SAND2011-0193C

ZnO buffered platinized silicon substrates for high temperature oxide thin film synthesis

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A portion of this work was funded under the LDRD Laboratory directed research and development program.

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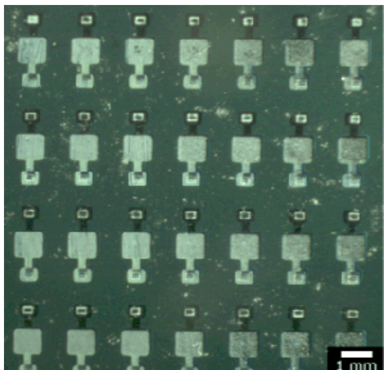
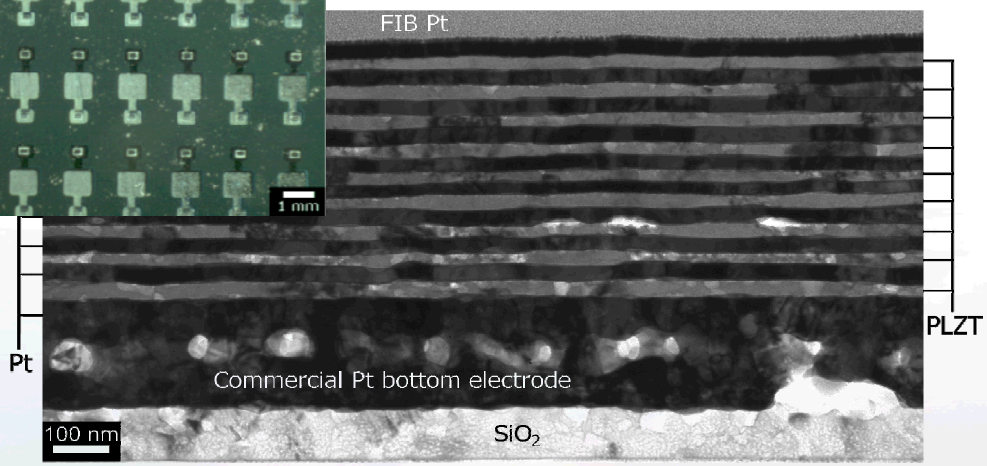
Outline

- Ferroelectric thin films
- Substrates and adhesion layers
- ZnO Adhesion layers
- $Pb(Zr,Ti)O_3$ integration
- $BaTiO_3$ thin films

Ferroelectric thin films

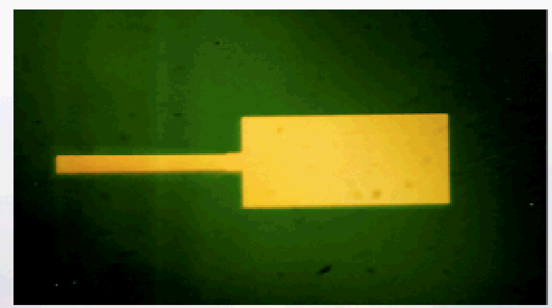


Functional PZT-based multilayer capacitor structures



Brennecka, et al, ***J. Mat. Res.***, (2008)

- Many commercial and emerging uses:
  - FE-RAM
  - Piezoelectric actuators and sensors
  - High-k dielectrics for energy storage
  - MEMS



PZT-MEMs Piezo Cantilever Beam for Energy Harvesting

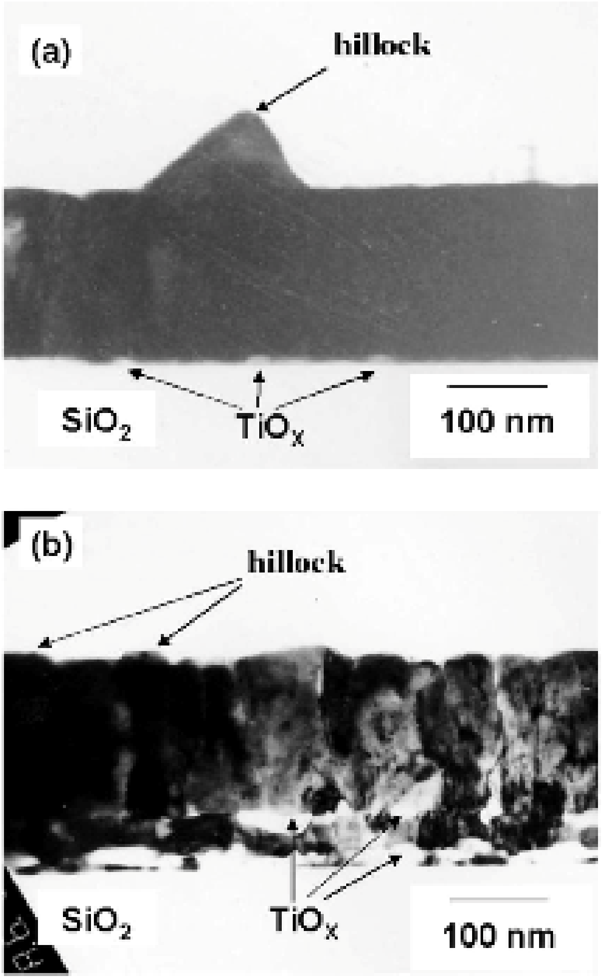
Substrates

- Most common substrate for oxide thin film synthesis is platinized silicon:
  - <100> or <111> Silicon wafer
  - 400 – 500 nm thermal SiO_2
  - 20 – 40 nm adhesion layer: commonly Ti or TiO_2
  - 100 – 200 nm Pt

- Platinum is an obvious choice for bottom electrode:
  - High Schottky barrier height = low leakage current
  - High-temperature oxidation resistant
  - Inert – will not react with deposited film

Substrates

- The adhesion layer is typically the weakest link:
  - Ti diffusion into Pt and oxidization
    - High compressive stress in Pt > hillocking
- Oxidize the adhesion layer?
  - Reactions with silicon substrate
  - Phase transitions = stress

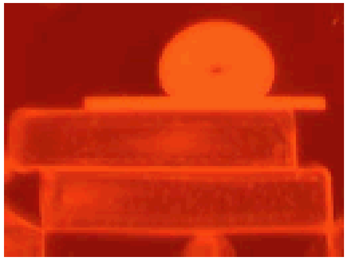


Nam et al., ***Thin Solid Films*** , (2000)

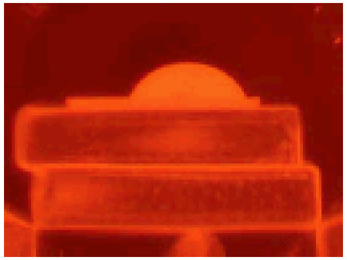
Alternative adhesion layers

- Replace Ti with more robust adhesion layer:
  - Zr or ZrO_2 – Al Shareef, H.N. et al *J. Mat. Res.* 12 (1997) 347; Zohni, O. et al. ***Thin Solid Films*** 516 (2008) 6052
  - Ta - Klissurska, R. et al. ***Microelectronic Engineering*** 29 (1995) 297
  - Al_2O_3 – Halder, S. et al. ***Appl. Phys. A*** 87, 705 (2007)
    - Al_2O_3 is an excellent high temperature adhesion layer – stable to 1000 °C
- Can we do better?

ZnO



Molten Cu on Al_2O_3



Molten Cu on ZnO

Substrate	Contact angle (°)	W_a (J/m^2)
Al_2O_3	133 ± 6	0.480 ± 0.142
ZnO	62 ± 5	2.012 ± 0.097

- Previous work has shown Cu wet ZnO very well:
  - W_a is *work of adhesion* and defines energy required to separate materials of interest
  - Determined experimentally from sessile drop tests
    - Cu is non-wetting on Al_2O_3 (contact angle > 90°) and wetting on ZnO (contact angle < 90°)
- Can we use ZnO as an adhesion layer for Pt?
  - Cu and Pt both Fm-3m metals

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

ZnO

- Pt/ZnO should provide a:
  - Non reactive substrate,
  - High temperature
- With:
  - Smoother interfaces
  - No hillocking or delamination
- Resulting in:
  - Ferroelectric oxide films with superior dielectric properties

ZnO buffered Pt/Si

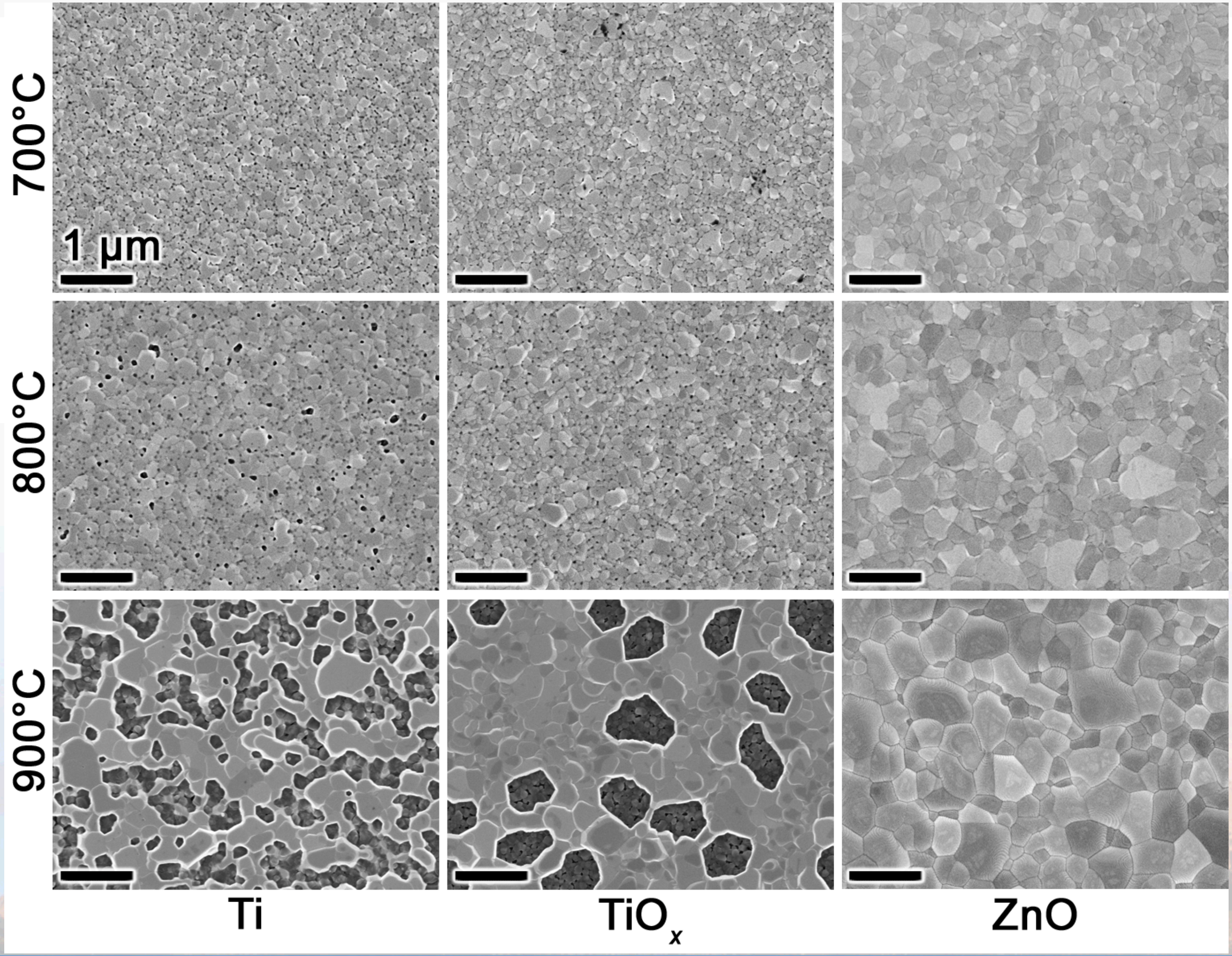
- RF sputter ZnO and Pt on commercially available 400 nm thermal oxide wafers

ZnO buffer layer	
RF power	150 W
Pressure	5 mTorr
Gas	50/50 Ar/O_2
Thickness	40 nm

Pt electrode	
RF power	300 W
Pressure	3 mTorr
Gas	Pure Ar
Thickness	100 nm

- Prepare Ti and TiO_x buffered platinized silicon for comparison
  - RF sputter 40 nm Ti metal
  - Oxidize in 15 mTorr flowing O_2 at 450 °C
- What happens to the substrate during thermal processing?

ZnO buffered Pt/Si vs temperature



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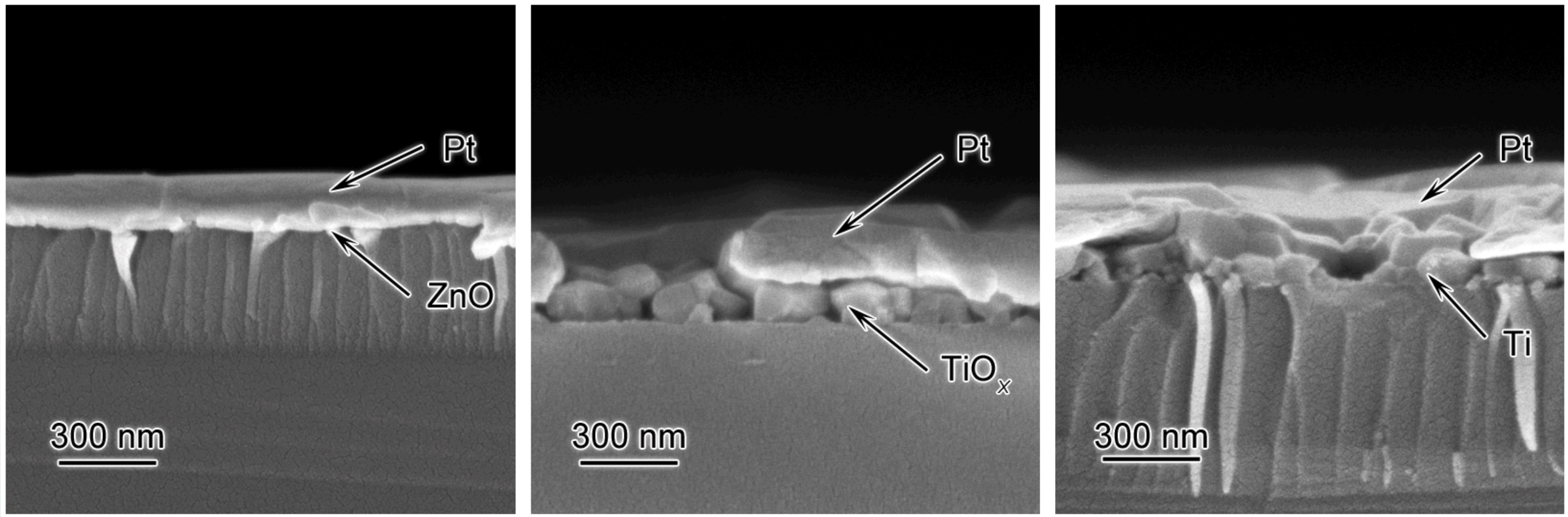
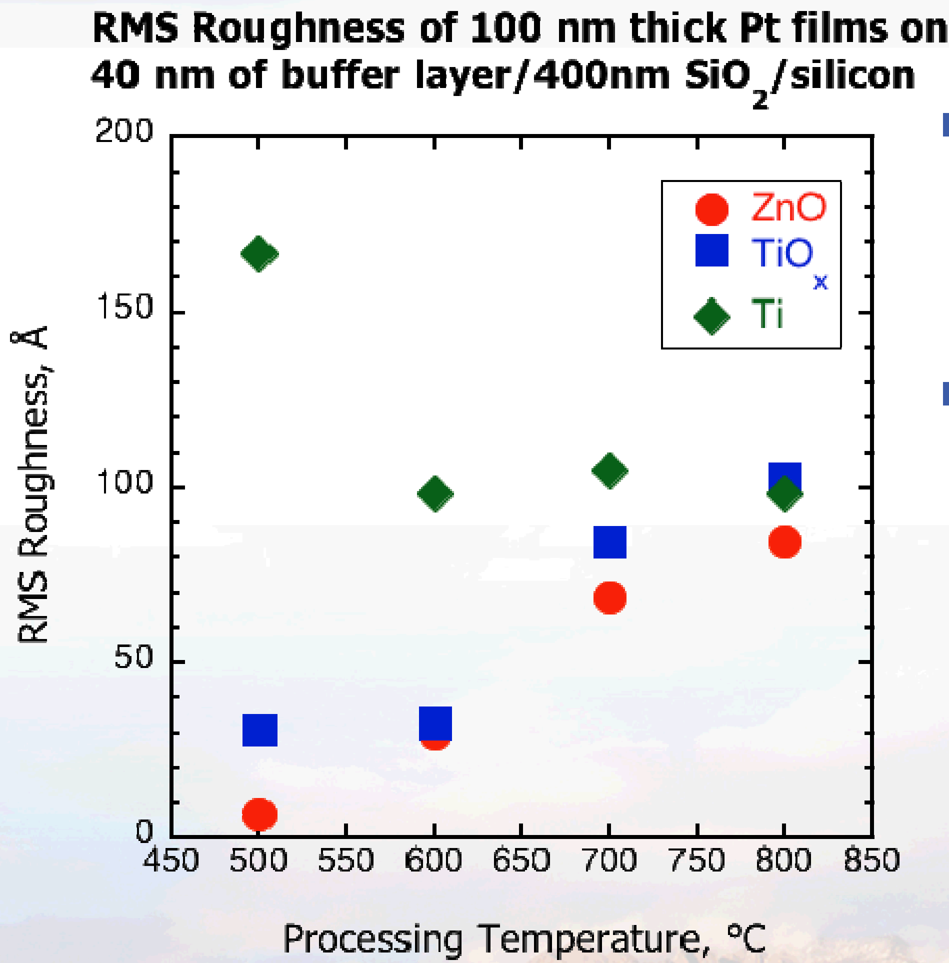
ZnO buffered Pt/Si cross-section



Surface roughness of Platinized Si



- RMS roughness of Pt/ZnO is lower for all temperatures
  - Smoother interface
- How do ferroelectric thin films perform on Pt / ZnO?

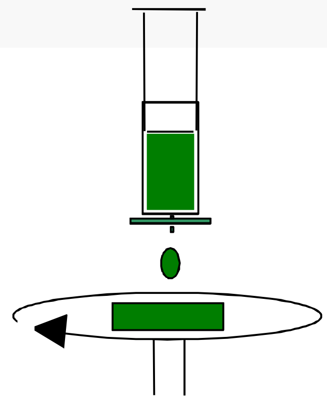
SNL IMO-based Solution Route

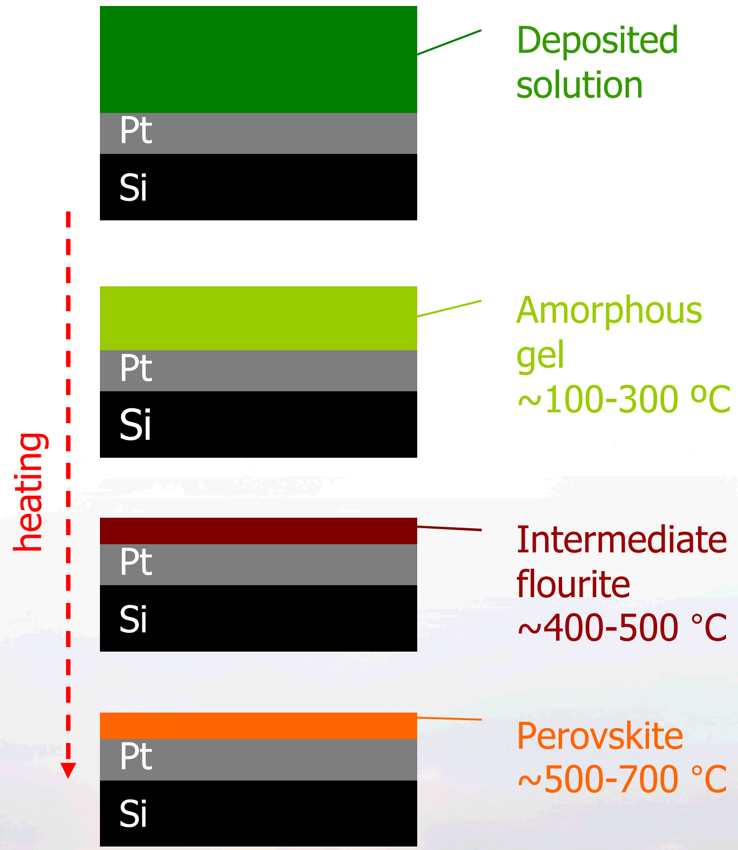
- **$Zr(OBu)_4 \cdot BuOH + Ti(OiPr)_4$**
  Blend 5 min
- **Acetic Acid / Methanol**
  Chelating agent / Solvent
- **$Pb(OAc)_4 + La(OAc)_3 \cdot H_2O$**
  Dissolve at ~90°C
- **Acetic Acid / Methanol**
  Adjust Molarity
- **Spin Coat Deposition**
  4000rpm/30sec
- Pyrolysis
- Crystallization
- *Sputter Pt Electrodes*

multiple depositions

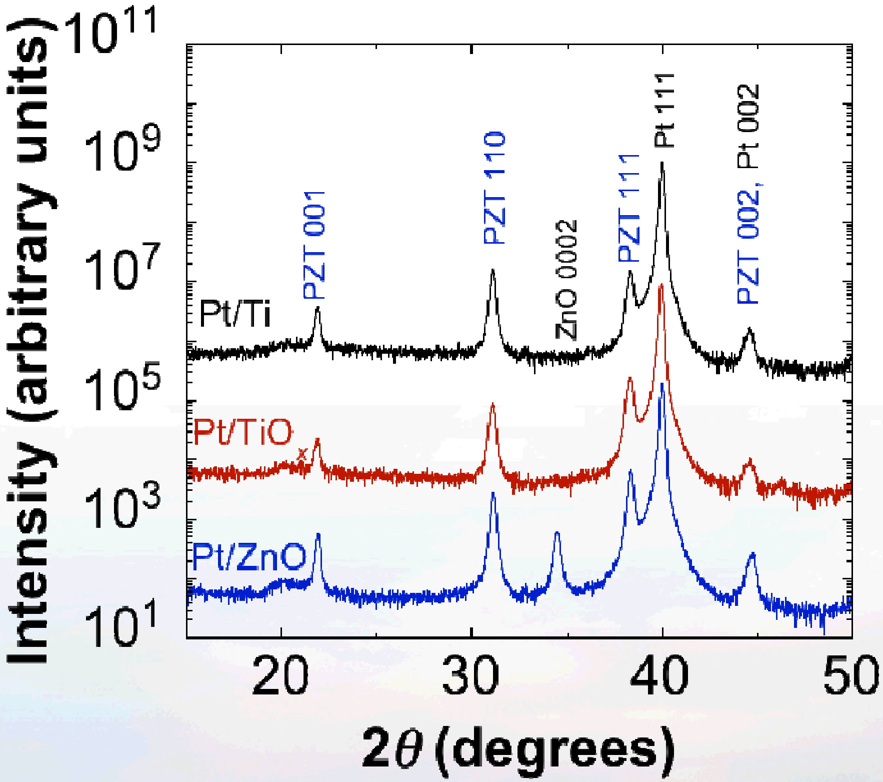
R.A. Assink and R.W. Schwartz; ***Chem. Mater.*** *(1993)*

G. Yi and M. Sayer; ***J. Appl. Phys.*** *(1988)*



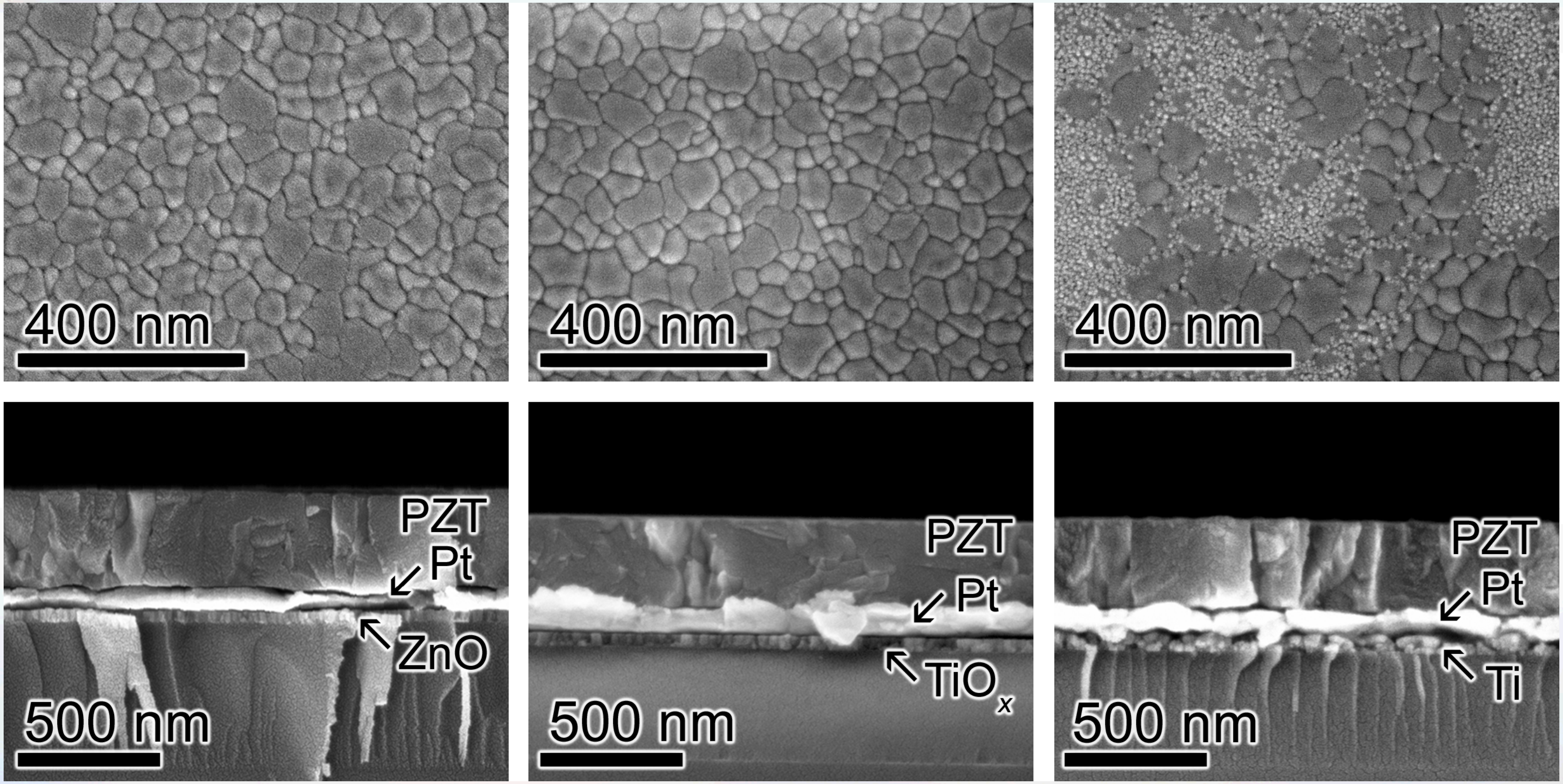


PZT Texture



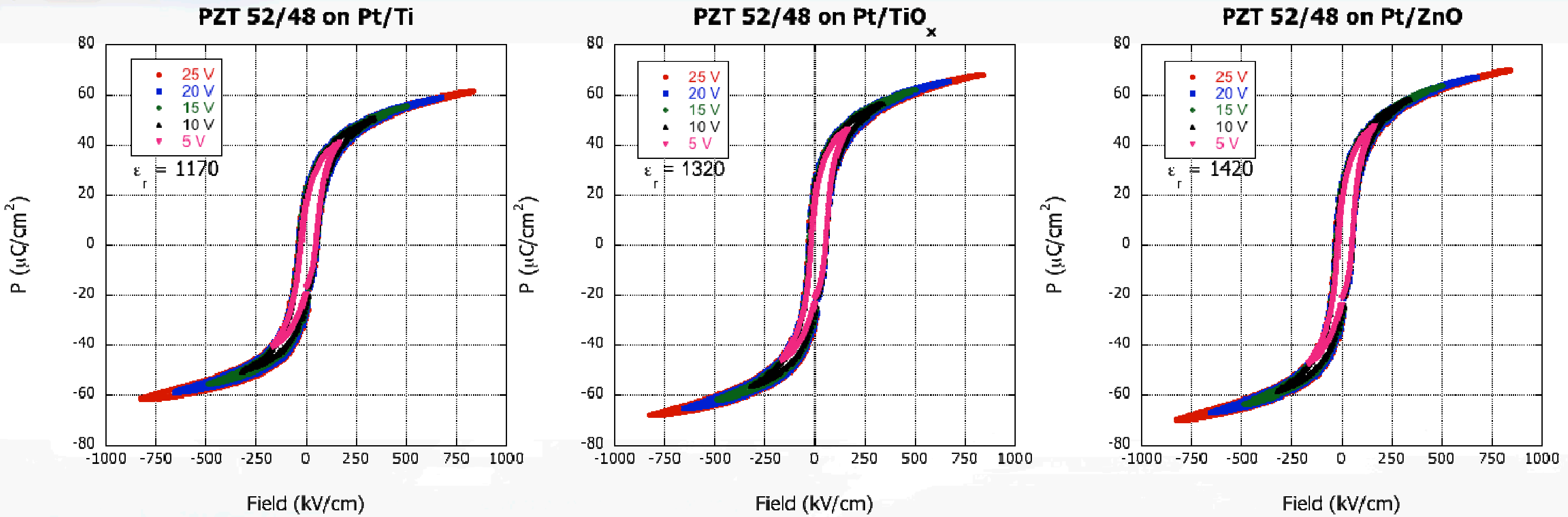
- PZT grows polycrystalline under these conditions - regardless of substrate

Surface topography



- A flourite second phase commonly occurs in PZT on Pt/Ti that dilutes permittivity
- PZT deposited on Pt/ZnO produces dense columnar microstructure with no evidence of flourite

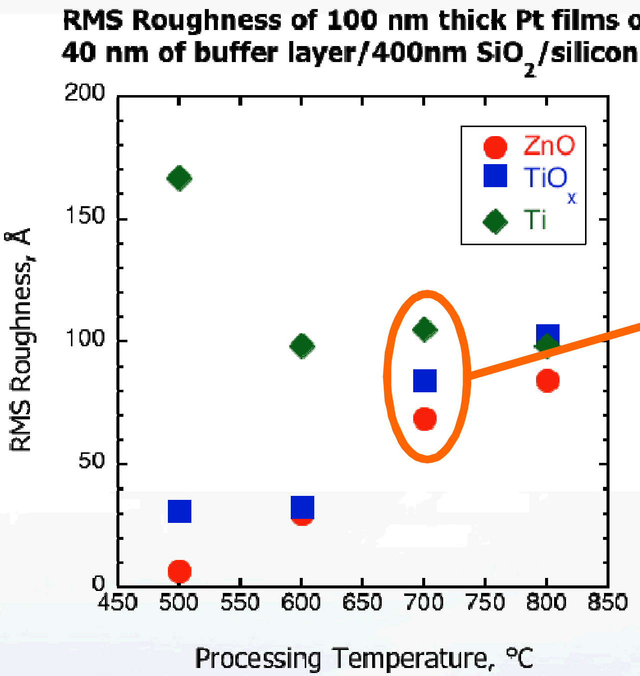
Dielectric and Ferroelectric properties

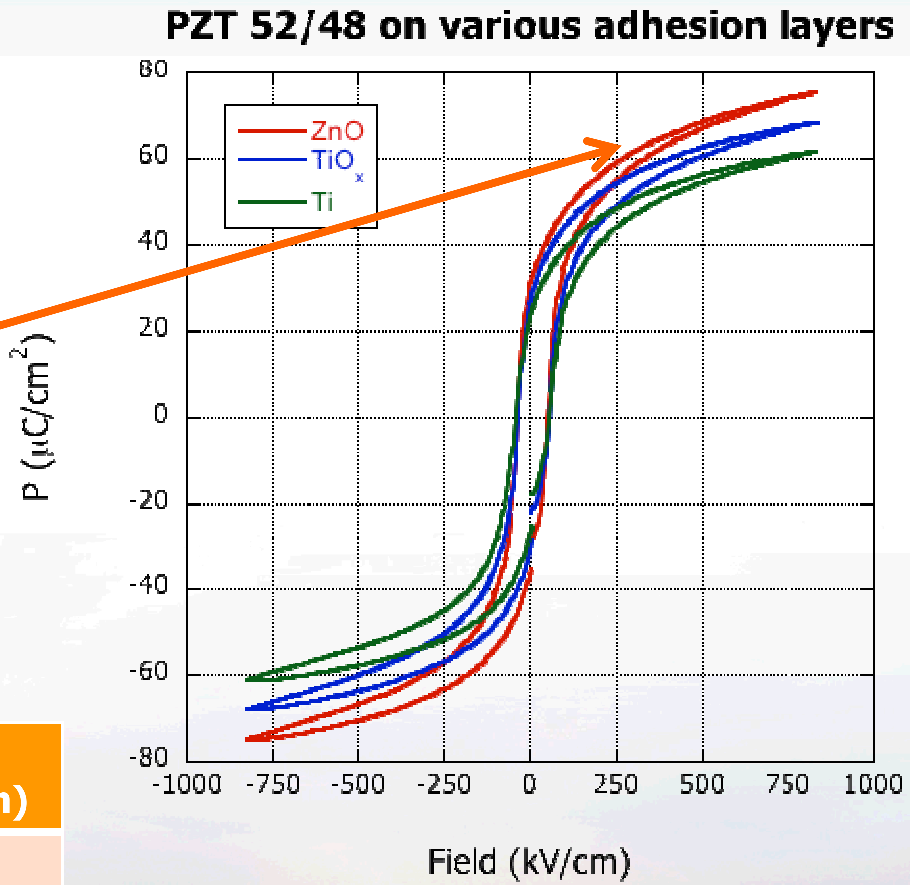


- Low field dielectric properties – 100 mV, 1kHz
  - Films on Pt/ZnO substrates have higher permittivity

- Polarization – field measurements – 10 Hz

Ferroelectric properties

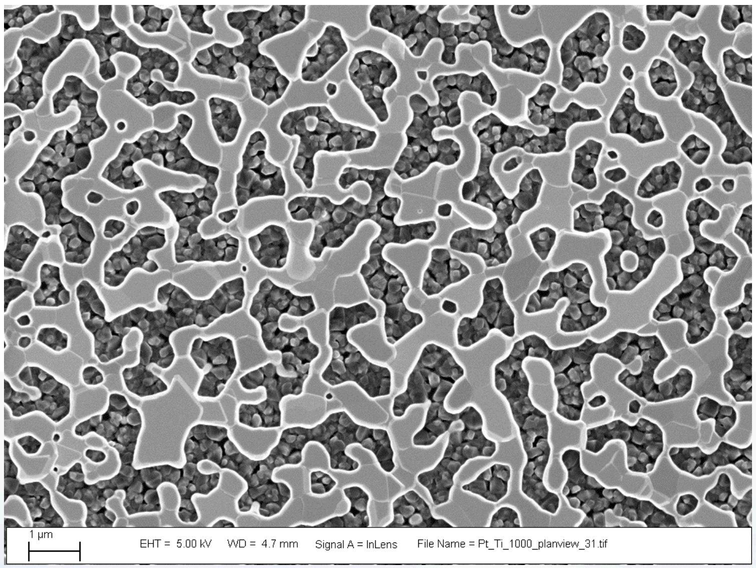




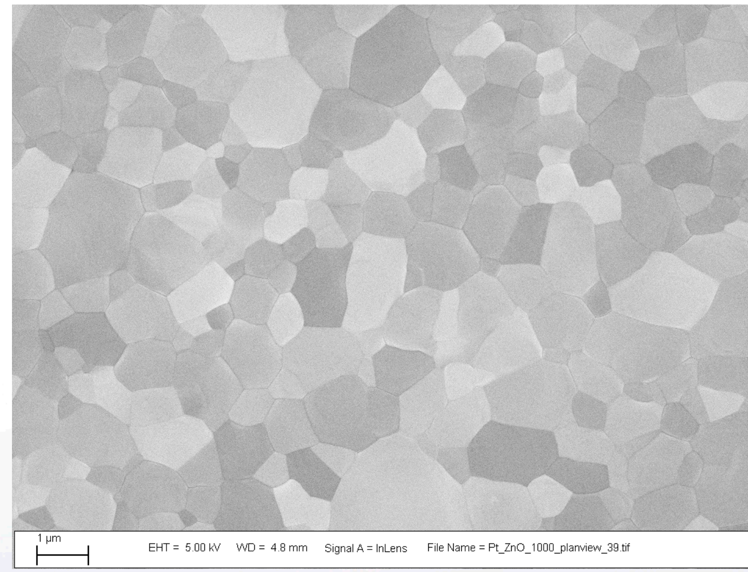
	P_{max} ($\mu C/cm^2$)	P_r ($\mu C/cm^2$)	E_c (kV/cm)
Pt/Ti	61.5	23.8	47.0
Pt/TiO_x	68.2	27.0	44.1
Pt/ZnO	75.3	32.2	43.8

Pt/ZnO as a high temperature substrate

Pt/Ti ⟶ Pt/ZnO



1000 ºC



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

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
3000rpm/30sec

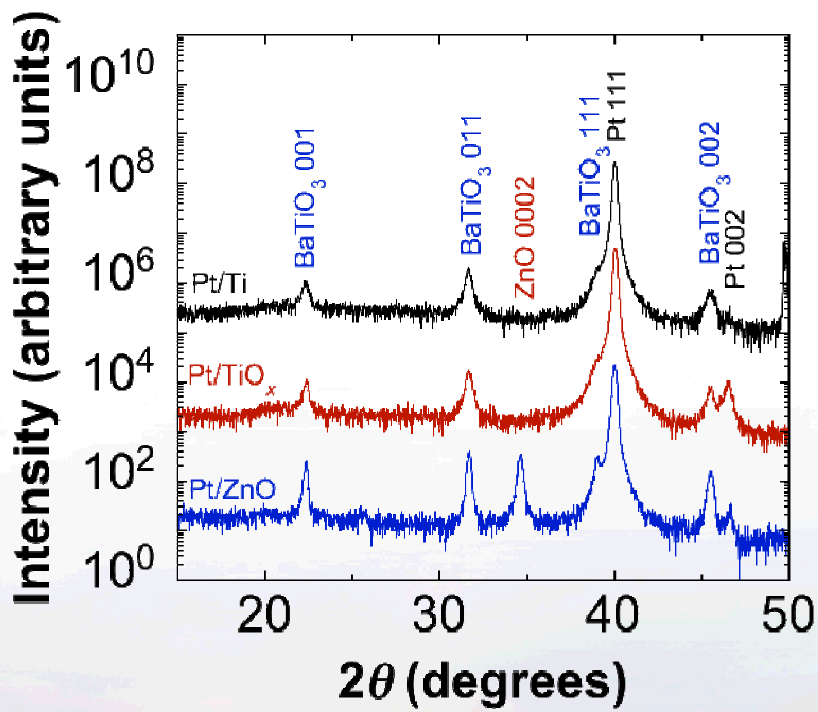
3 layers

Dry ~ 250 °C

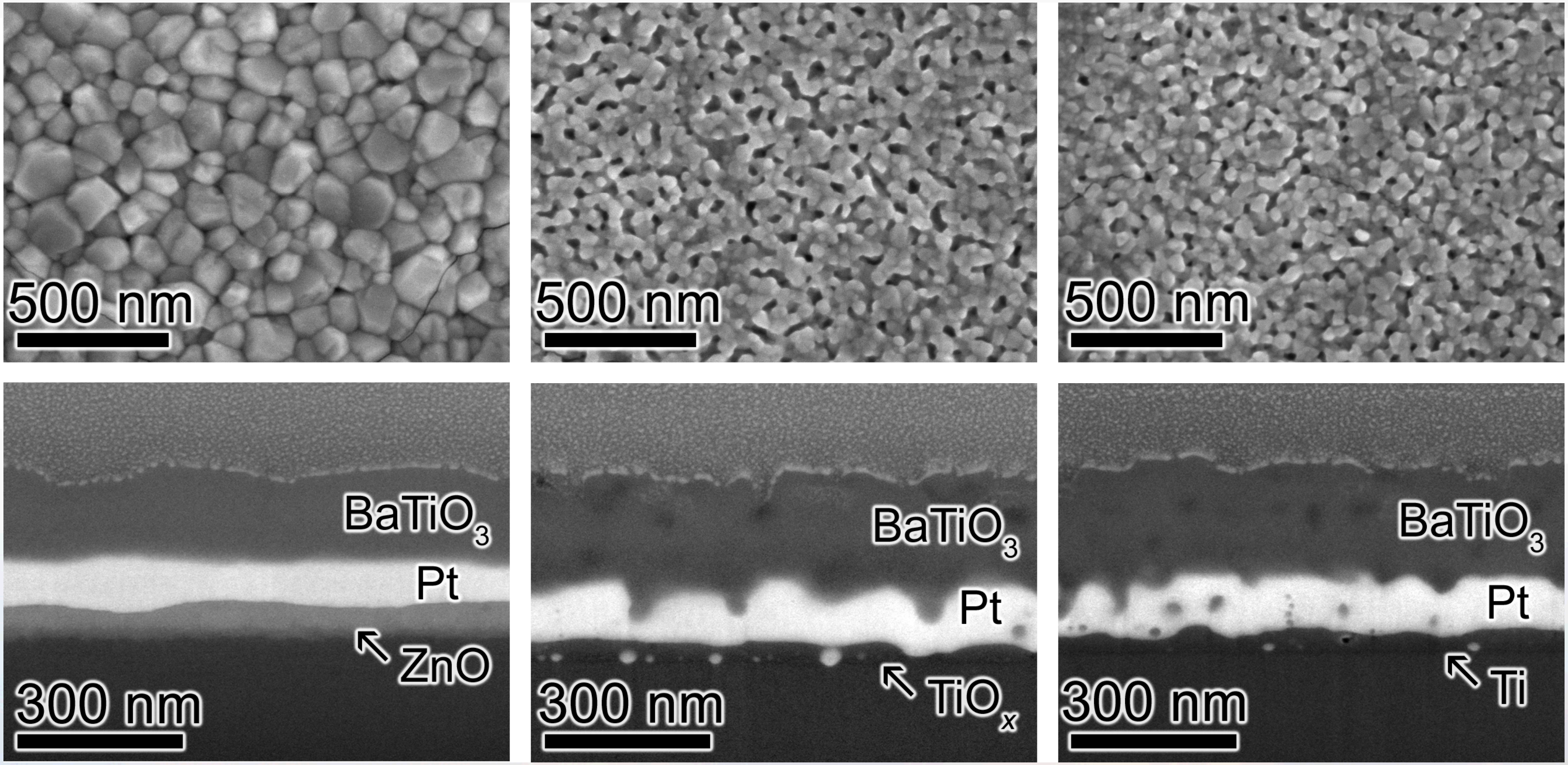
Repeat 3x

Fire 900 °C

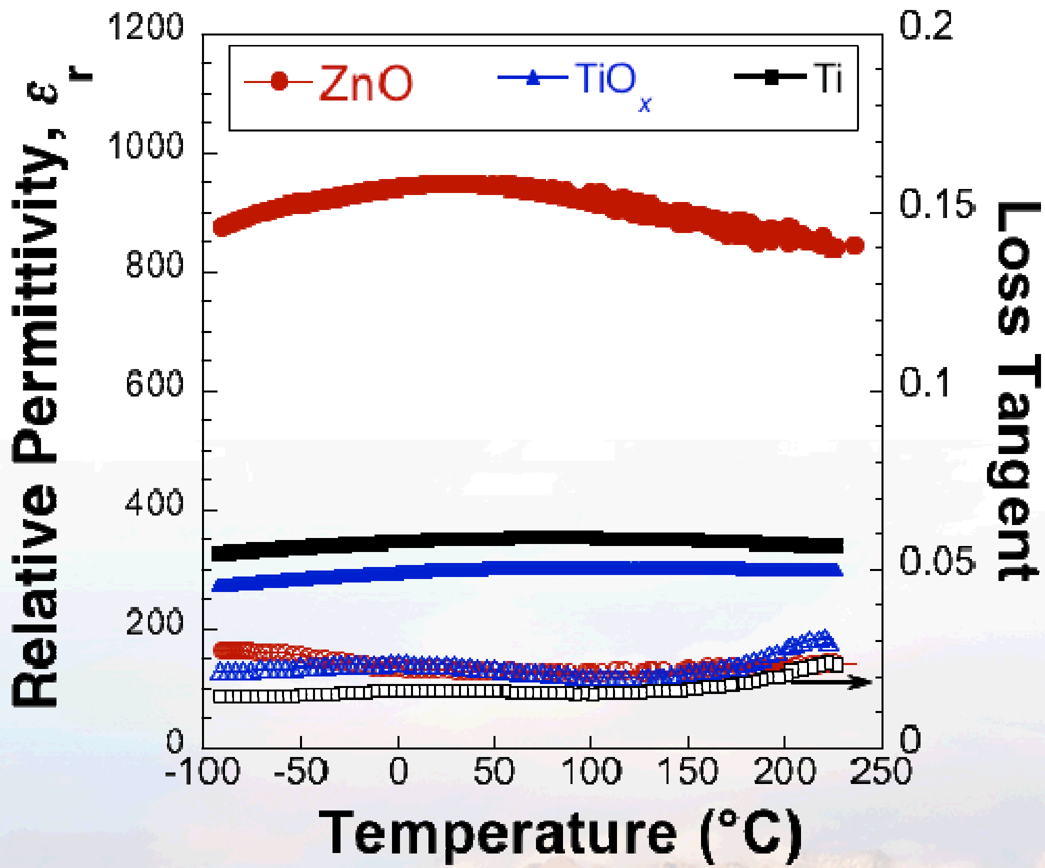
Sputter Pt Electrodes



Topography and microstructure



$BaTiO_3$ C-T by substrate



- Reduced porosity + larger grain size in films on Pt/ZnO = Higher permittivity
  - Comparable to high quality - fiber textured BT films (Hoffman and Waser; **J. Eur. Cer. Soc.** 19, (1999) 1339)
  - 3x comparable thickness MOCVD BST films (Parker et. al.; **APL** 81 (2002) 340)
- Temperature of max ε_r is lower than for bulk BaTiO3
  - Possible ZnO doping?
  - Thickness effect? Film is only 175 nm thick

Summary

- ZnO buffered Pt/Si may be a significant upgrade to Pt/Si with Ti adhesion layers:
  - Smoother oxide/electrode interfaces
  - Higher k
  - Better ferroelectric properties
- Future uses:
  - Fatigue resistant films
  - High temperature processing of other oxide systems