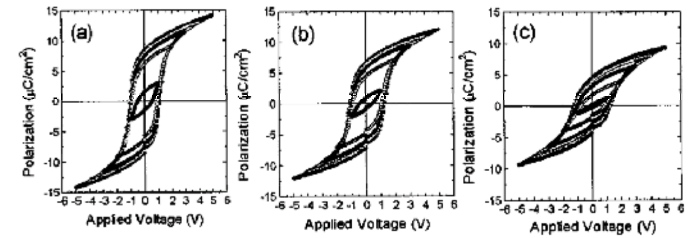
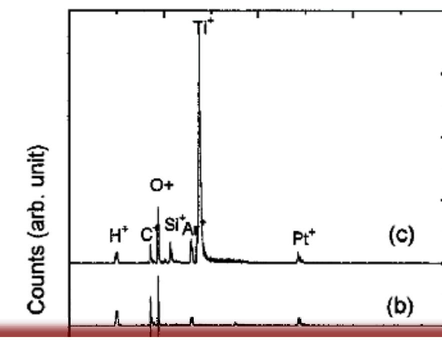


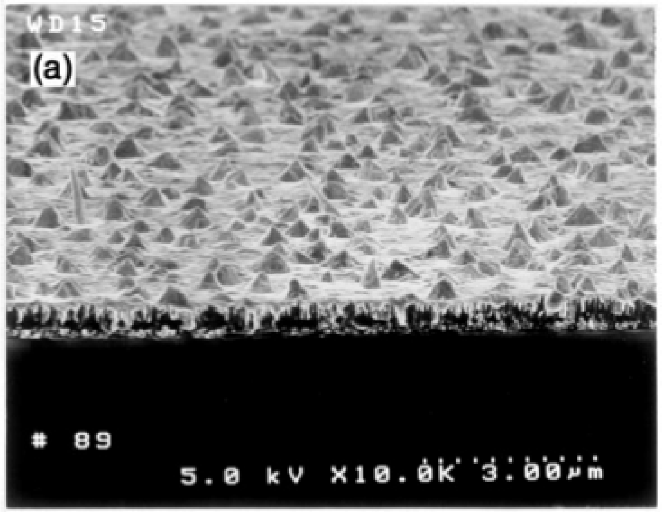
FIG. 2. $P-V$ hysteresis loops of SBT thin films (a) on Pt/ZrO_2/SiO_2/Si, (b) Pt/TiO_2/SiO_2/Si, and (c) Pt/Ti/SiO_2/Si substrates.

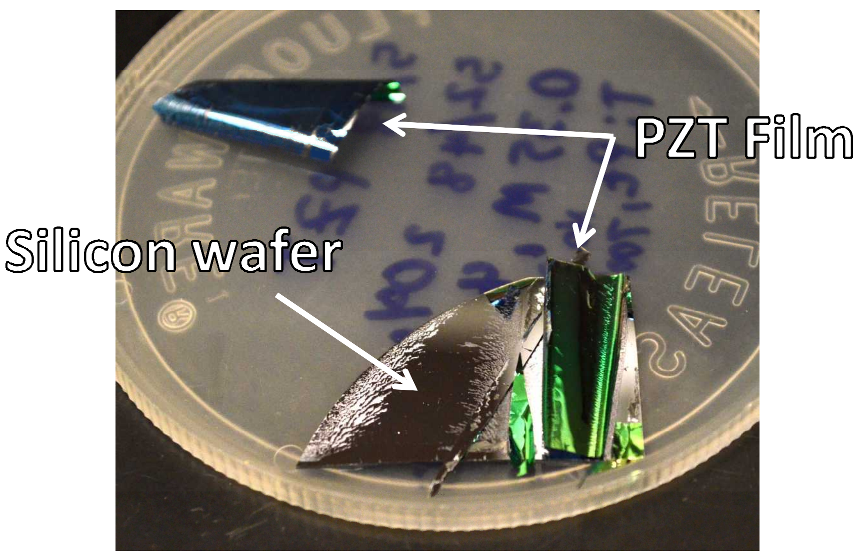


$_2$/Si, simu-

- Electrode/adhesion layer stacks cannot be considered as inert bystanders!
- Titanium-based adhesion layers are known to diffuse through platinum

Pt/Ti remains state of the art in platinized silicon:



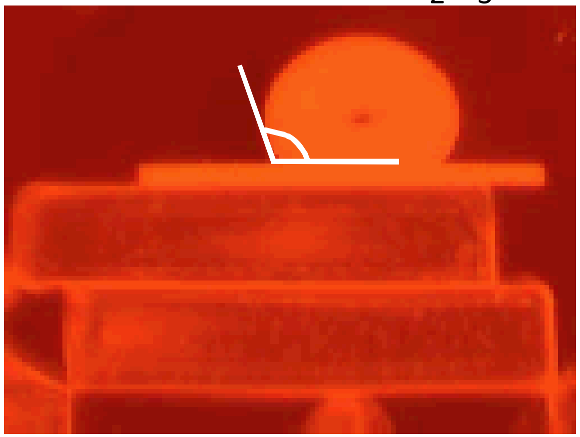


- Titanium 'adhesion' layers by far the most common
  - Adhesion of Pt/ZrO_2 and Pt/TiO_2 not as good as Pt/Ti
- Titanium expands upon oxidation causing hillocks
- Adhesion layer still fails with large temperature swings (>700°)
- ***>20 years of research and small improvements made***
- ***There must be a better solution!***

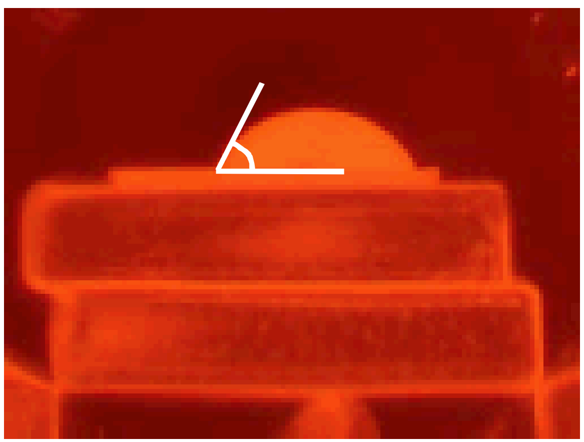
Al-Shareef, *et al.*, *J. Mat. Research*, **12** (2), 347-354 (1997)

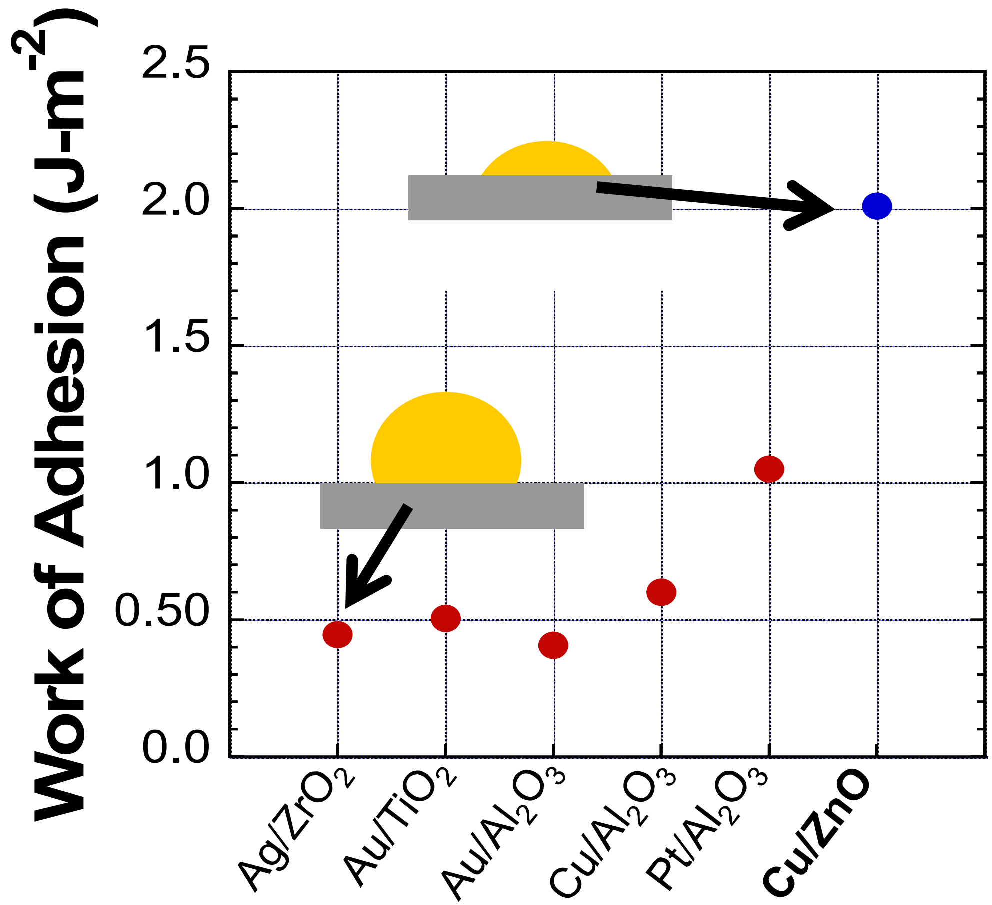
Metal Wetting and Adhesion

Molten Cu on Al_2O_3



Molten Cu on ZnO

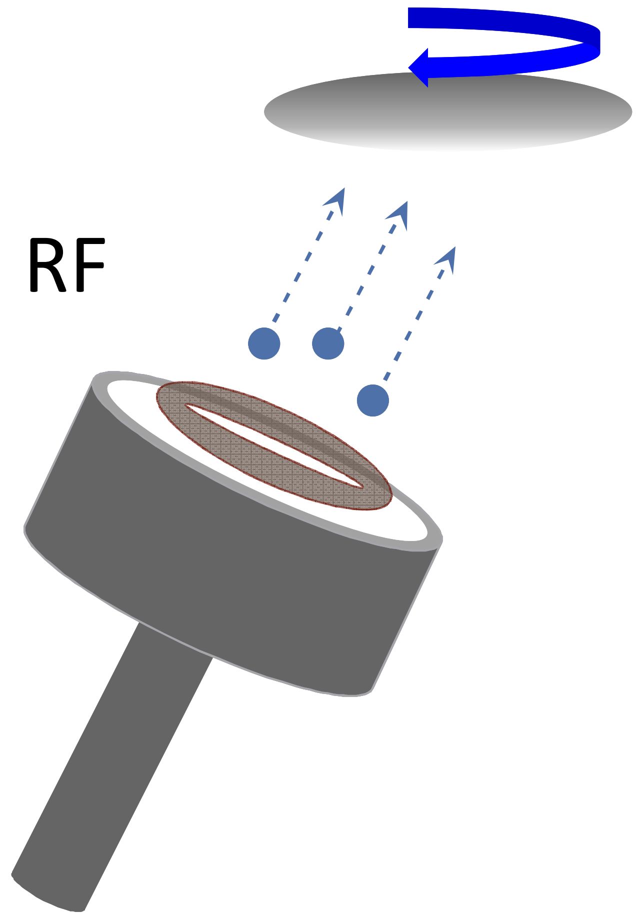




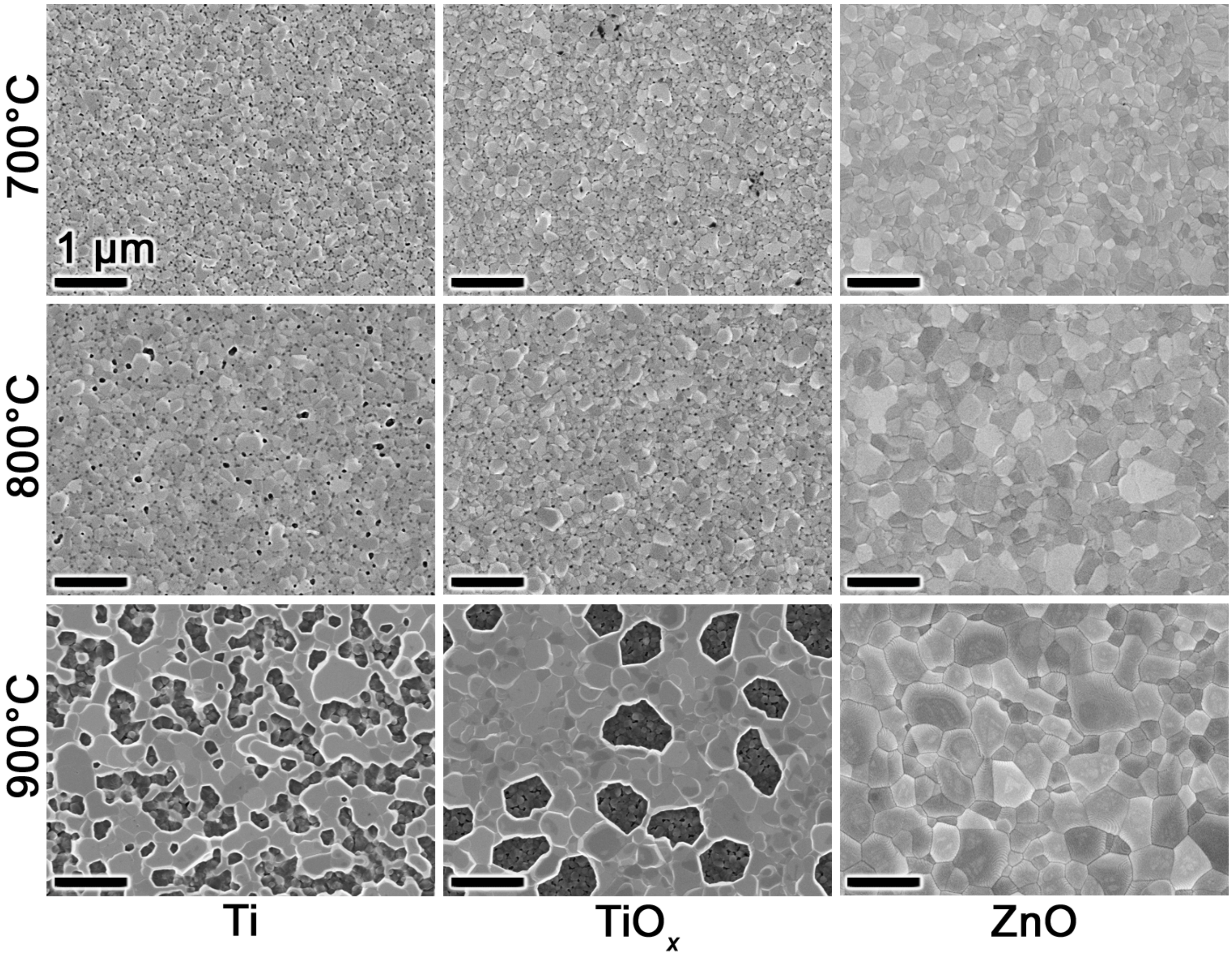
Can we use lessons learned from wetting experiments to guide selection of improved adhesion layers?

Pt/Si Substrate Preparation

- 100 nm Pt/40 nm buffer/400 nm SiO_2/Si
- 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



Electrode Temperature Stability



SNL IMO PZT CSD Film Preparation

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

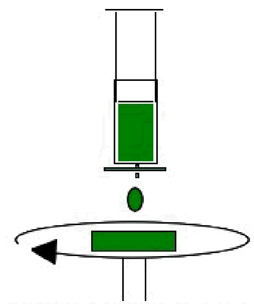
Spin Coat Deposition
4000rpm/30sec

multiple depositions

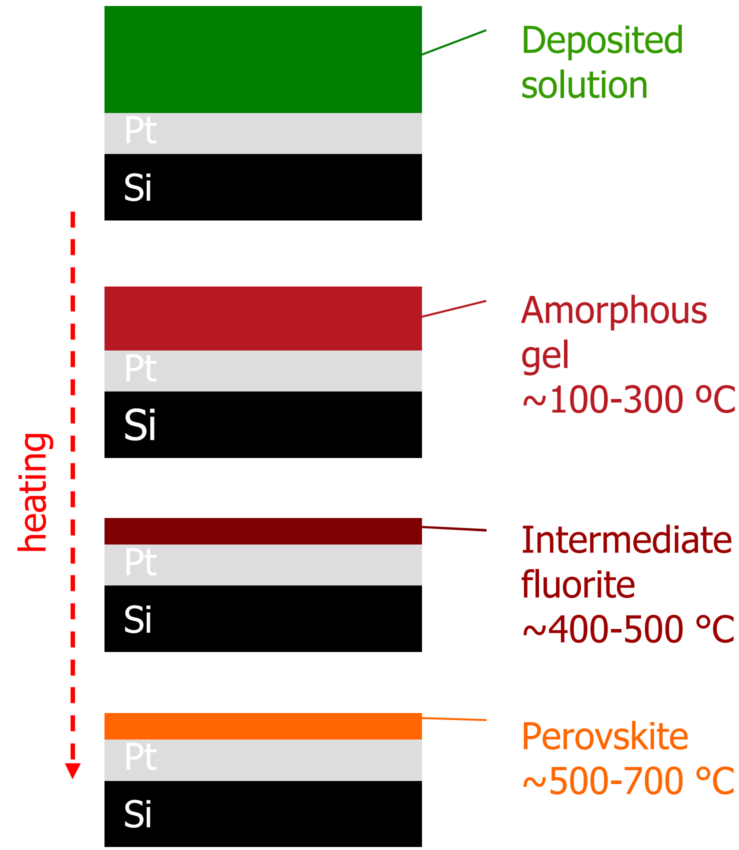
Pyrolysis

Crystallization

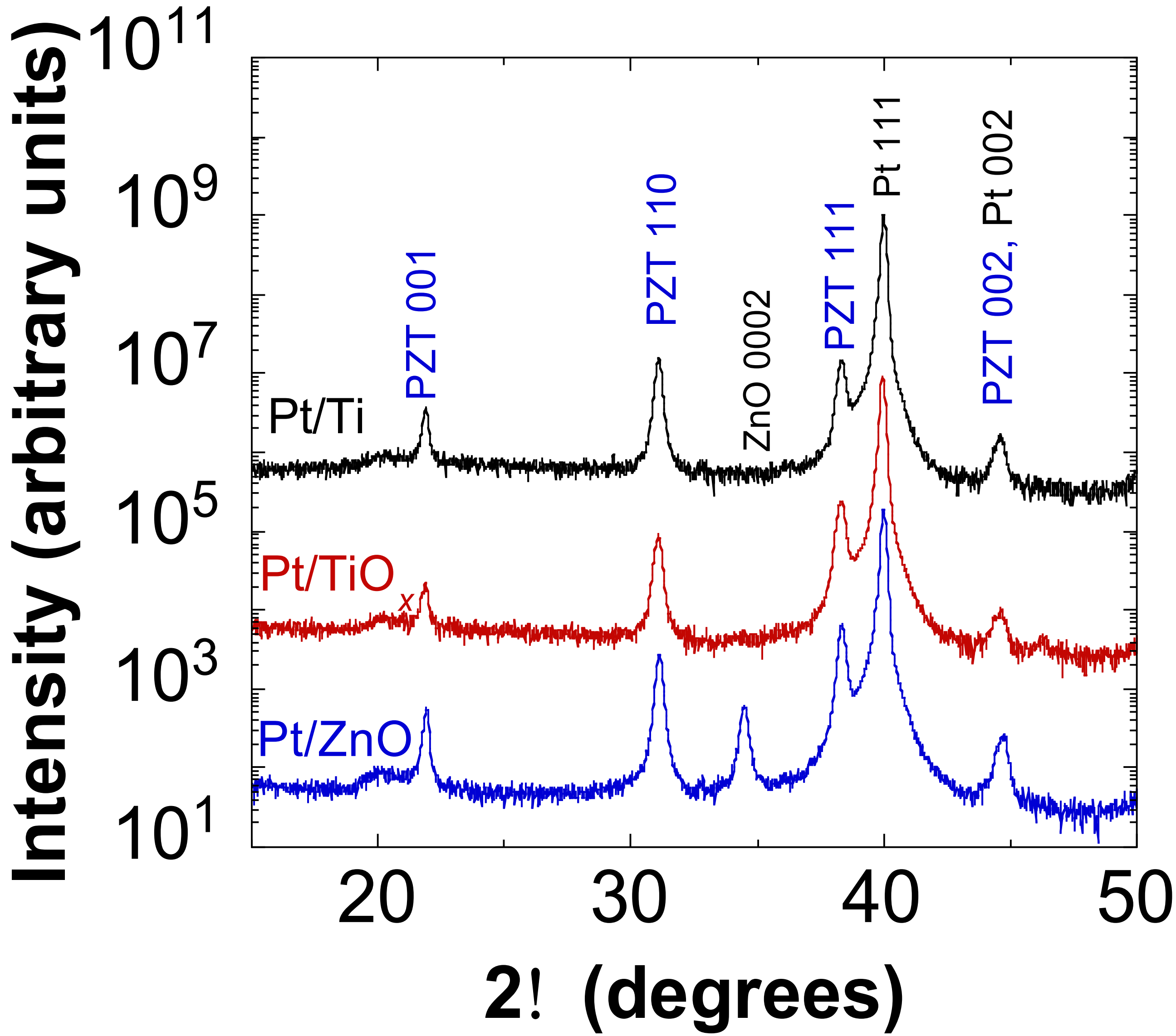
Sputter Pt electrodes



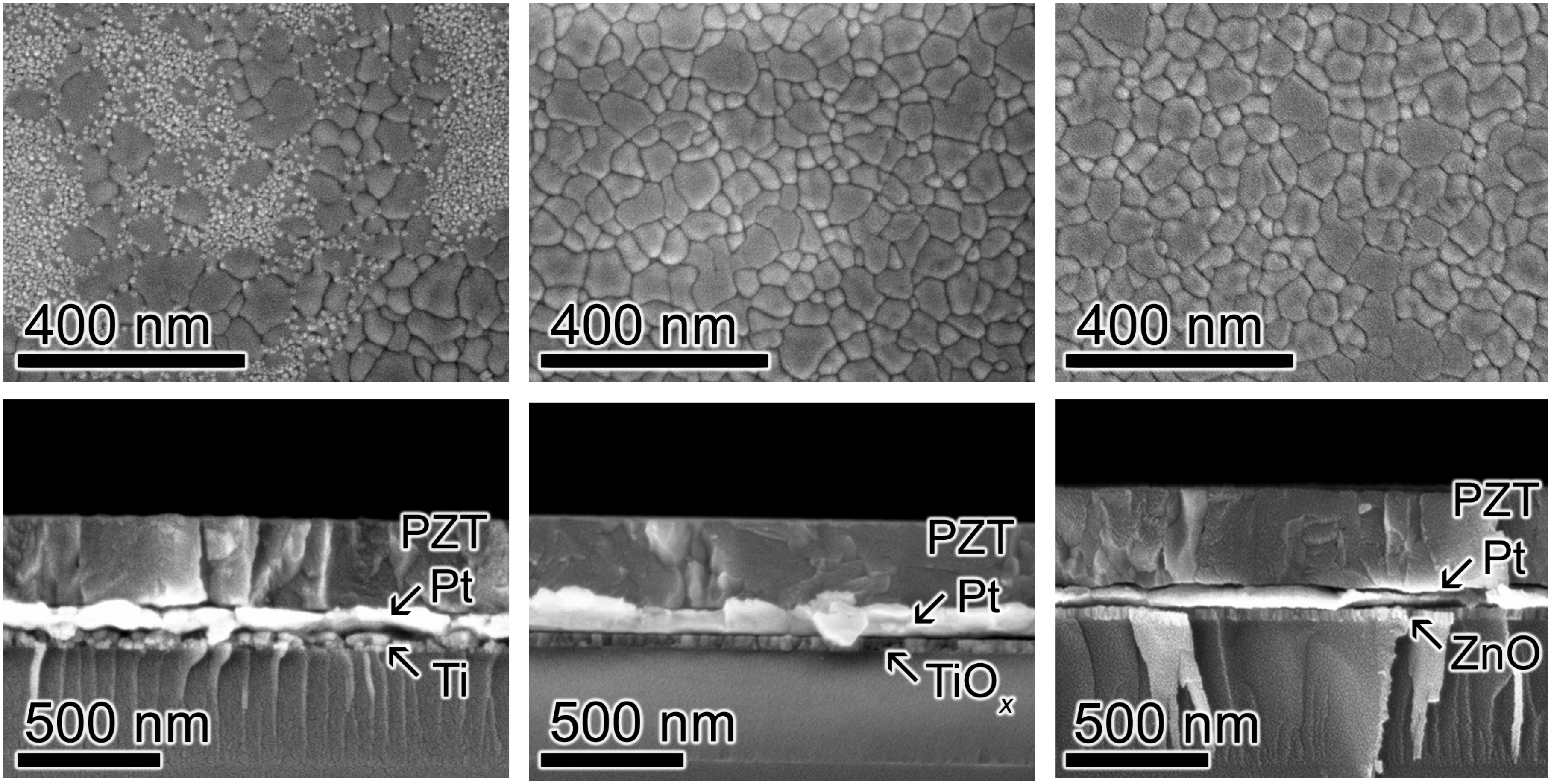
Spin Deposition



Film Phase/Crystallographic Properties

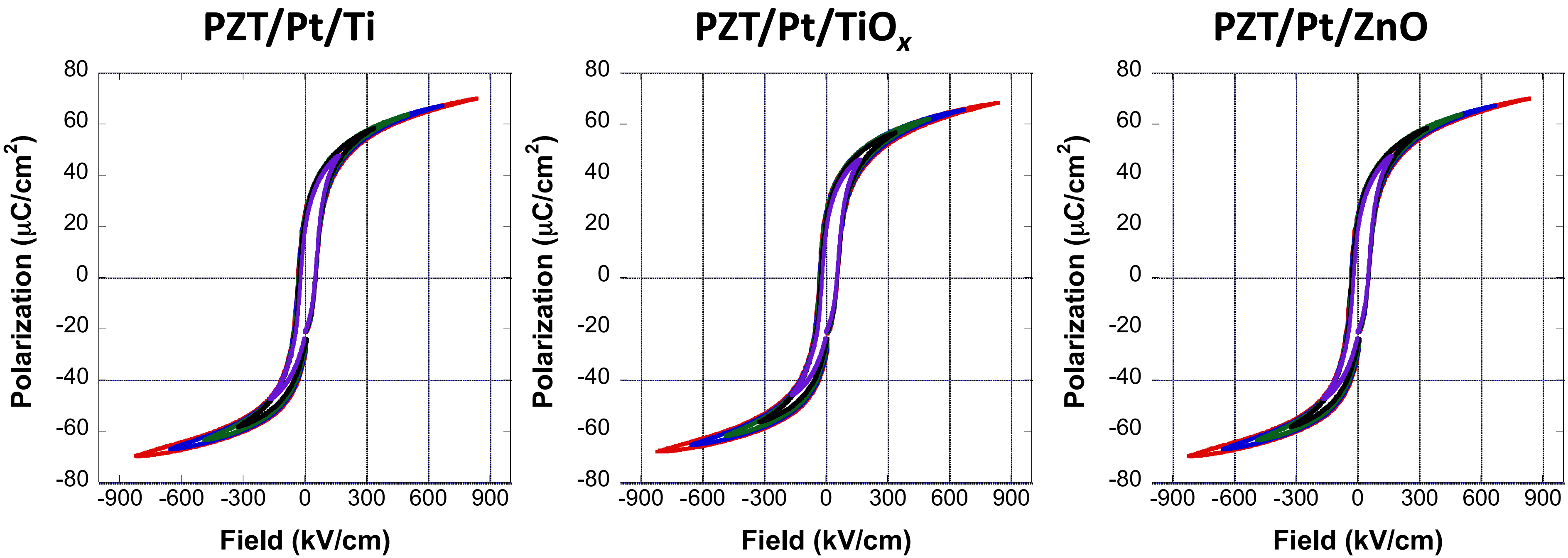


PZT Film Microstructure



C.T. Shelton and J.F. Ihlefeld *et. al.*, *Adv. Funct. Mater*. **22**, 2295-2302 (2012)

Dielectric and Ferroelectric properties

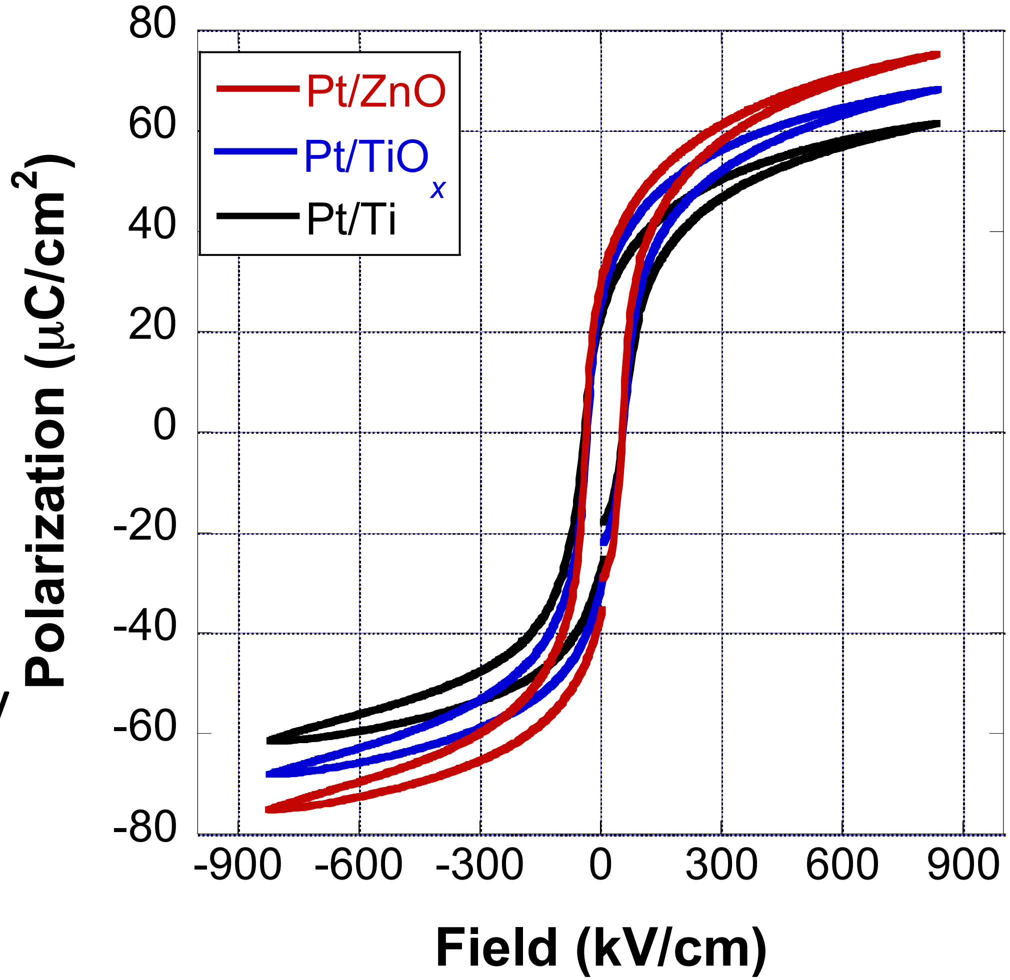


- Measurements conducted at 10 Hz
- All films saturate well
- Low leakage

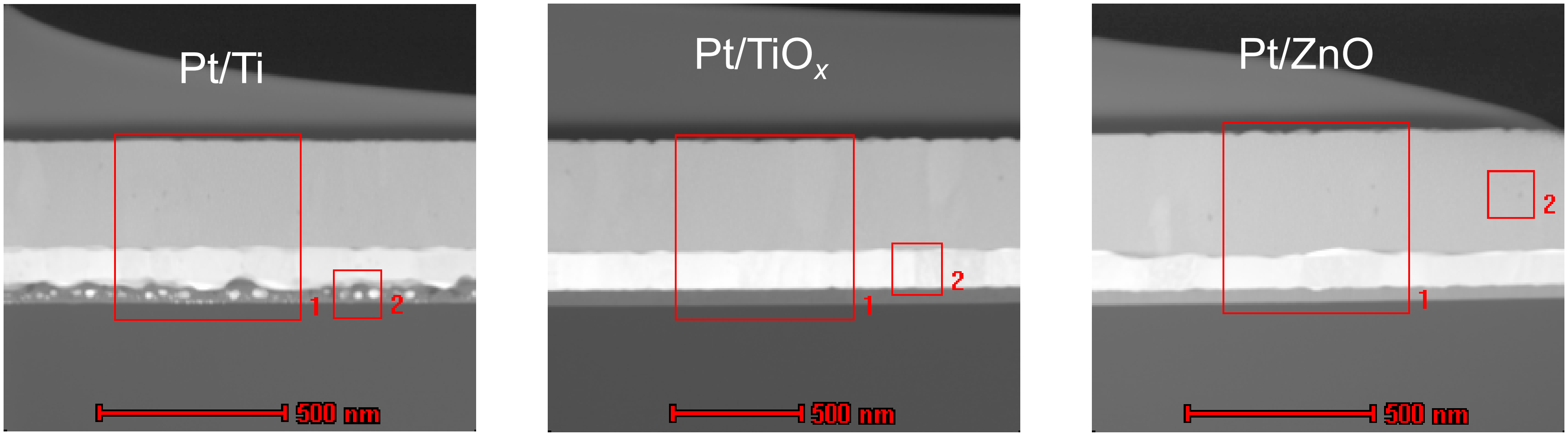
PZT Films Ferroelectric Properties: Pt/ZnO Substrates Superior

	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**

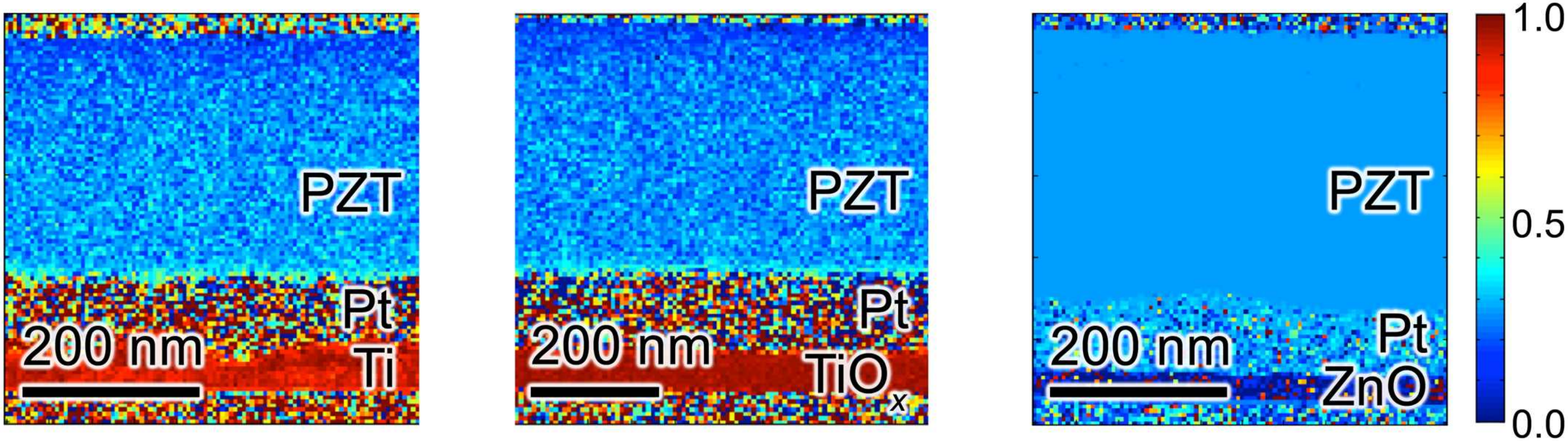
- Both P_r and K increase on ZnO-buffered substrates
- Coercive field decreases slightly for PZT on ZnO-buffered substrates



PZT Composition Analysis: No Composition Gradient on Pt/ZnO

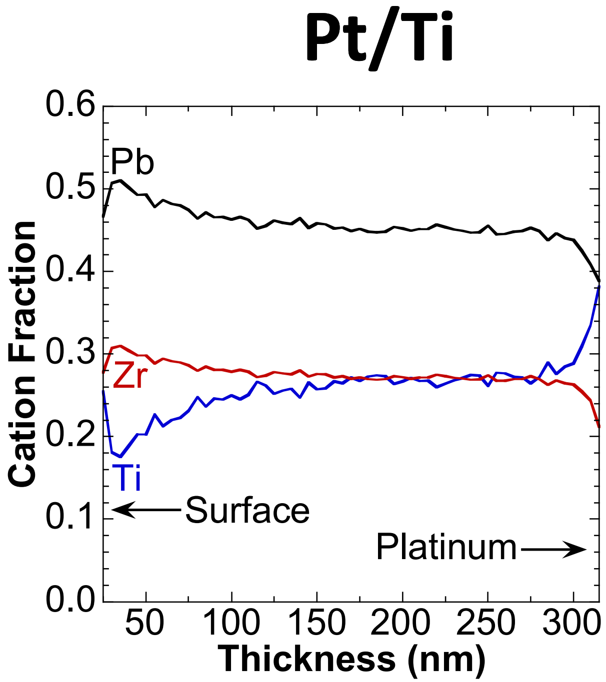


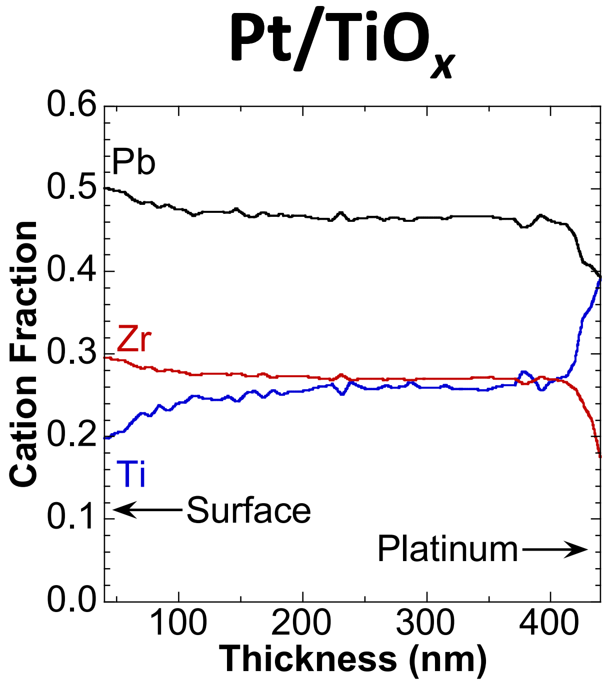
Titanium Distribution

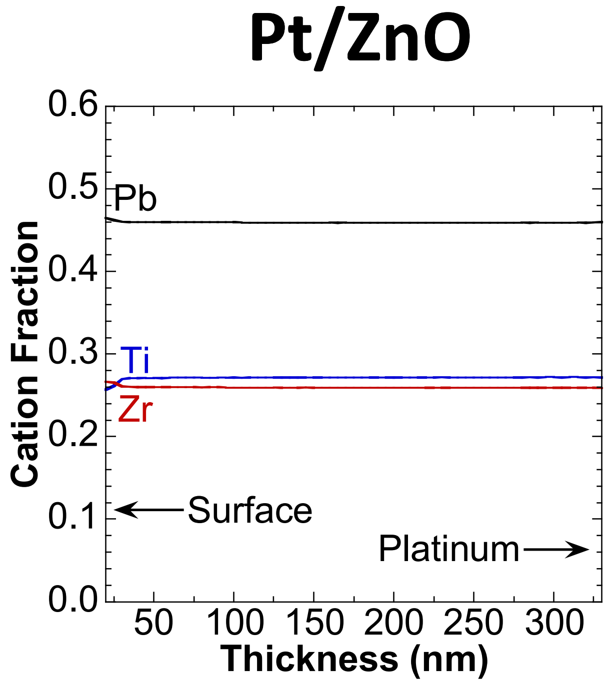


C.T. Shelton and J.F. Ihlefeld *et. al.*, *Adv. Funct. Mater*. **22**, 2295-2302 (2012)

PZT Composition Analysis: No Composition Gradient on Pt/ZnO







Substantially improved chemical homogeneity in films on Pt/ZnO substrates

Chemical Homogeneity Effects on Electronic Properties

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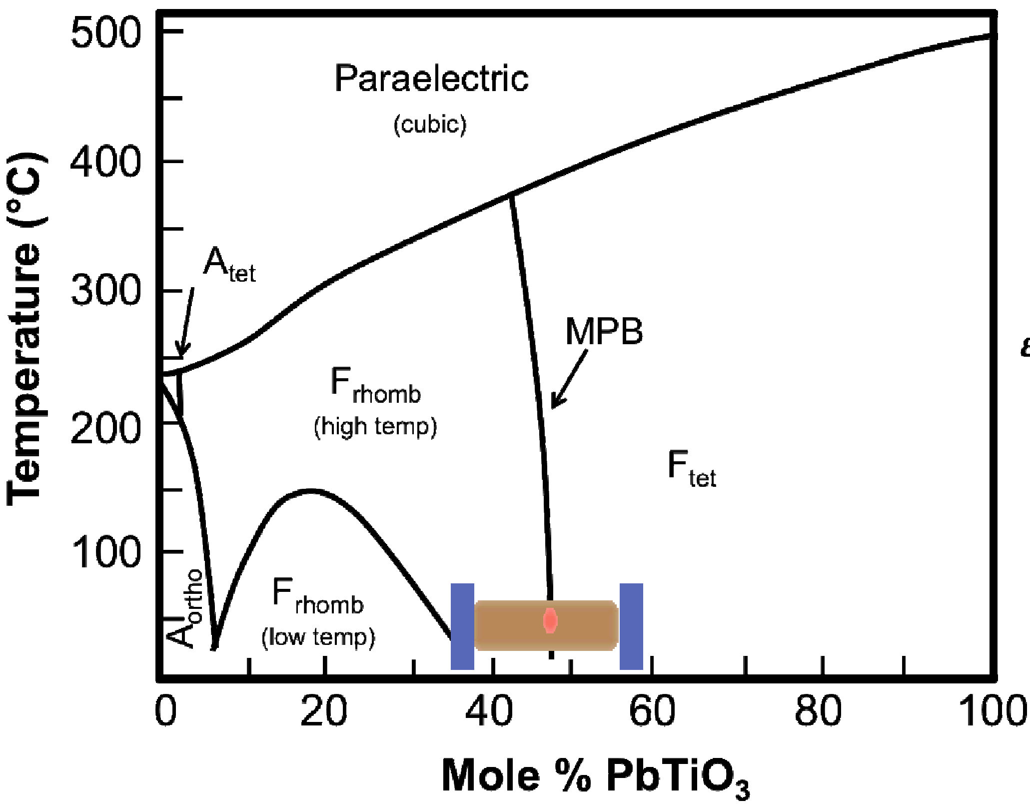
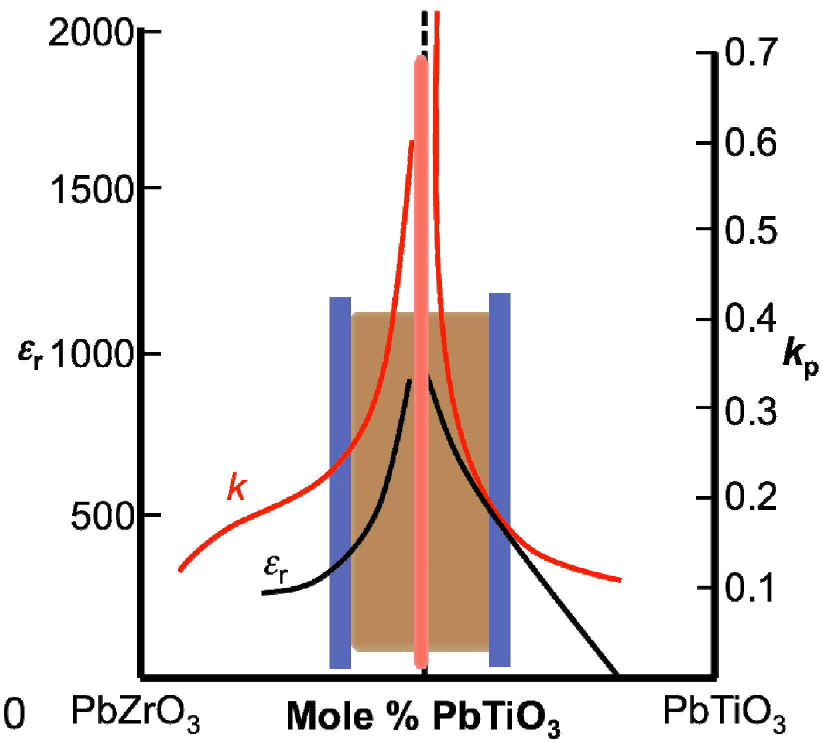
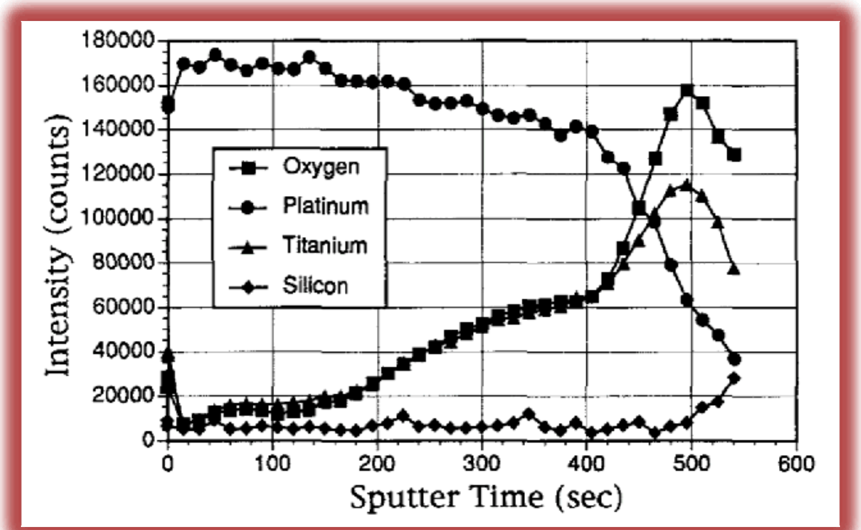


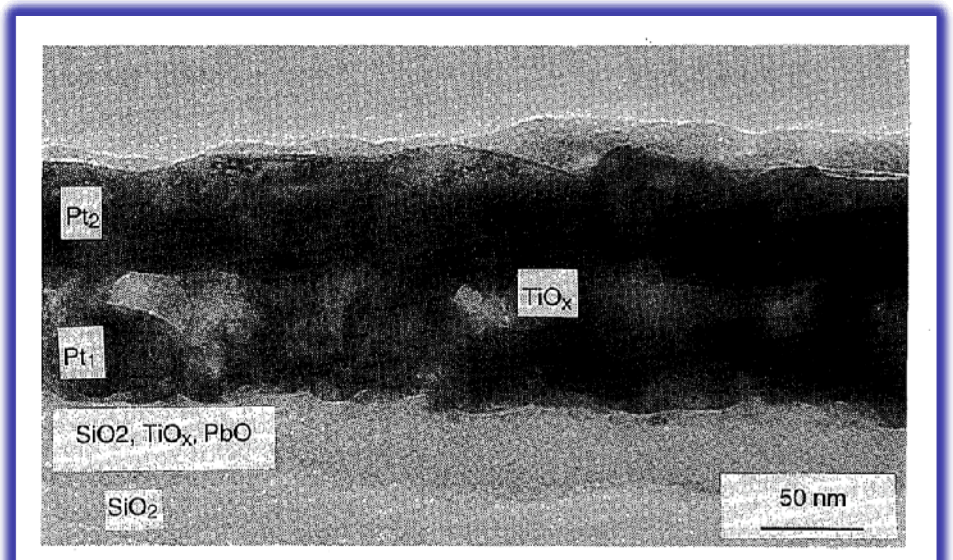


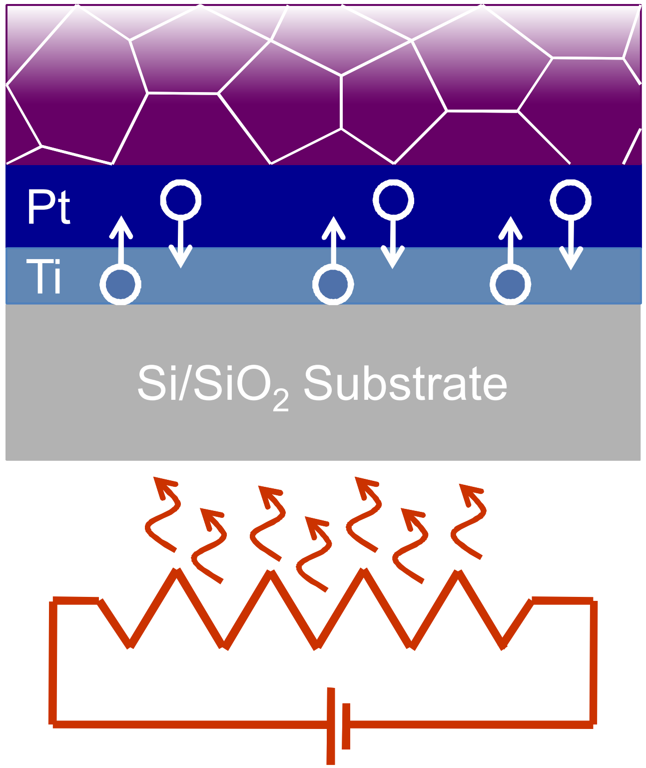
Increased dielectric and ferroelectric response directly correlates with improved homogeneity*

* Consistent with Calame and Muralt, *Appl. Phys. Lett*. **90**, 062907 (2007)

Revising prior art: Ti diffuses into Pt!



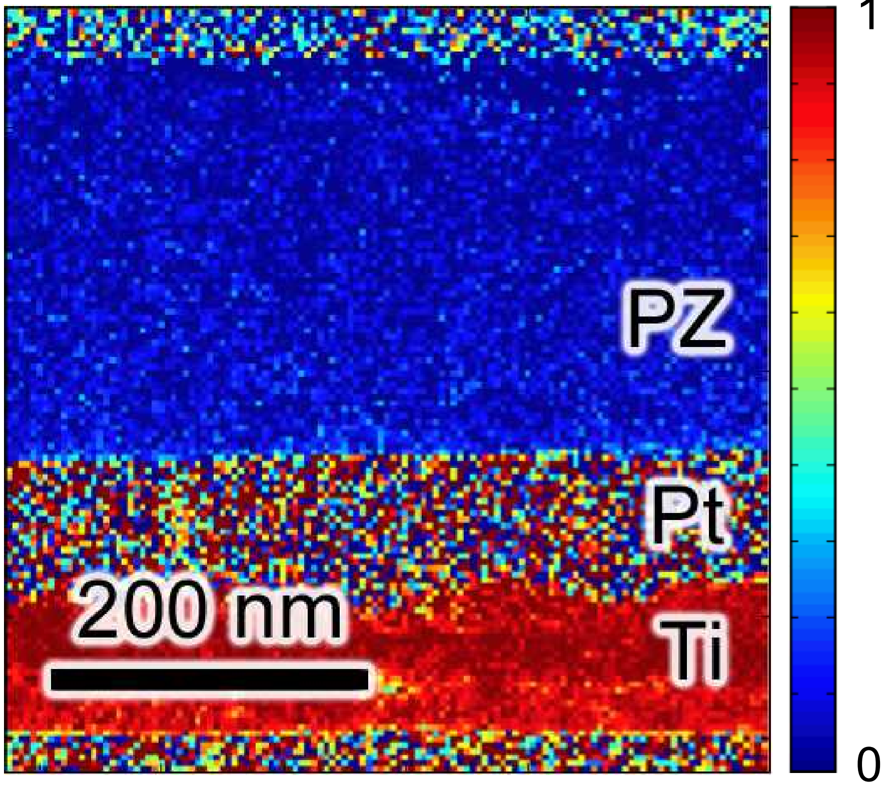




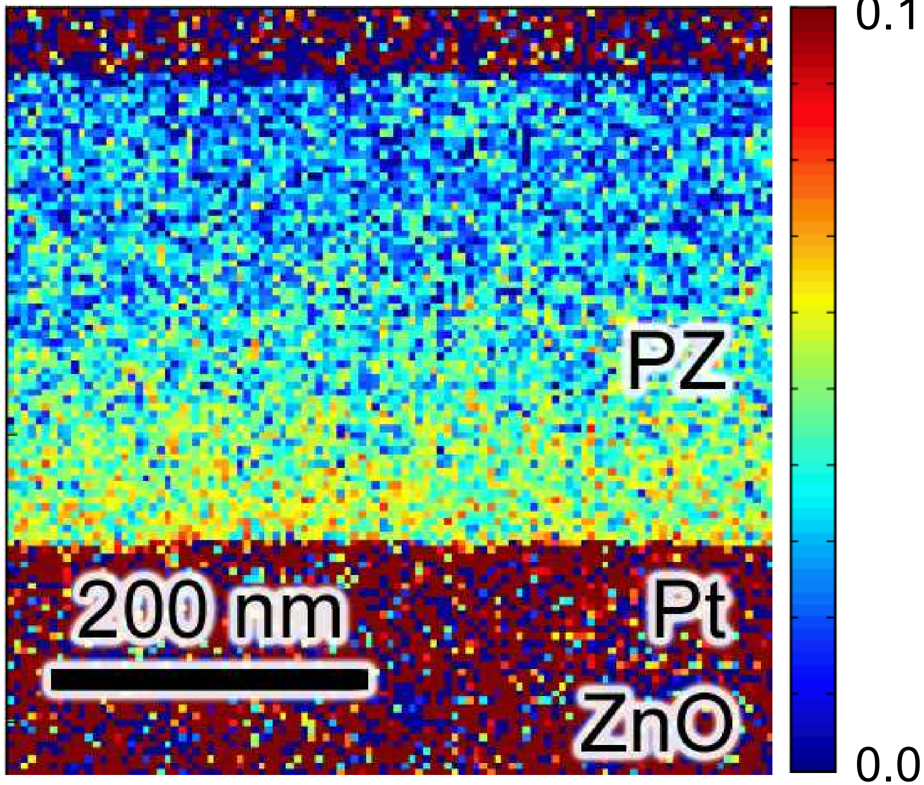
Ti diffusing through Pt can incorporate into the PZT Film

Test for Gradient Mechanism: $PbZrO_3$

PZ/Pt/Ti

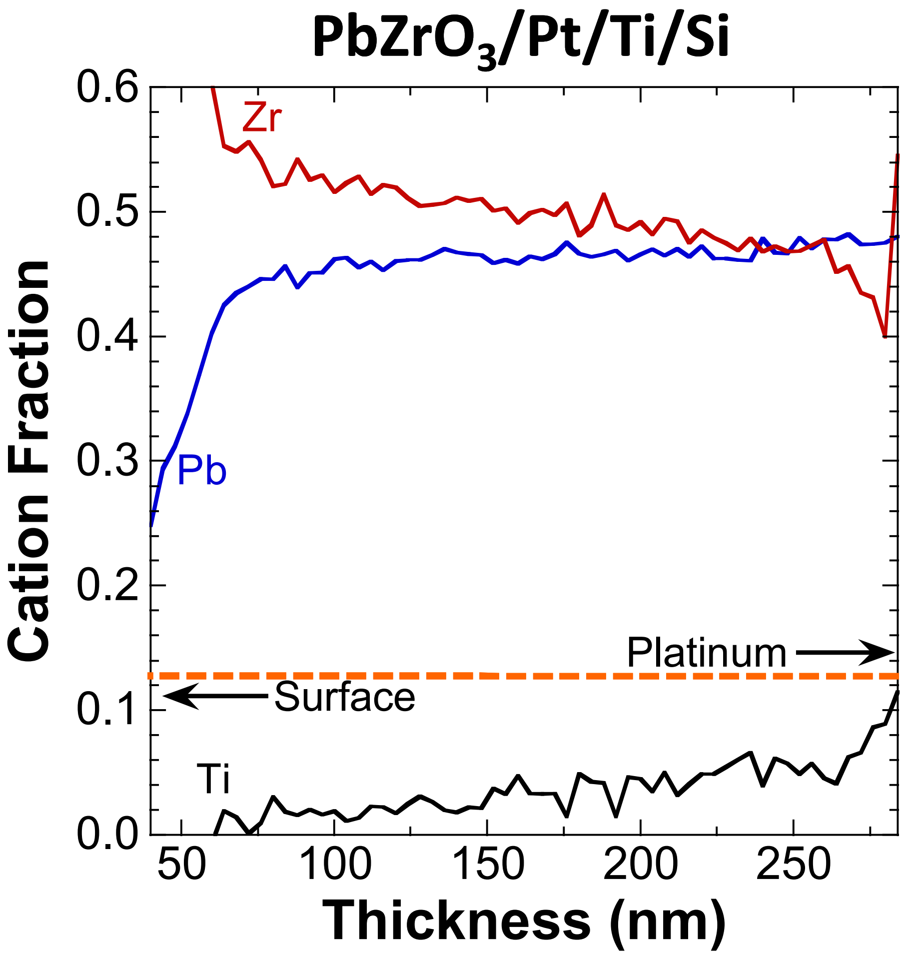


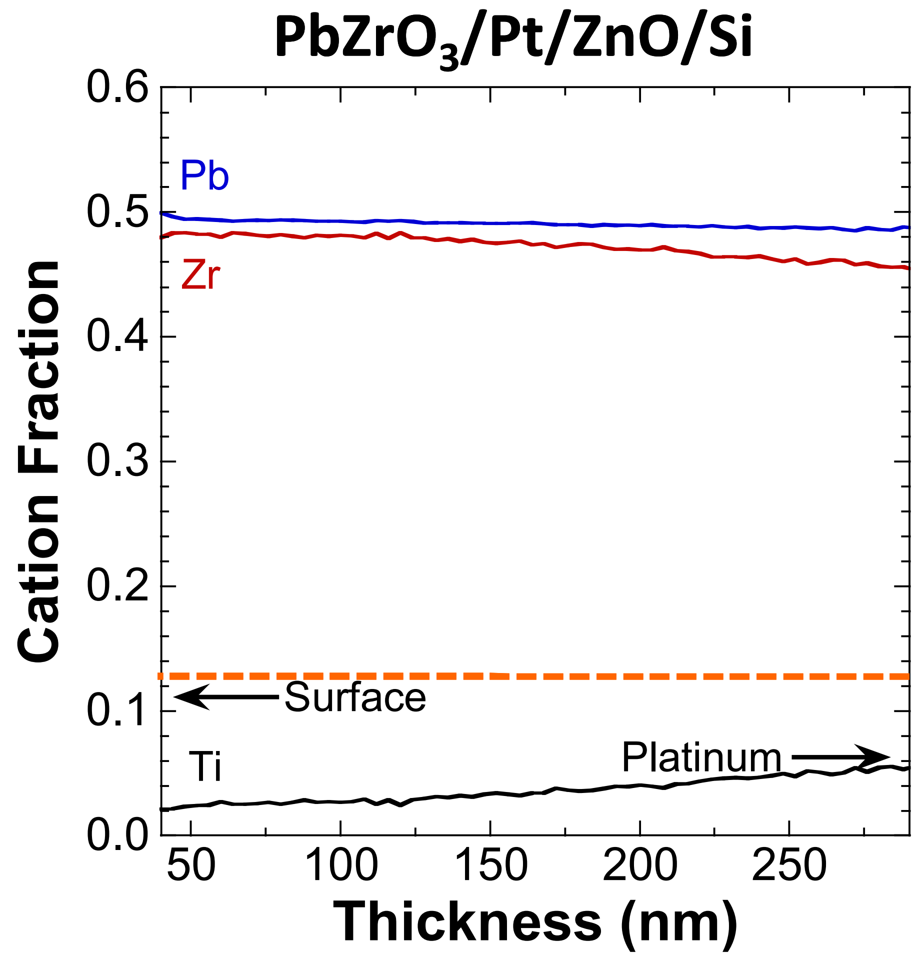
PZ/Pt/ZnO



Note Scale Difference

Mechanism: Ti Diffusion from Adhesion Layer: Test with $PbZrO_3$



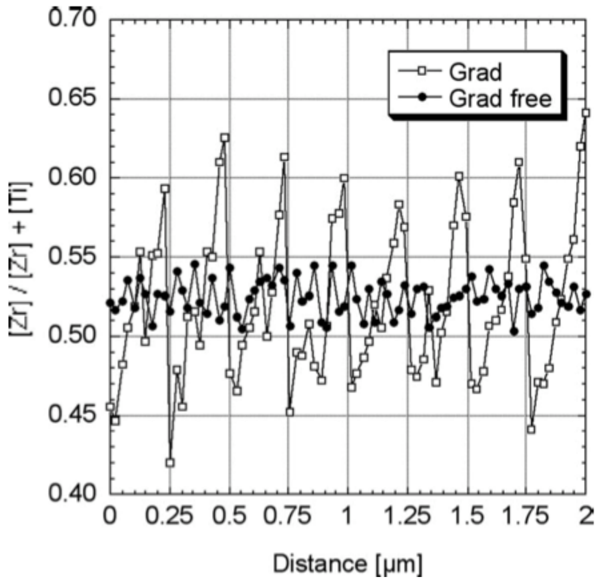


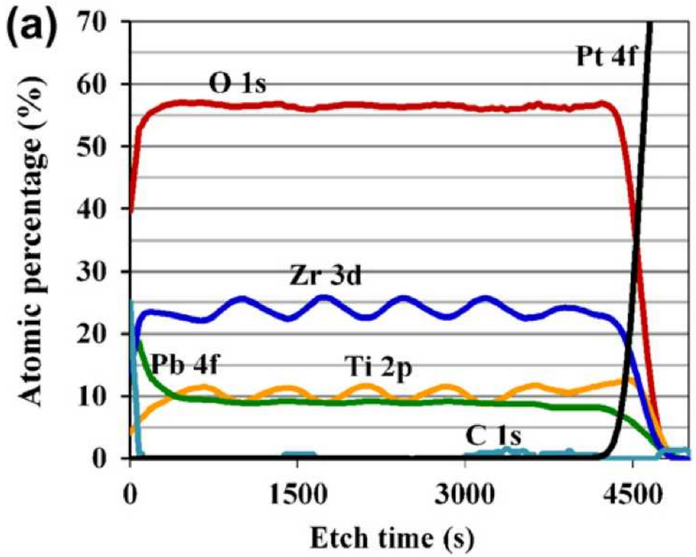
Less Ti and smaller gradient on Pt/ZnO

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
  - Heating Method/Rate: 15, 50, 200°C/s





*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)

‡Based upon: C.D.E. Lakeman and D.A. Payne, JACerS, **75(11)**, 3091 (1992)

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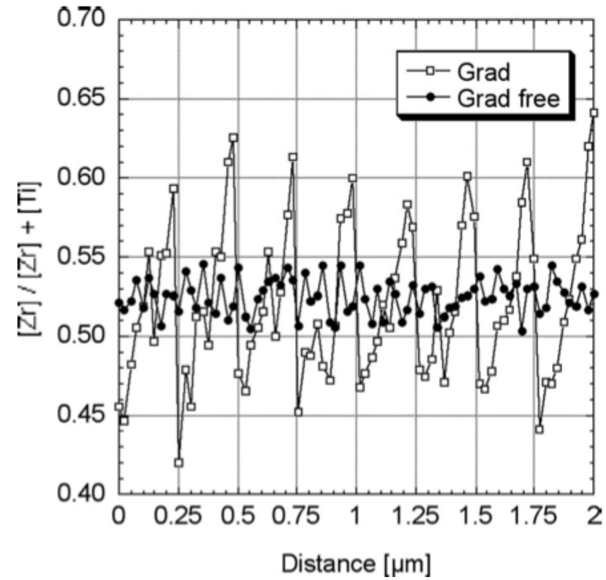

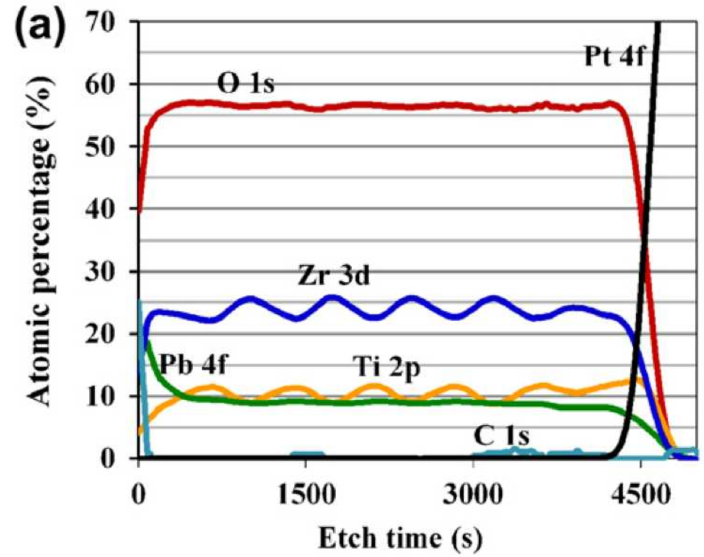

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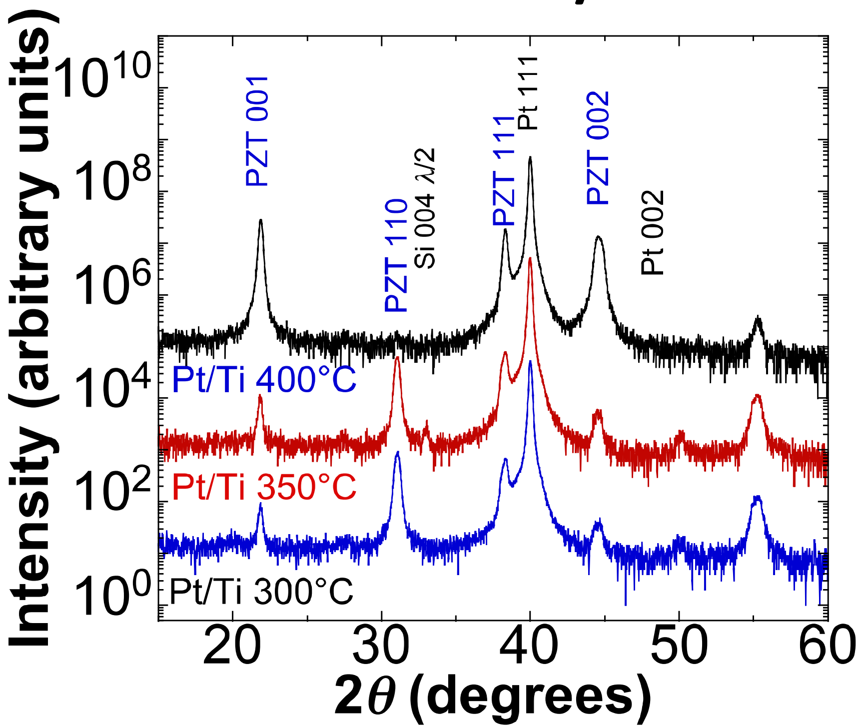
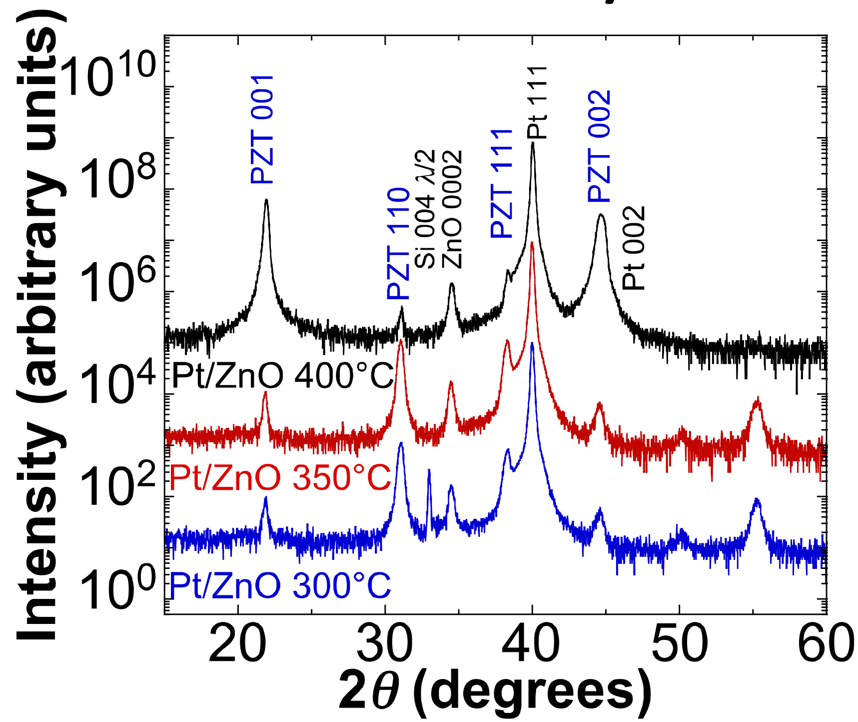
Pyrolysis Effects: Texture

IMO on Pt/Ti



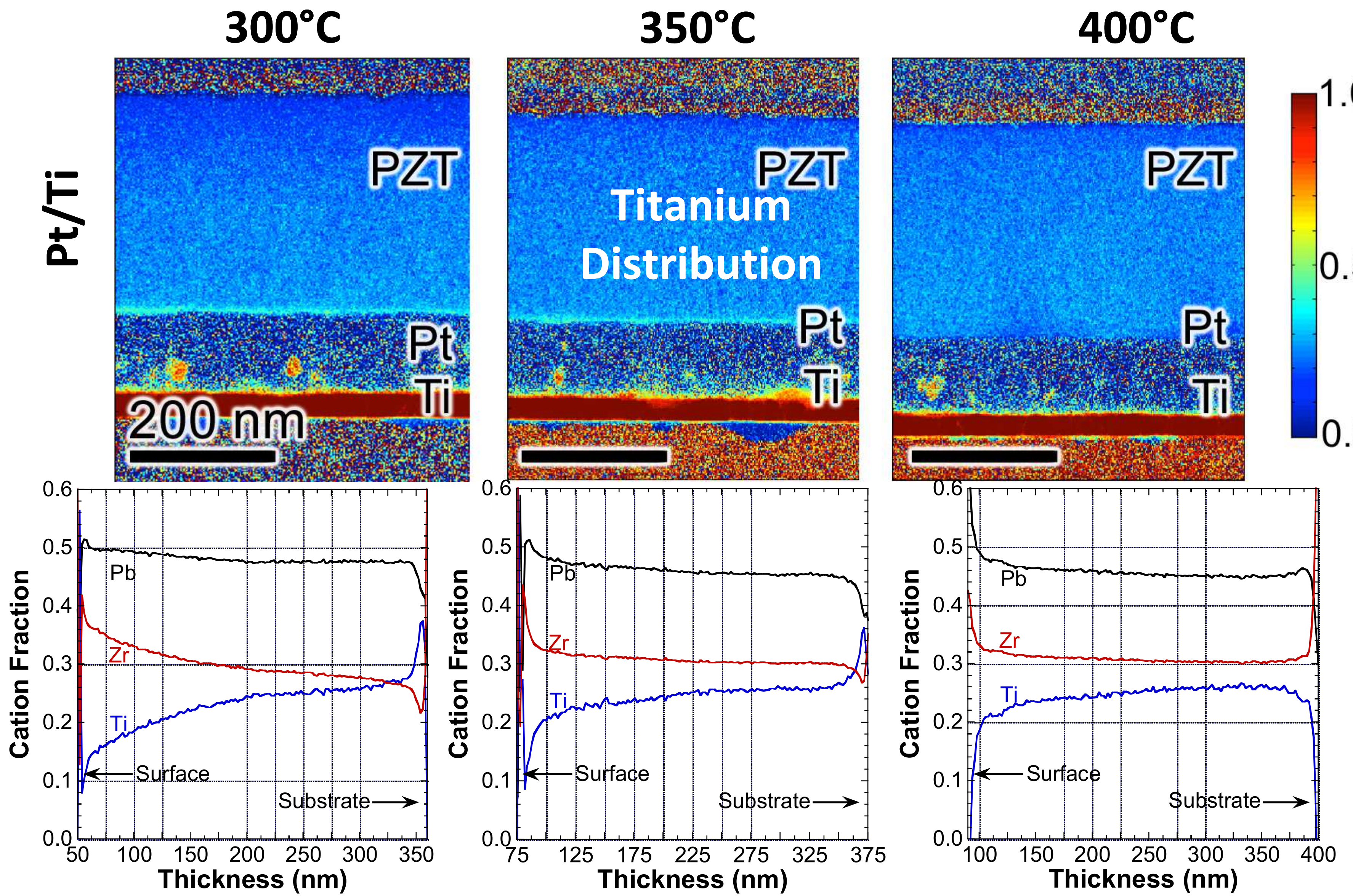
2-MOE on Pt/ZnO



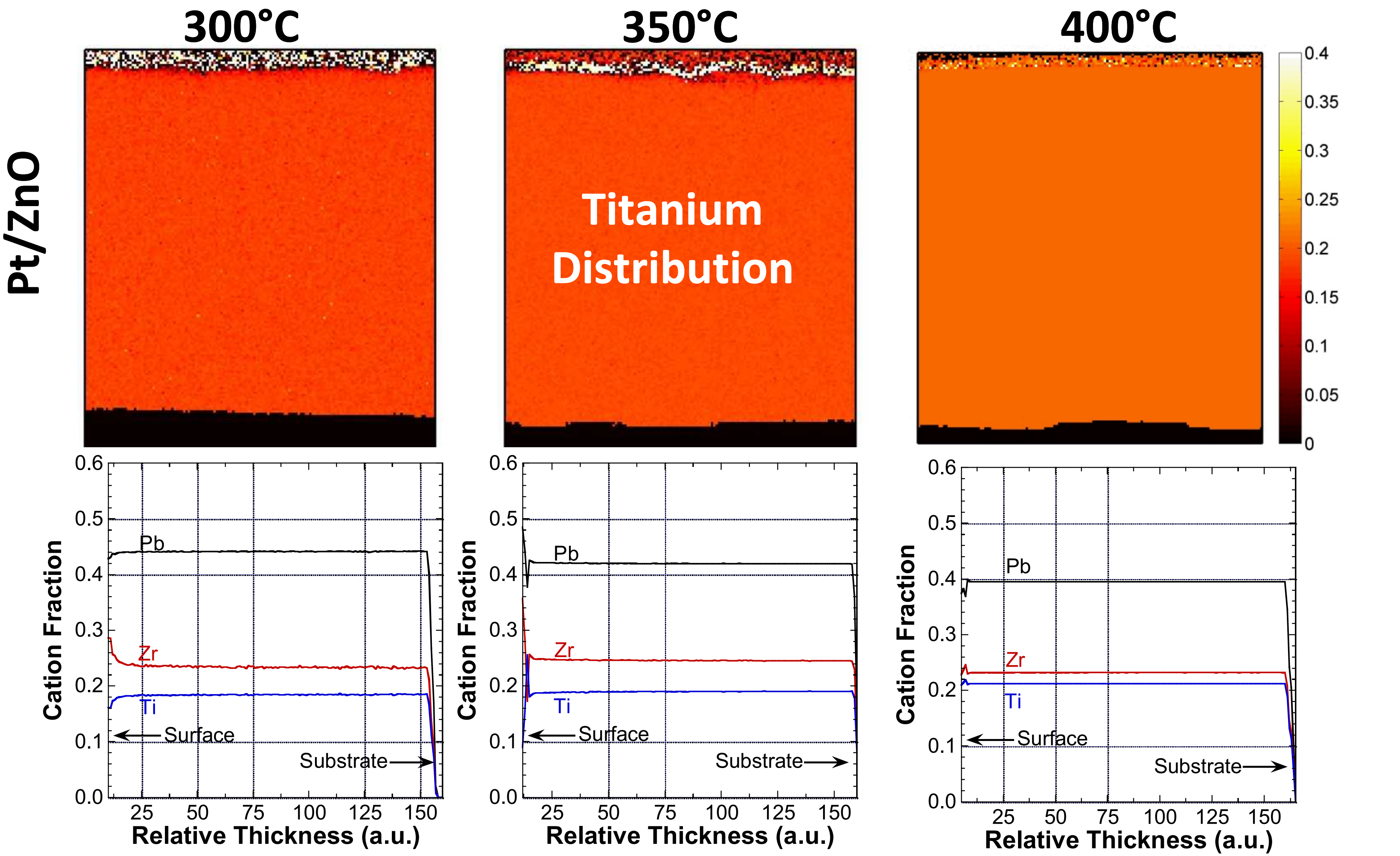
- Pyrolysis temperature affects texture
- No apparent difference with substrate or chemistry
- Consistent with previous work*

*Brennecka, et *al.*, *Proc. 14th US-Japan*, 136 (2009) *Chen and Chen, *JACerS*, **81** (1) 97-105 (1998)

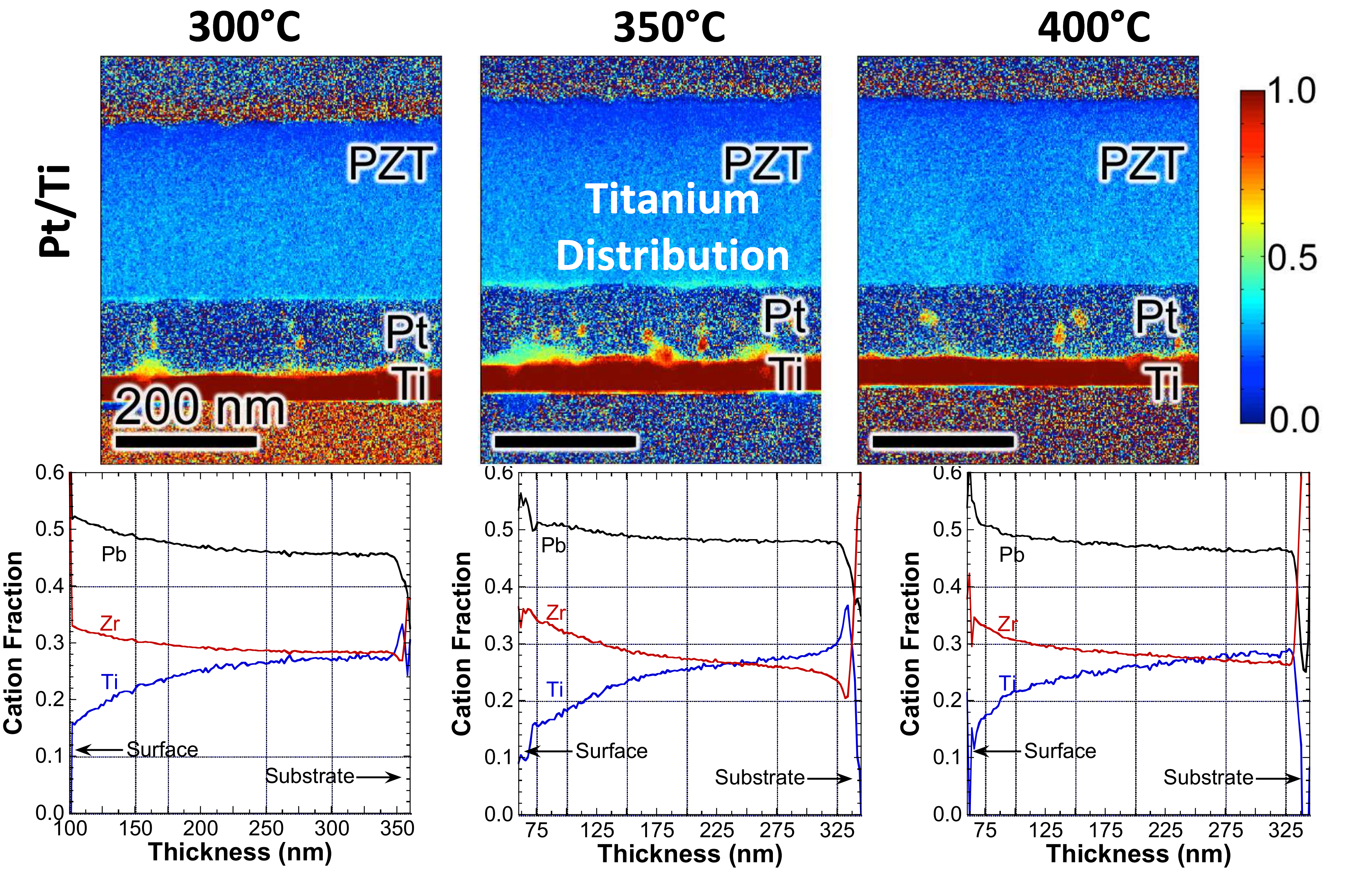
Solution Chemistry Effect: IMO films



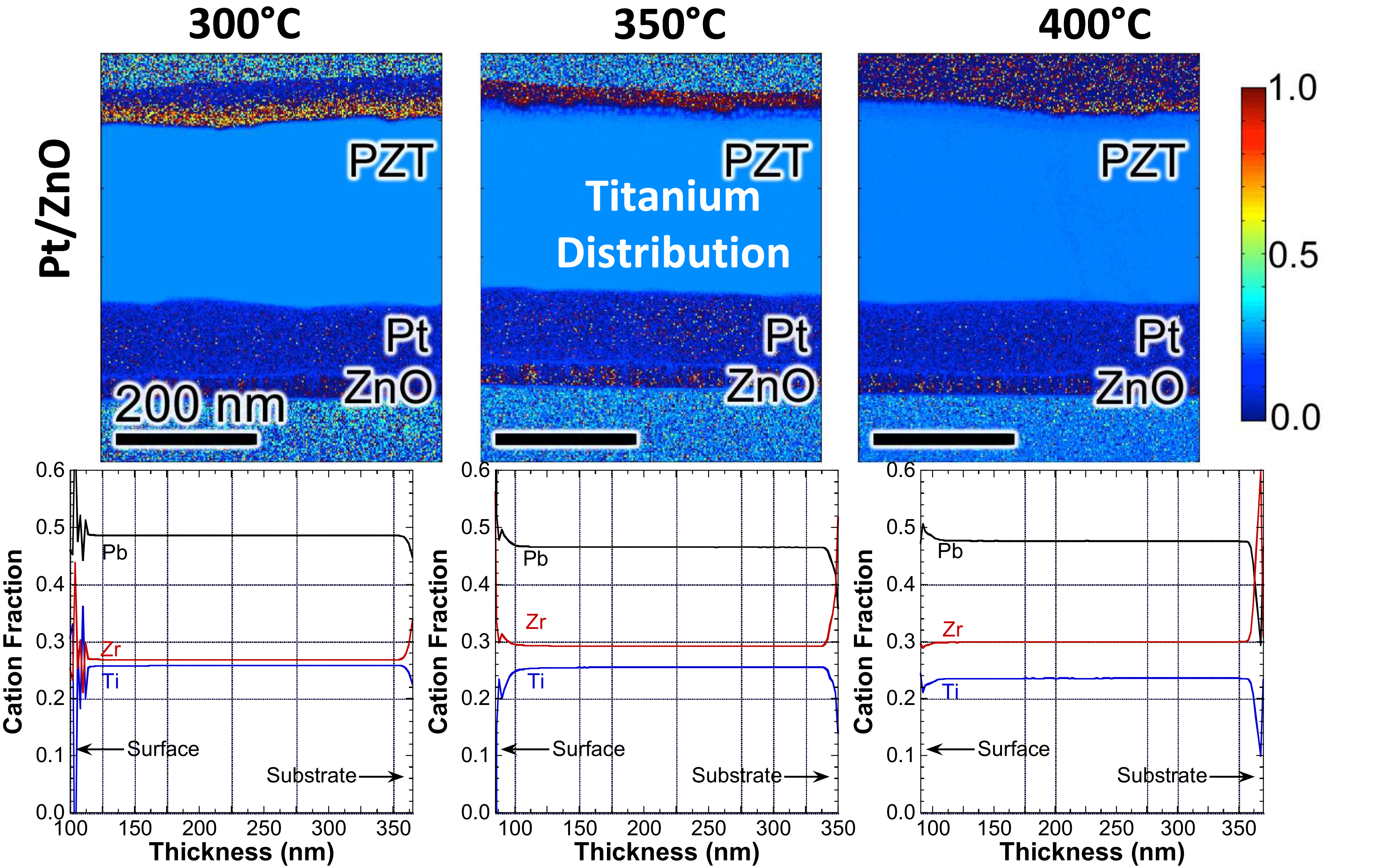
Solution Chemistry Effect: IMO Films



Solution Chemistry Effect: 2-MOE films



Solution Chemistry Effect: 2-MOE films



Solution Chemistry Effects?

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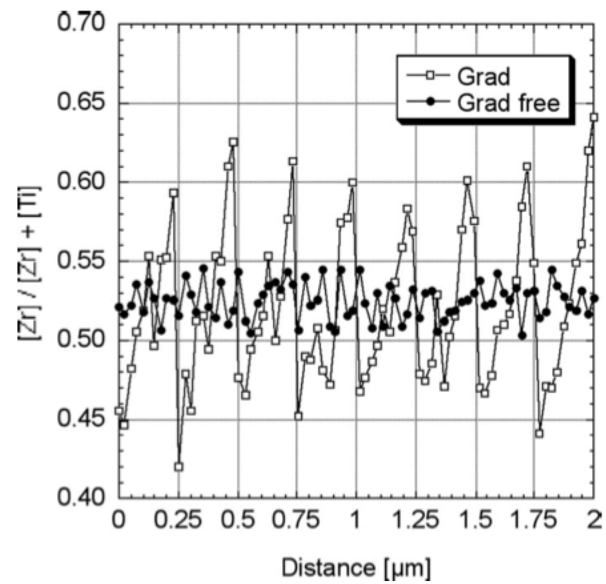
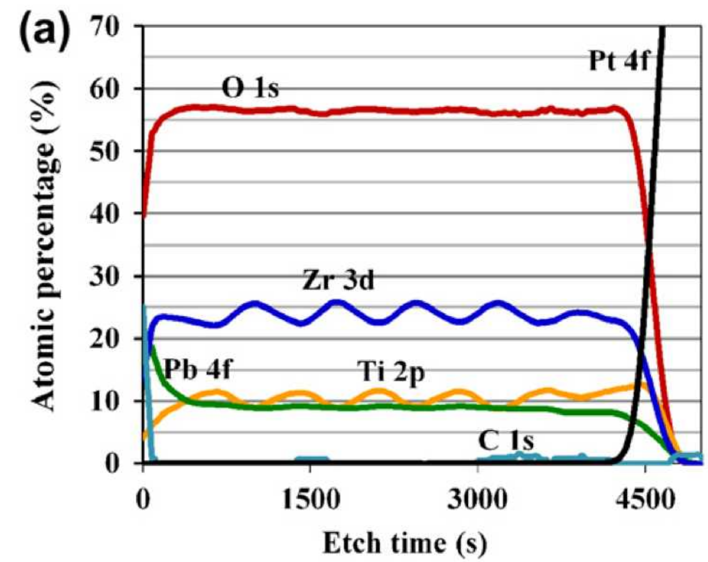
- This model cannot explain ‘saw-tooth’ profiles observed by other groups*
- What roles do solution chemistry and processing conditions play in gradient formation?
- More experiments necessary to isolate controlling variables
  - ~~Substrate: Pt/Ti vs Pt/ZnO~~
  - ~~Chemistry: IMO vs 2-MOE~~‡
  - ~~Pyrolysis: 300, 350, 400°C~~
  - ***Heating Method/Rate: 15, 50, 200°C/s via RTA***





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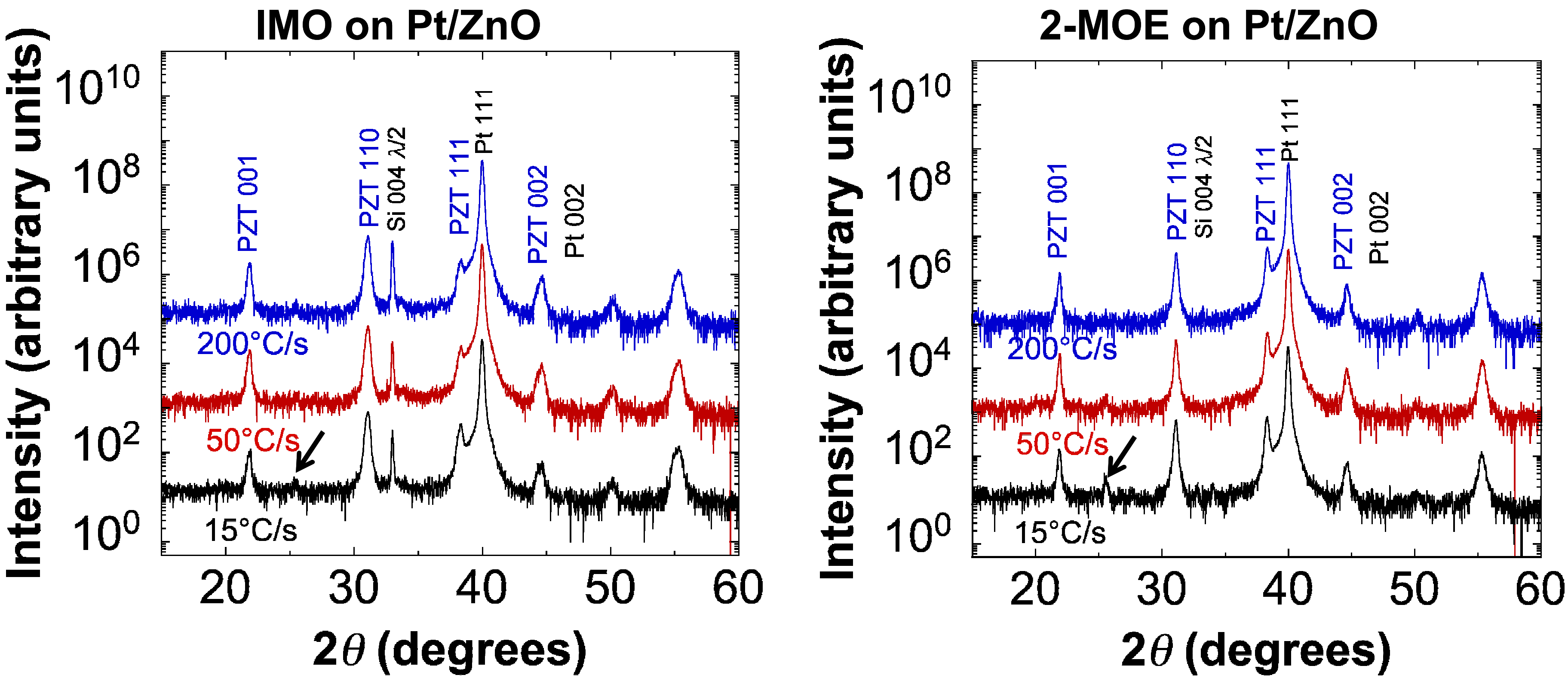
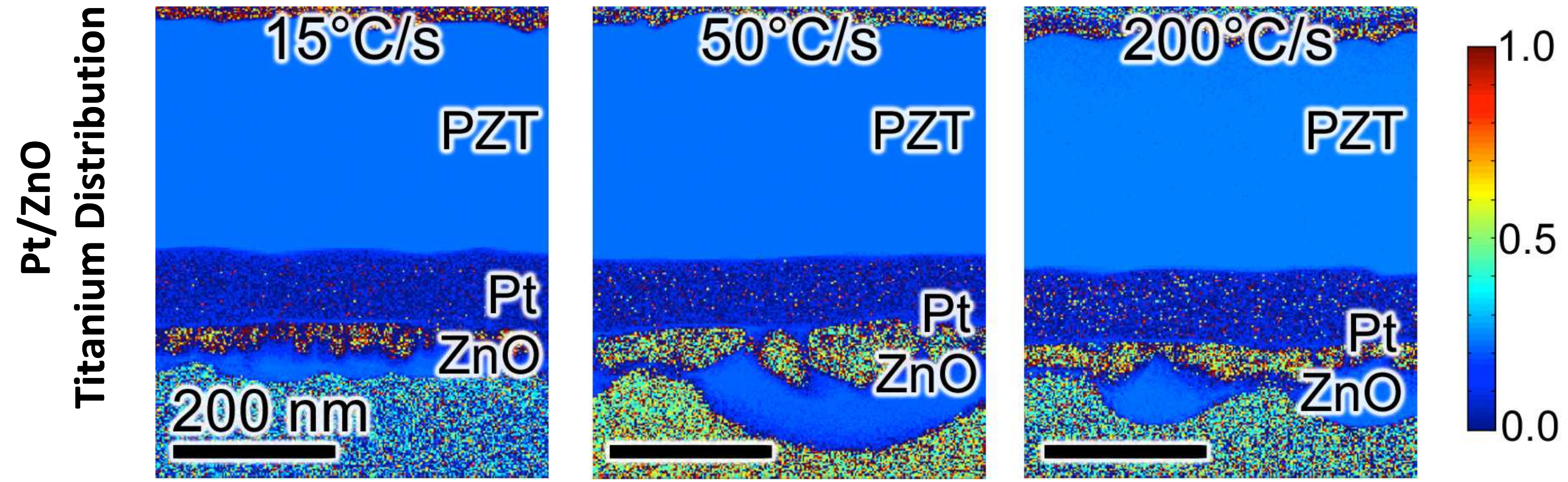
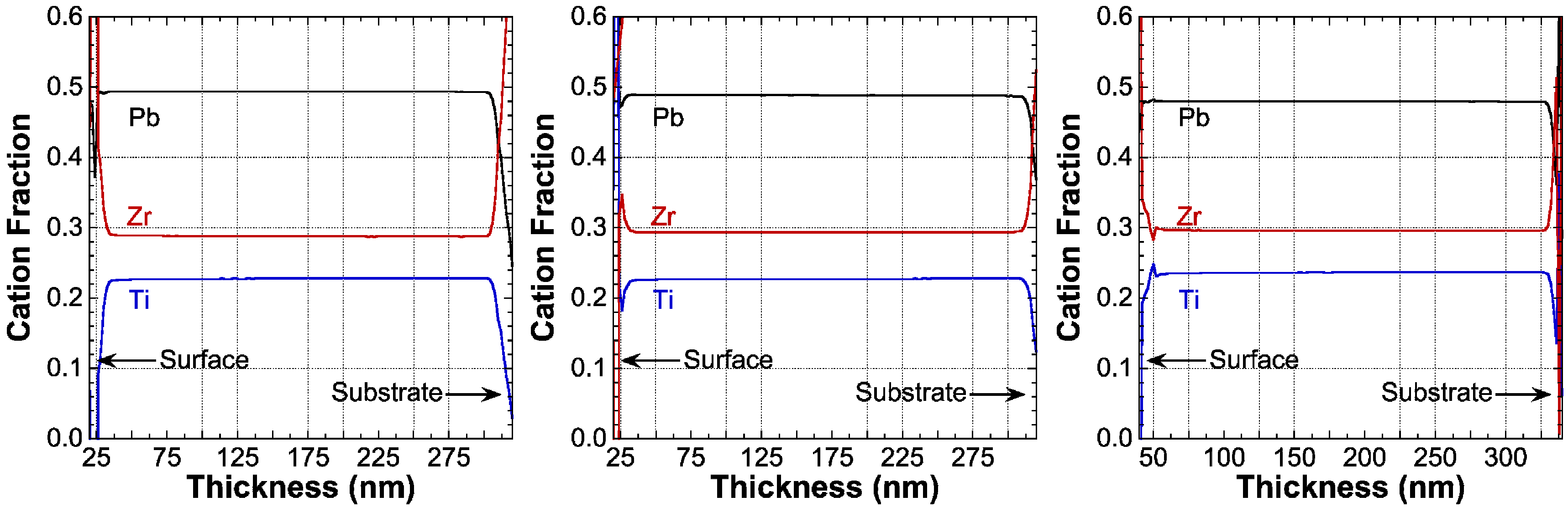
RTA Heating Rate Effects: Texture



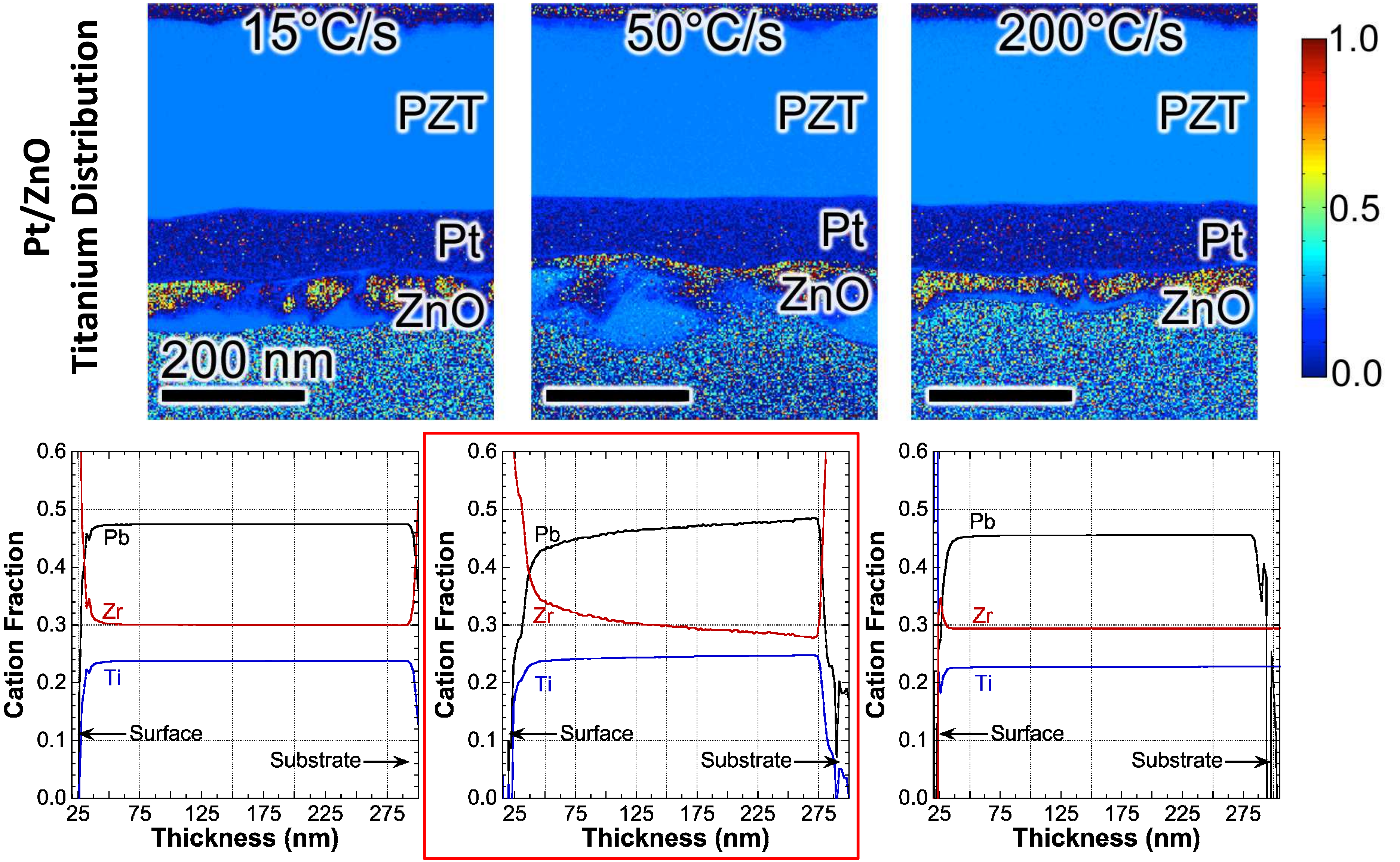
- No apparent heating rate dependence to texture
  - Consistent with previous studies*
- ZnO diffraction peaks no longer visible
- Additional peaks present in low ramp rate samples

Ramp Rate Effect: IMO Films

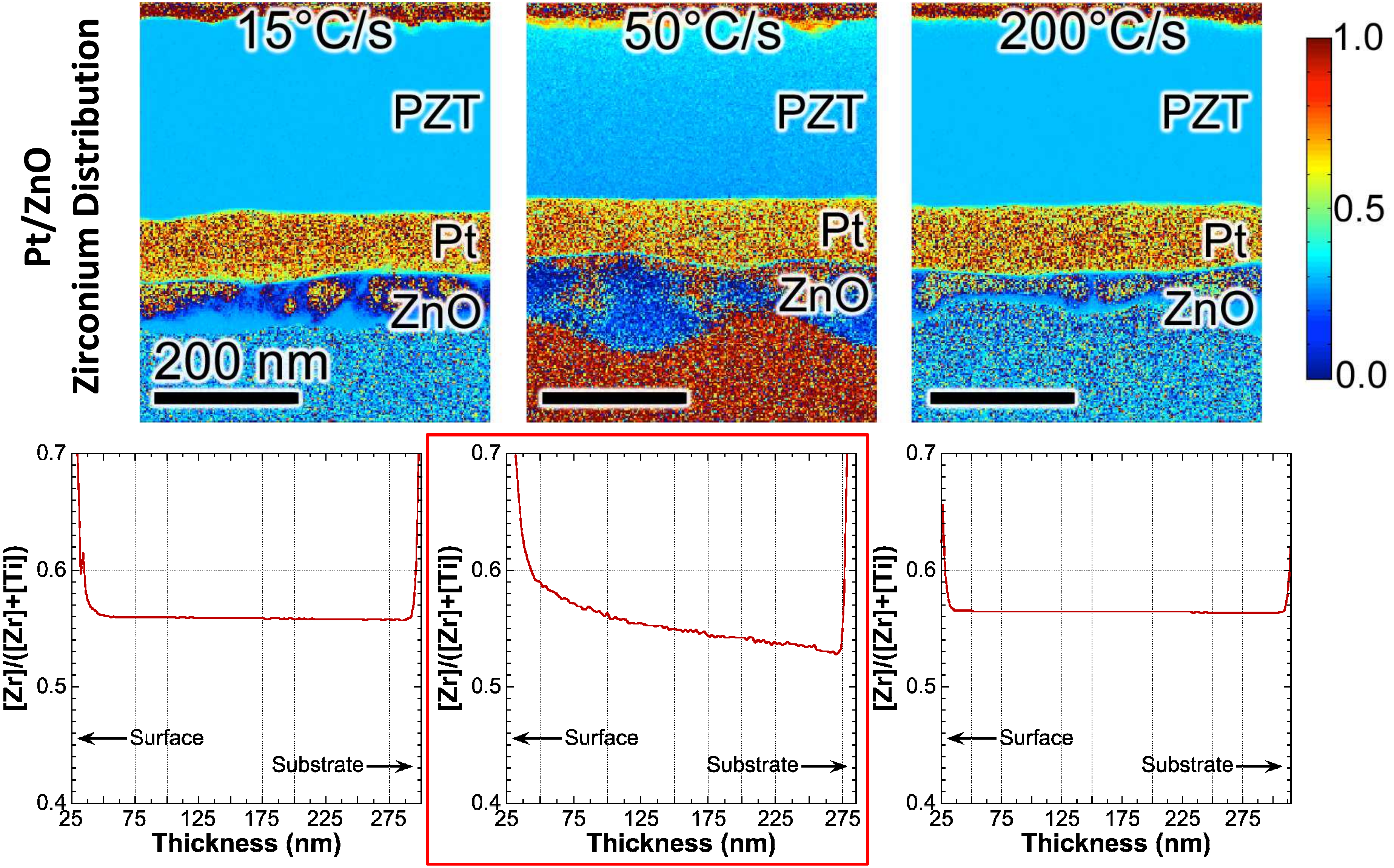




Ramp Rate Effect: 2-MOE Films

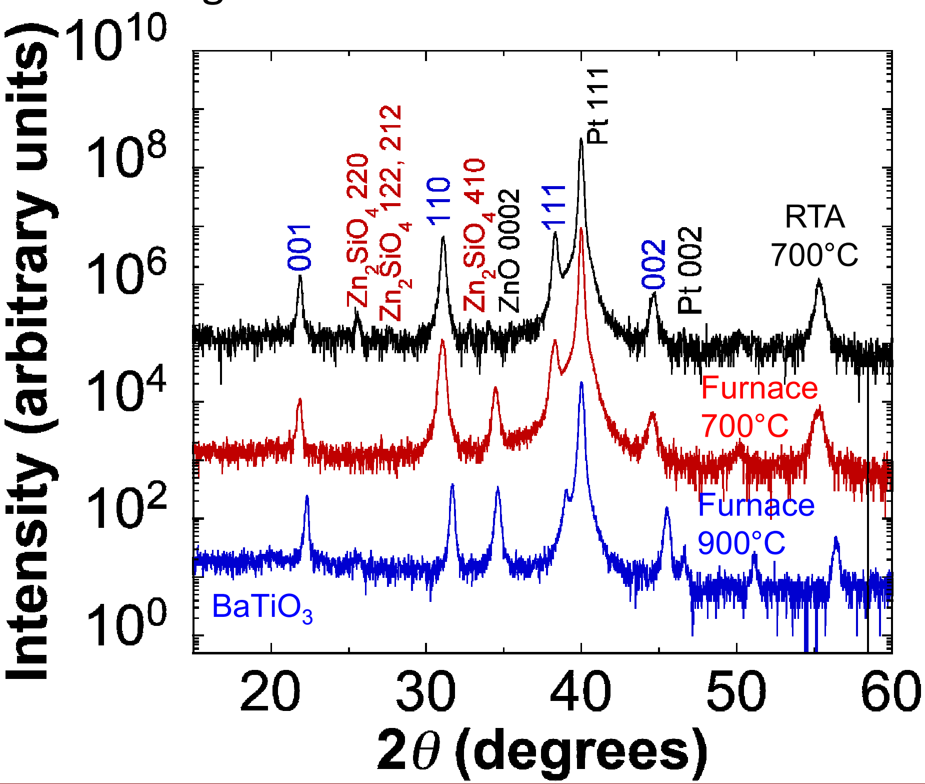


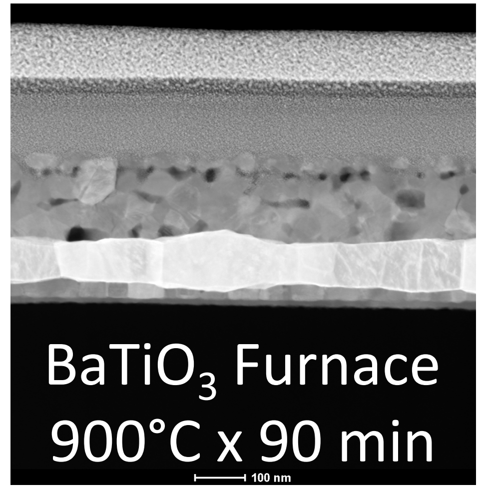
Ramp Rate Effect: 2-MOE Films

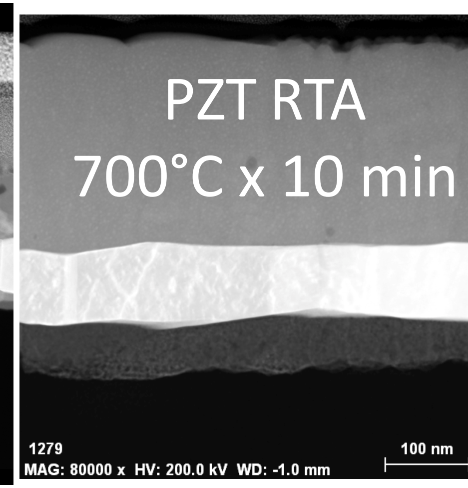


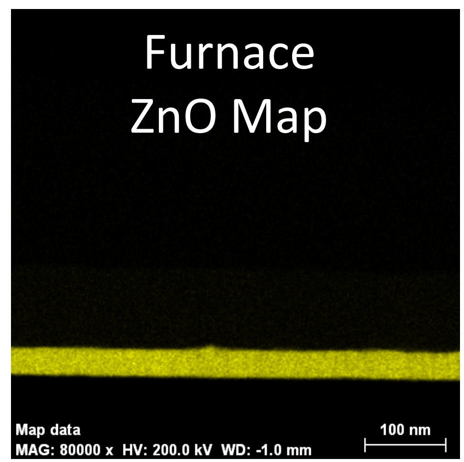
Interesting Observation: ZnO-SiO_2 Reaction

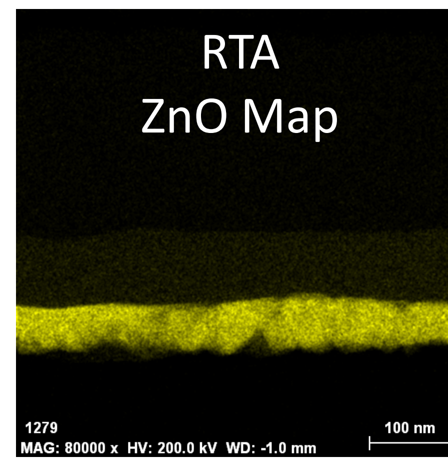
- Observe formation of secondary Zn_2SiO_4 phase in RTA samples
- Only previously observed this in films subjected to significantly higher thermal budgets





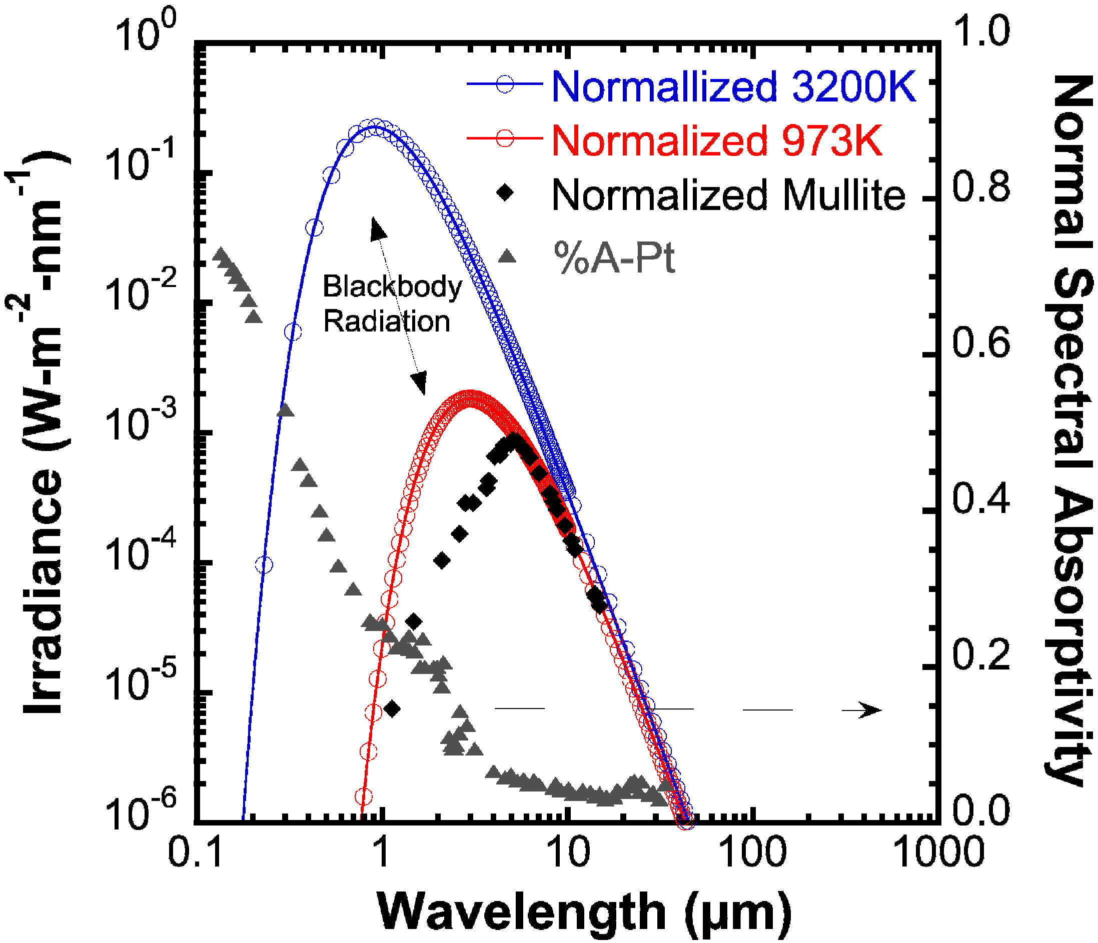






Interesting Observation: $ZnO-SiO_2$ Reaction

- Heating mechanism differs
  - RTA=Optical absorption
  - Furnace=optical+conductive
- ***Pt electrode may get substantially hotter than RTA thermocouple***
- ***Locally heating Pt likely affects film crystallization processes***



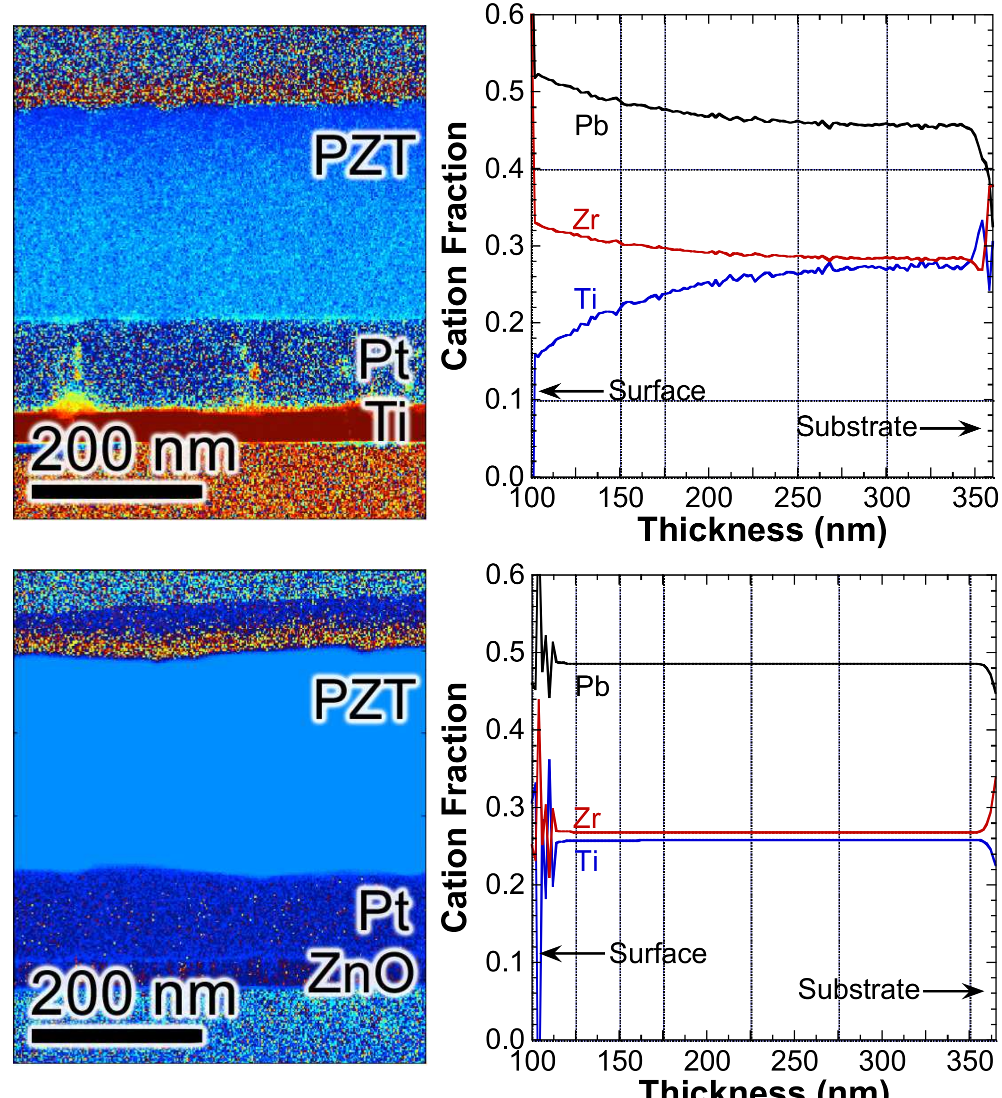
*Thermo-optical data calculated from: "Thermal Radiative Properties: Metallic Elements and Alloys," and "Thermal Radiative Properties of Nonmetallic Solids" by Y.S. Touloukian and D.P. Dewitt (1972)

Processing of PZT Film: Lessons Learned To Date

Sandia National Laboratories

<u>Open Issues:</u>

- Pyrolysis temperature does not significantly effect gradient formation
- On substrates devoid of a titanium adhesion layer, gradient formation appears to be hindered – even for 2-MOE sol-gel chemistries
- ***Heating rate and method*** ***does** appear to matter*
  - Slight gradient observed in RTA samples with 50°C/s ramp rate



Summary

- IMO PZT films prepared on Pt/ZnO substrates possess improved electronic properties compared to traditional substrates
- ZnO as an adhesion layer enables chemically homogeneous films for most processing conditions
- Titanium/TiO_x may be poor choices for Pt adhesion layers for the high performance device development
- ***If a chemically homogeneous film is required, then furnace anneals are preferable***