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

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Collaborators

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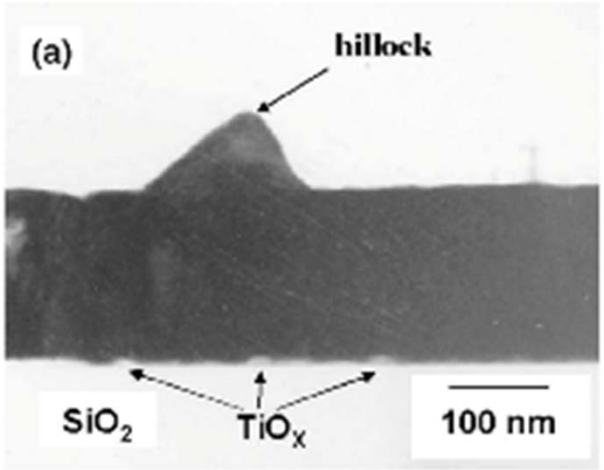
Microscopy

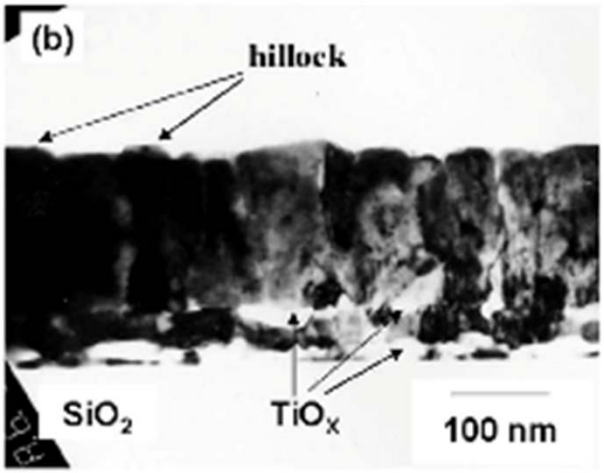
- Paul Kotula
- Bryan Gauntt
- Ping Lu
- Bonnie McKenzie
- Amy Allen
- Michael Rye

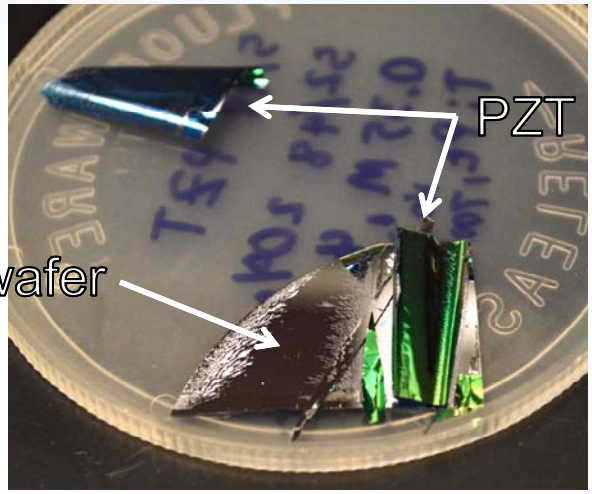
Solution/Film Preparation

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

Issues with Platinized Silicon Substrates





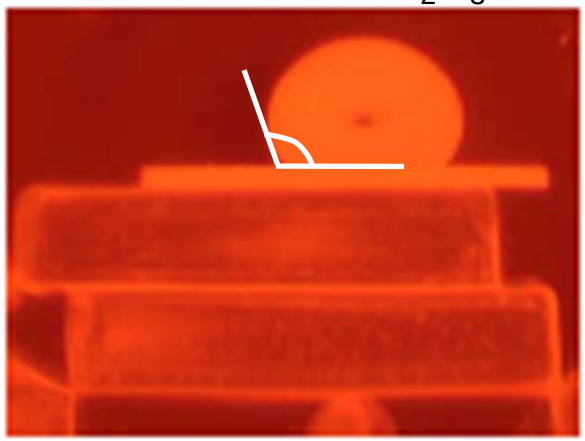


- Titanium 'adhesion' layers by far the most common
- Titanium expands upon oxidation causing hillocks
- Adhesion layers fail with large temperature swings (>700°)

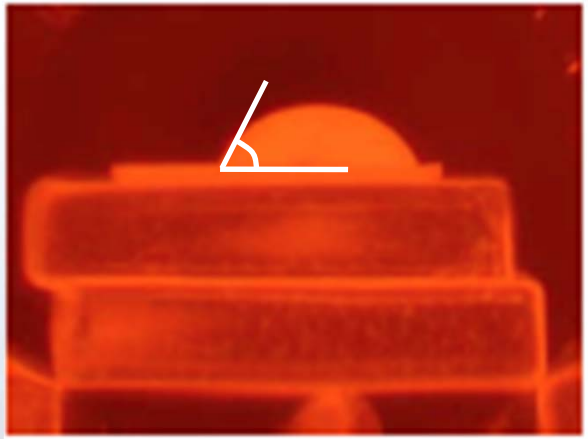
Nam et al., *Thin Solid Films* (2000)

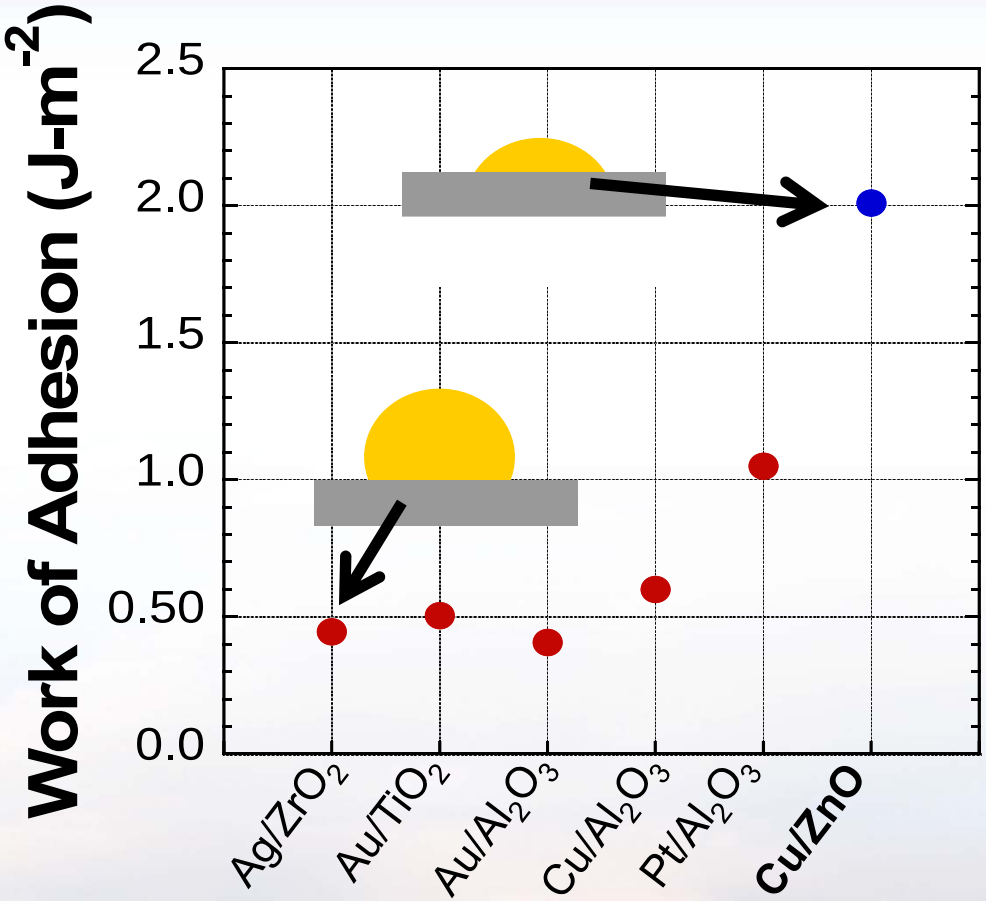
Metal Wetting and Adhesion

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. Dissertation, NCSU 2006

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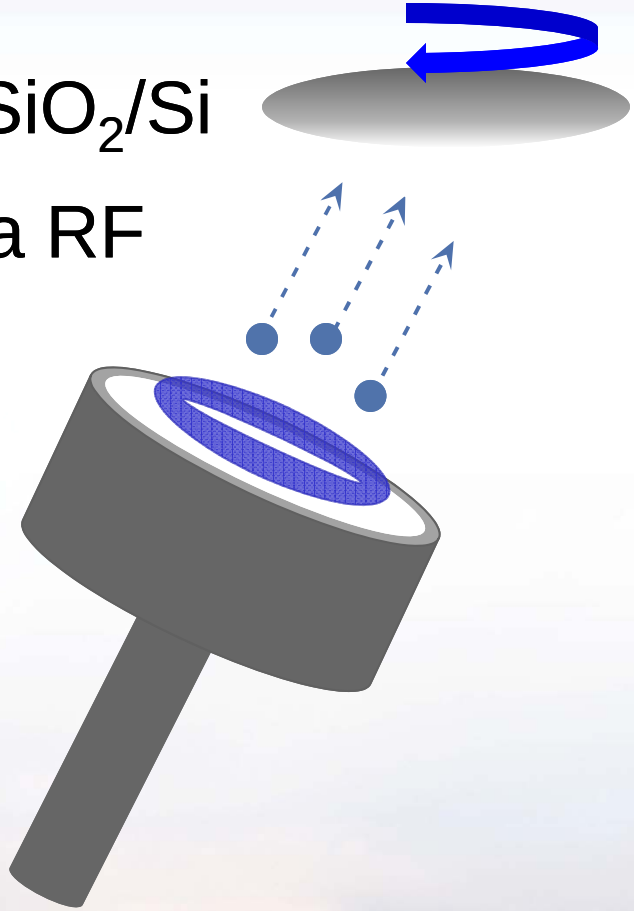
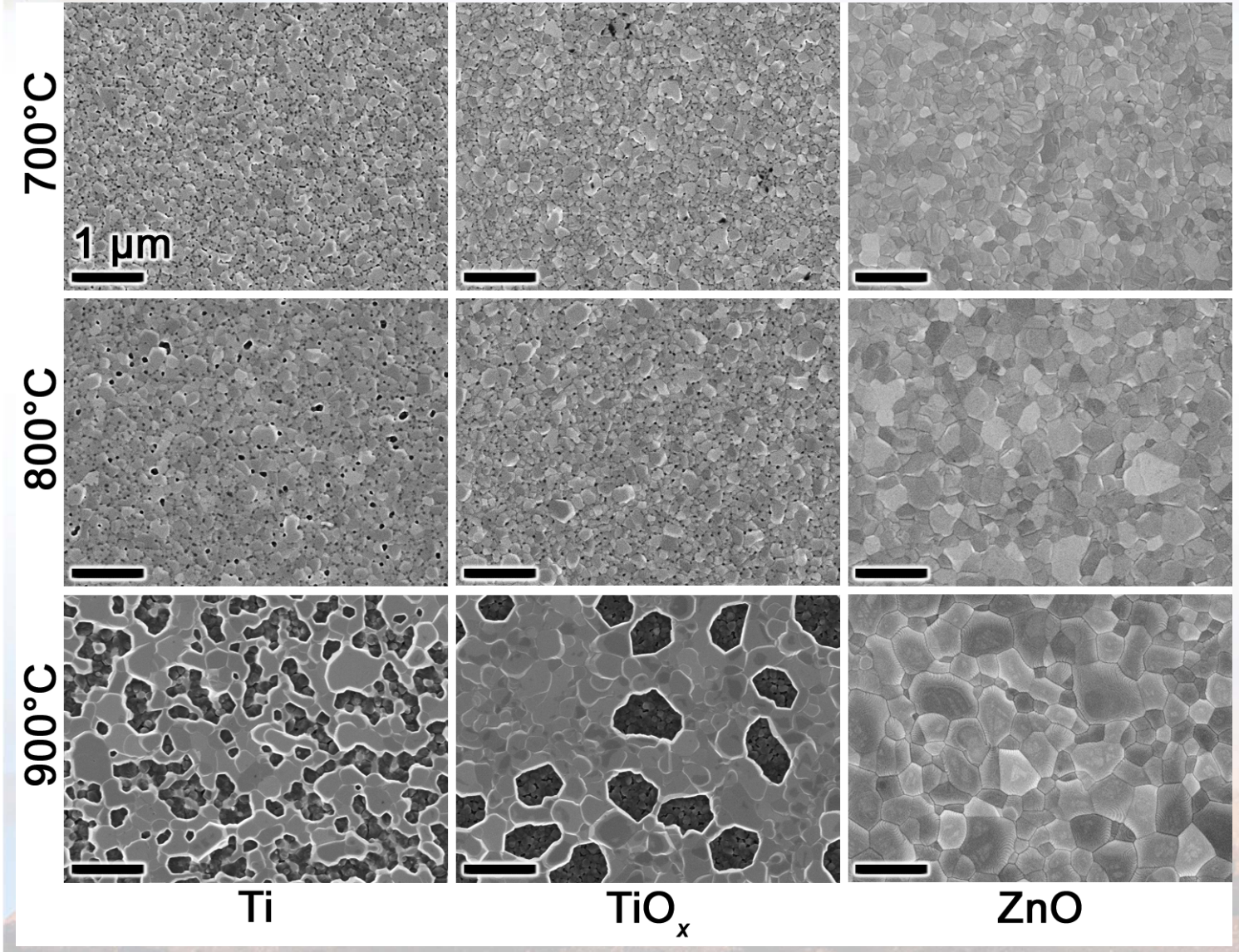
Pt/Si Substrate Preparation

- 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



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SNL IMO PZT CSD Film Preparation

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

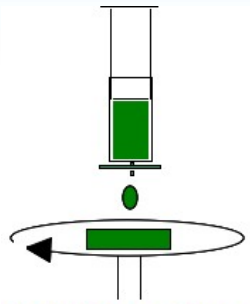
Spin Coat Deposition
4000rpm/30sec

multiple depositions

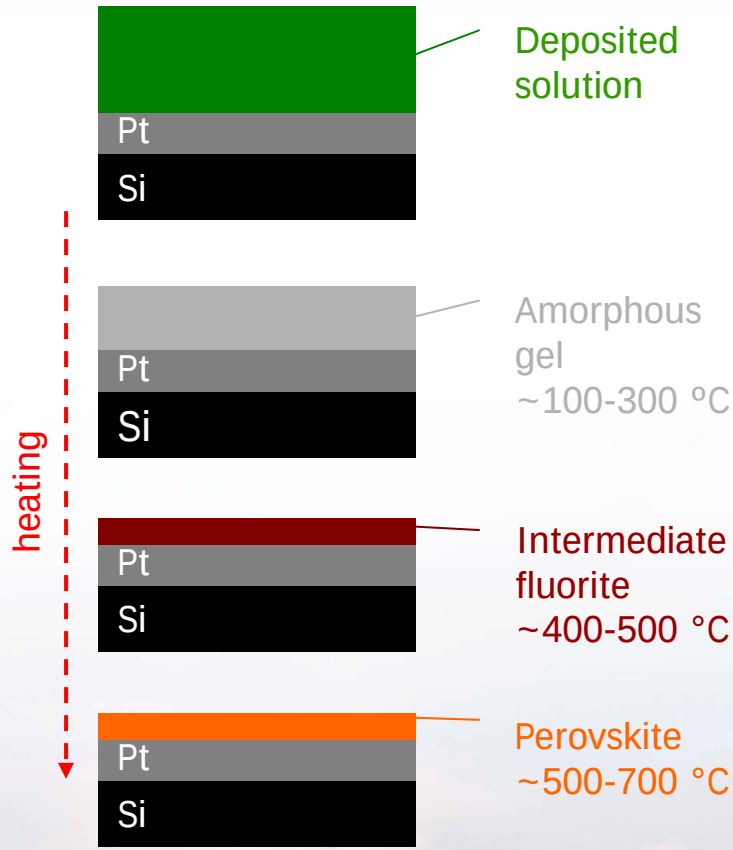
Pyrolysis

Crystallization

Sputter Pt electrodes

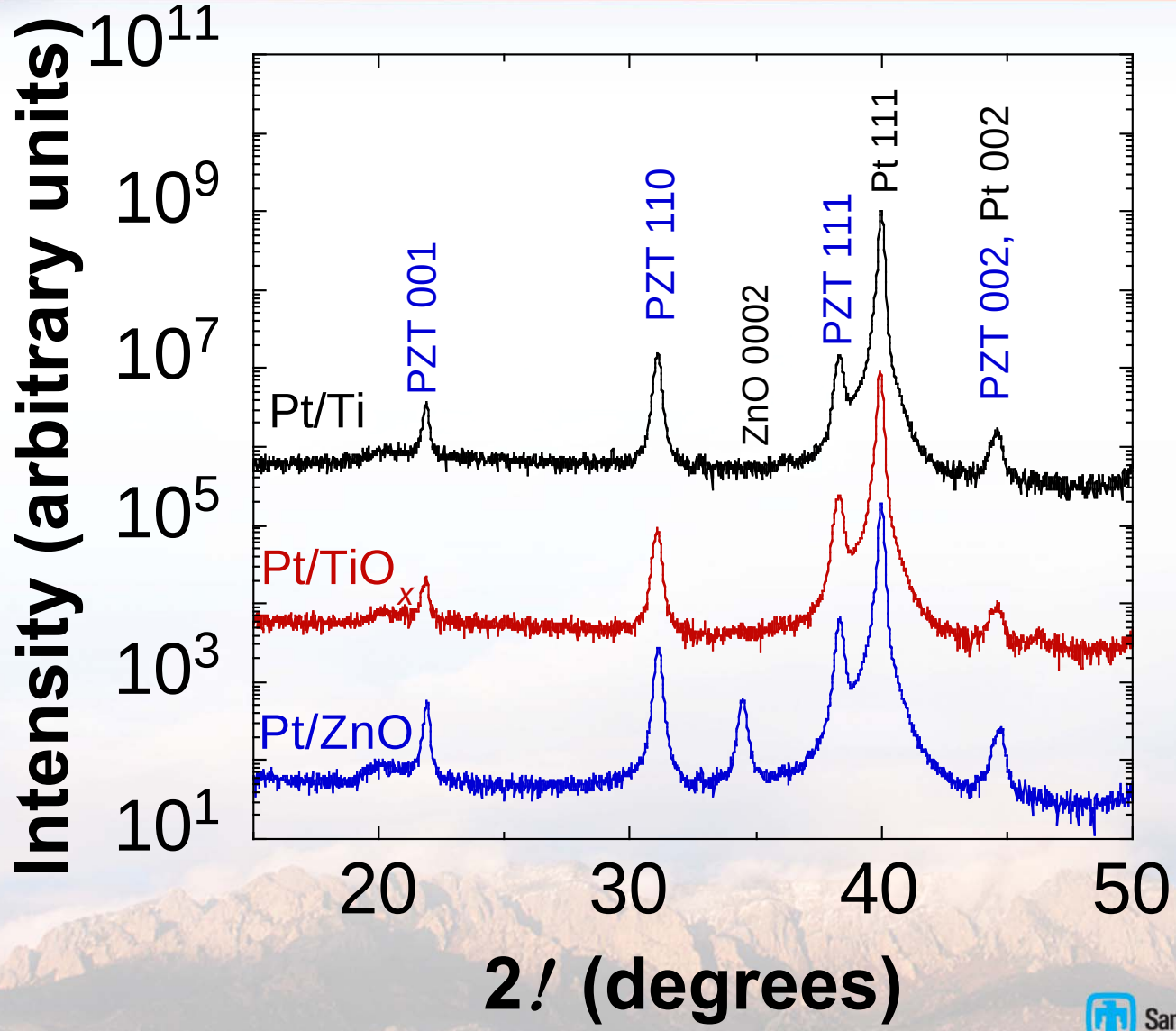


Spin Deposition



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

Film Phase/Crystallographic Properties



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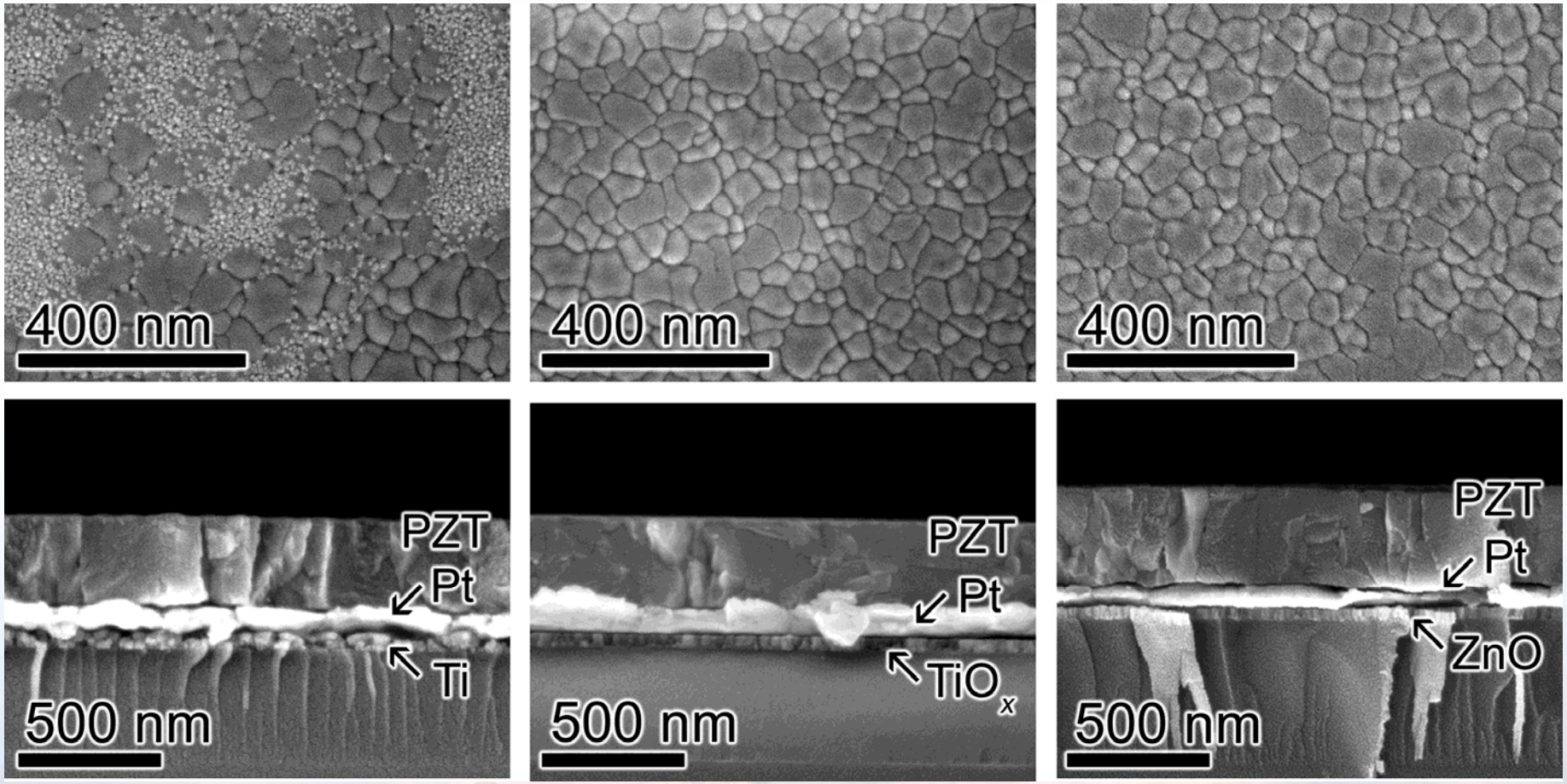
PZT Film Microstructure



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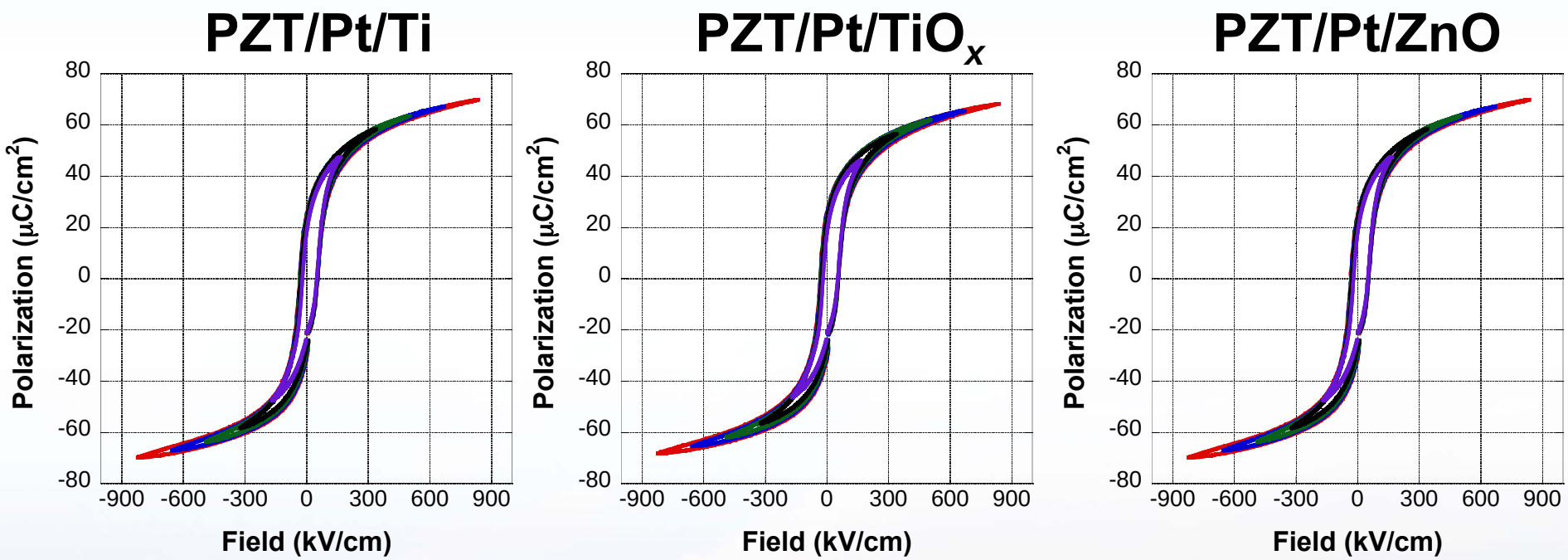
Dielectric and Ferroelectric properties



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

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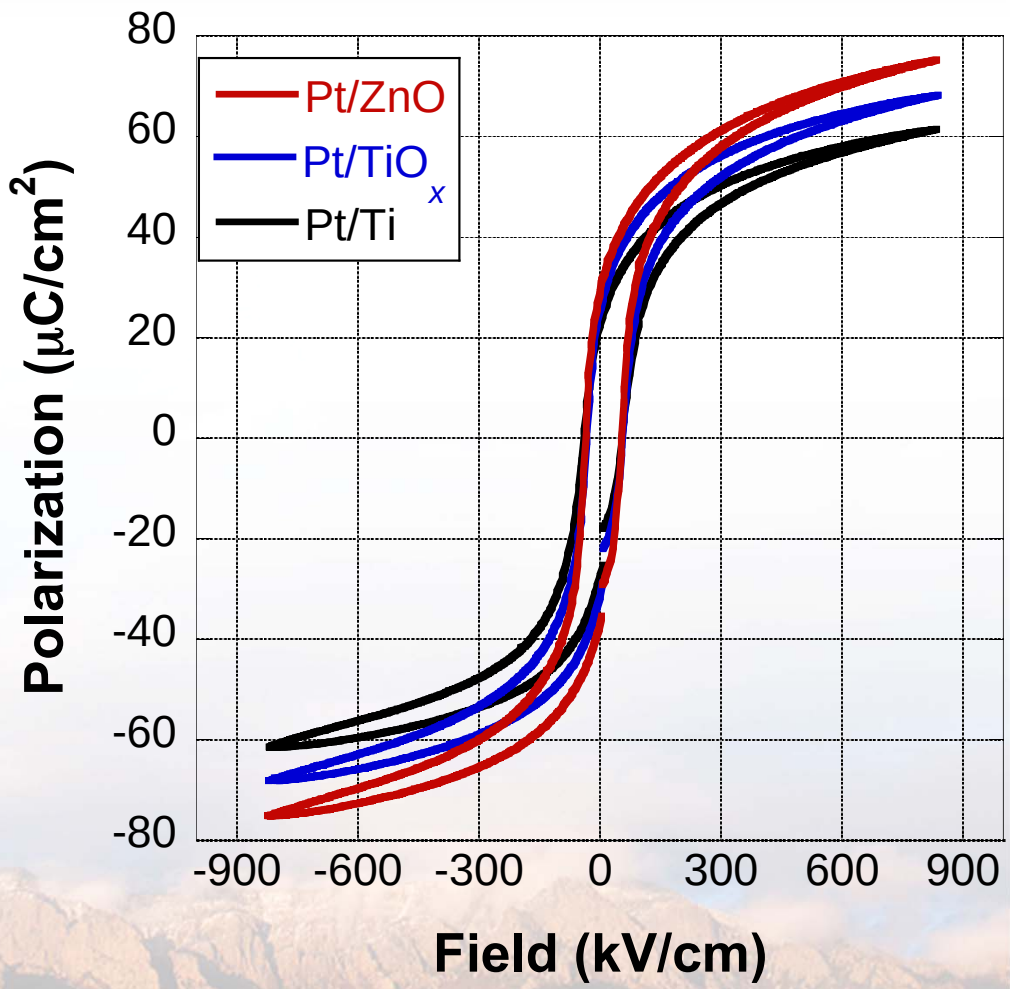
PZT Films Ferroelectric Properties: Pt/ZnO Substrates Superior

	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



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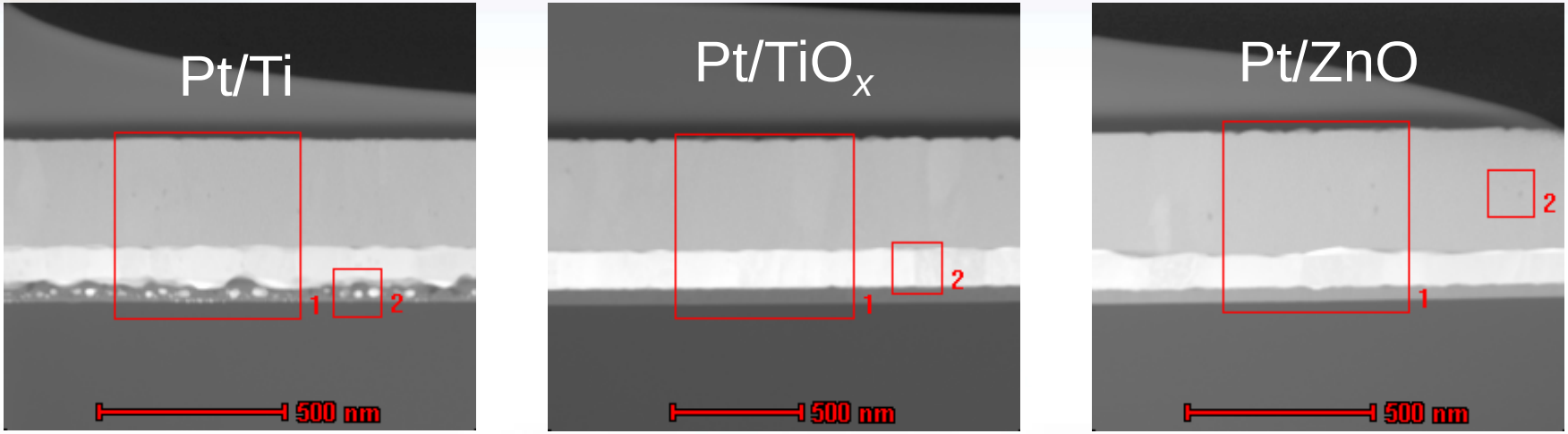
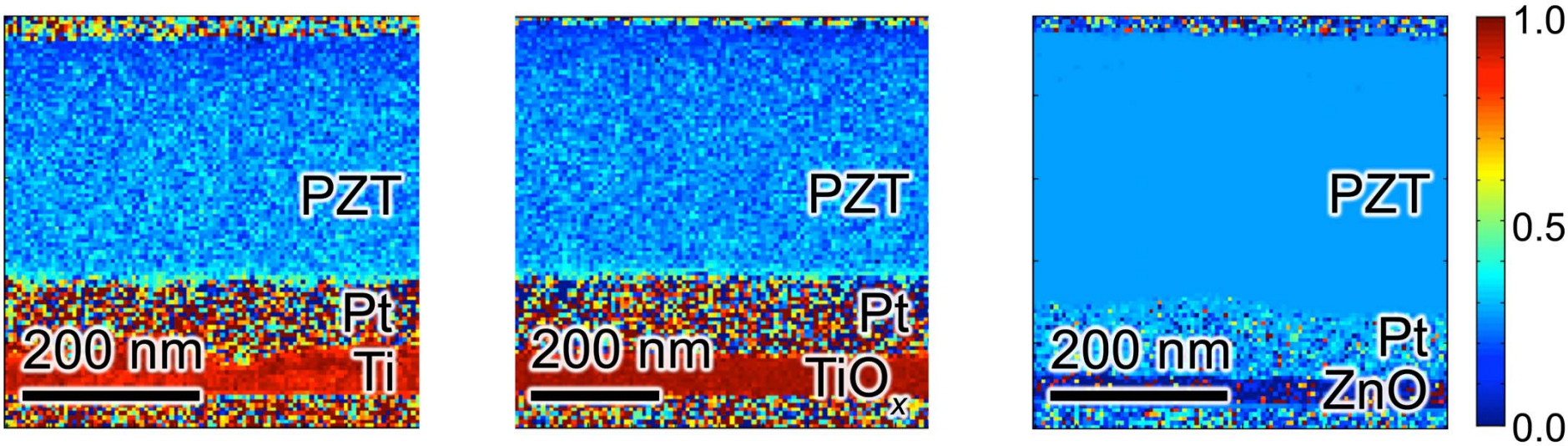
PZT Composition Analysis: No Composition Gradient on Pt/ZnO



Titanium Distribution



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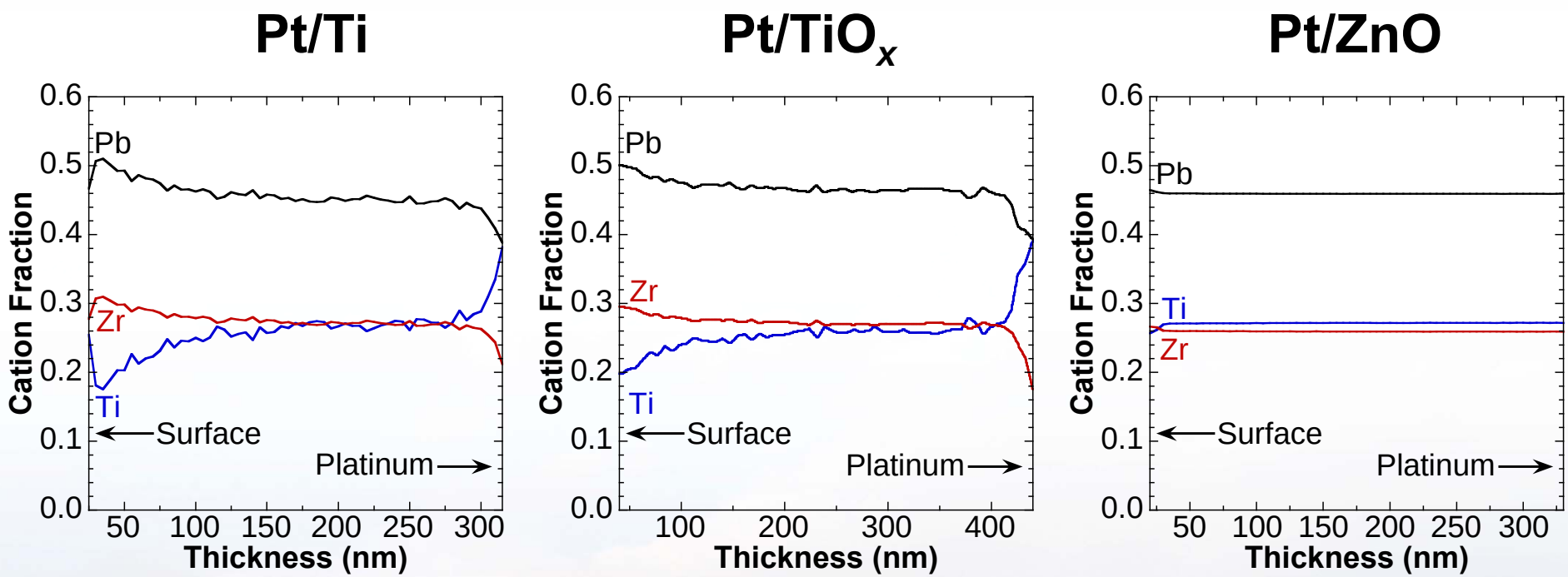

Substantially improved chemical homogeneity in films on Pt/ZnO substrates

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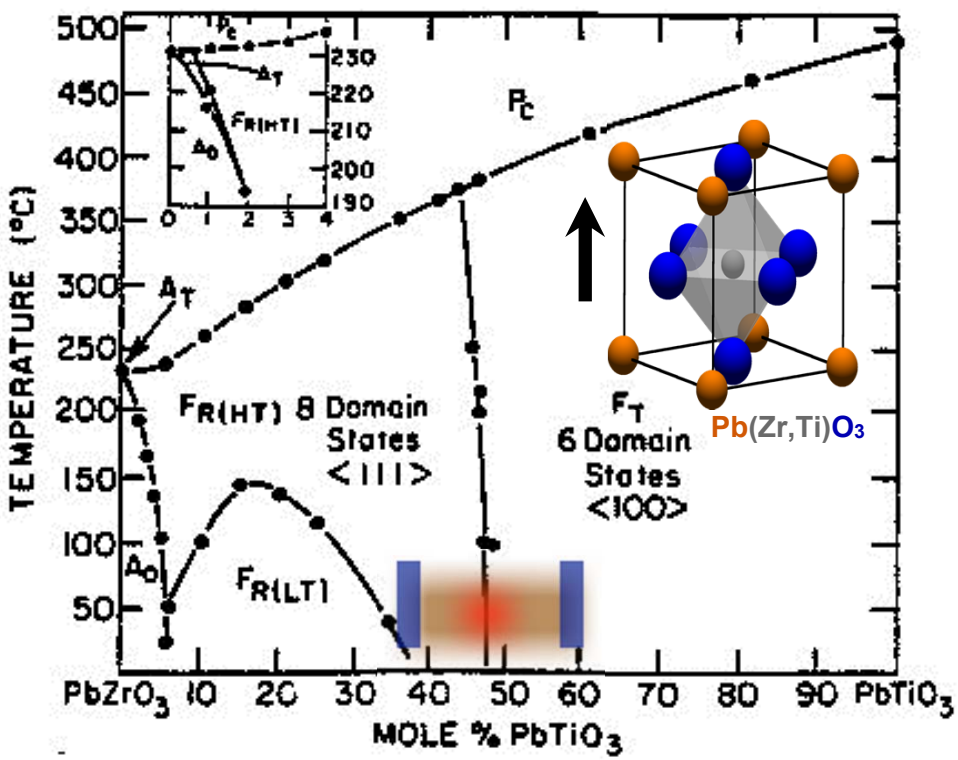
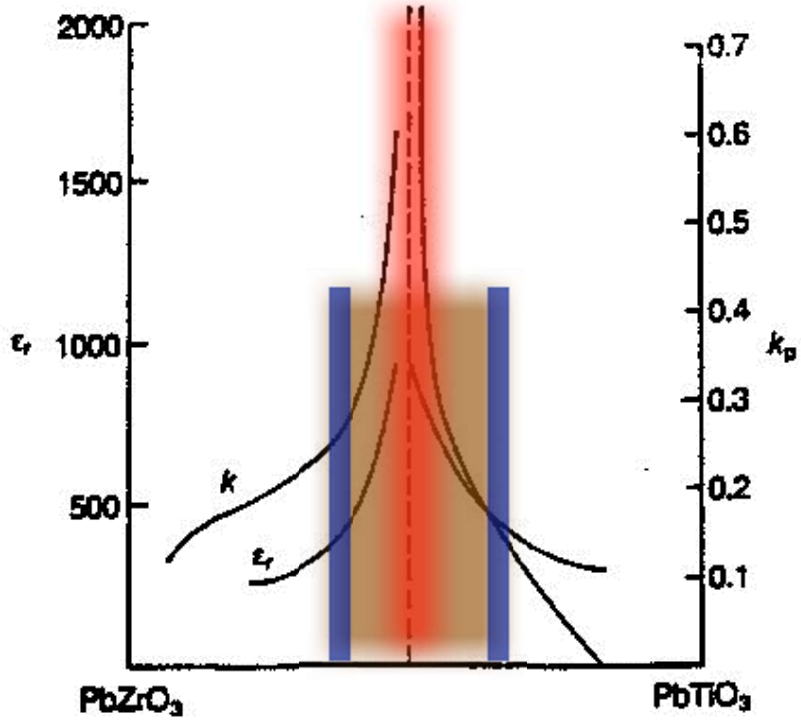
Chemical Homogeneity Effects on Electronic Properties



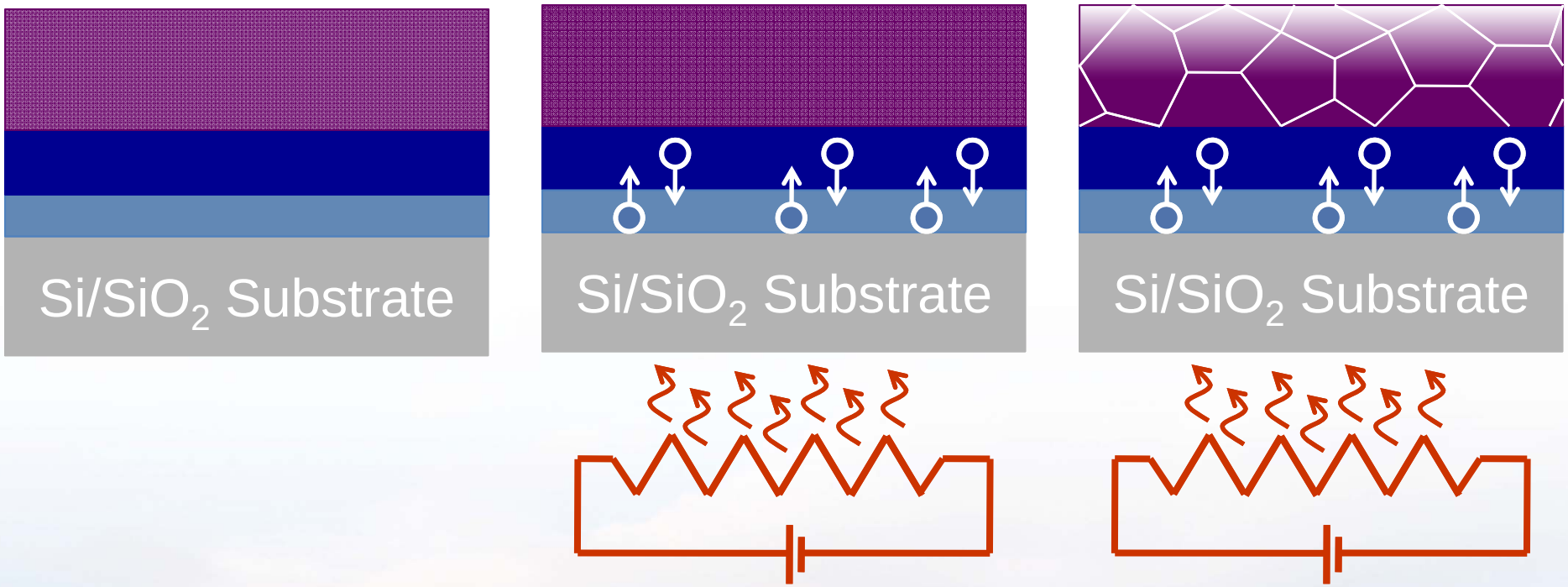


Good enough (too many to mention)

Better (Bastani and Bassiri-Gharb via MOE)

Better (Calame and Muralt via MOE, Shelton *et al.* via IMO)

Our Model

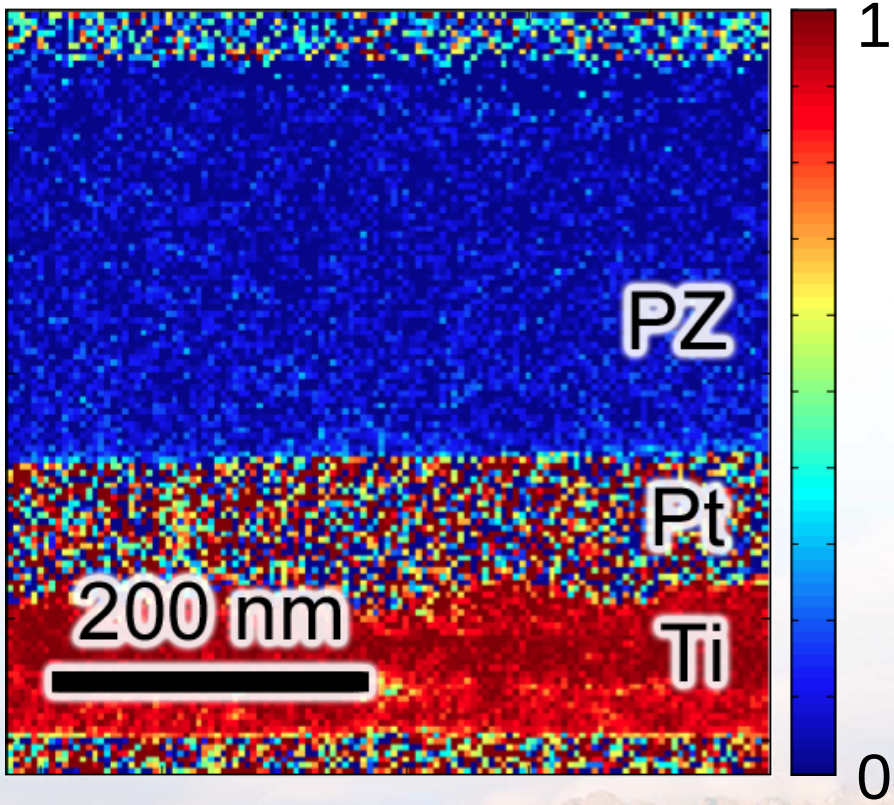


<u>Hypothesis:</u>

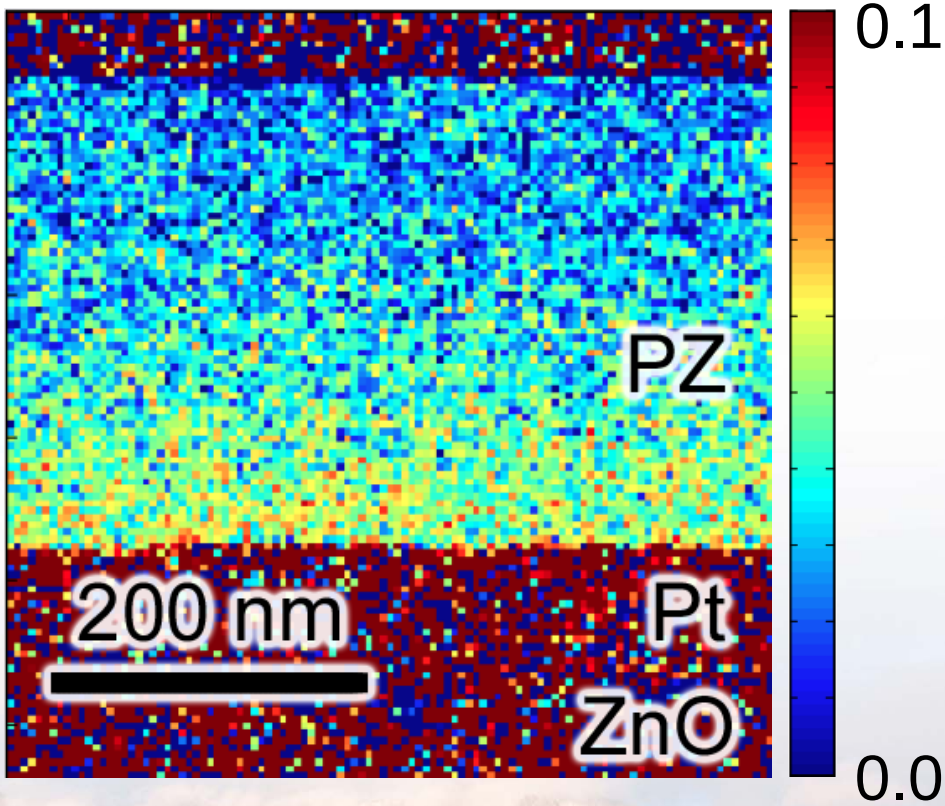
Titanium diffuses through platinum and to film/Pt interface

Test for Gradient Mechanism: $PbZrO_3$

PZ/Pt/Ti

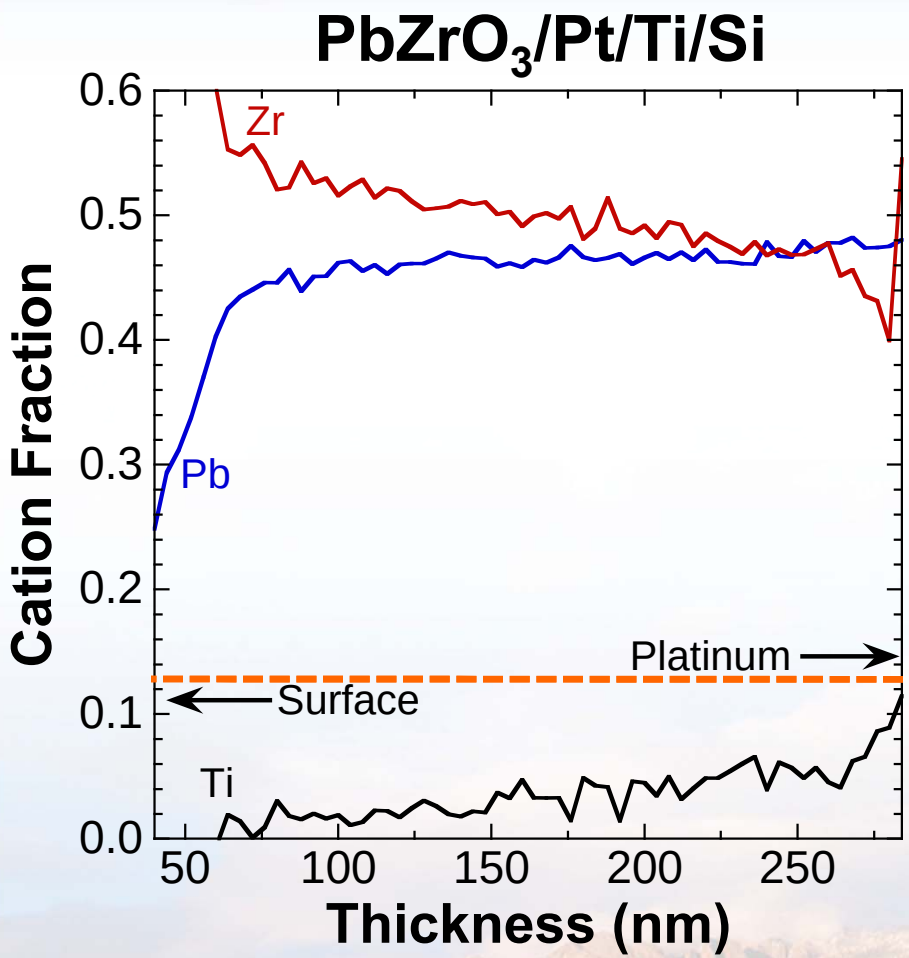


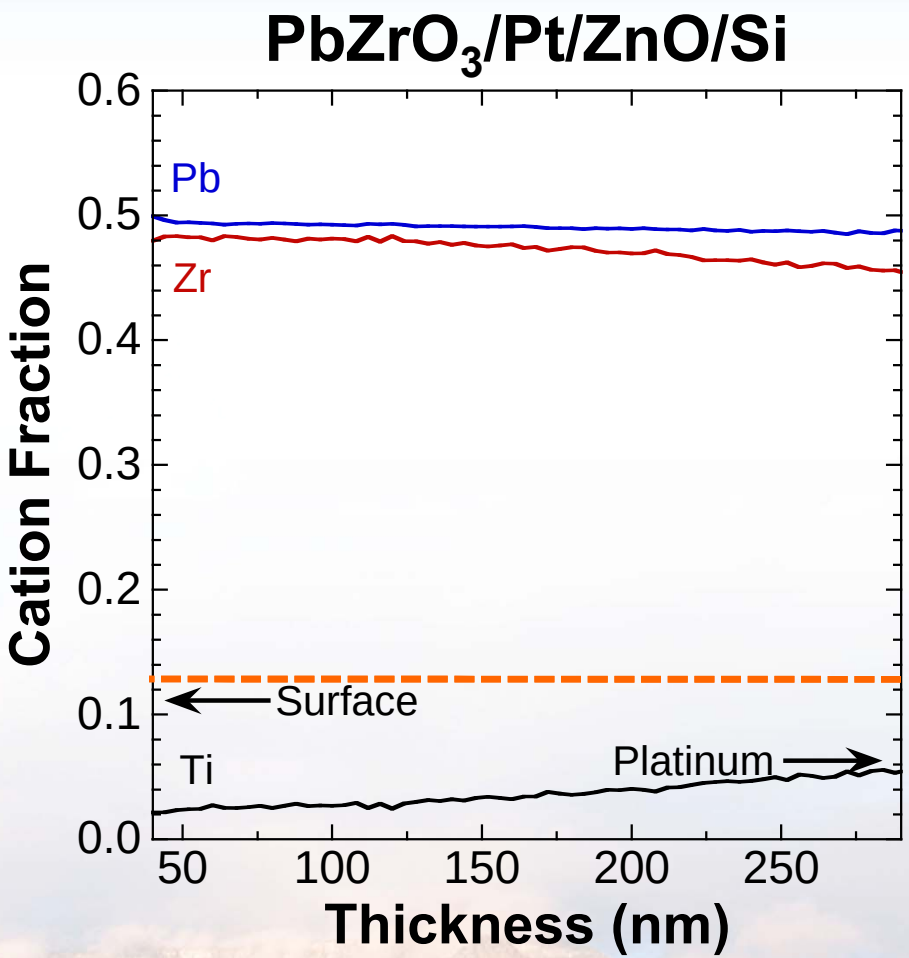
PZ/Pt/ZnO



Note Scale Difference

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





Less Ti and smaller gradient on Pt/ZnO

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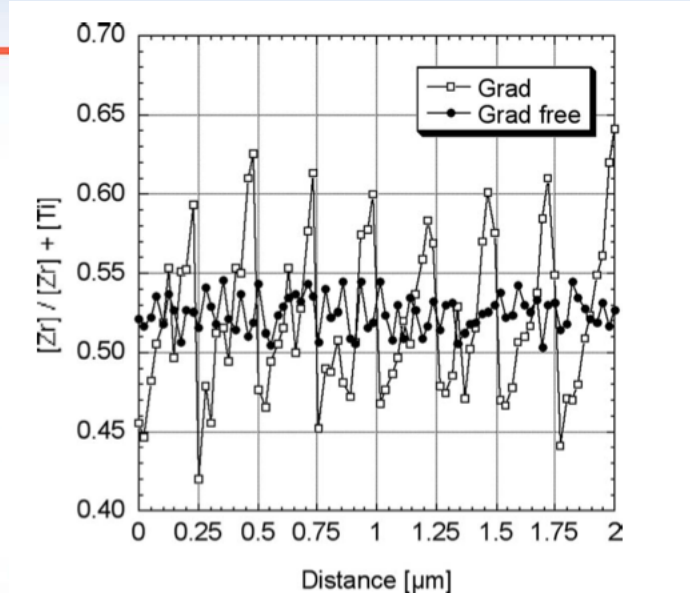
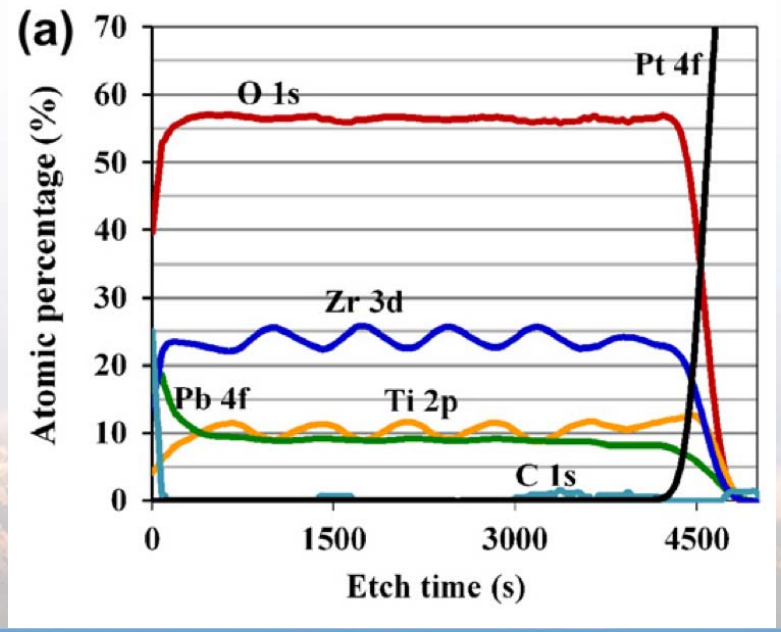
Solution Chemistry Effects?

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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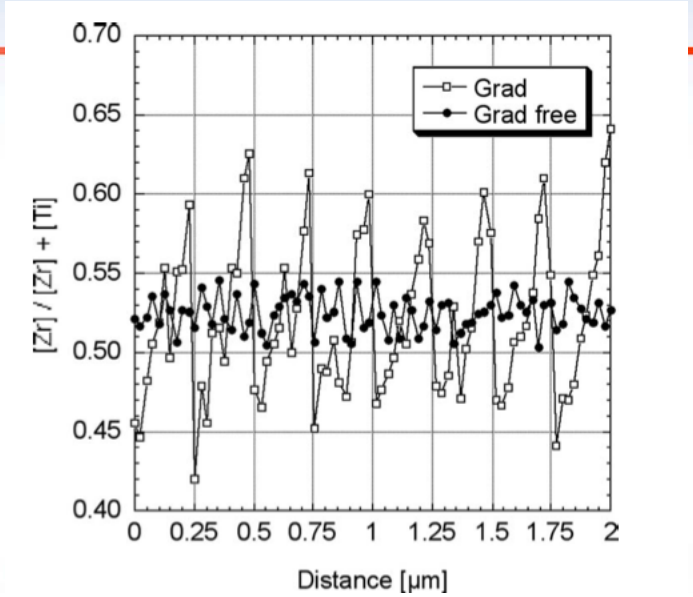

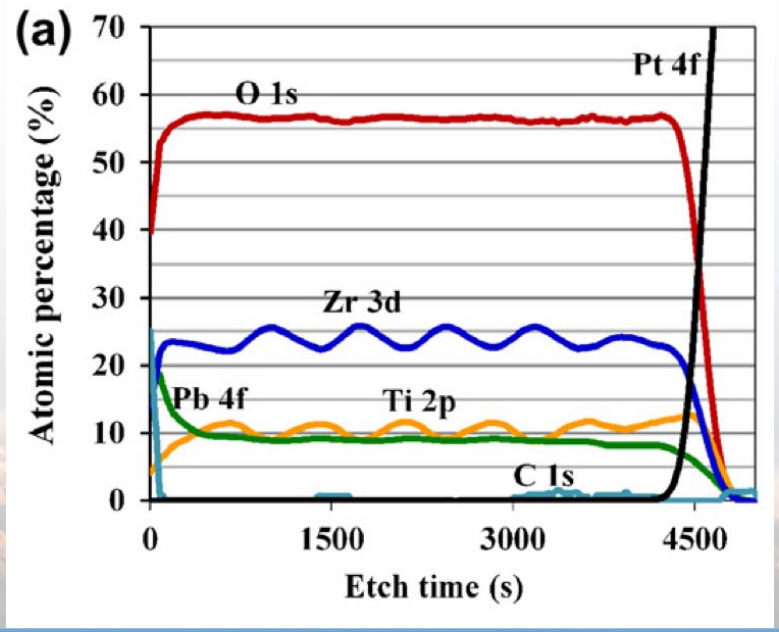

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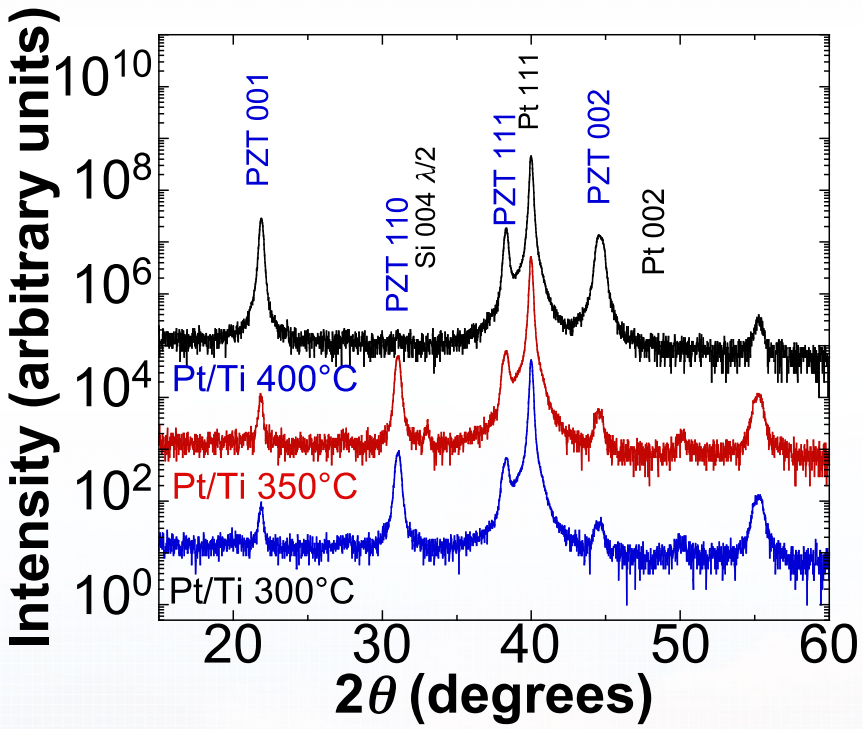
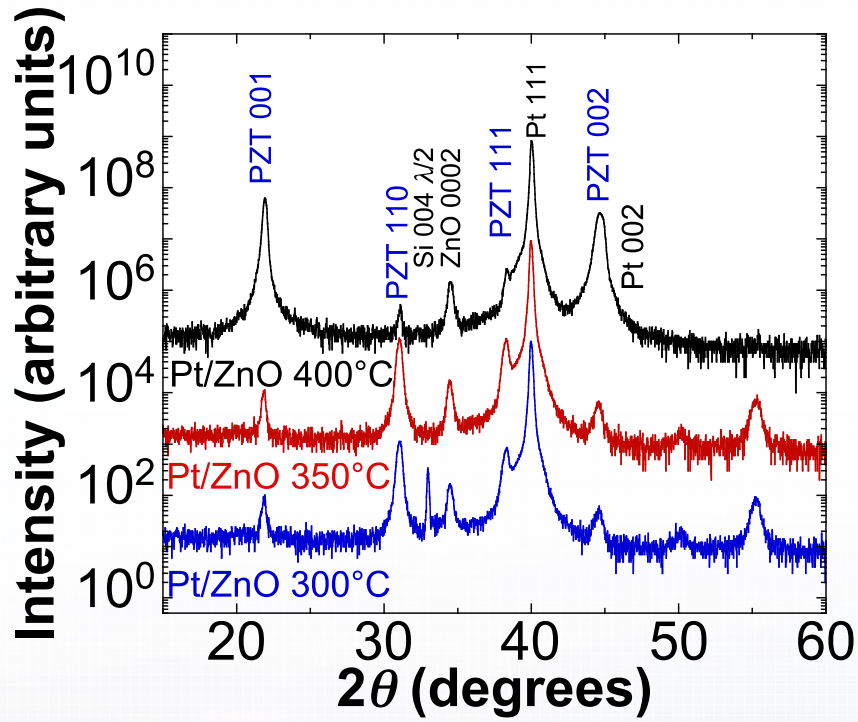
Pyrolysis Effects: Texture

IMO on Pt/Ti



2-MOE on Pt/ZnO



- ***Pyrolysis temperature 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)

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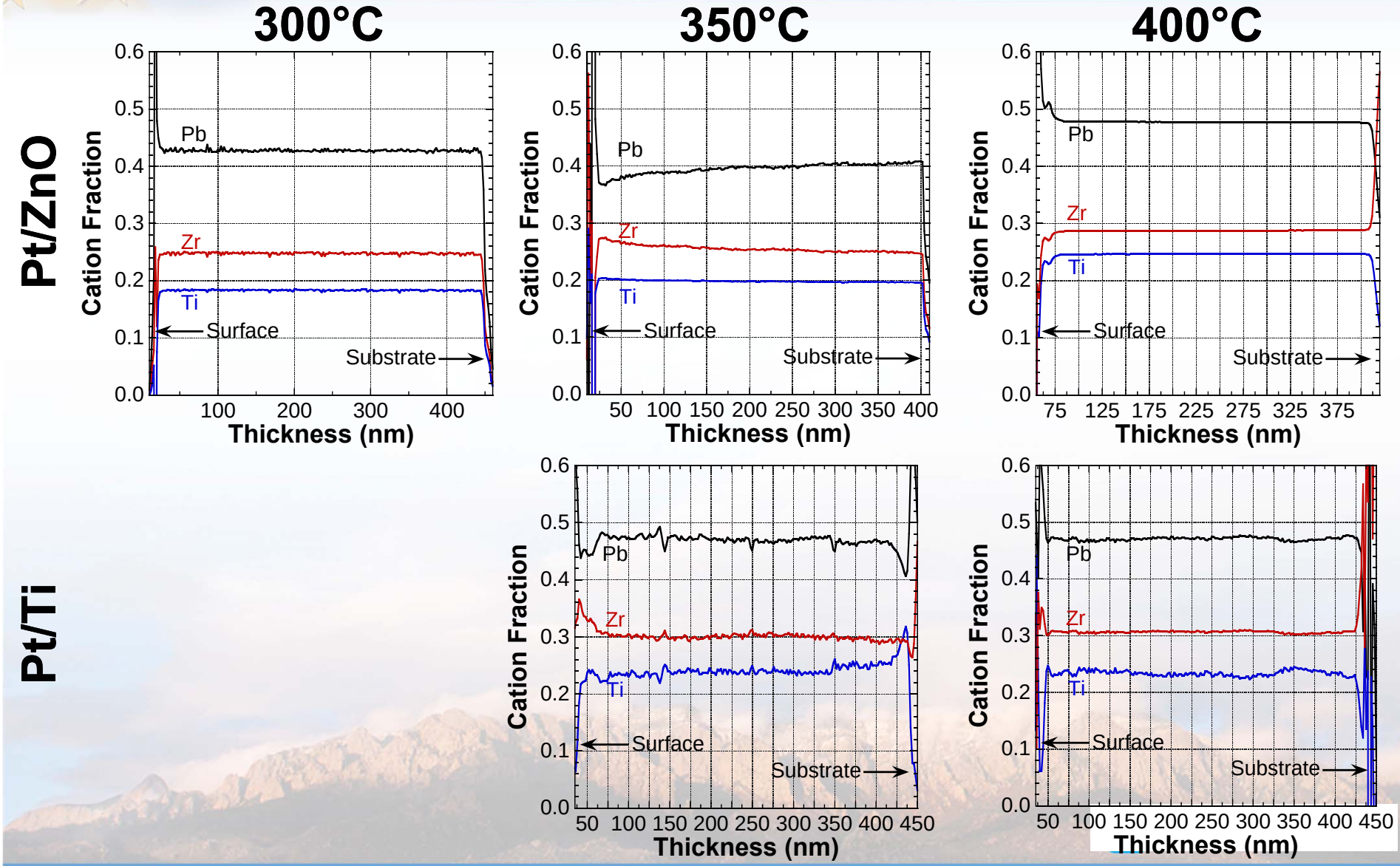
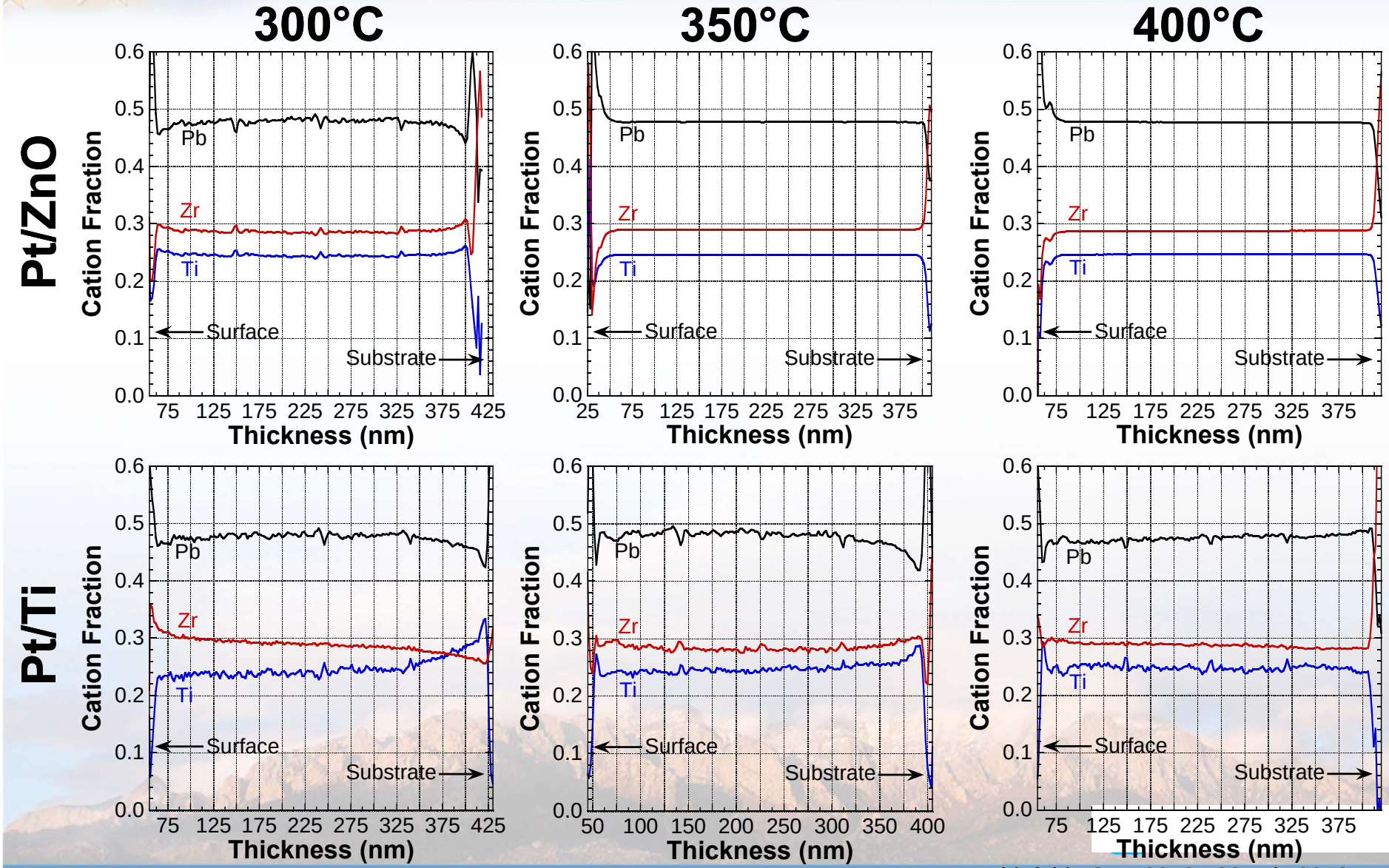
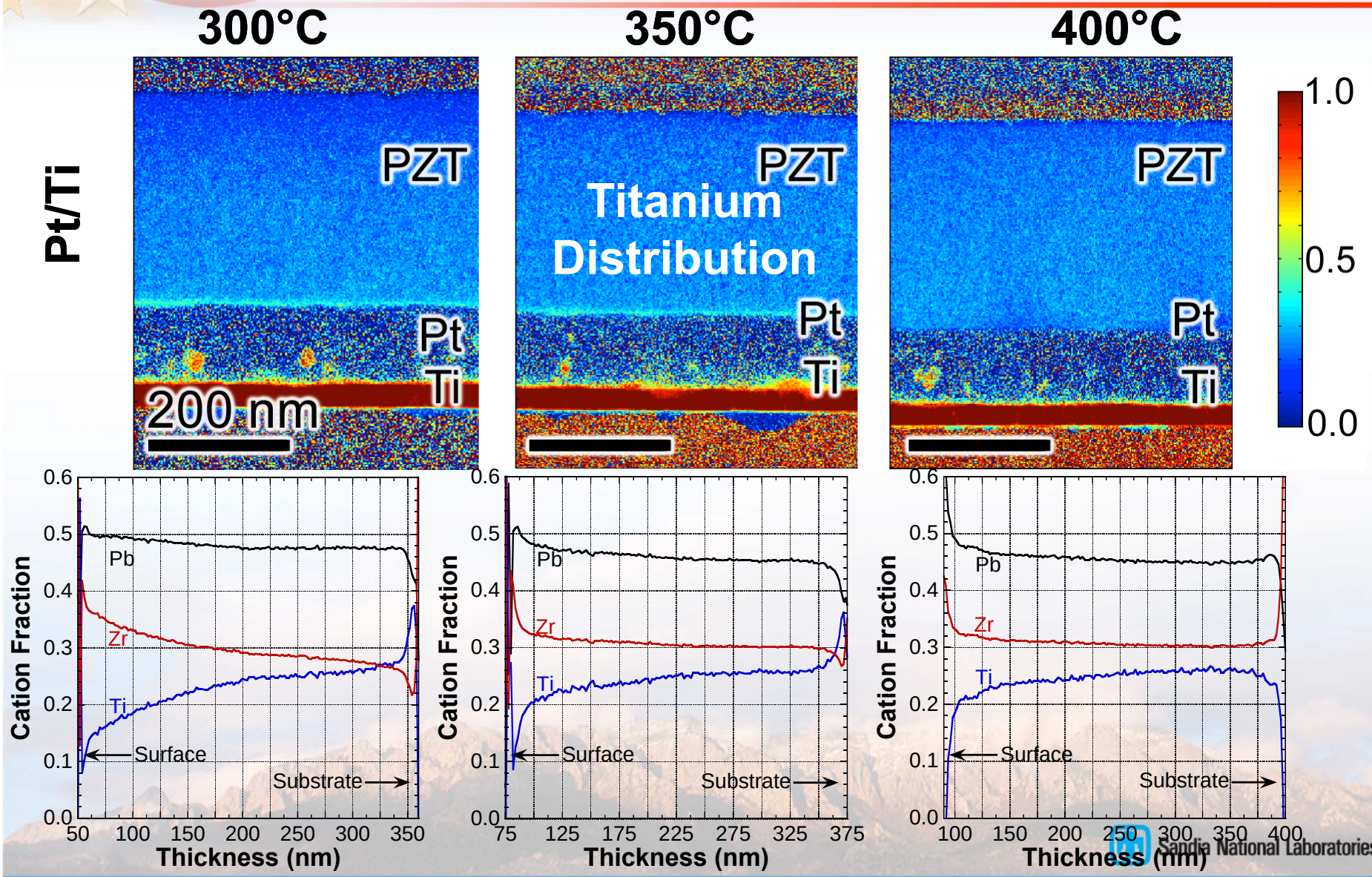
Unfired Chemical Distribution: IMO Films



Unfired Chemical Distribution: 2-MOE Films



Solution Chemistry Effect: IMO films



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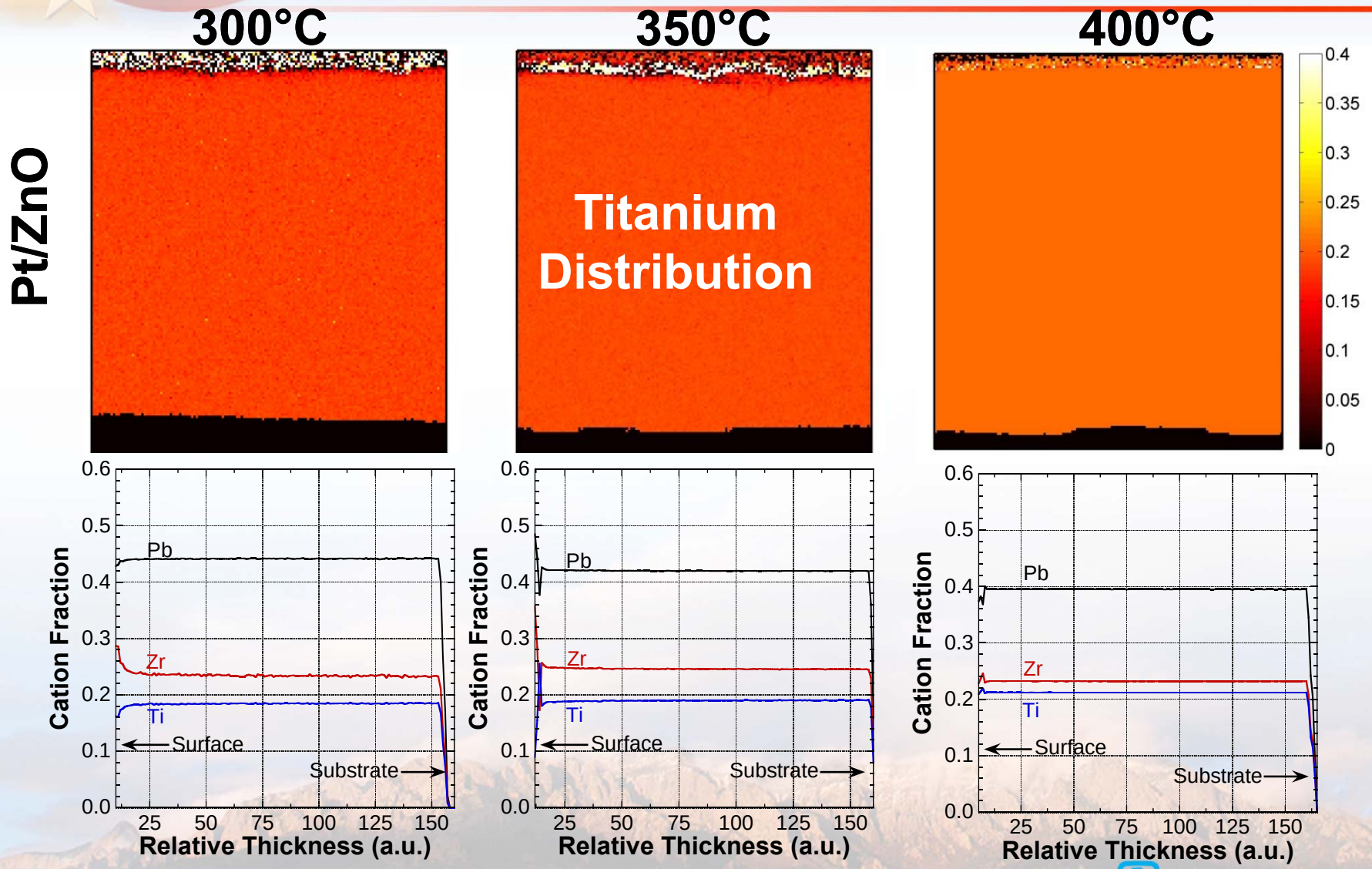

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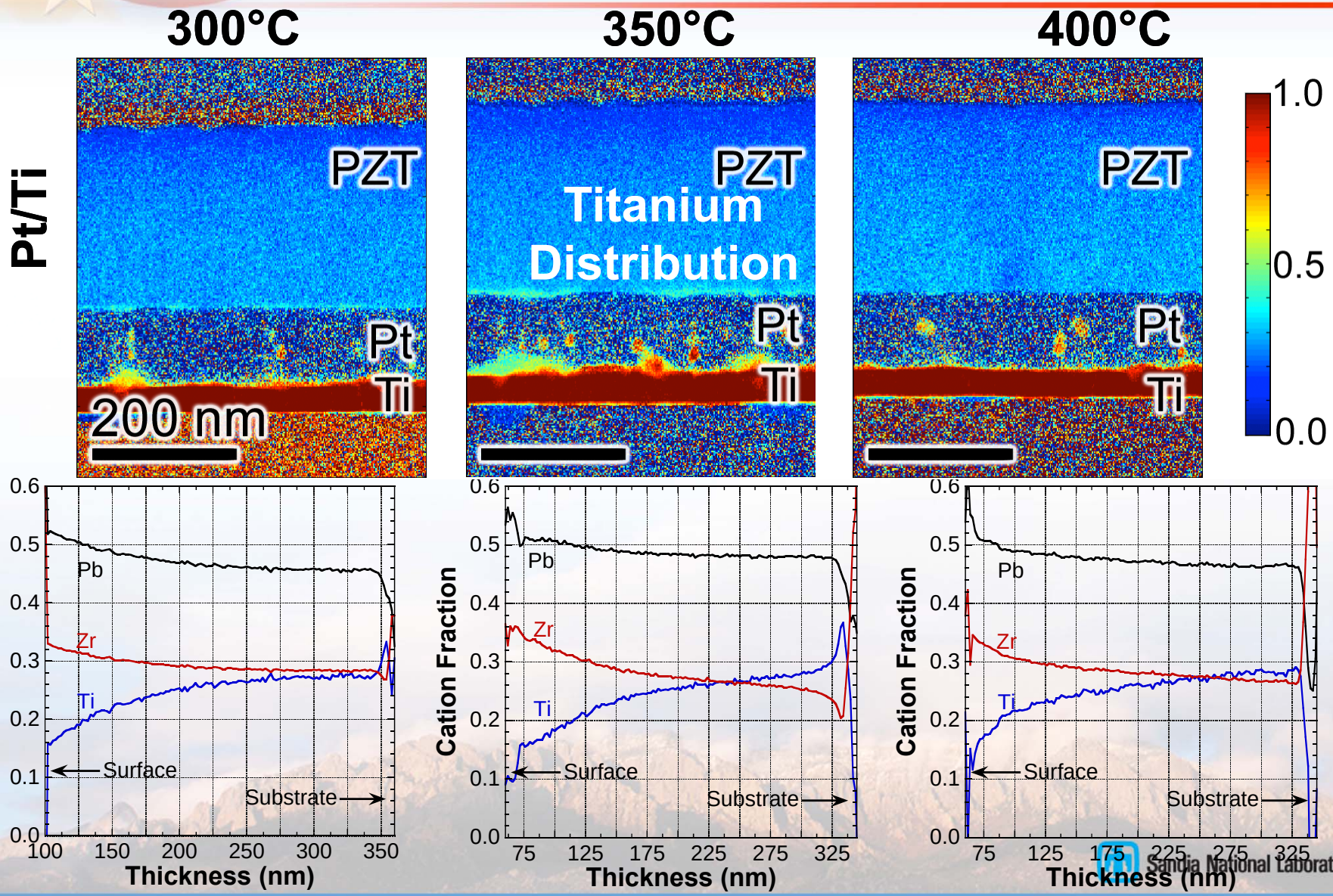
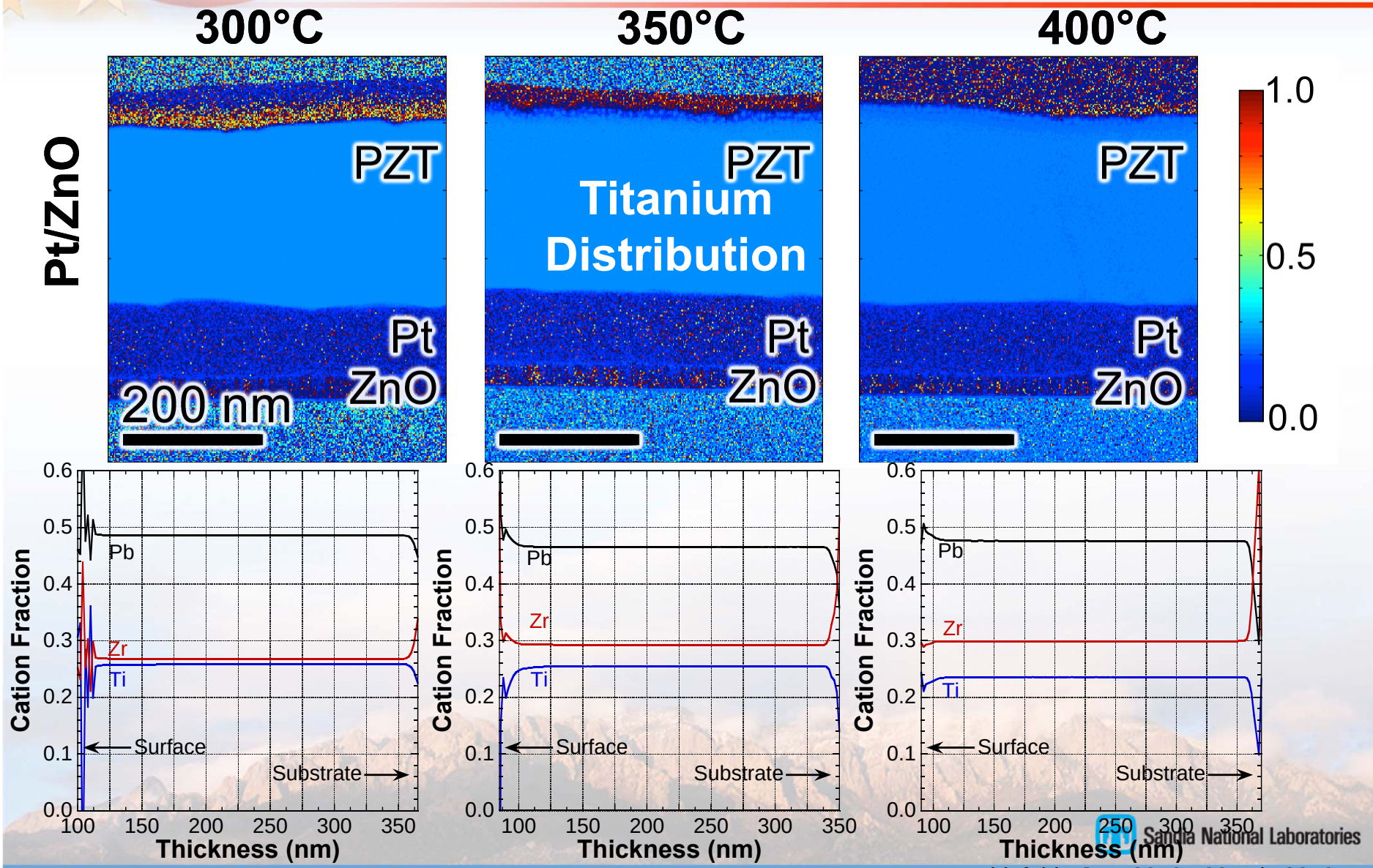
Solution Chemistry Effect: 2-MOE films



Solution Chemistry Effect: 2-MOE films



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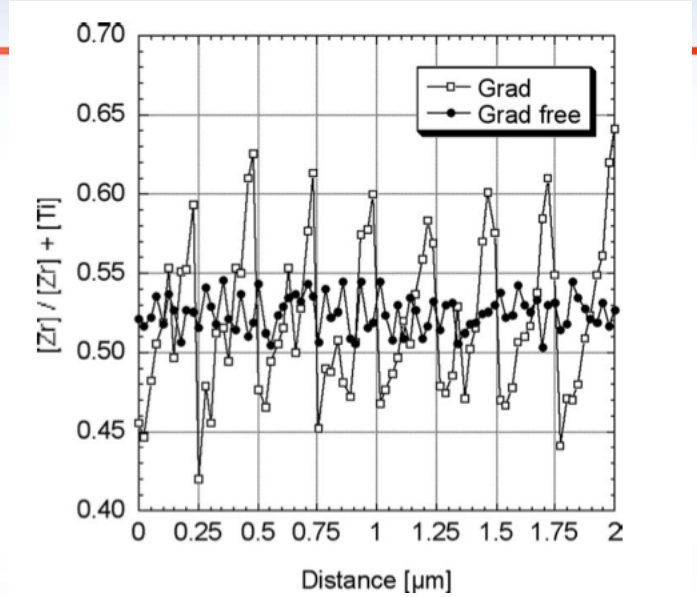
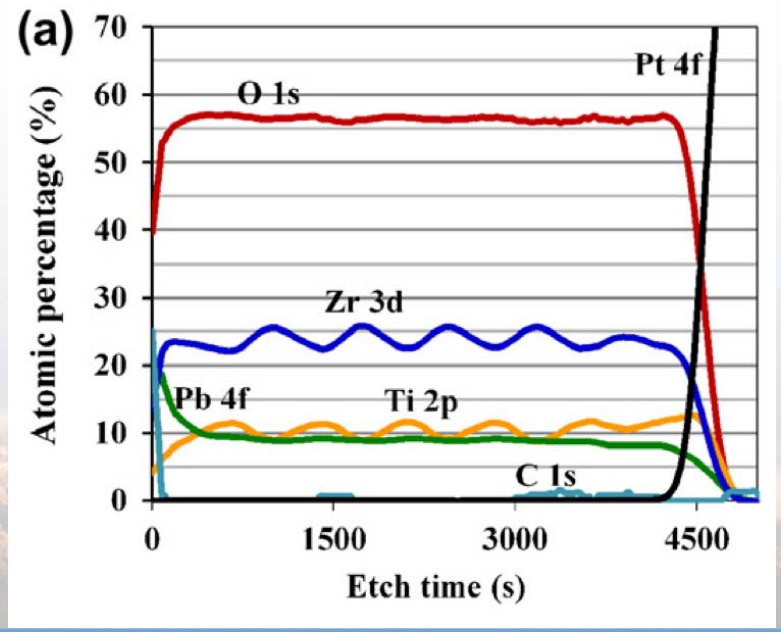
  - Substrate: **Pt/Ti** vs **Pt/ZnO**
  - Chemistry: **IMO** vs **2-MOE**‡
  - Pyrolysis: **300**, **350**, **400° C**
  - **Heating Method/Rate: 15, 50, 200° C/s**
    - **RTA: Solaris 150 (Tungsten Halogen Lamp)**





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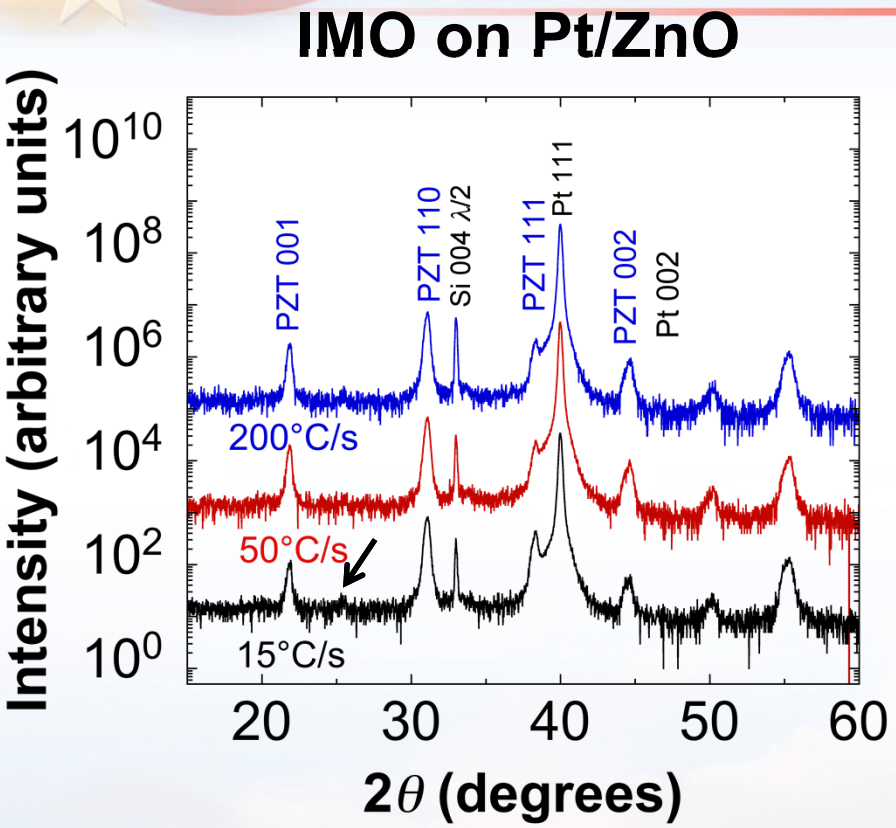
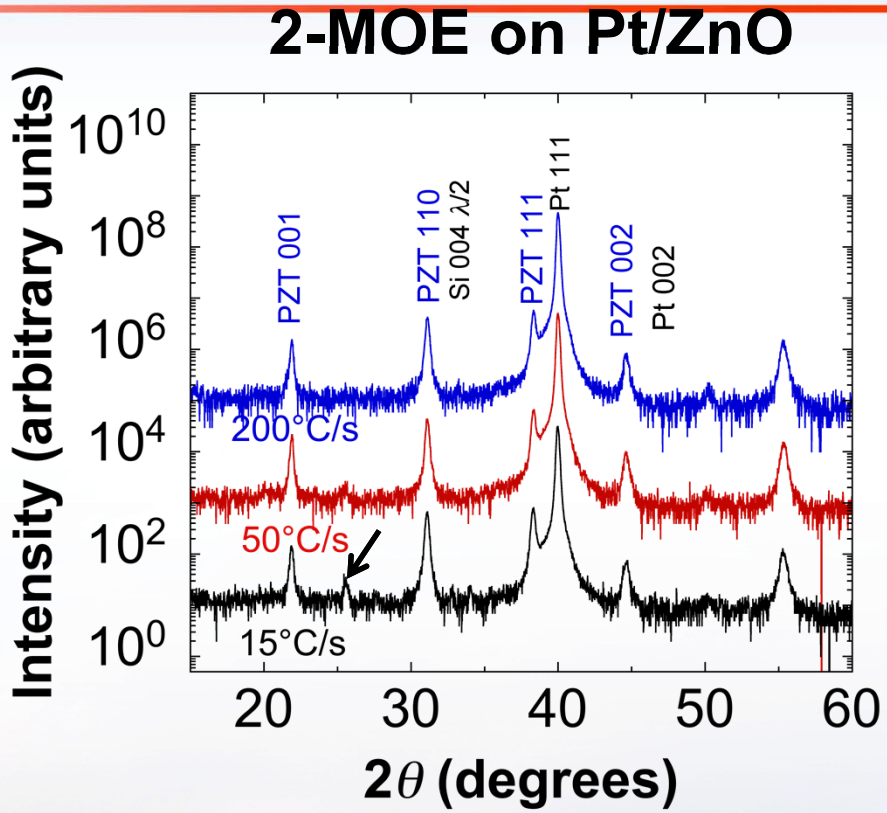
RTA Heating Rate Effects: Texture



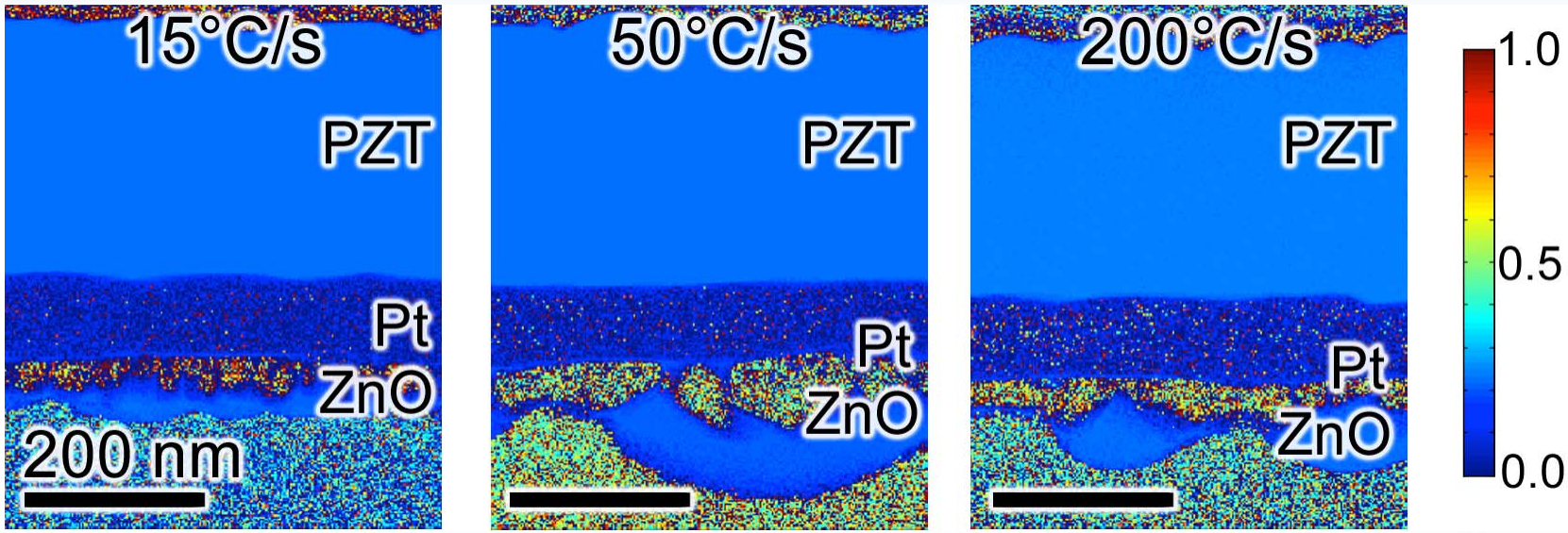


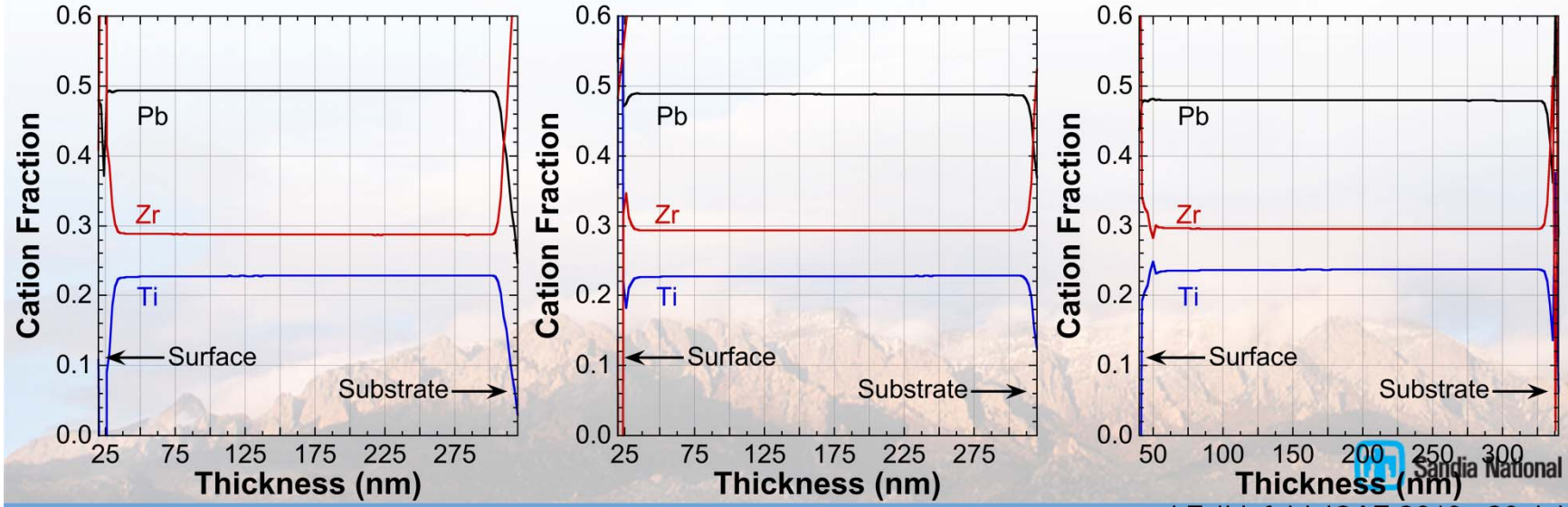
- ***No apparent heating rate dependence to texture***
  - ***Consistent with previous studies****
- ***ZnO diffraction peaks no longer visible***
- ***Additional peaks present in low ramp rate samples***

*K. Nittala and J.L. Jones, *et al.*, *J. Appl, Phys.*, **113**, 244101 (2013)

Ramp Rate Effect: IMO Films

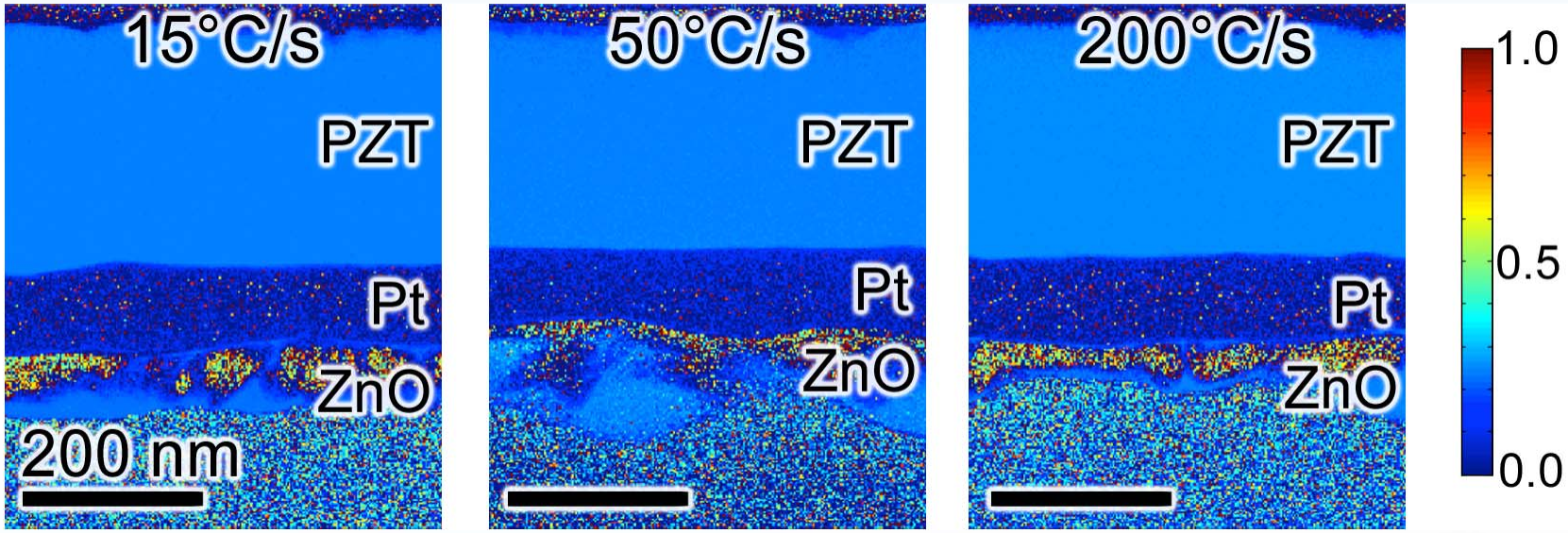
Pt/ZnO Titanium Distribution

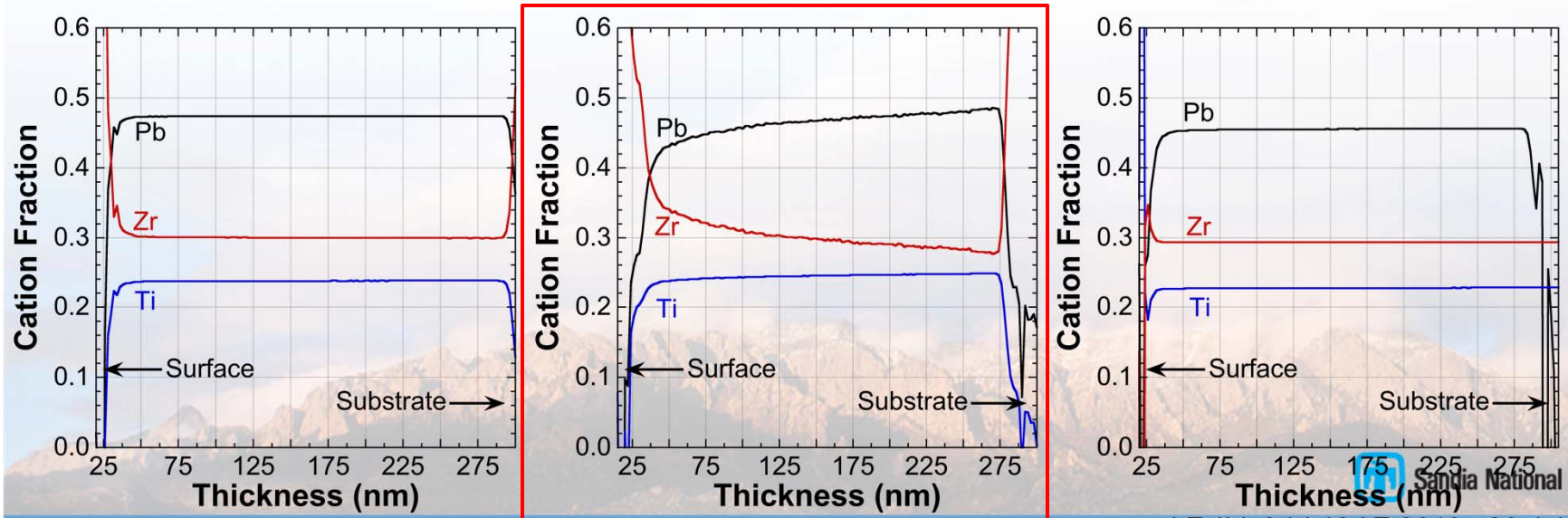




Ramp Rate Effect: 2-MOE Films

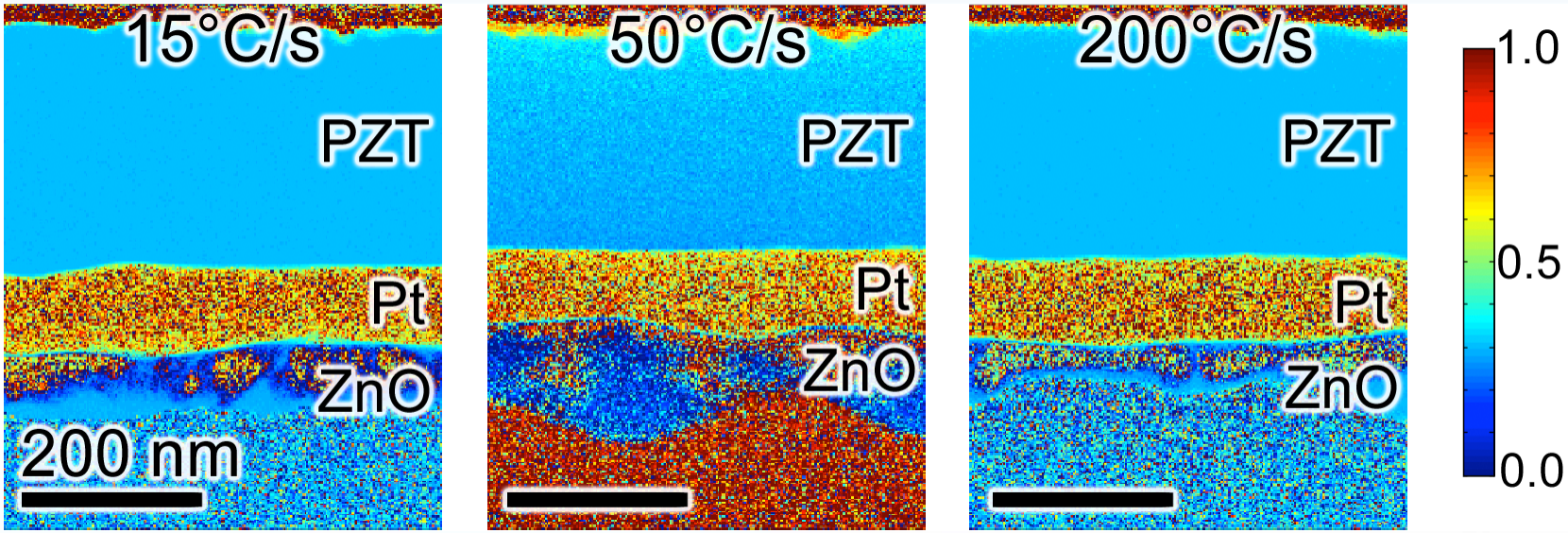
Pt/ZnO
Titanium Distribution

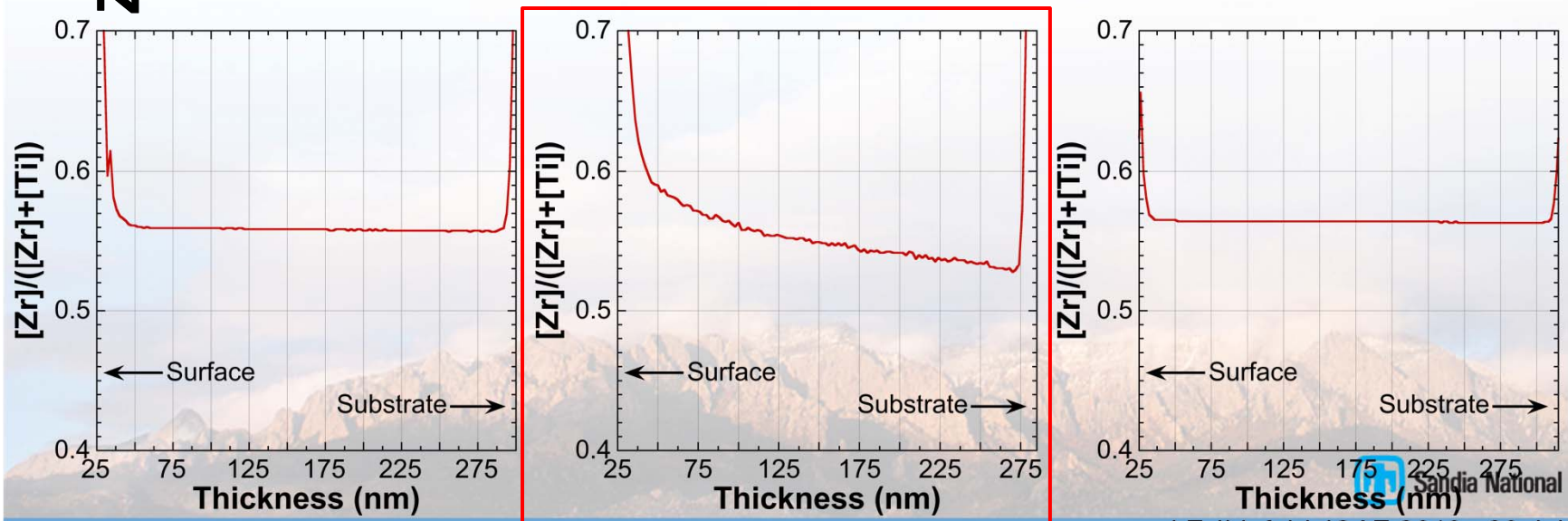




Ramp Rate Effect: 2-MOE Films

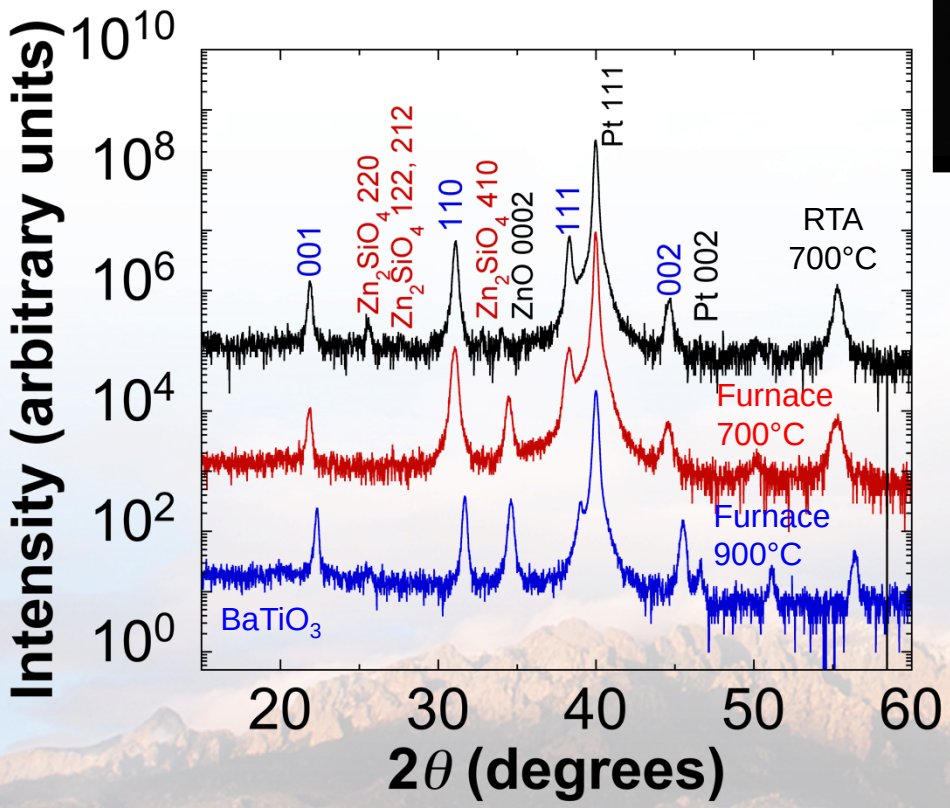
Pt/ZnO Zirconium Distribution

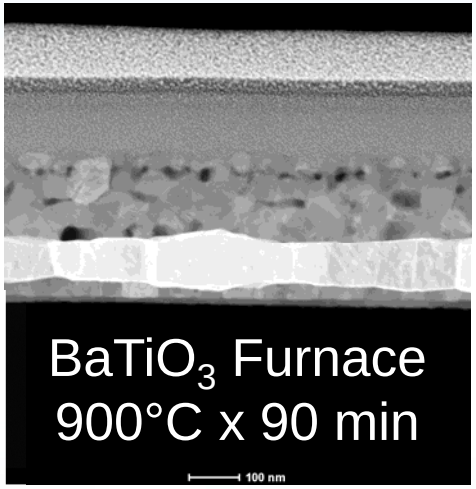


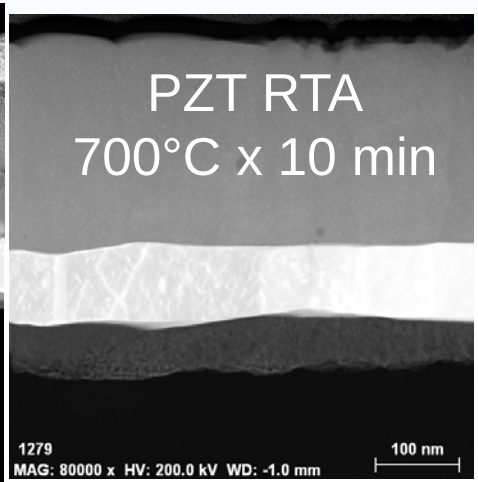


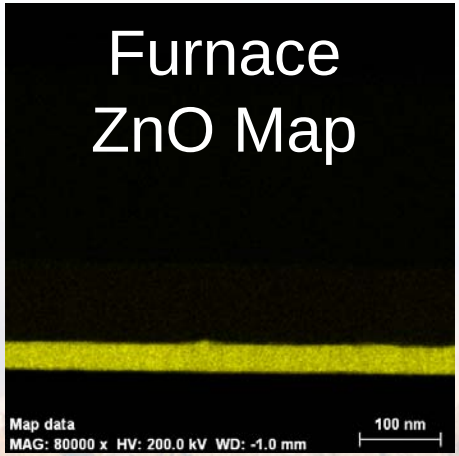
Interesting Observation: $ZnO\text{-}SiO_2$ Reaction

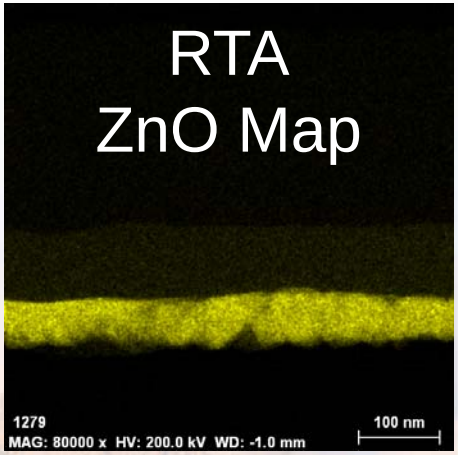
- Observe formation of secondary Zn_2SiO4 phase in RTA samples
- Only previously observed this in films subjected to significantly higher thermal budgets











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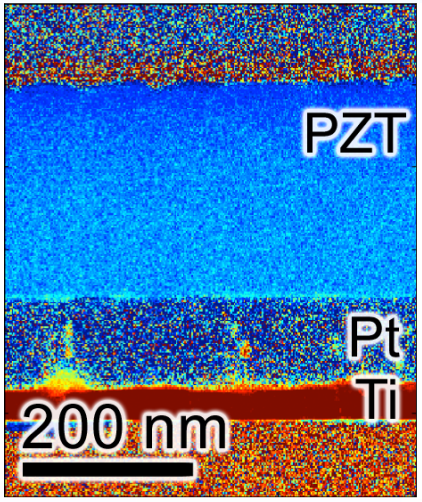
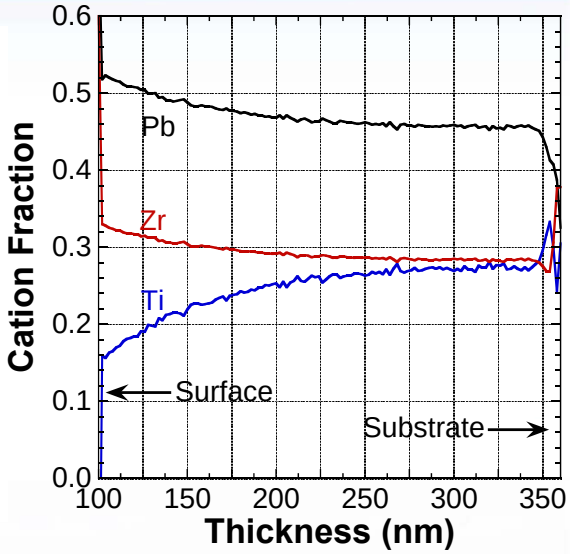
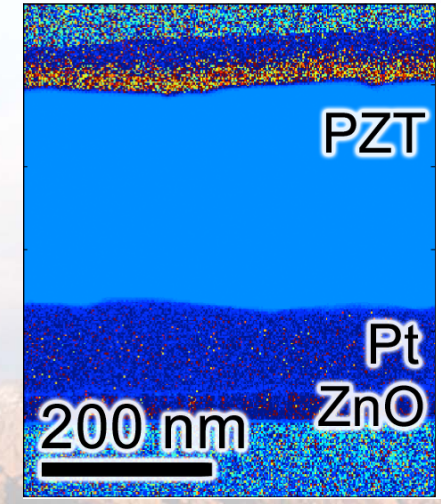
Processing of PZT Film: Lessons Learned To Date

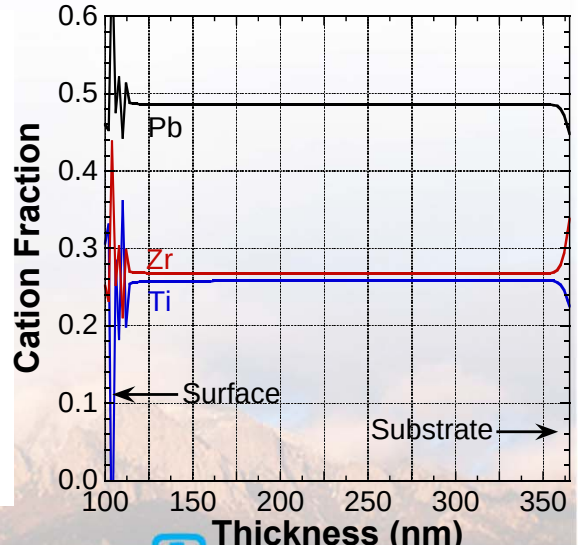
Open Issues:

- Pyrolysis temperature does not significantly effect gradient formation
- On substrates devoid of a titanium adhesion layer, no gradients form – even for 2-MOE sol-gel chemistries
- Heating rate and method ***does*** appear to matter
  - Gradient observed in RTA samples with 50° C/s ramp rate









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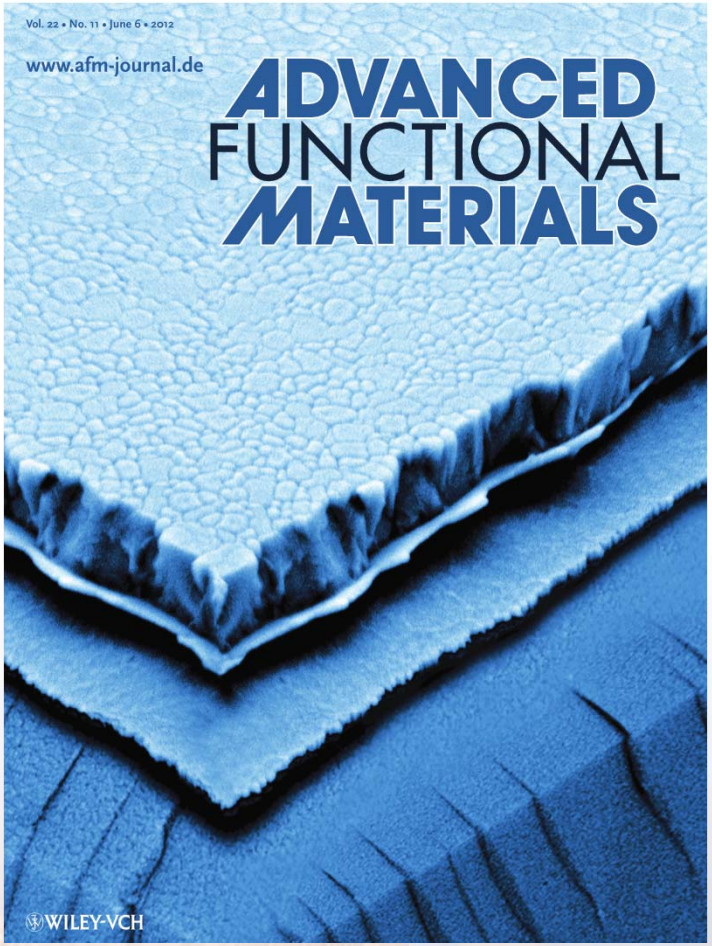
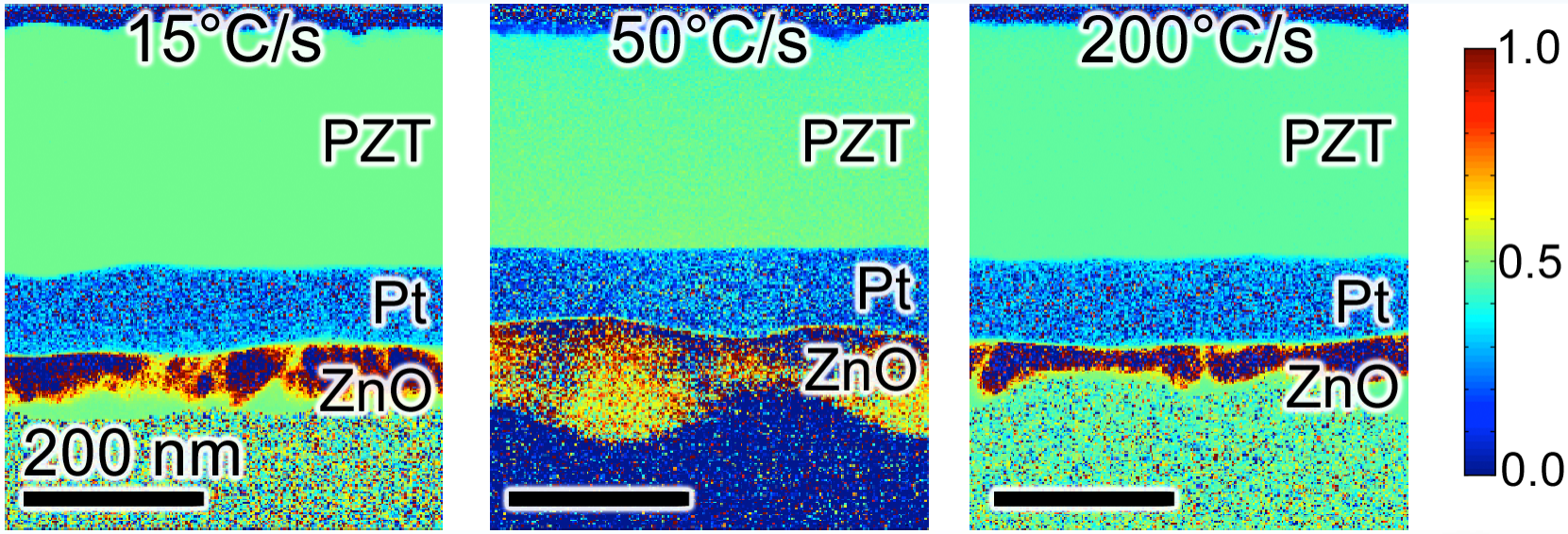
Summary

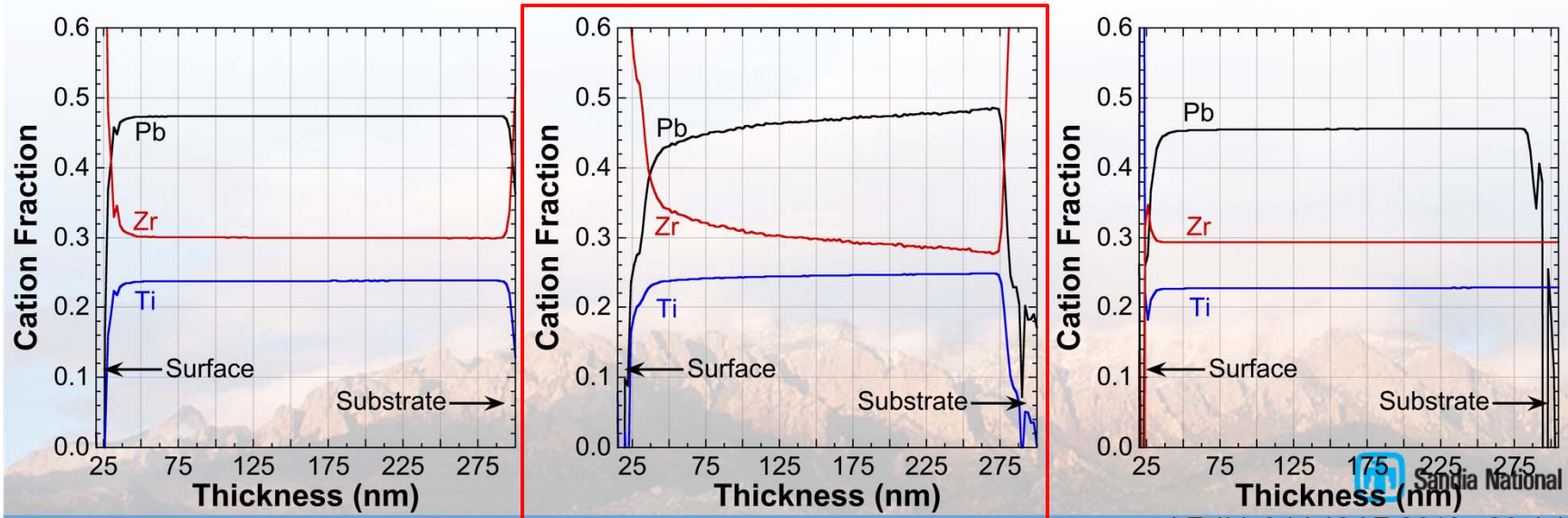
- IMO PZT films prepared on Pt/ZnO substrates possess improved electronic properties compared to traditional substrates
- ZnO as an adhesion layer enables chemically homogeneous films
- Even traditional sol-gel PZT films did not possess composition gradients on Pt/ZnO substrates: *heating rate effect?*
- *Stay tuned….*



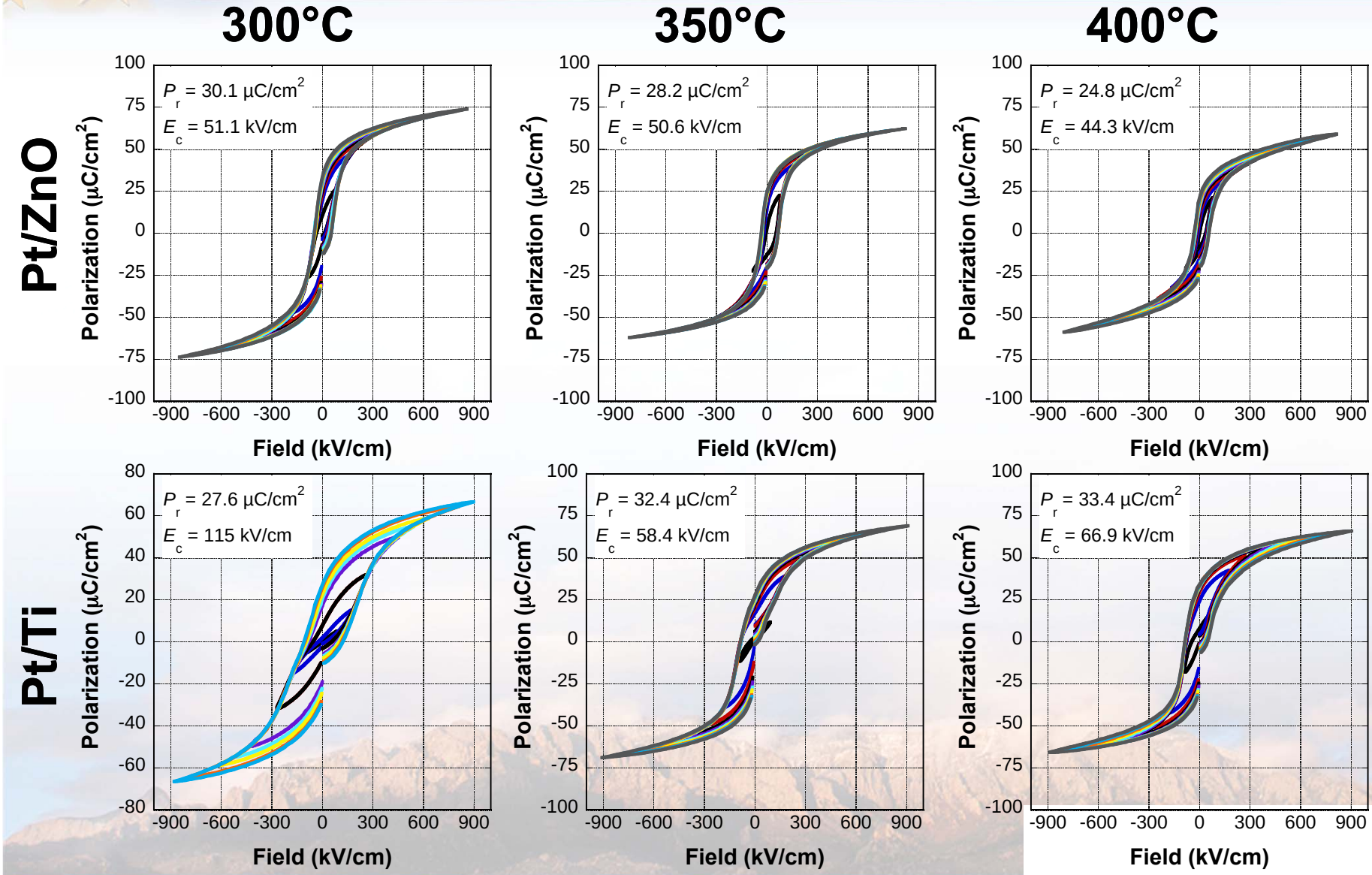
Ramp Rate Effect: 2-MOE Films

Pt/ZnO Lead Distribution





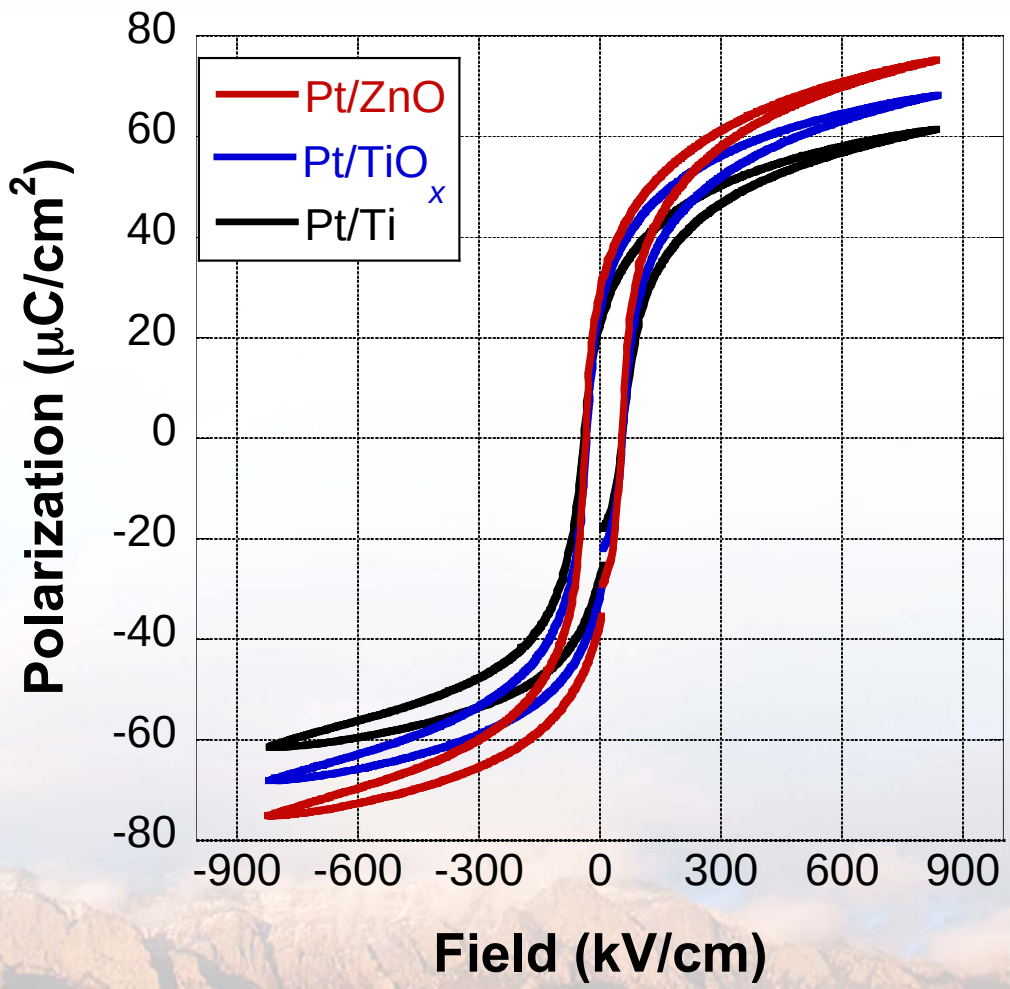
Ferroelectric Properties: IMO Films



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**

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



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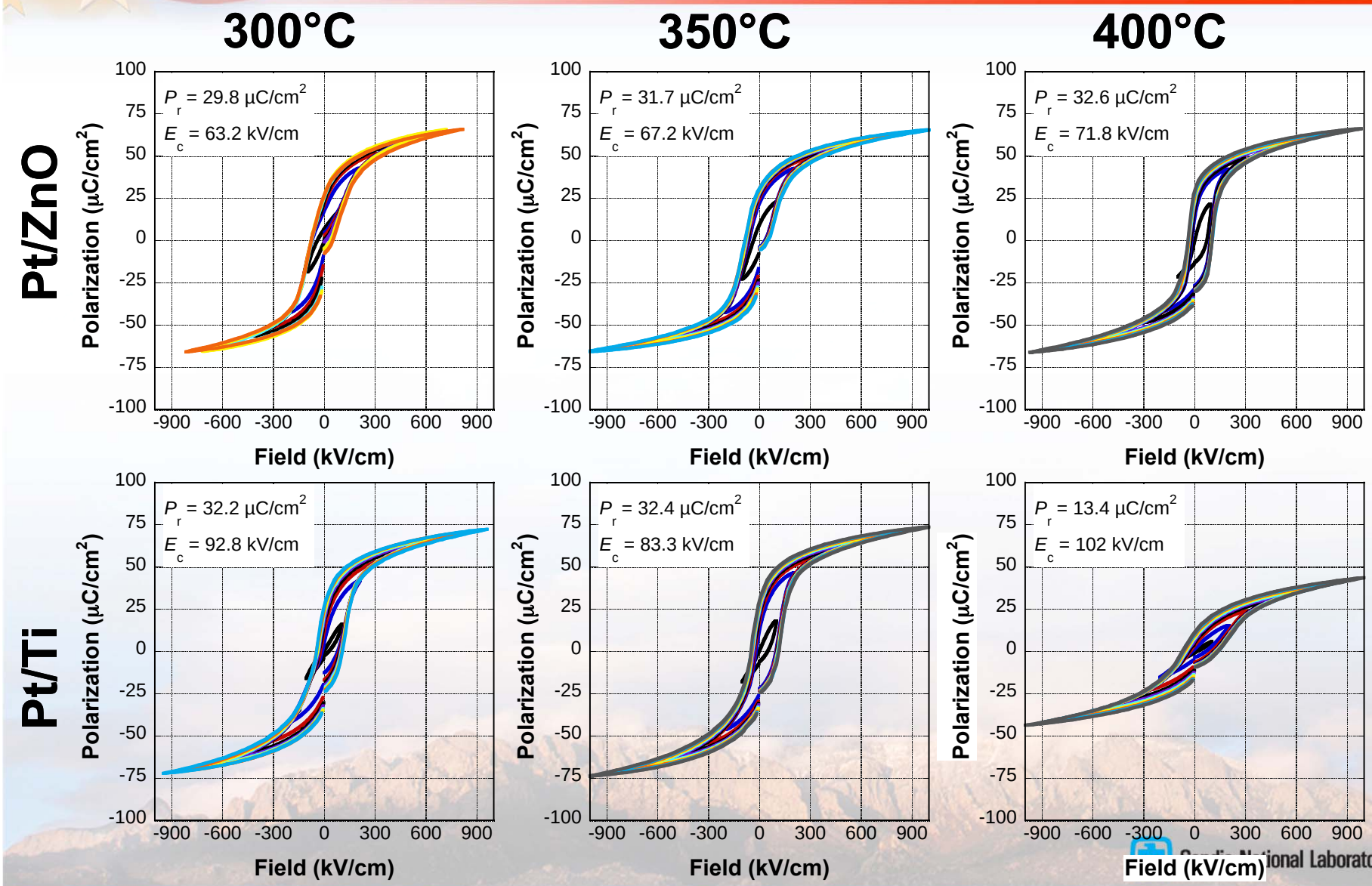
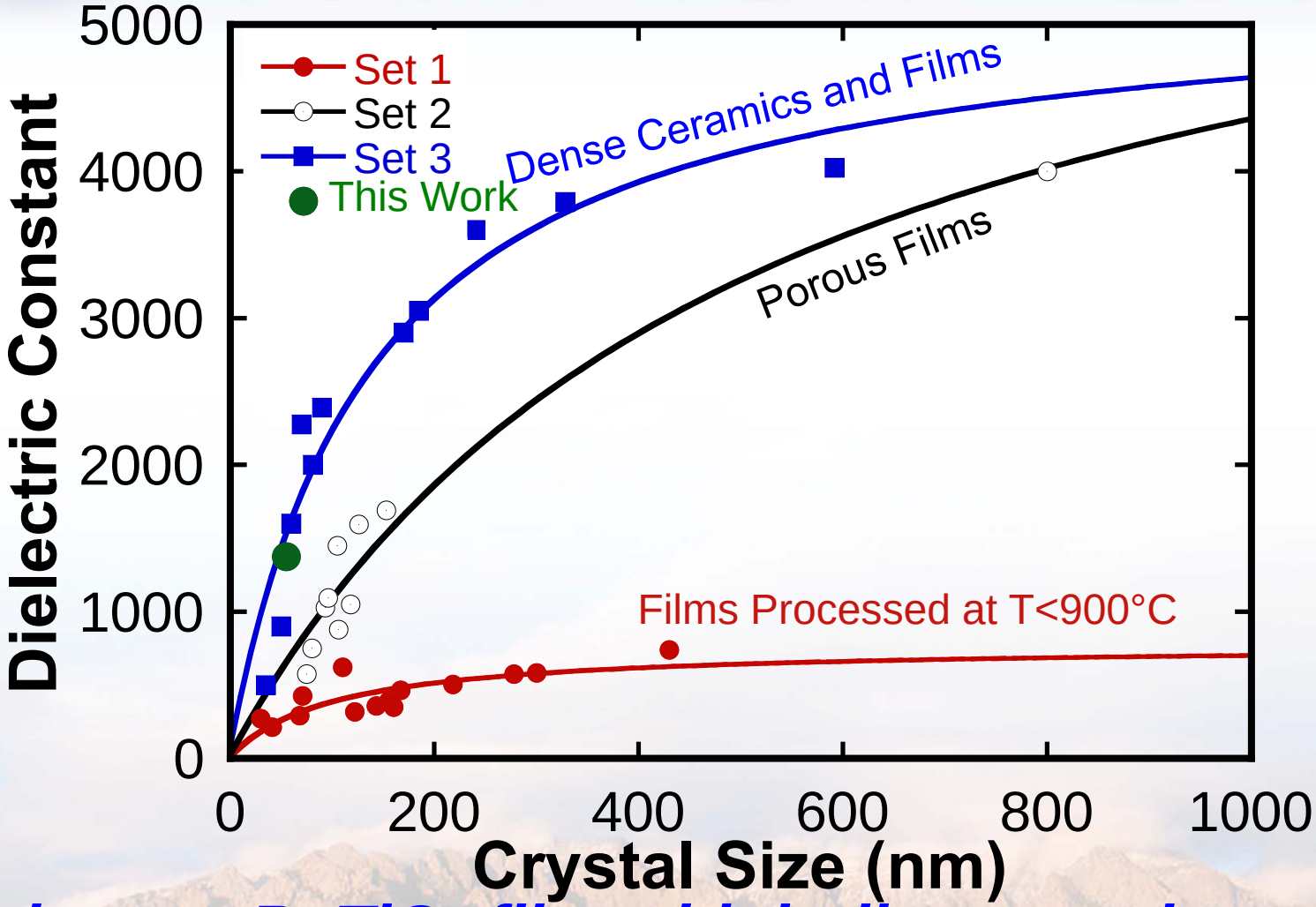
Ferroelectric Properties: 2MOE Films



$BaTiO_3$ Scaling Effects



First known $BaTiO_3$ film with bulk properties on Si

Plot adapted from Aygün *et. al. J. Appl. Phys.* (2011)

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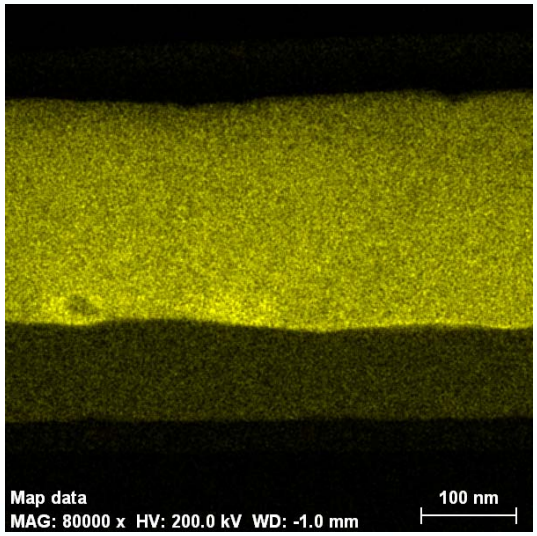
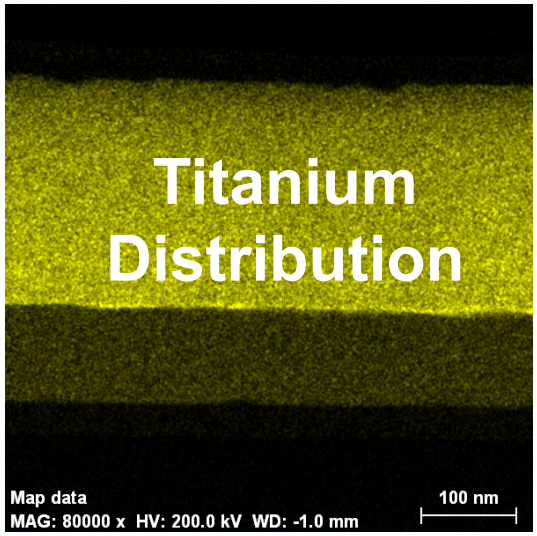
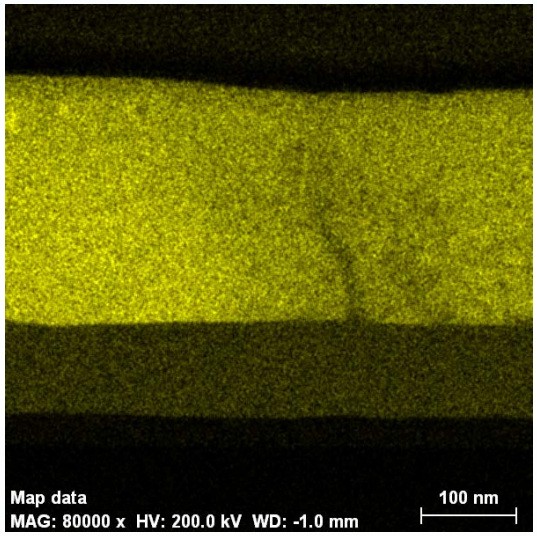
Solution Chemistry Effect: 2-MOE films

300°C | 350°C | 400°C

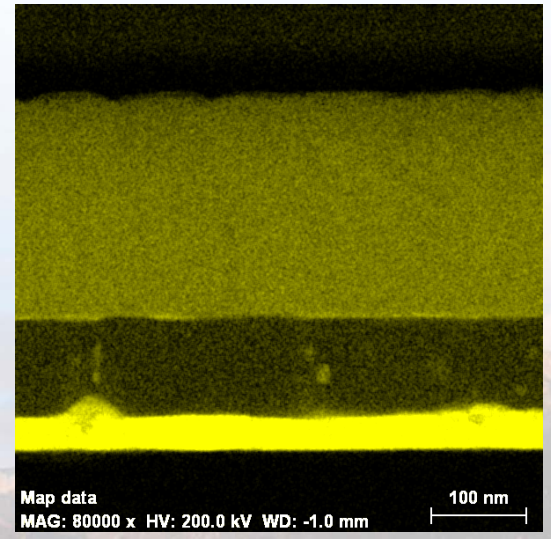
Pt/ZnO

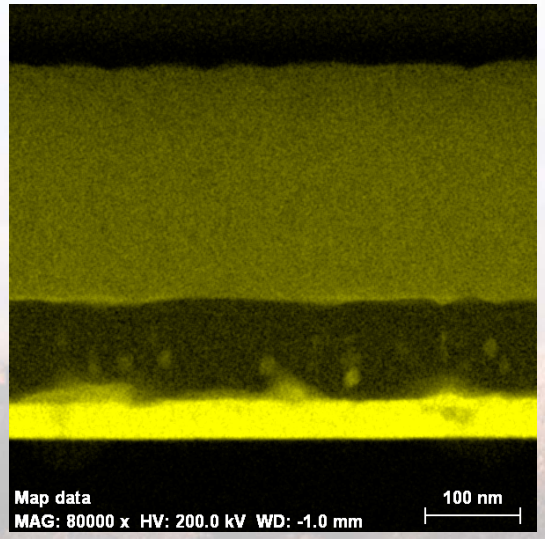


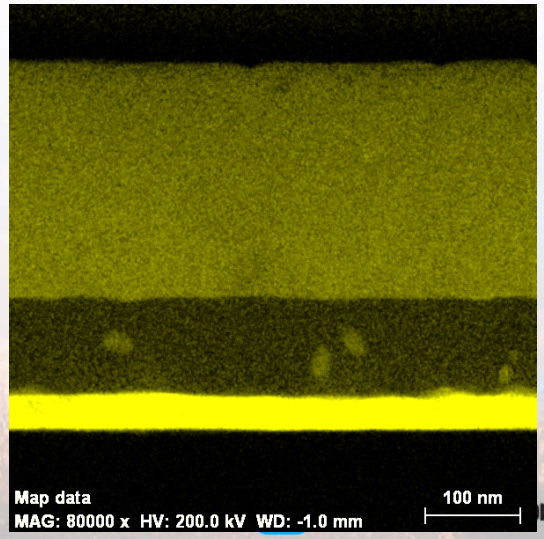




Pt/Ti



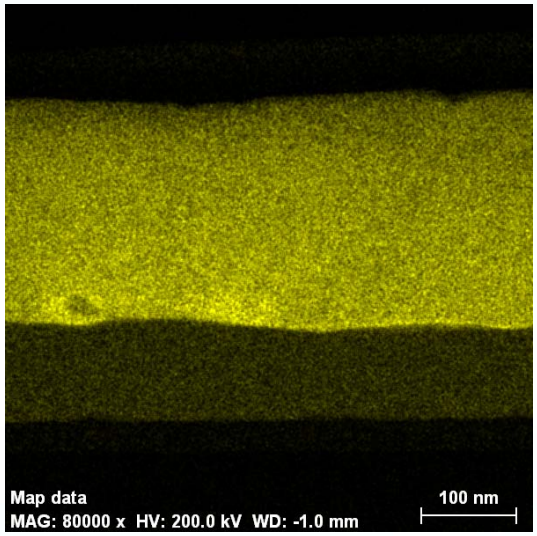


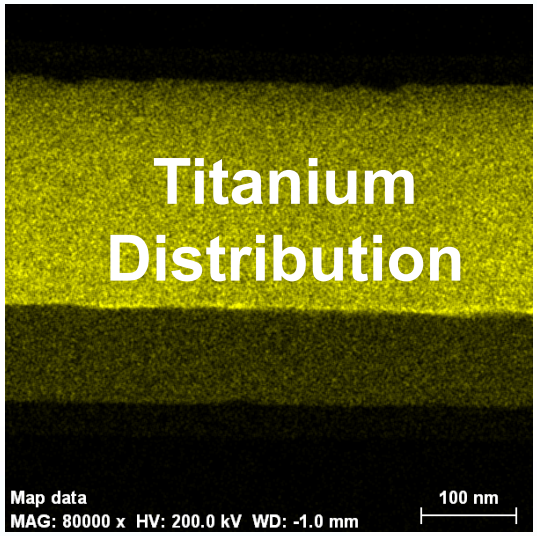


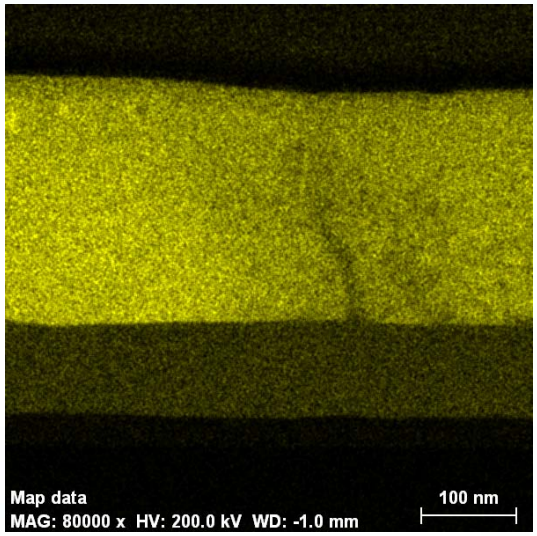
Solution Chemistry Effect: 2-MOE films

300°C | 350°C | 400°C

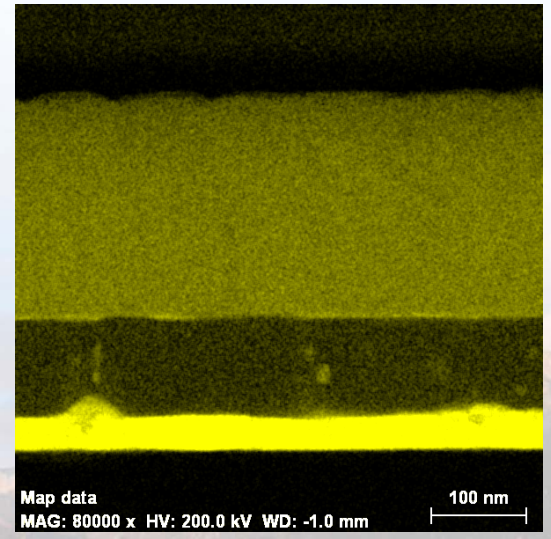
Pt/ZnO

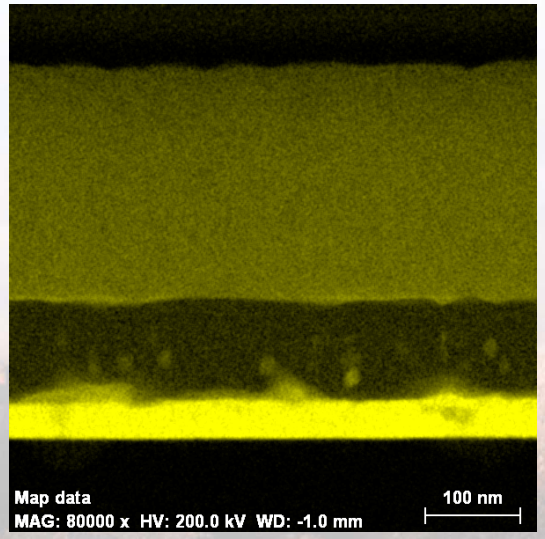


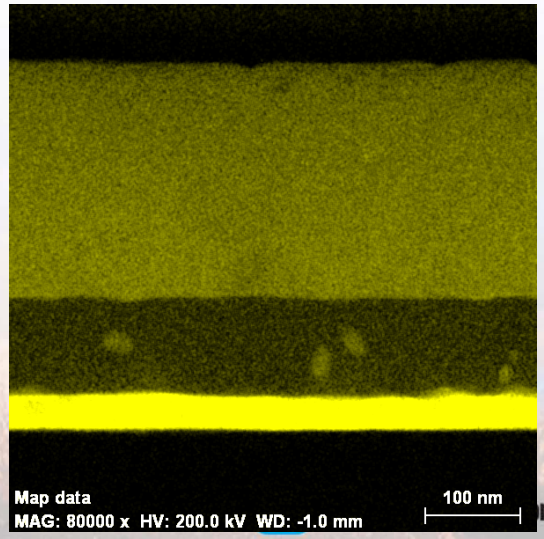




Pt/Ti



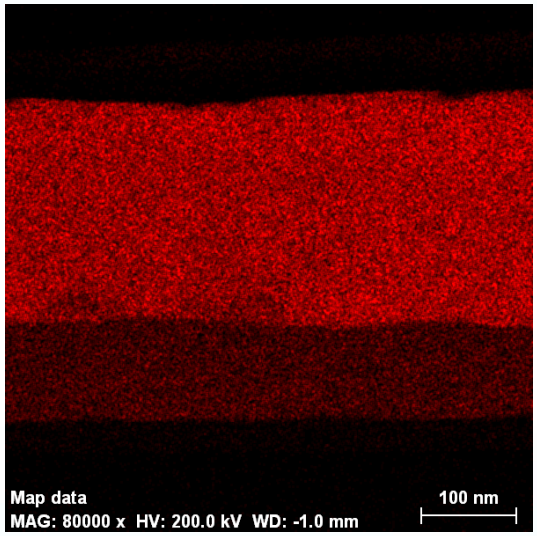


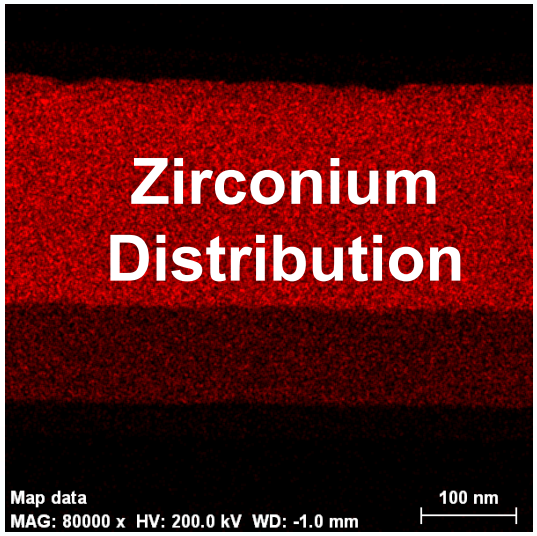


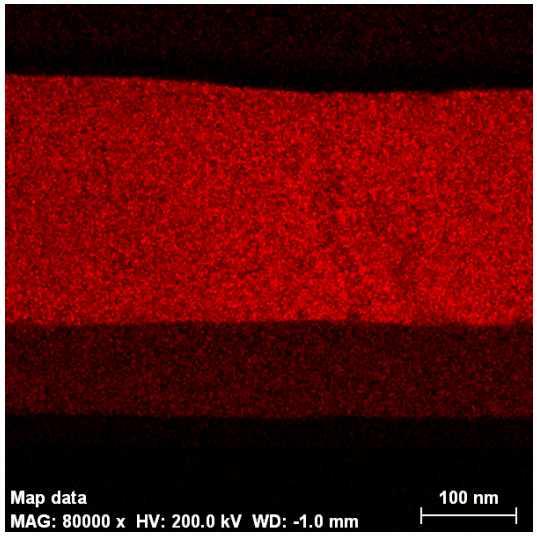
Solution Chemistry Effect: 2-MOE films

300°C | 350°C | 400°C

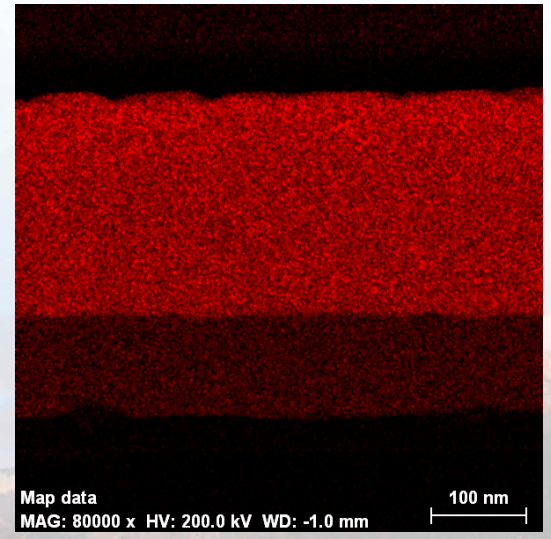
Pt/ZnO

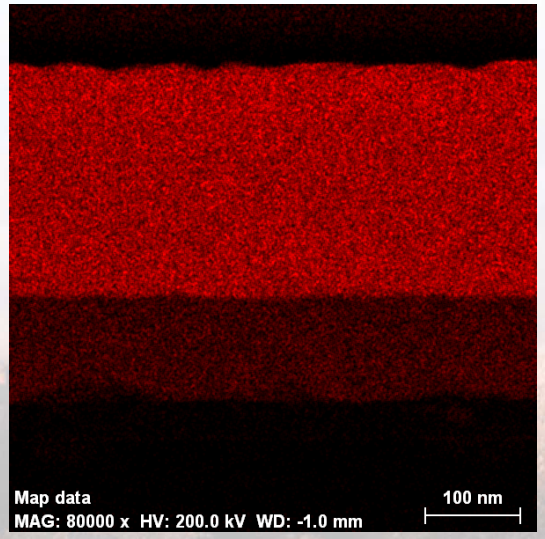


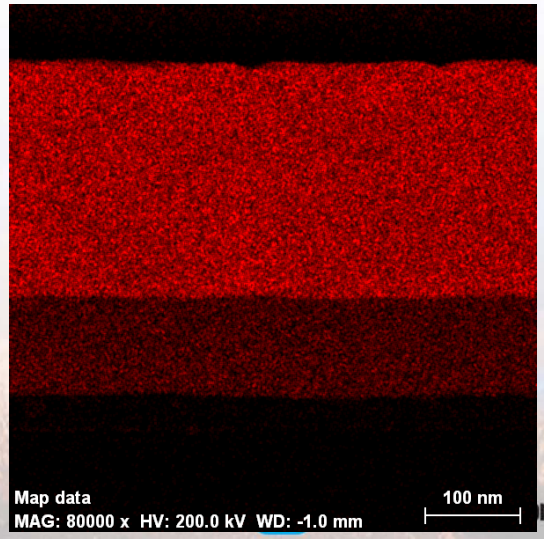




Pt/Ti



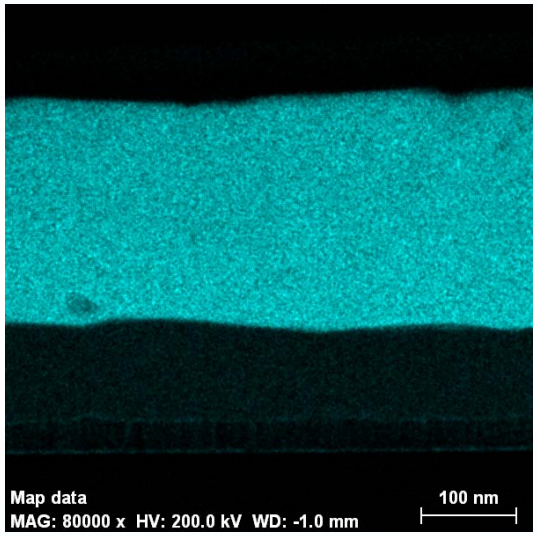


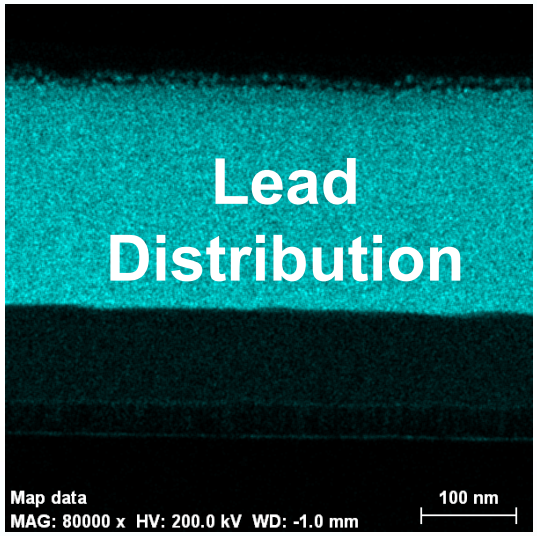


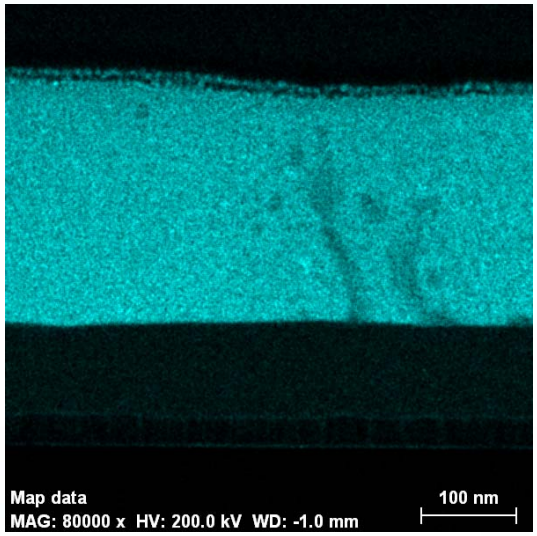
Solution Chemistry Effect: 2-MOE films

300°C | 350°C | 400°C

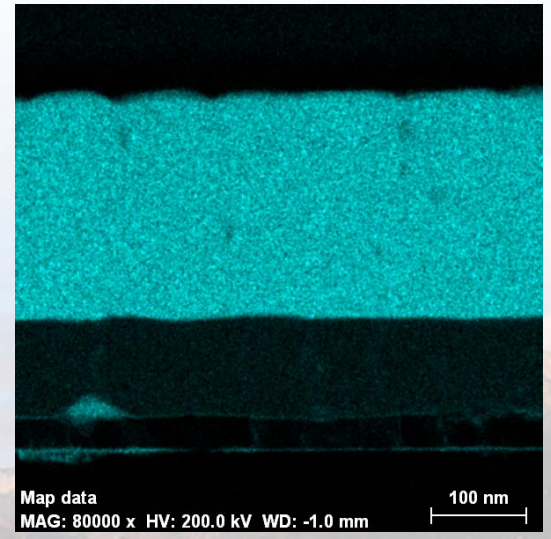
Pt/ZnO

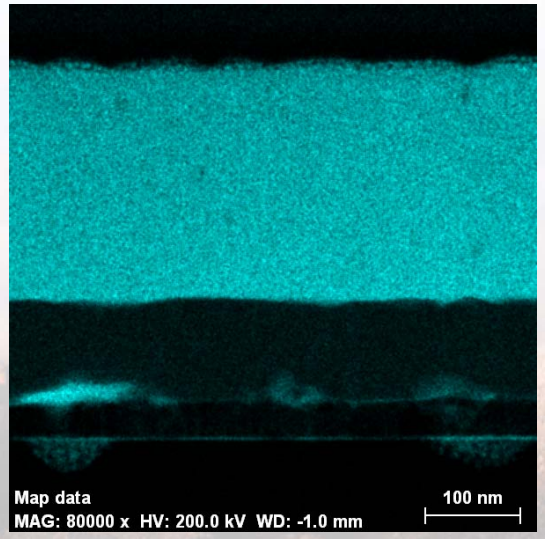


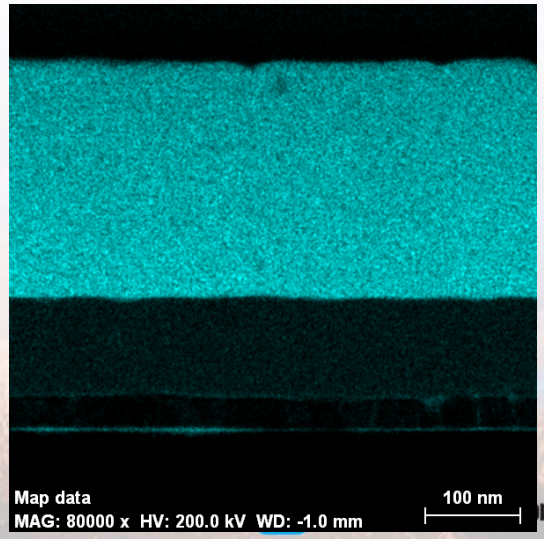




Pt/Ti



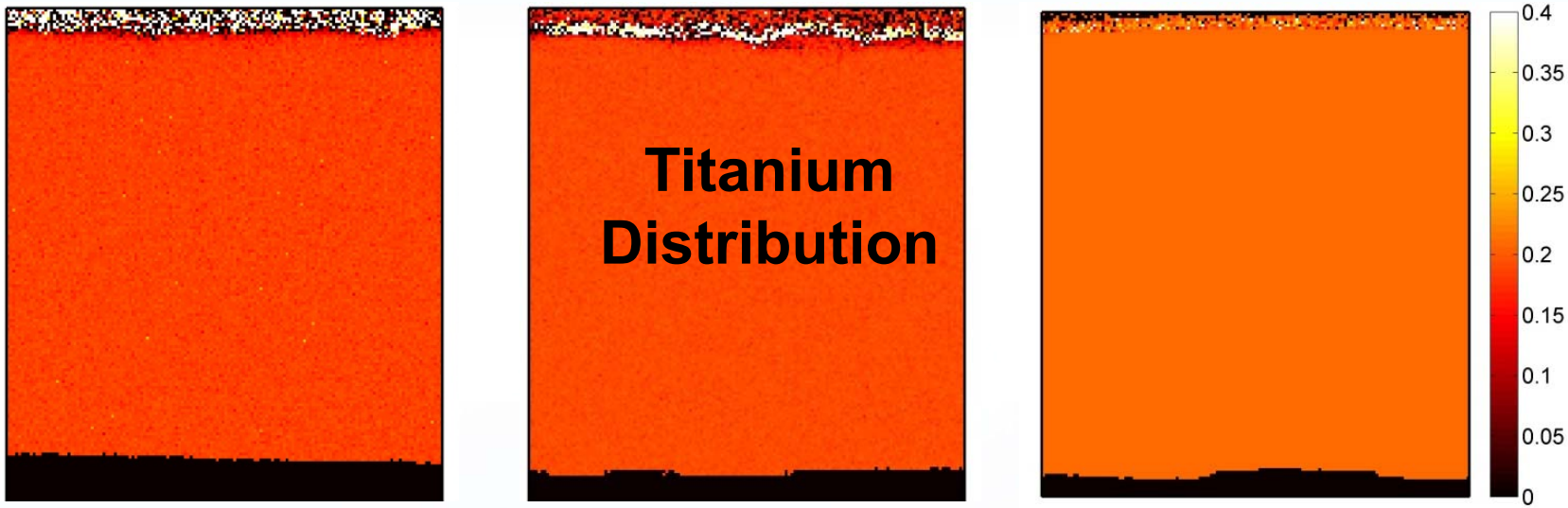




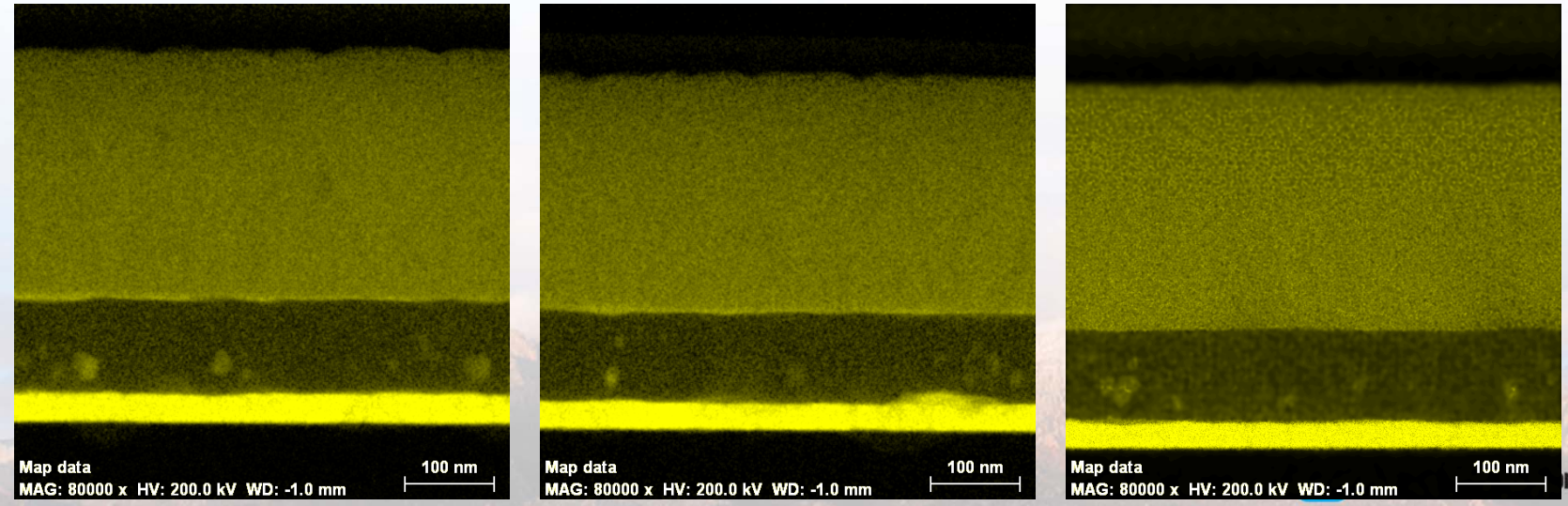
Solution Chemistry Effect: IMO Films

300°C 350°C 400°C

Pt/ZnO



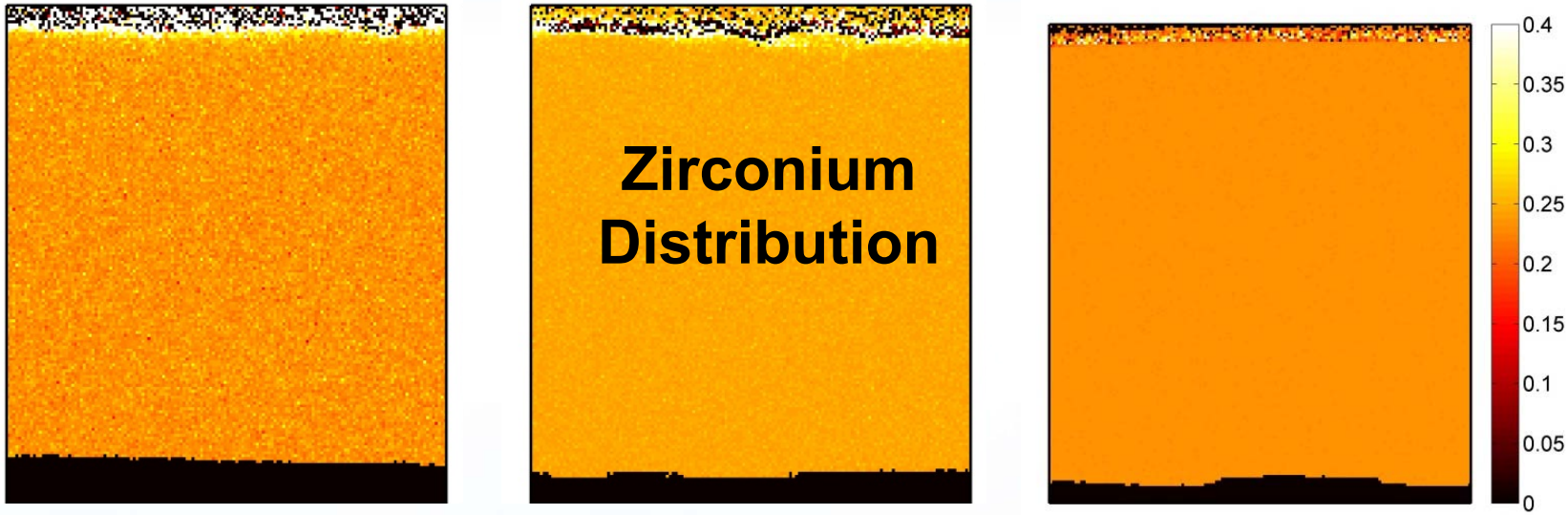
Pt/Ti



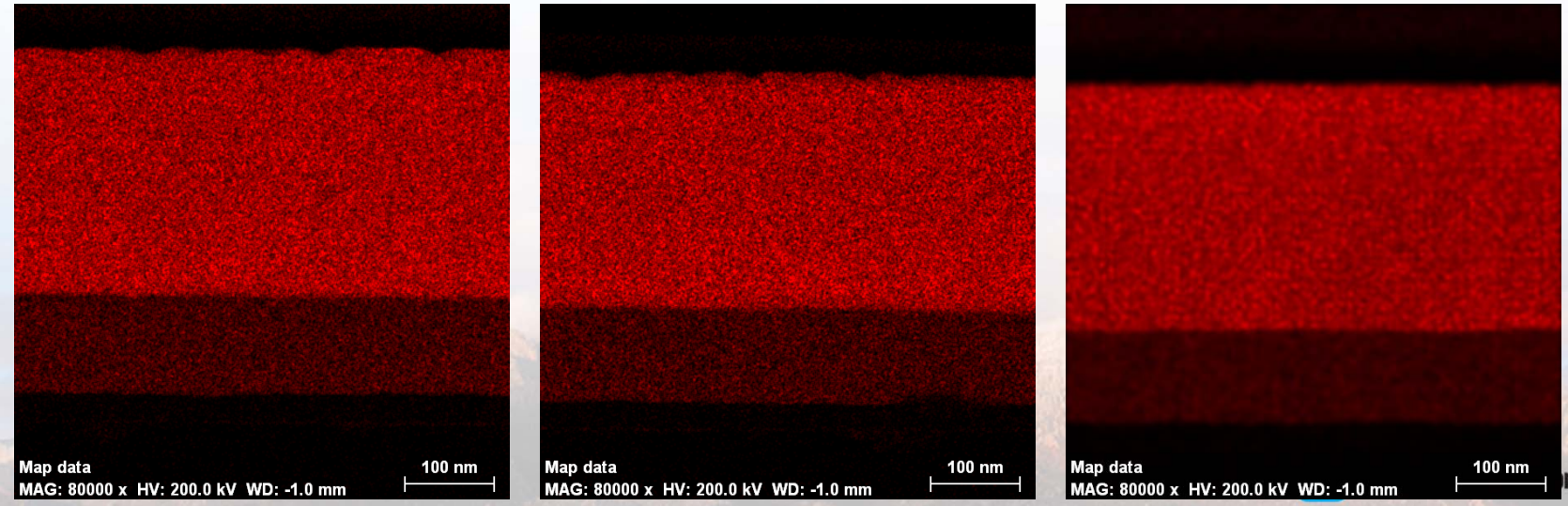
Solution Chemistry Effect: IMO Films

300°C 350°C 400°C

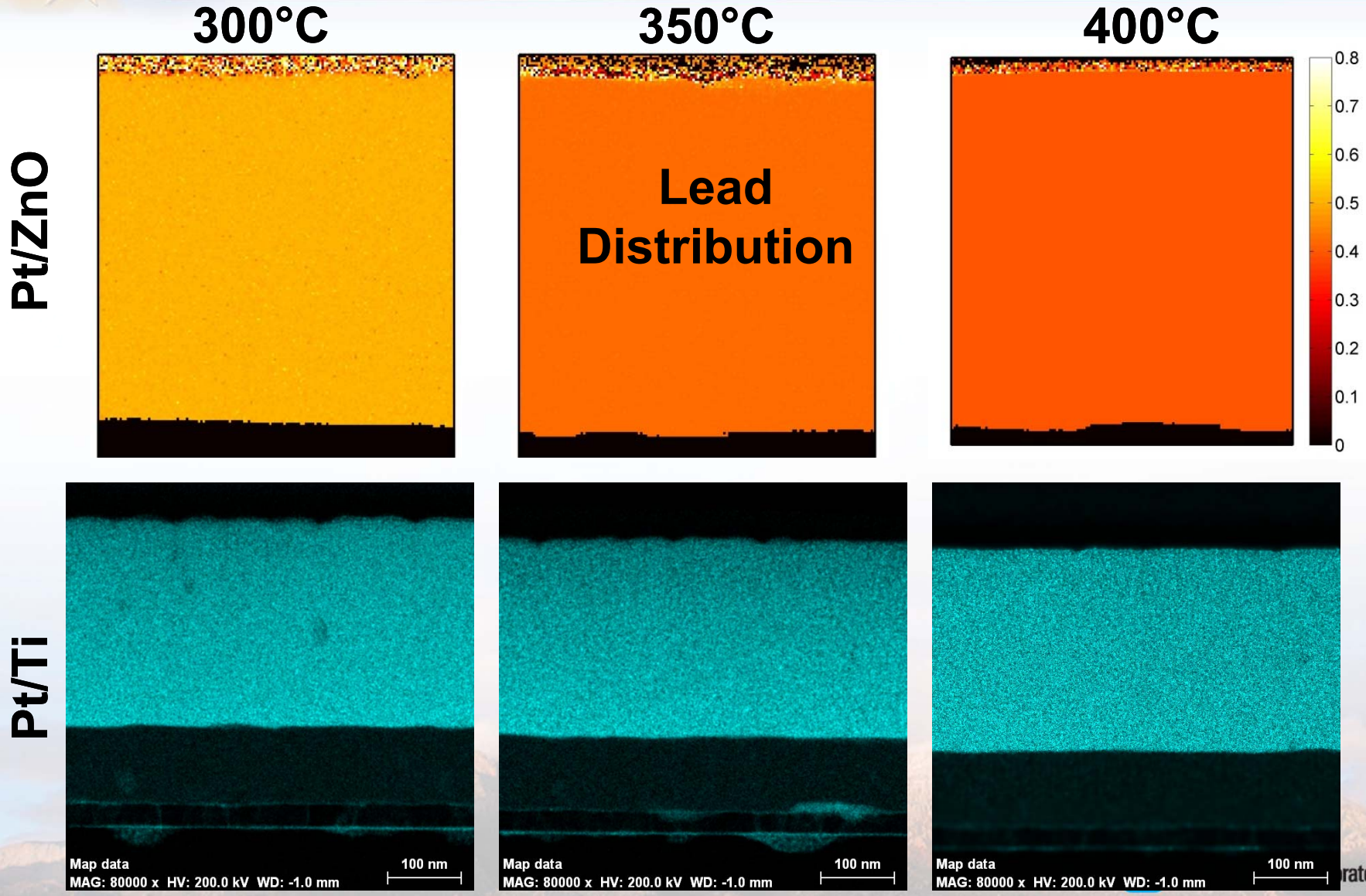
Pt/ZnO

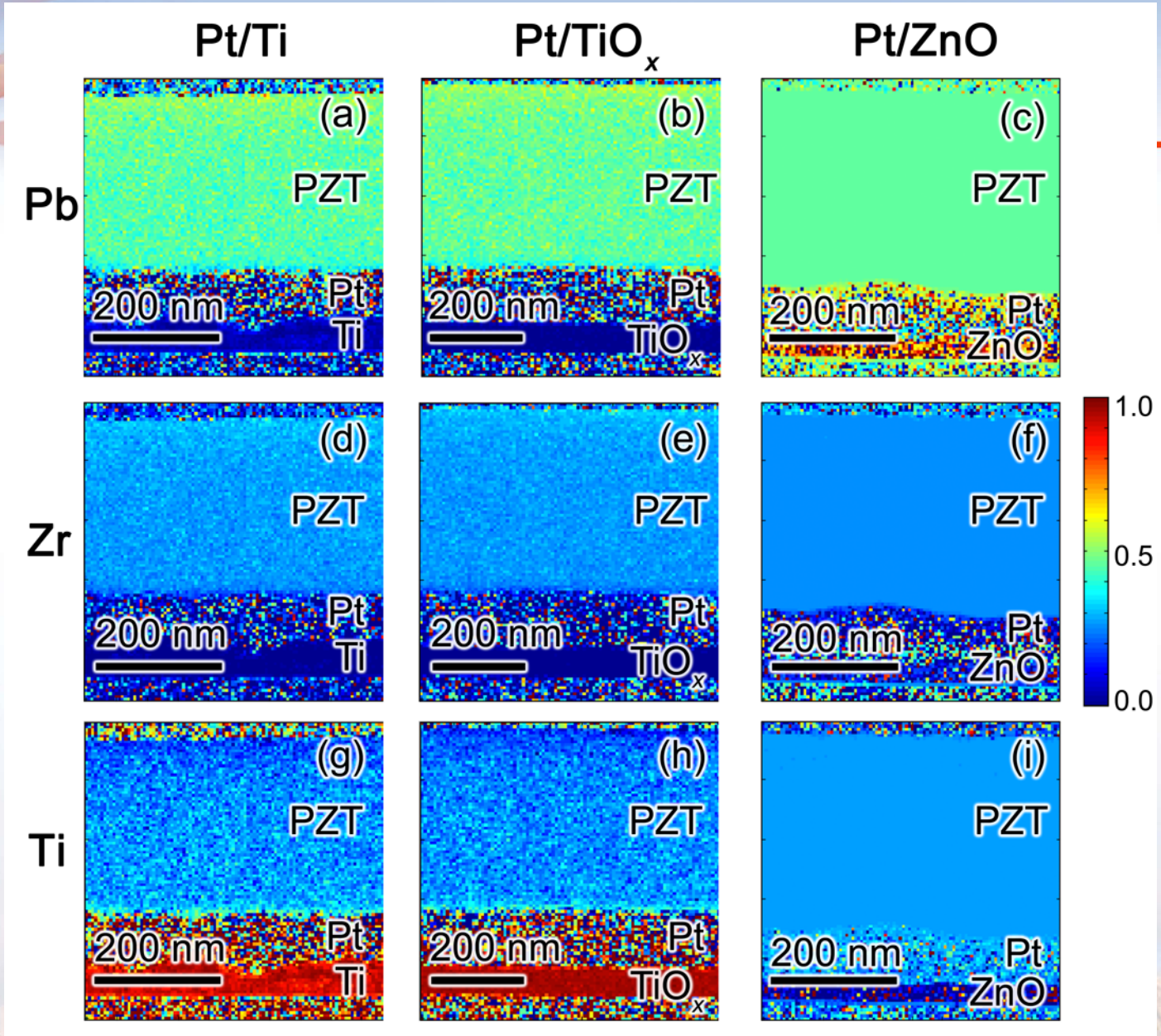


Pt/Ti



Solution Chemistry Effect: IMO Films

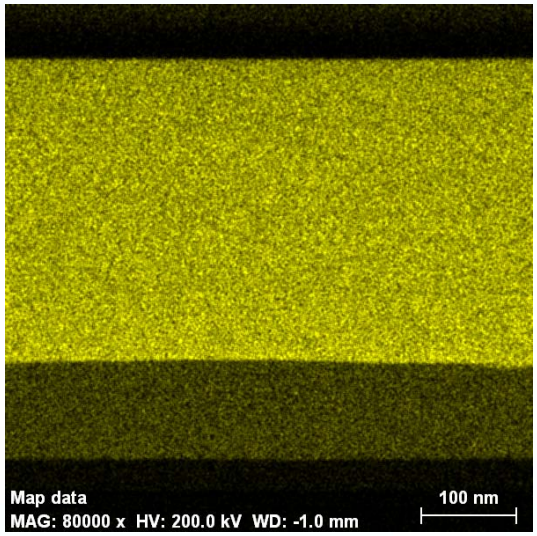


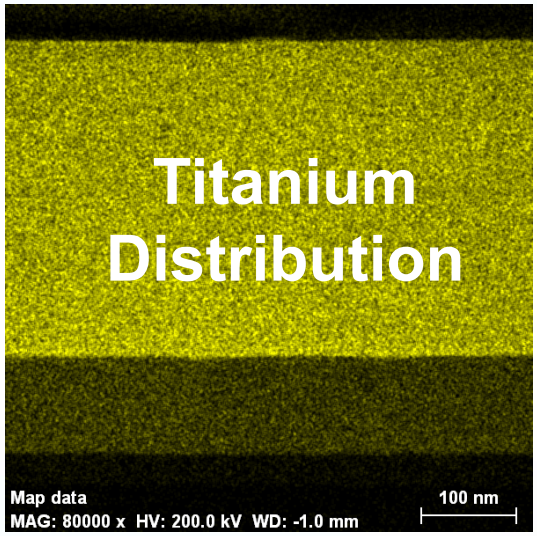

Pt/Ti
Pt/TiO$_x$
Pt/ZnO
Pb
Zr
Ti
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
PZT
Pt
Ti
TiO$_x$
ZnO
200 nm
1.0
0.5
0.0

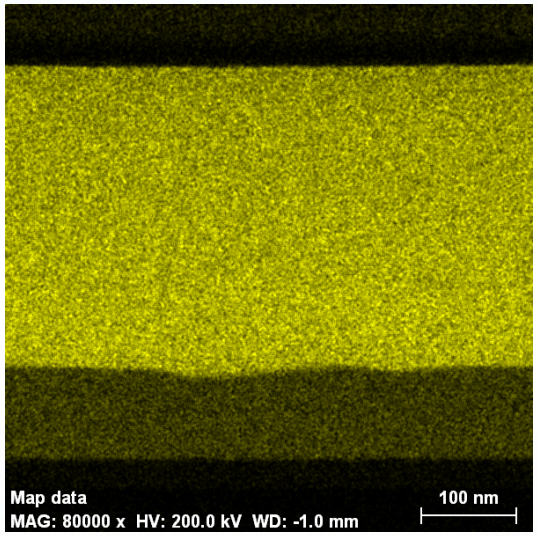
Solution Chemistry Effect: 2-MOE films Prior to Crystallization

300°C 350°C 400°C

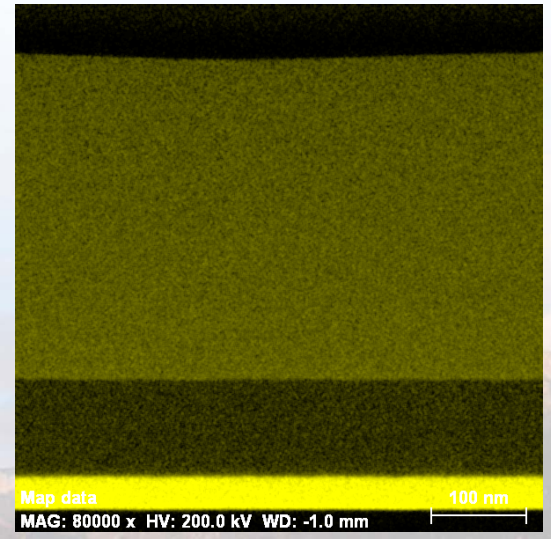
Pt/ZnO

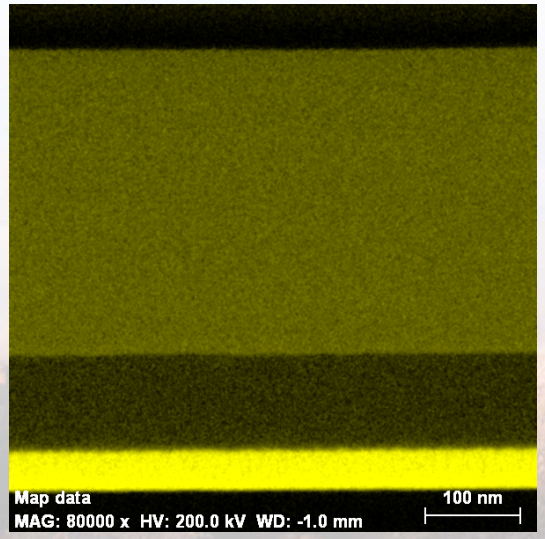


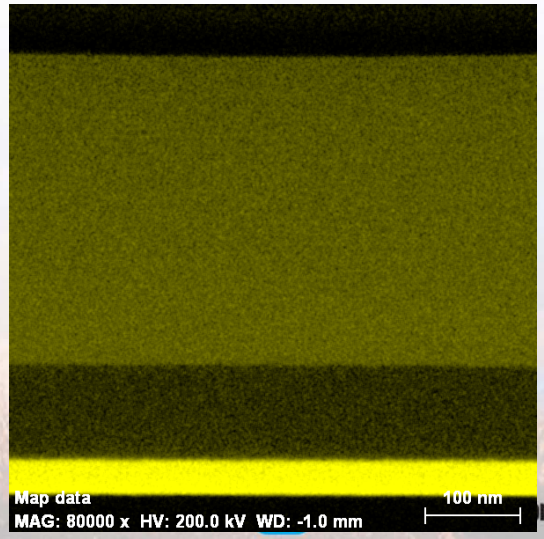




Pt/Ti





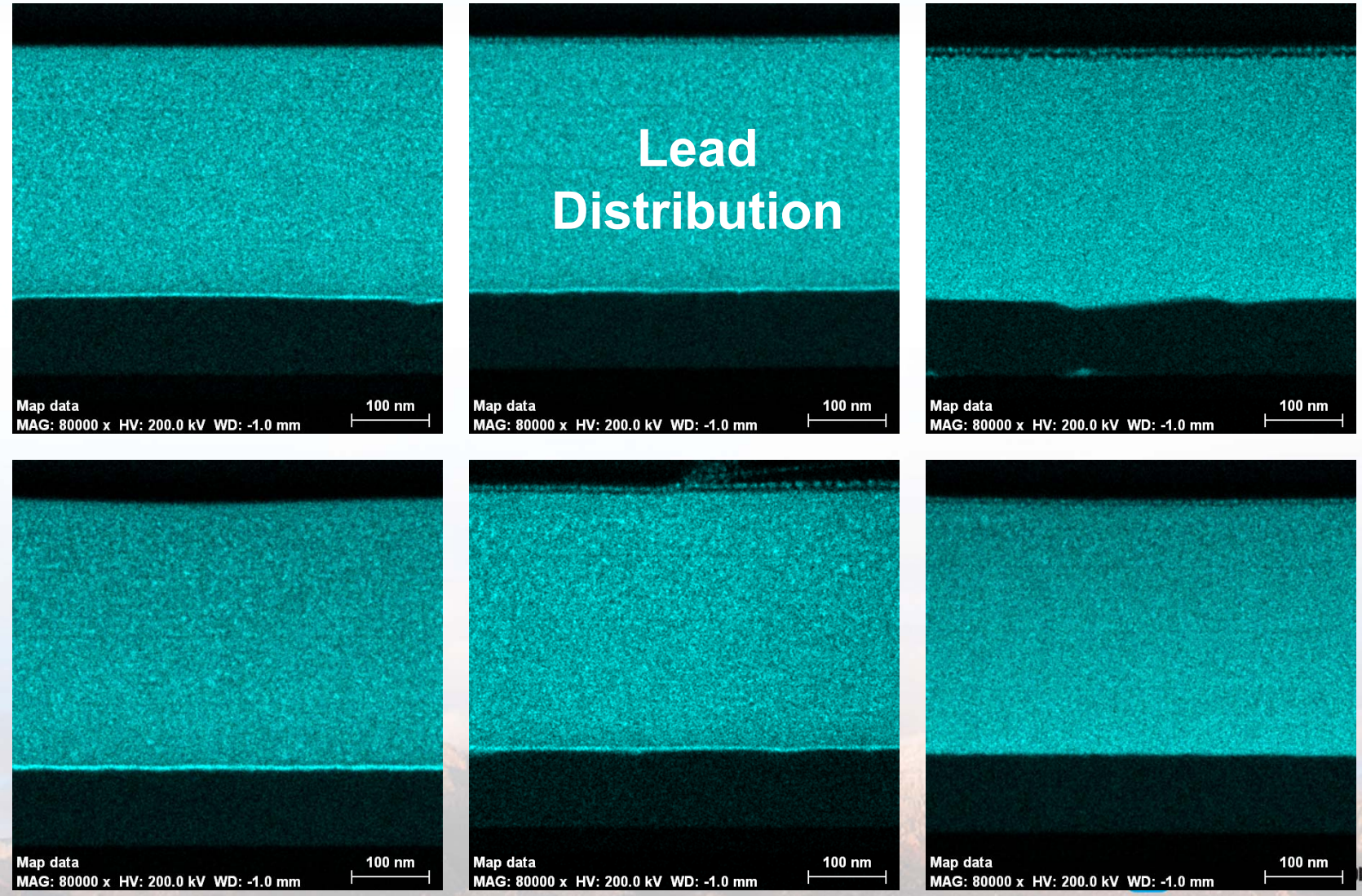


Solution Chemistry Effect: 2-MOE films Prior to crystallization

300°C 350°C 400°C

Pt/ZnO

Pt/Ti

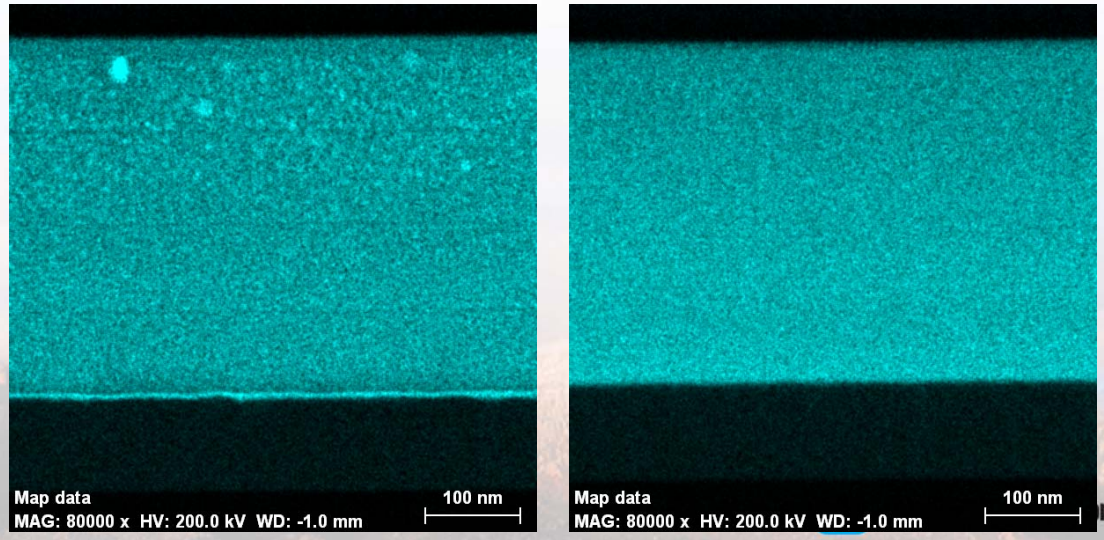


Solution Chemistry Effect: IMO Films Prior to Crystallization

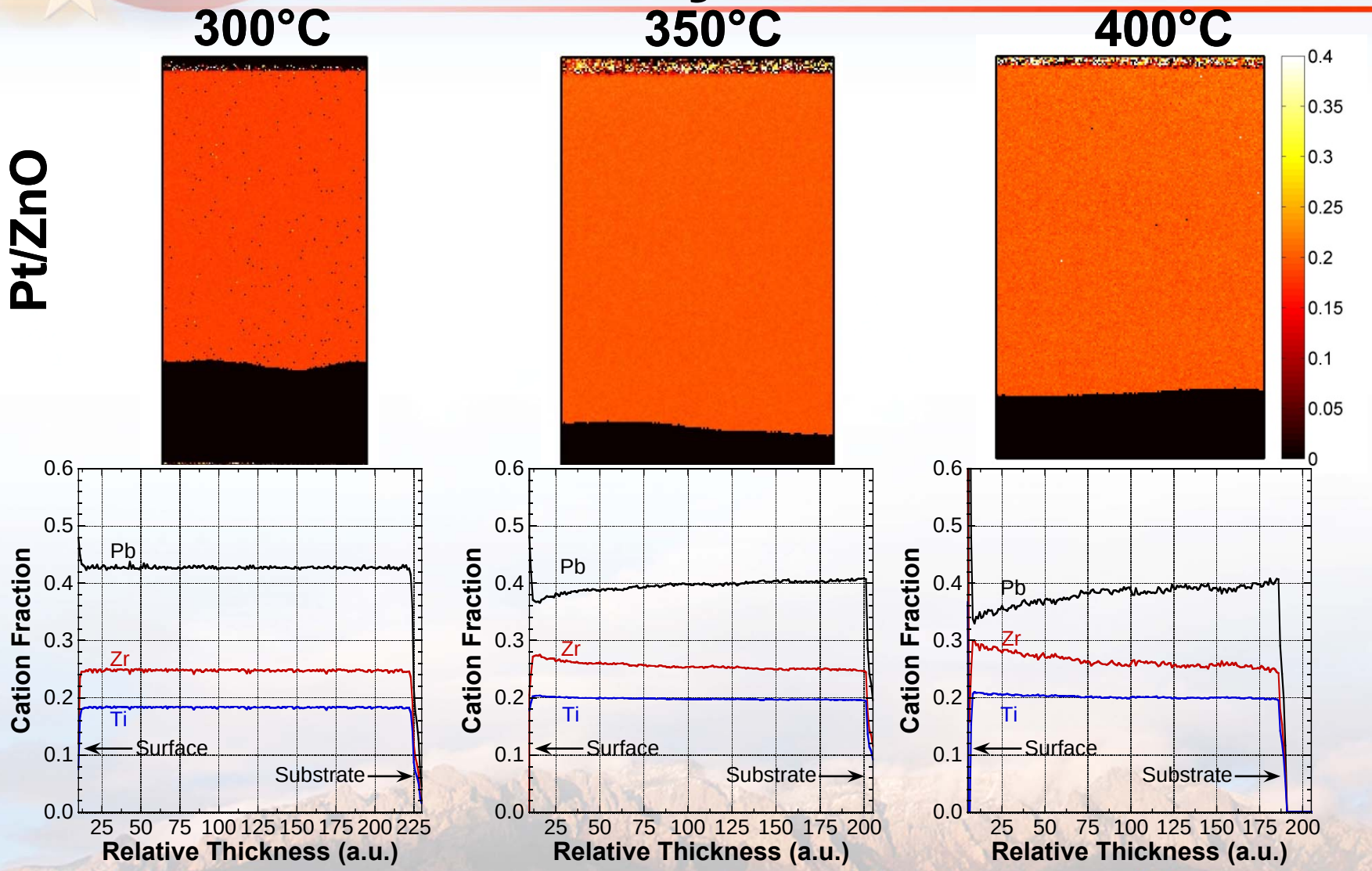
300°C 350°C 400°C

Pt/ZnO

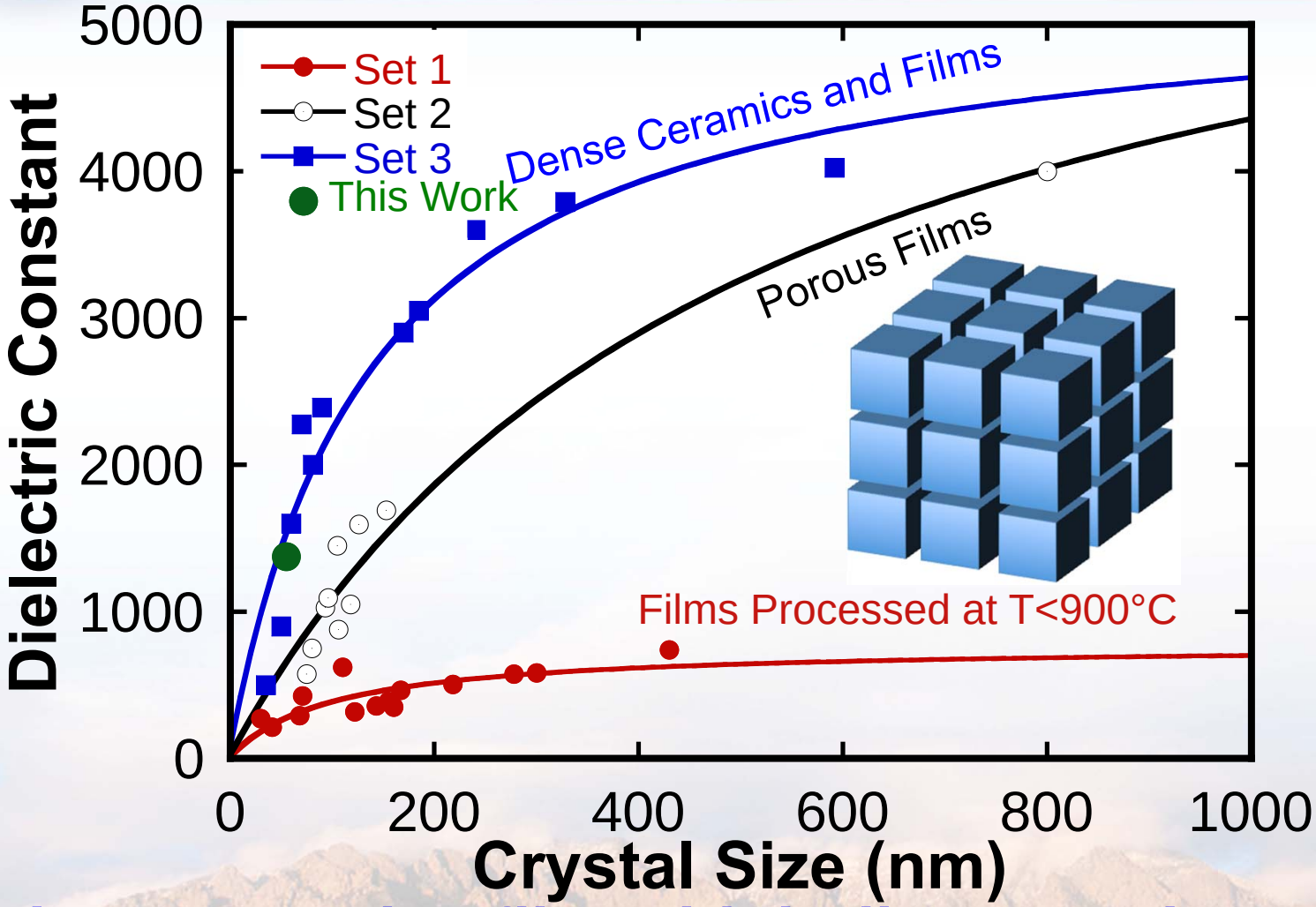
Pt/Ti



Solution Chemistry Effect: IMO Films Prior to crystallization



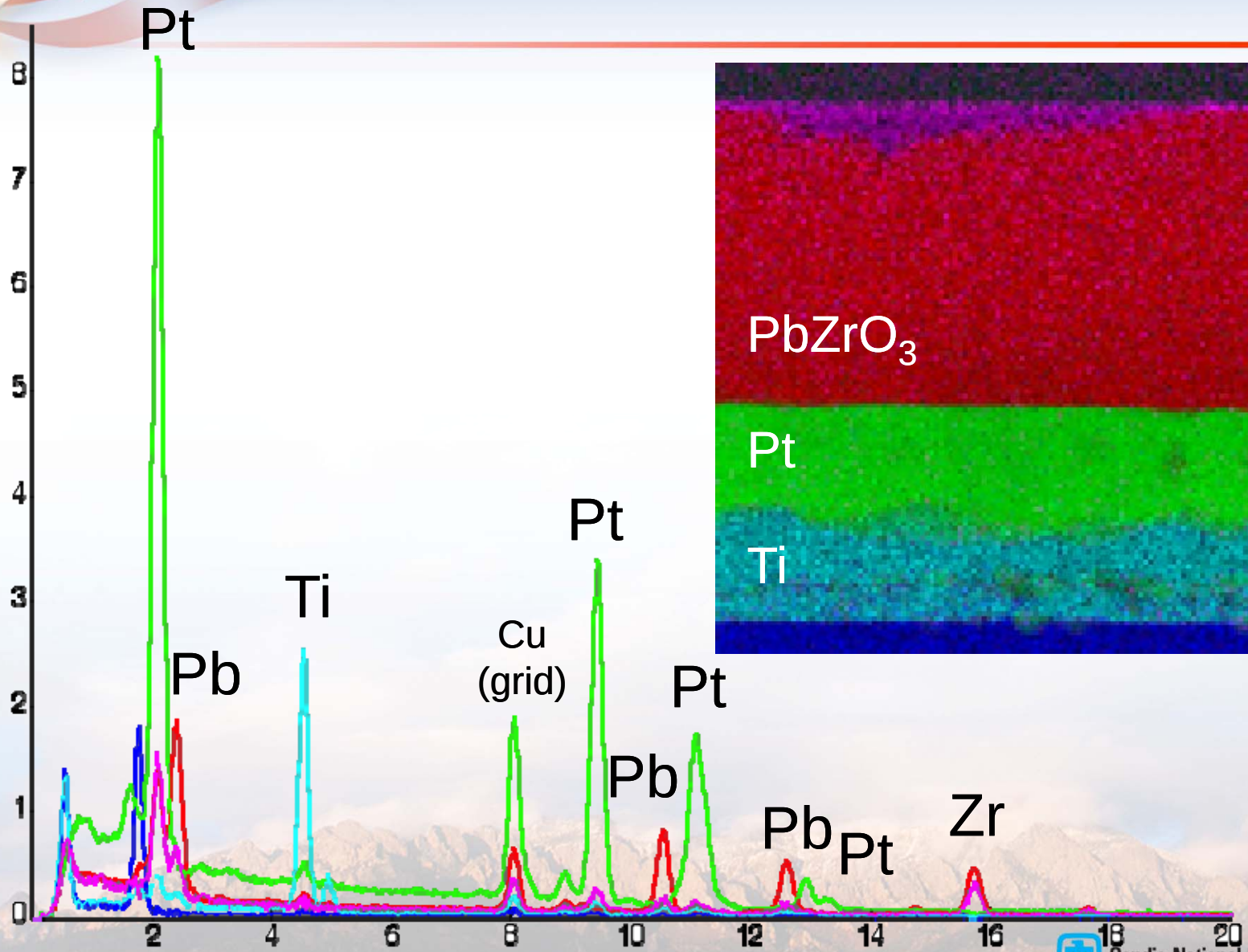
$BaTiO_3$ Scaling Effects

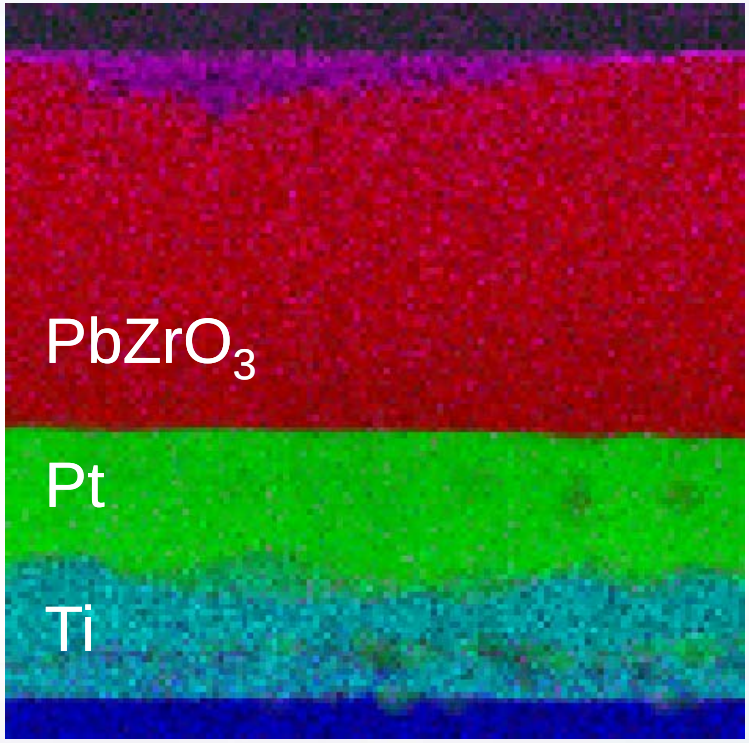


First known $BaTiO_3$ film with bulk properties on Si

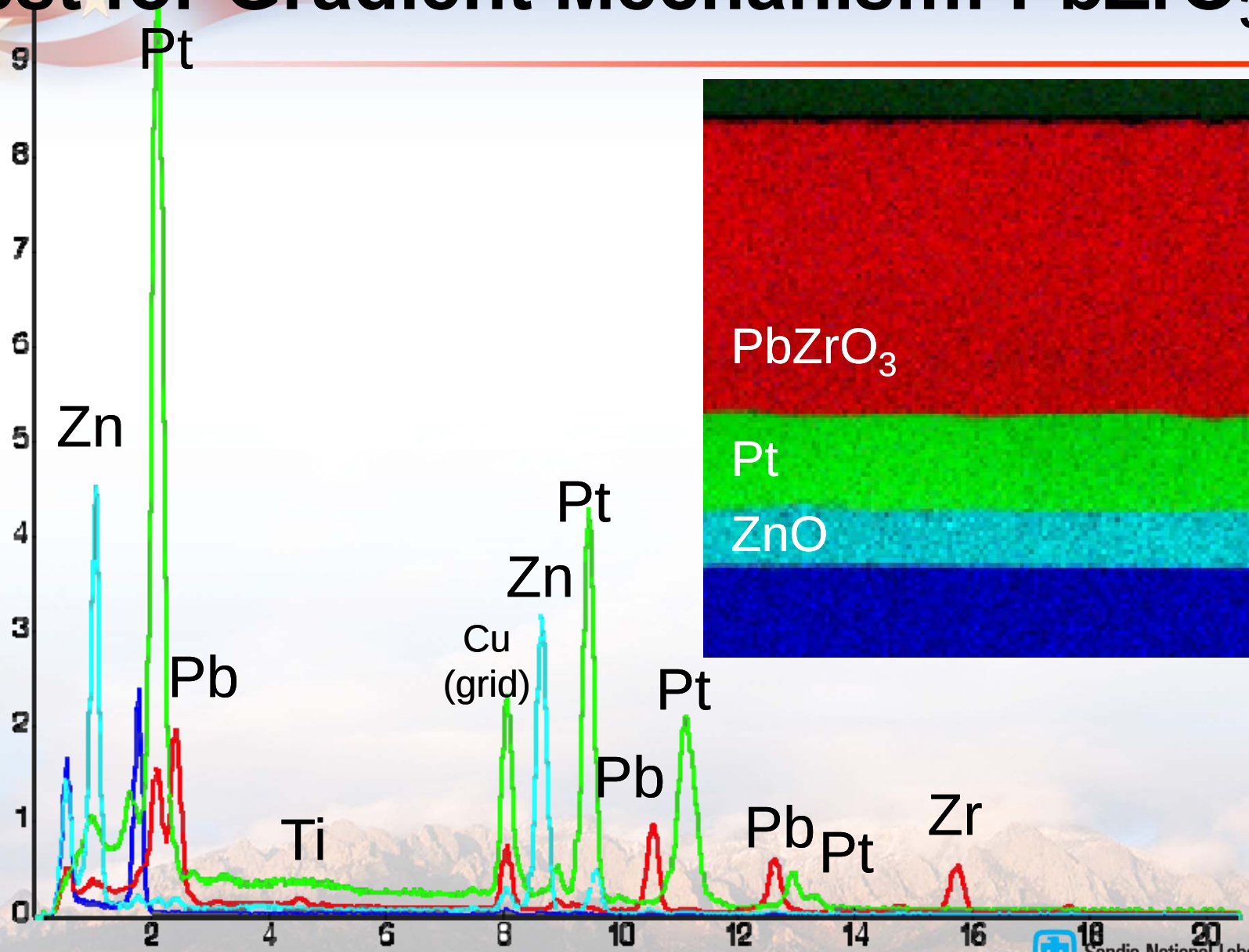
Plot adapted from Aygün *et. al. J. Appl. Phys.* (2011)

Test for Gradient Mechanism: $PbZrO_3$





Test for Gradient Mechanism: $PbZrO_3$



Crystallite vs. Grain Size

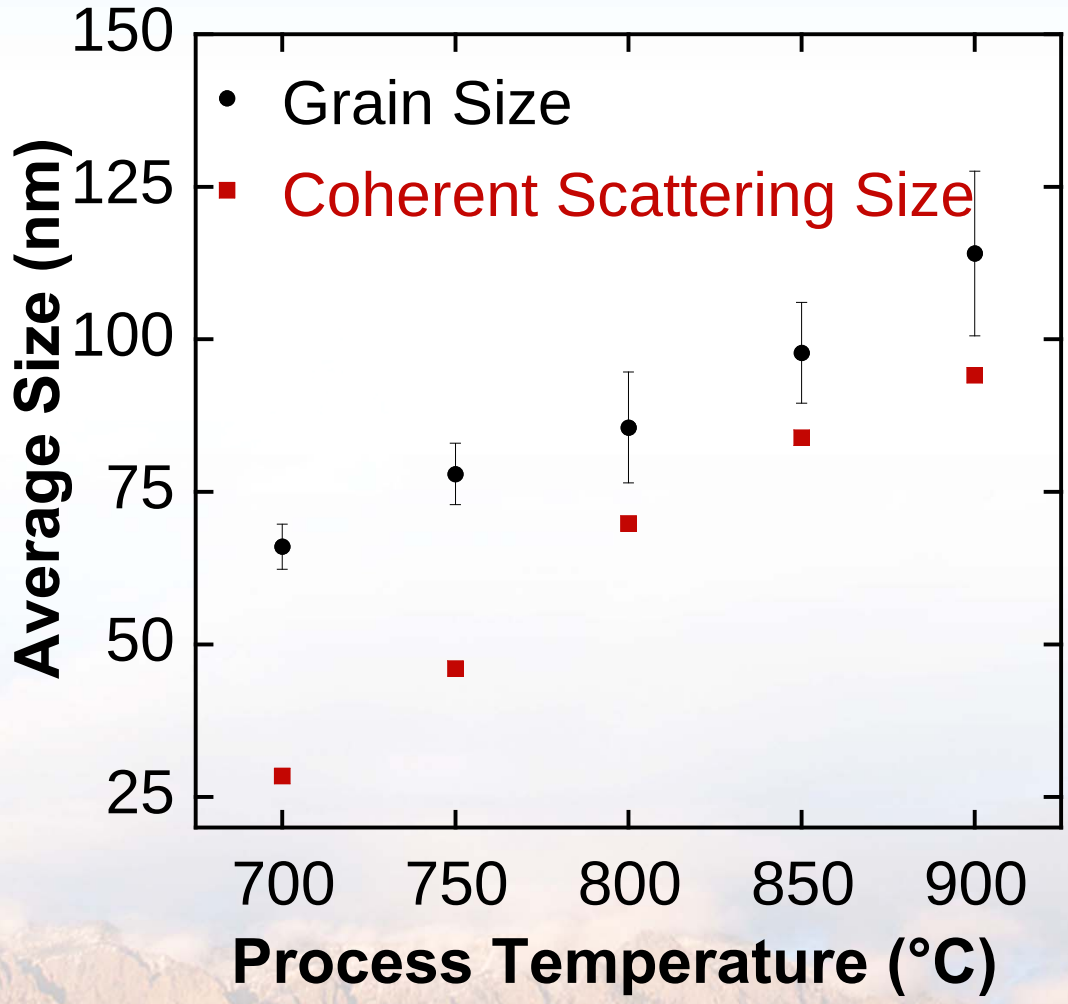
Grain Size

- AFM and FE-SEM
- 95% confidence interval

Coherent Scattering Size

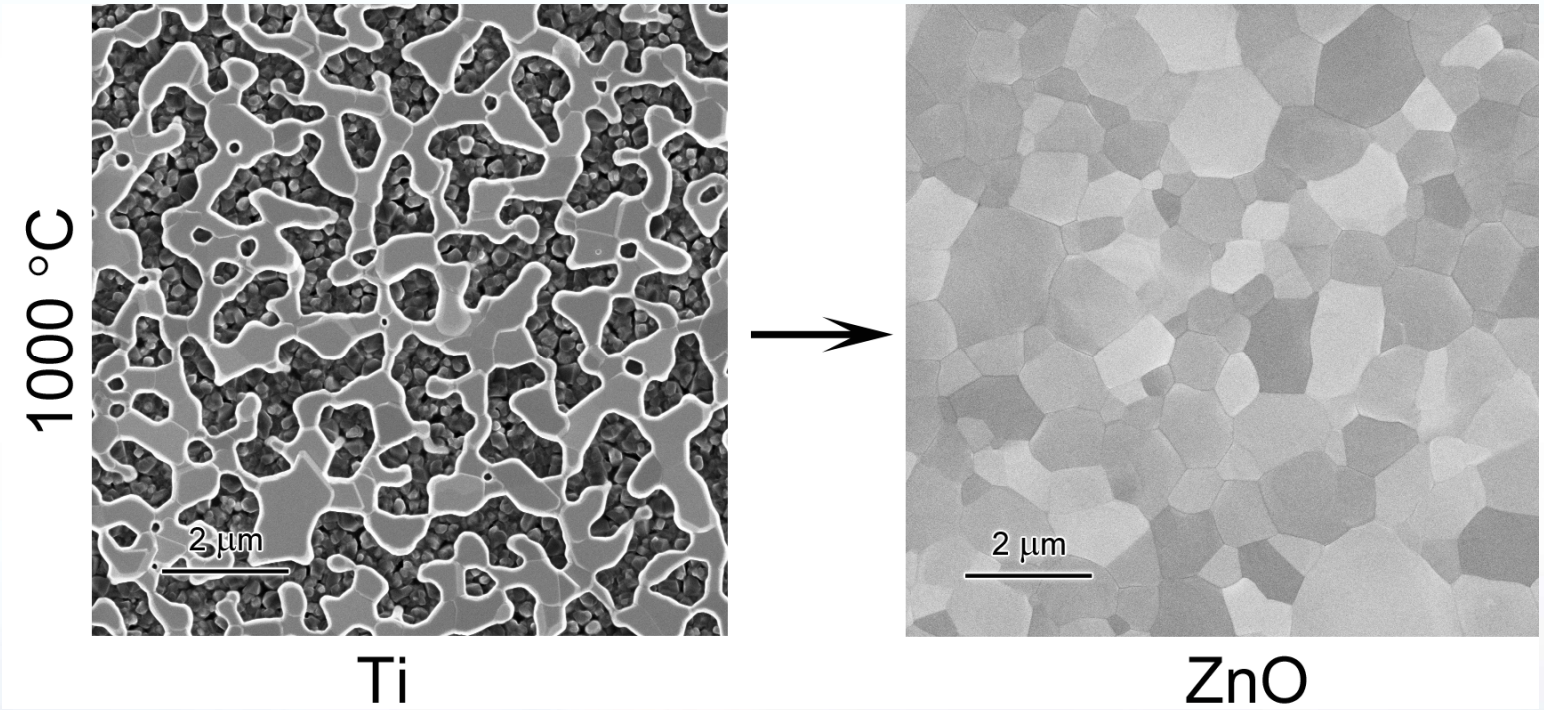
- CHESS
- Scherrer's Formula on 111 reflections

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:
  - $BaTiO_3$
  - $(Ba,Sr)TiO_3$

MLC Scaling History

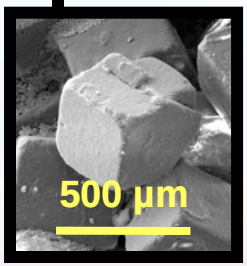
0603: 1600 µm X 800 µm
Most popular pre-2002 size

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

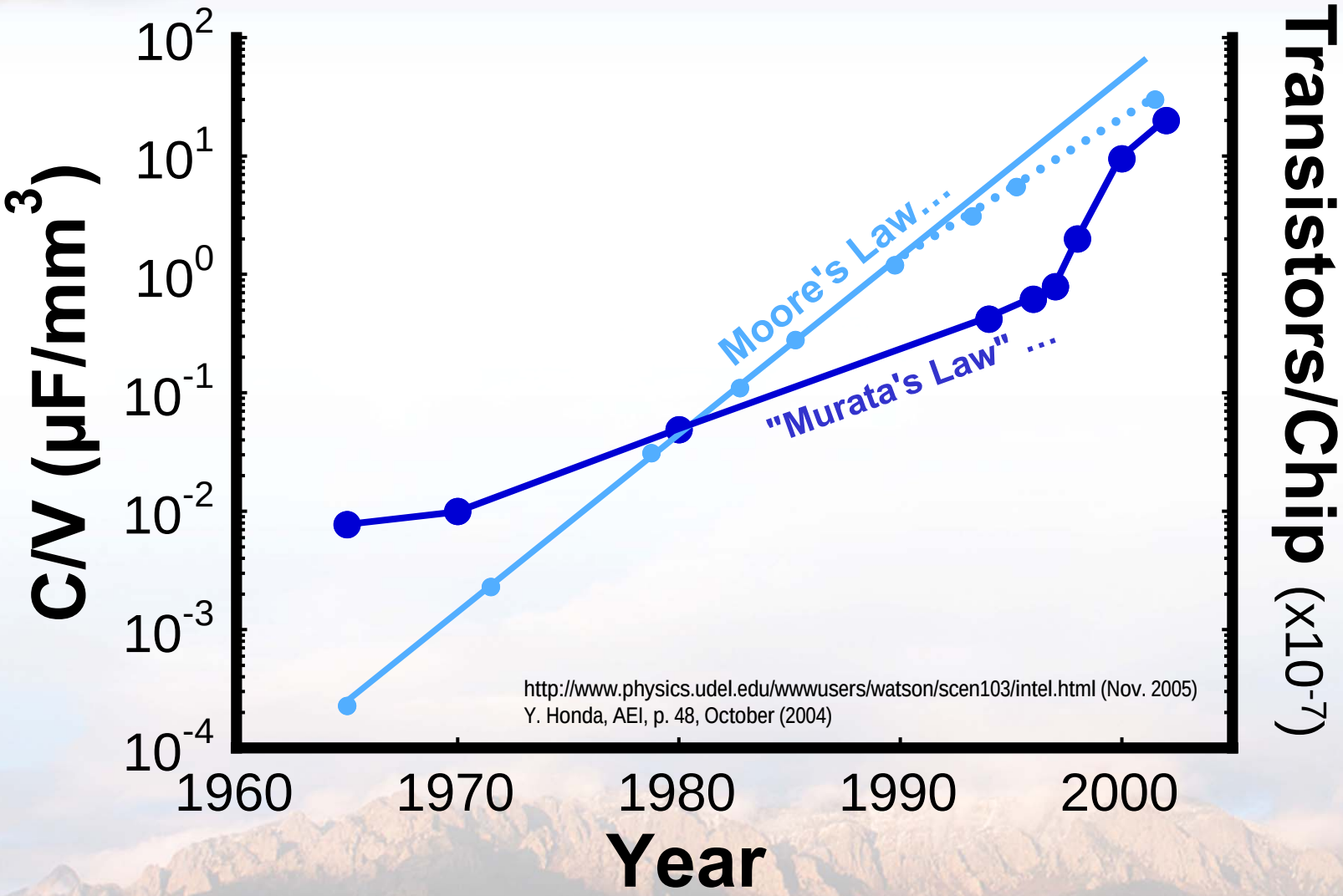
***to-scale* image of salt grain**



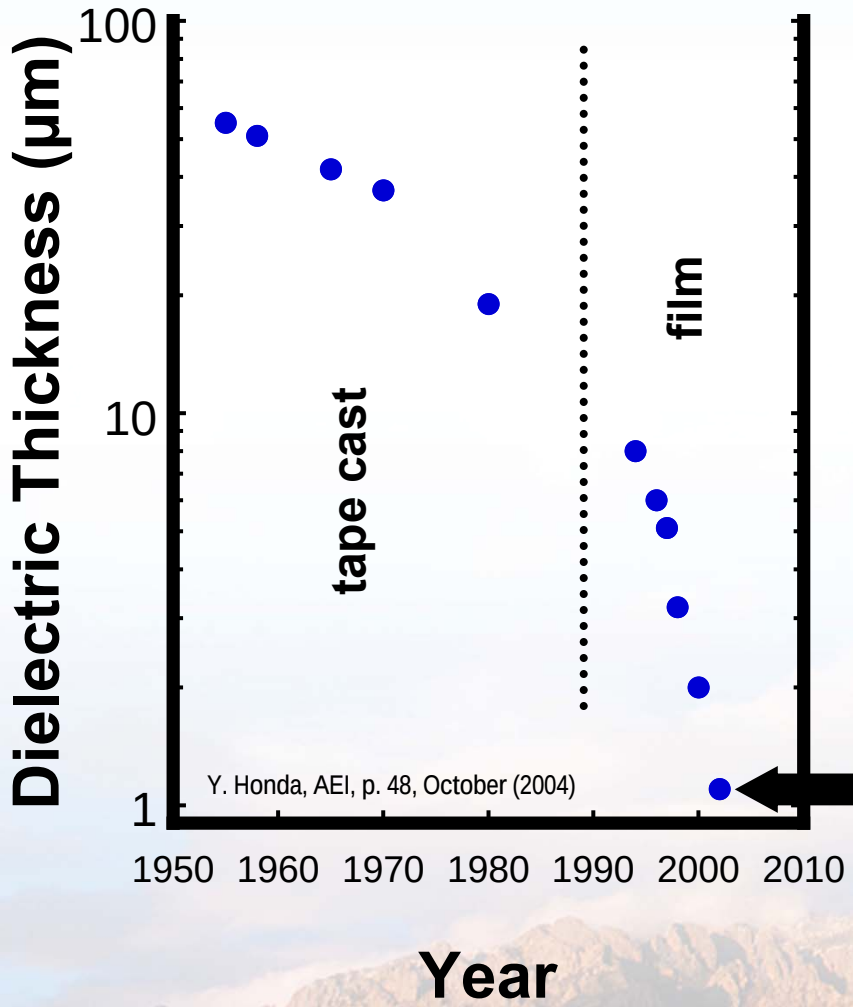
still 10^2 layers!

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!***