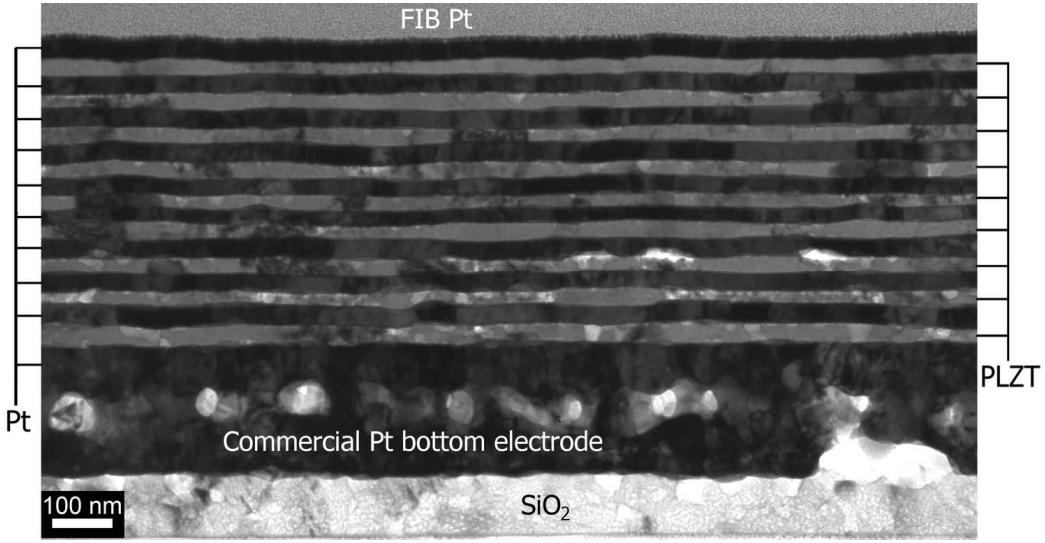
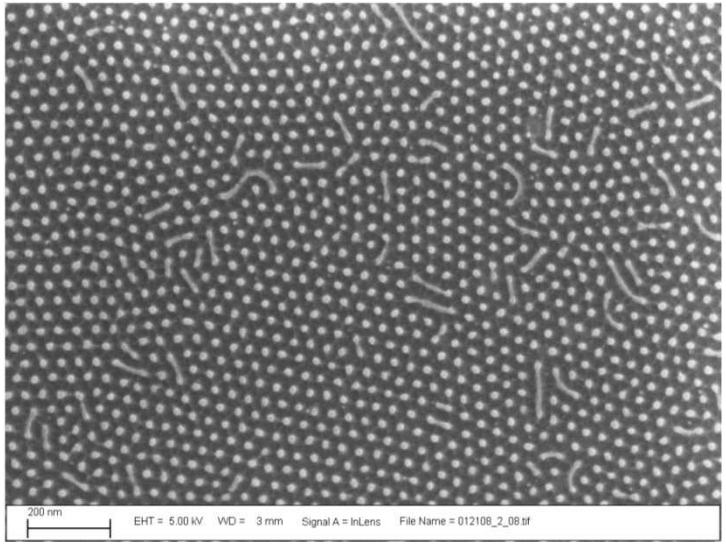
SAND2008-5660P

Functional Solution-Derived Nanoscale Electronic Oxides

Geoff Brennecka, J.S. Wheeler, C.M. Parish, and B.A. Tuttle
Sandia National Laboratories





National Nuclear Security Administration

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Acknowledgments

Sandia

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- Wyatt Winkenwerder

U. Wisconsin

- Paul Nealey
- Padma Gopalan
- Shengxiang Ji

U. Florida

- Jacob Jones

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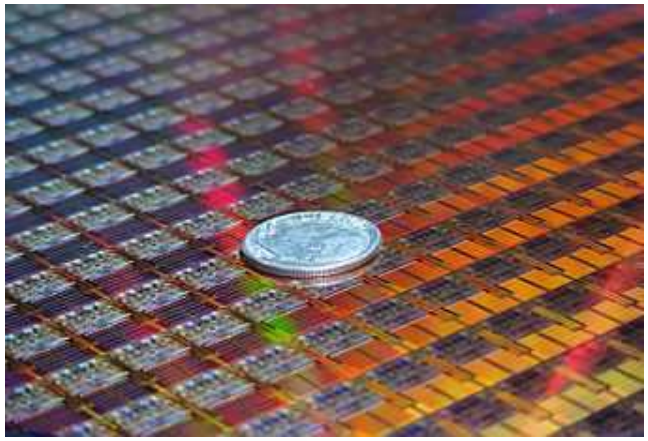
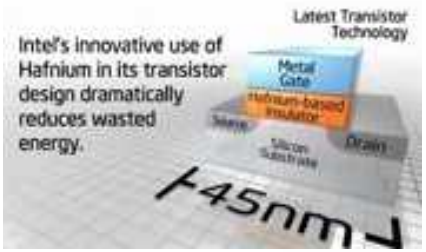
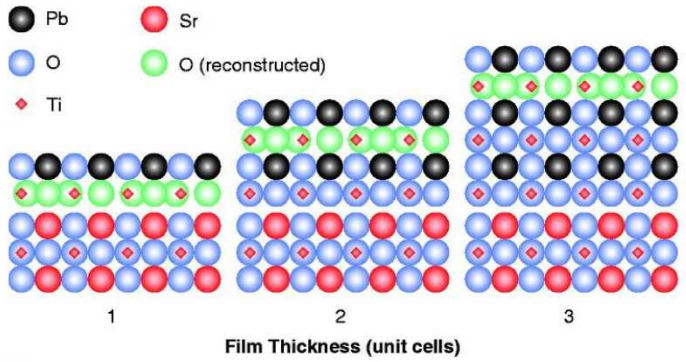
Background & Motivation



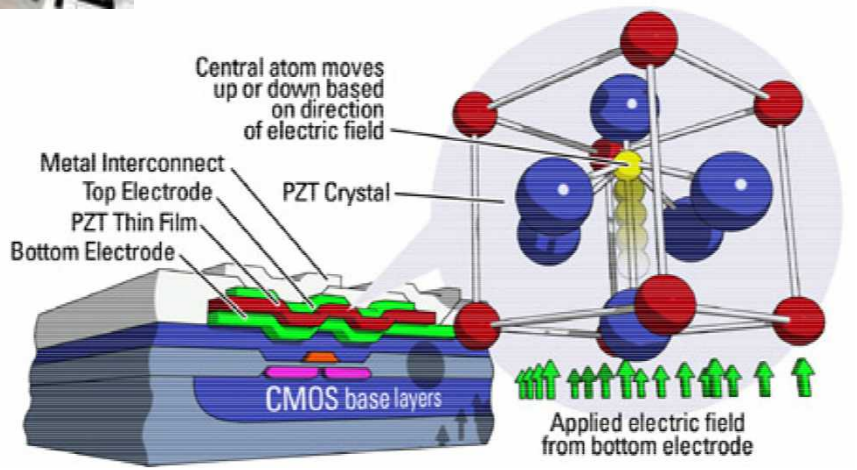


intel now using HfO_2 in their processors (45nm transistors)

- Reduce physical size
- Increase function(s)
- Reduce power consumption



Fong et al., Science (2006)



Ramtron FERAM

- Process/architecture
- Materials/integration

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SNL 'IMO' 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

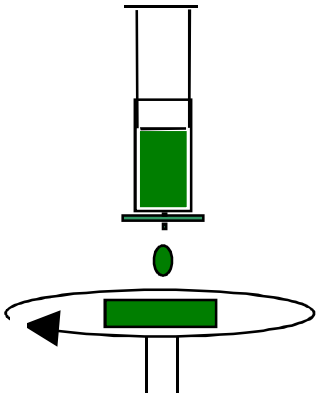
Pyrolysis

Crystallization

Sputter Pt Electrodes

multiple depositions

multiple layers



Spin Deposition

heating

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

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

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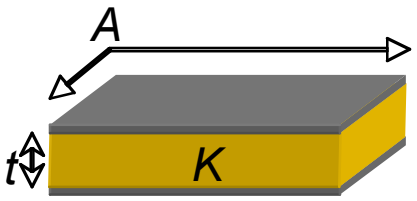
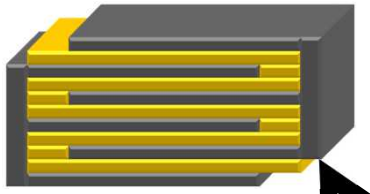
High-Value Integrated Capacitors

Multilayers



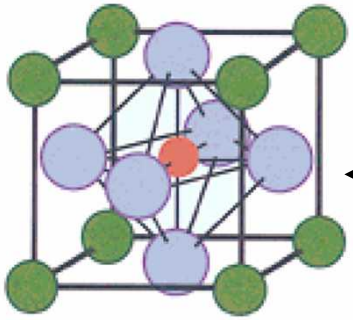


- Pulse discharge
- Remote sensors
- Medical devices

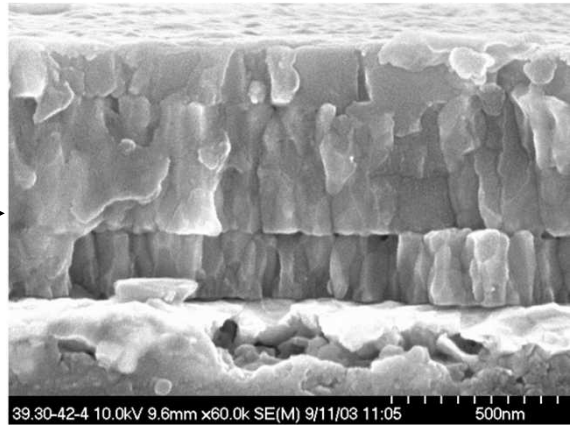
–any application that needs rapid access to a large amount of electrical energy in a small volume

$$C = \varepsilon_0 K \frac{A}{t}$$

Thin films



High-K materials



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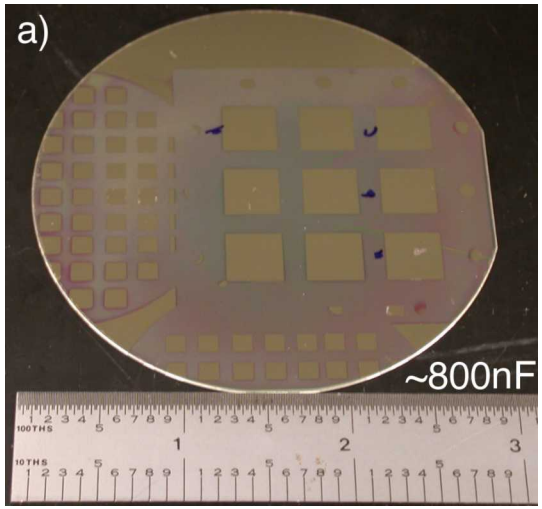
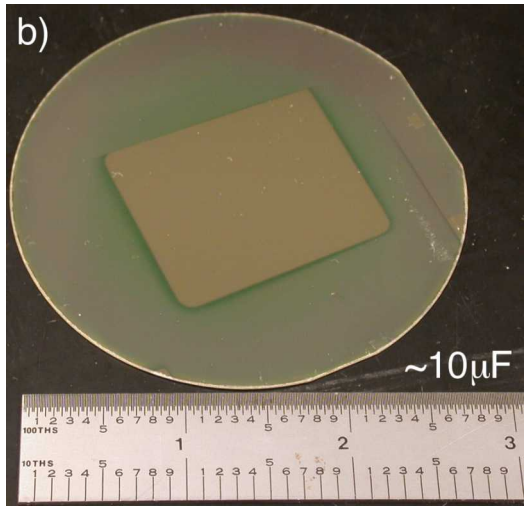
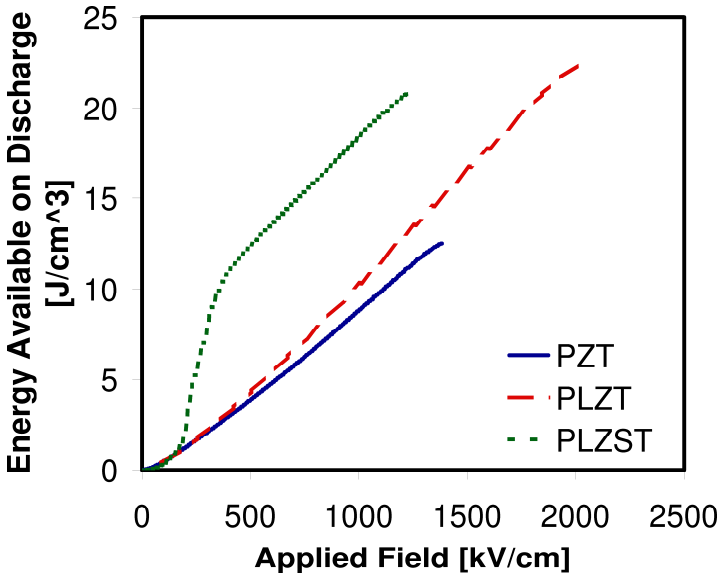
High Energy Density Pulse Discharge Capacitors

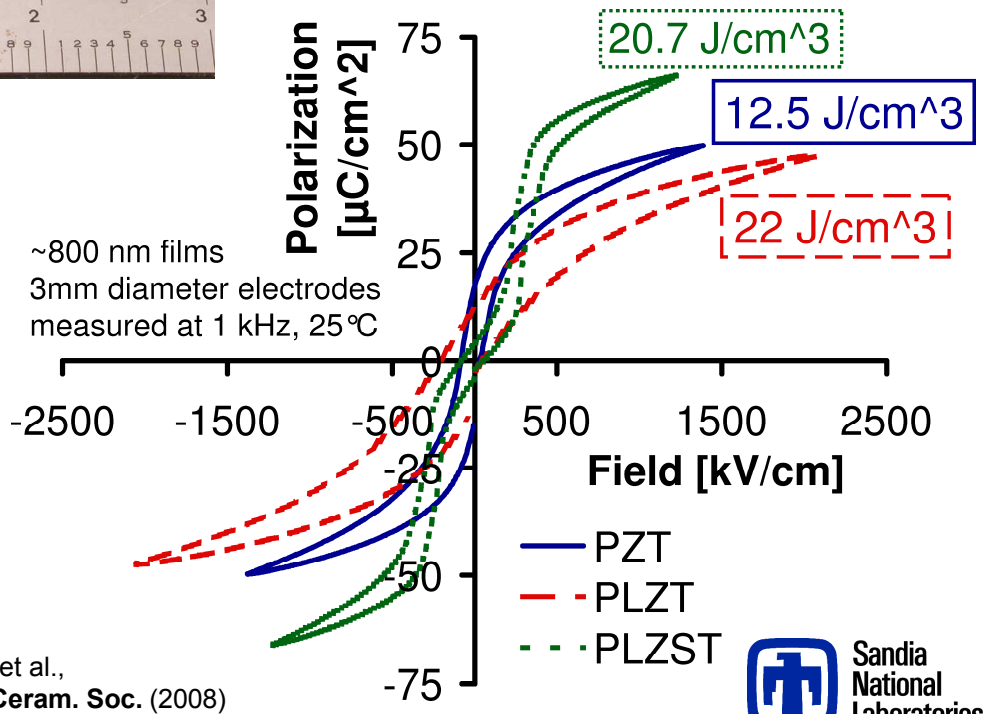




‘Standard’ thin films

- *~250 - 1000nm thick*
- *applications >50V*
- *high energy density*
- *pulse discharge*





Sigman et al.,
J. Am. Ceram. Soc. (2008)

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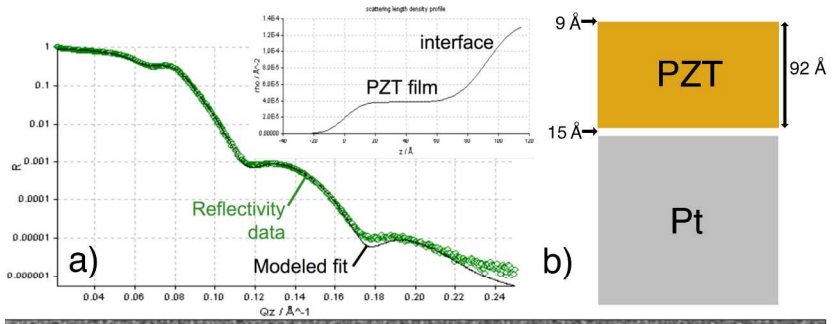
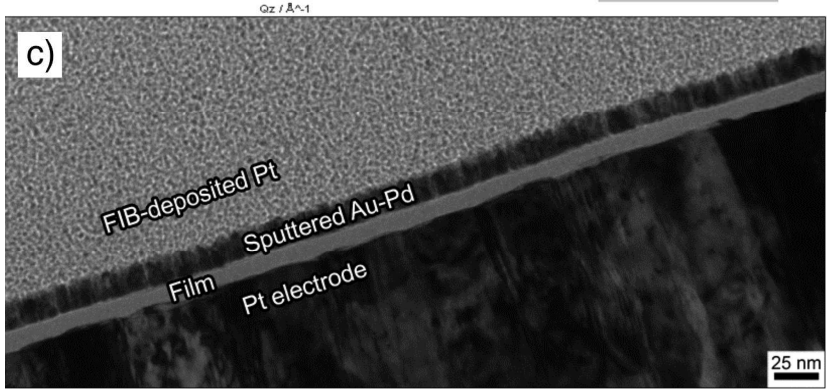
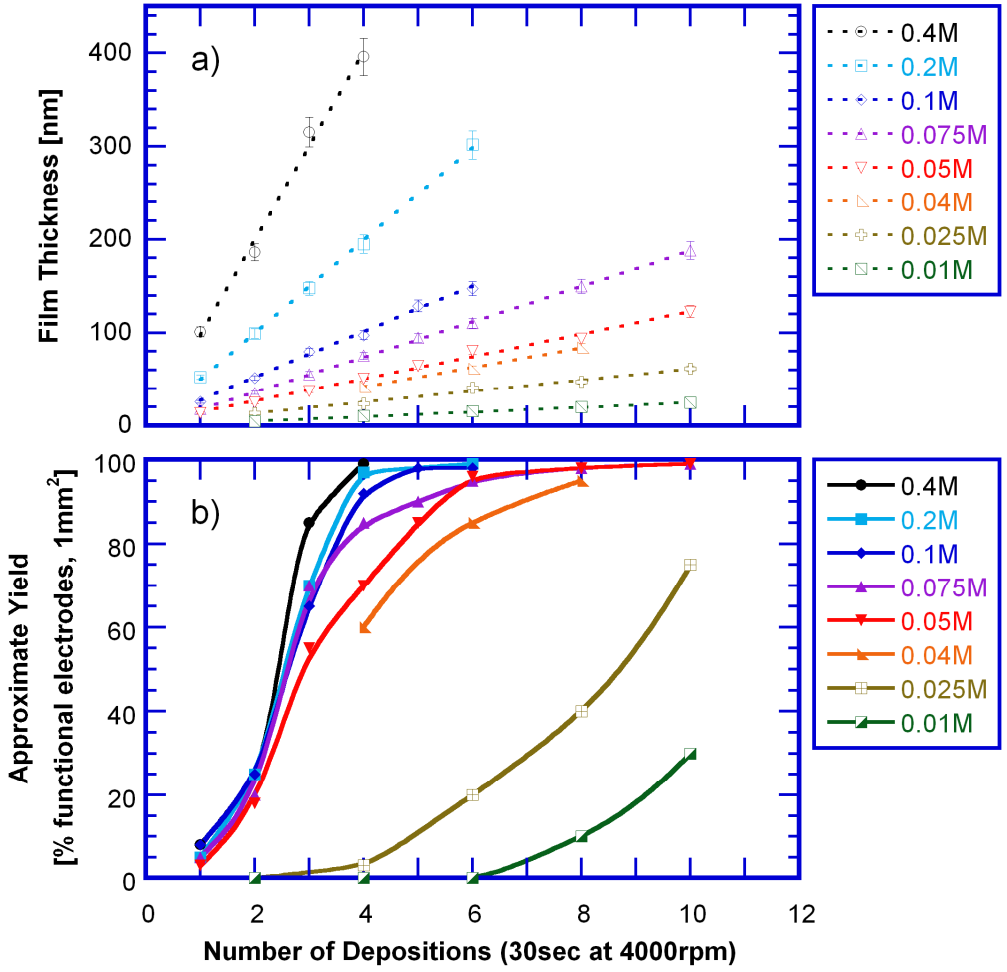
High Capacitance Ultrathin Films







- Single-phase continuous PZT films as thin as 9nm fabricated via spin coating
- Minimum thickness ultimately limited by islanding during crystallization

Sigman et al., ***J. Am. Ceram. Soc.*** *(2008)*
Brennecka, et al., ***J. Mater. Res.*** *(2007)*

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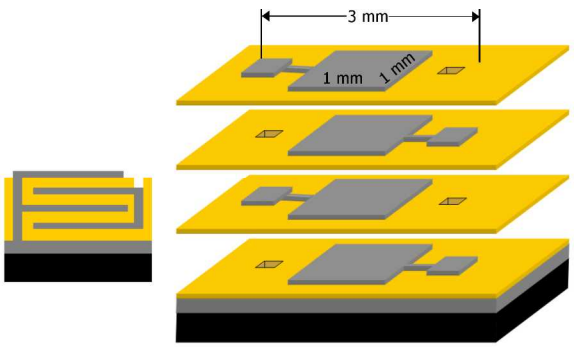
Multilayer Structures



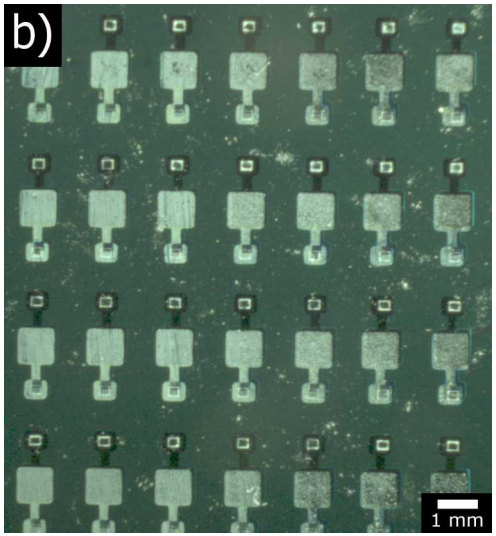
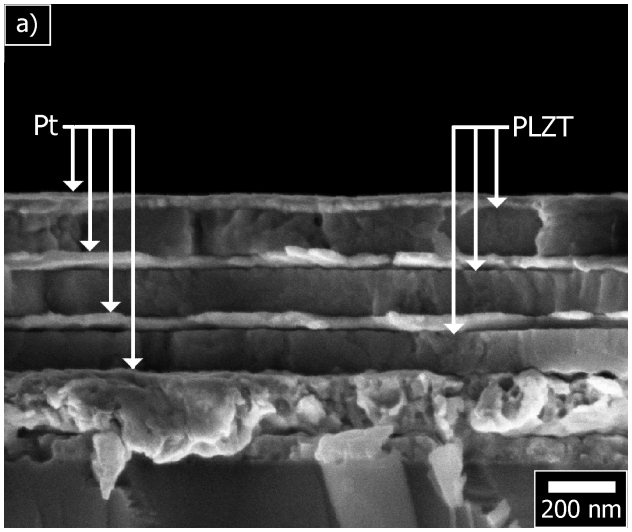
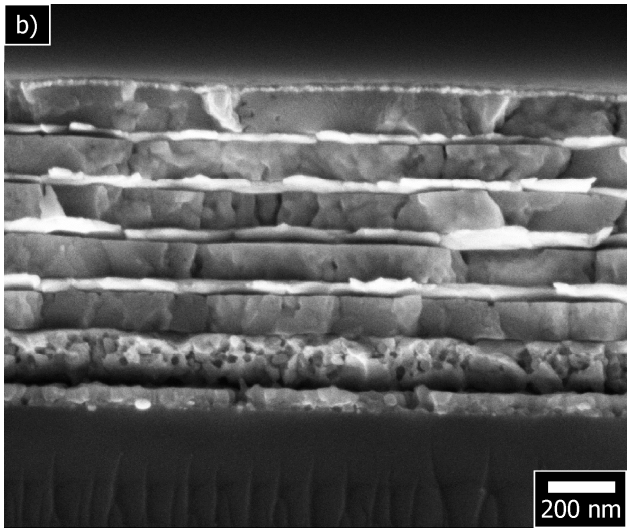
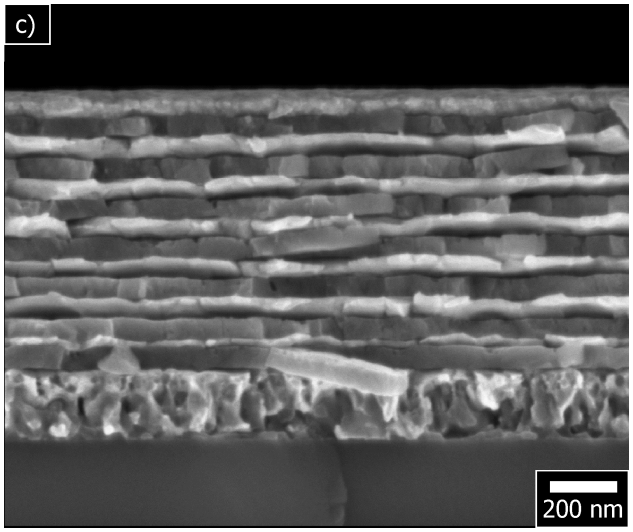
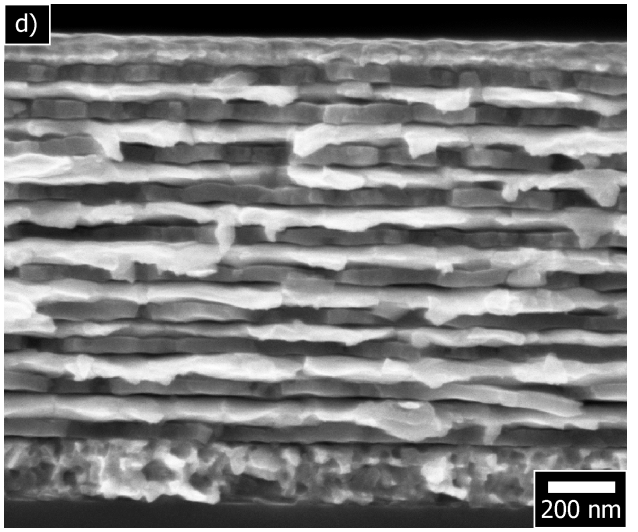


Photo-resist masked wet etch enables connections between alternate layers









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

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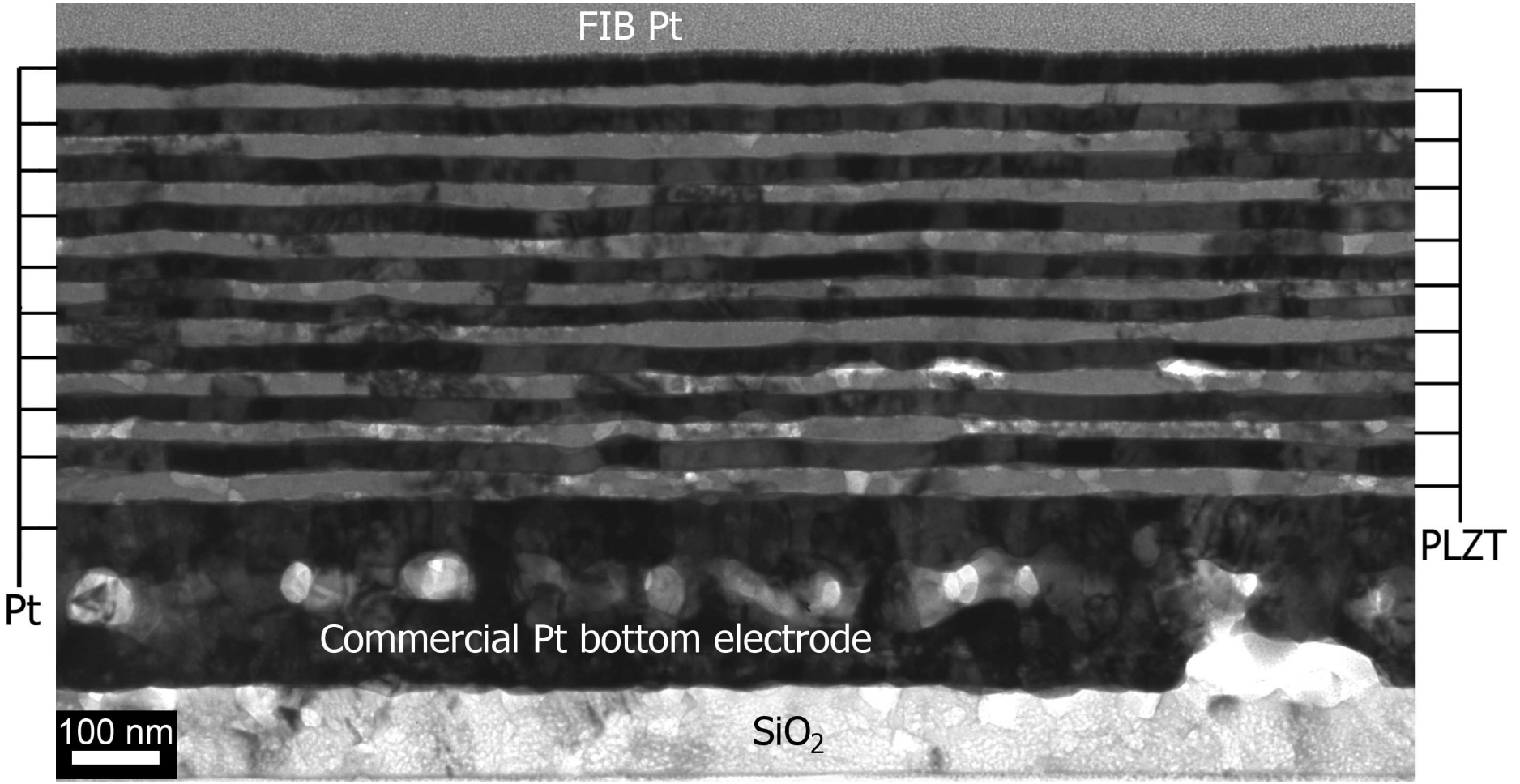
Multilayer Structures



9 layer capacitor structure with ~20nm solution-deposited PLZT layers and ~20nm sputtered Pt electrodes

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

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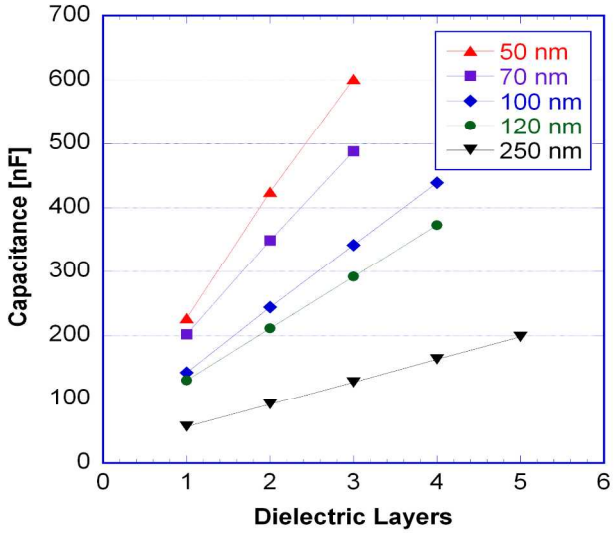
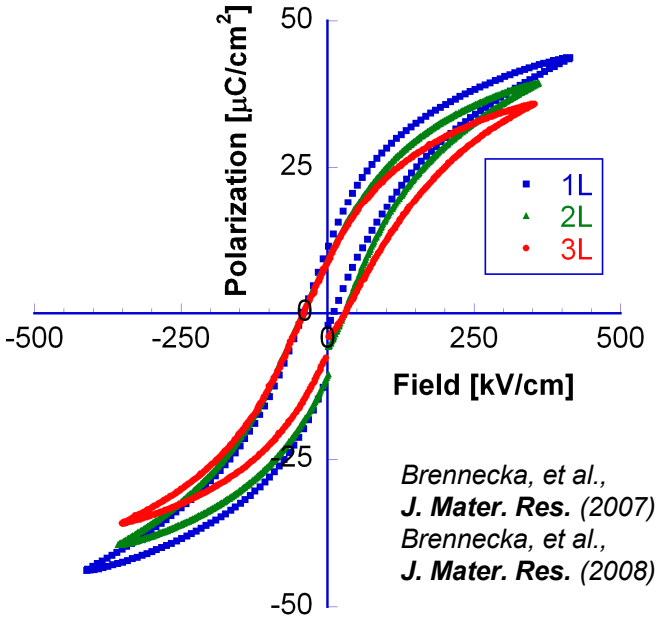
Electrical Performance



Good news:

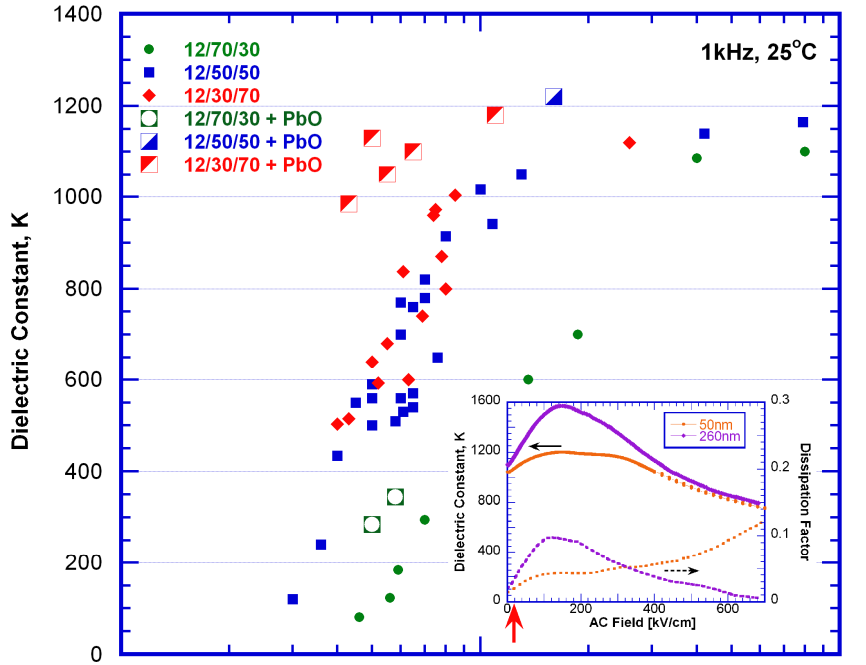
Properties scale well with number of layers

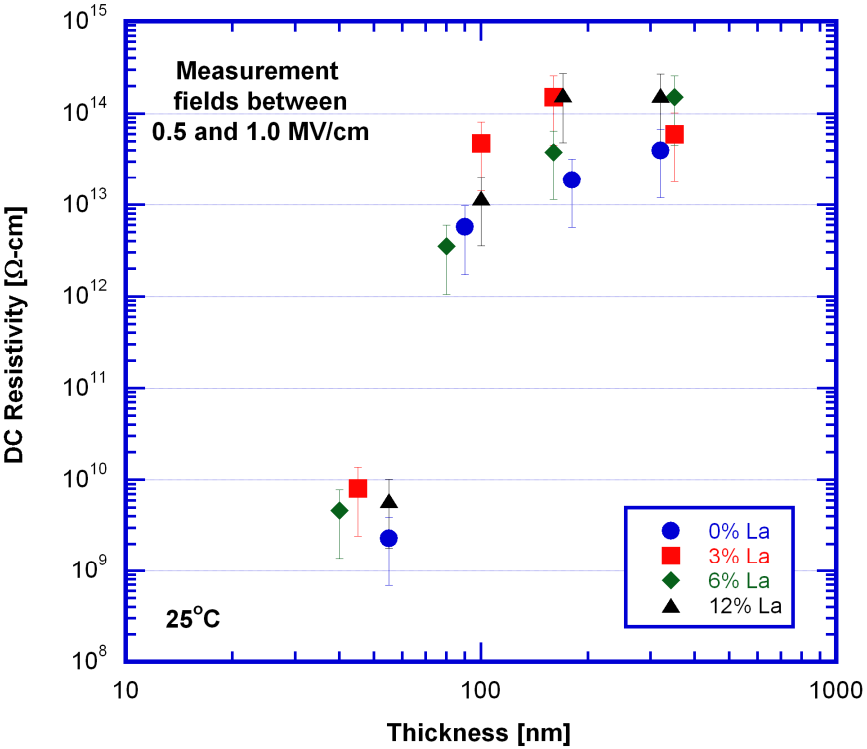


Brennecka, et al., ***J. Mater. Res.*** *(2007)*
Brennecka, et al., ***J. Mater. Res.*** *(2008)*

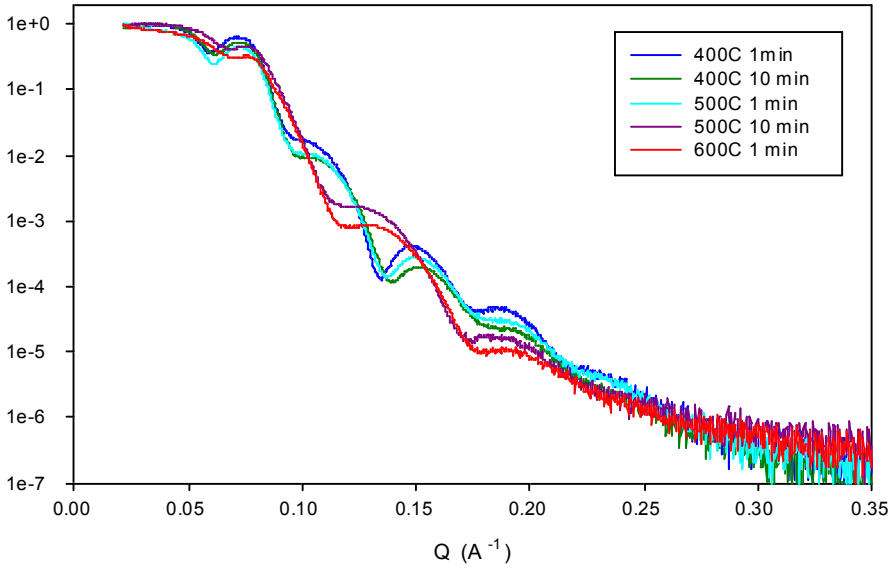
Bad news:

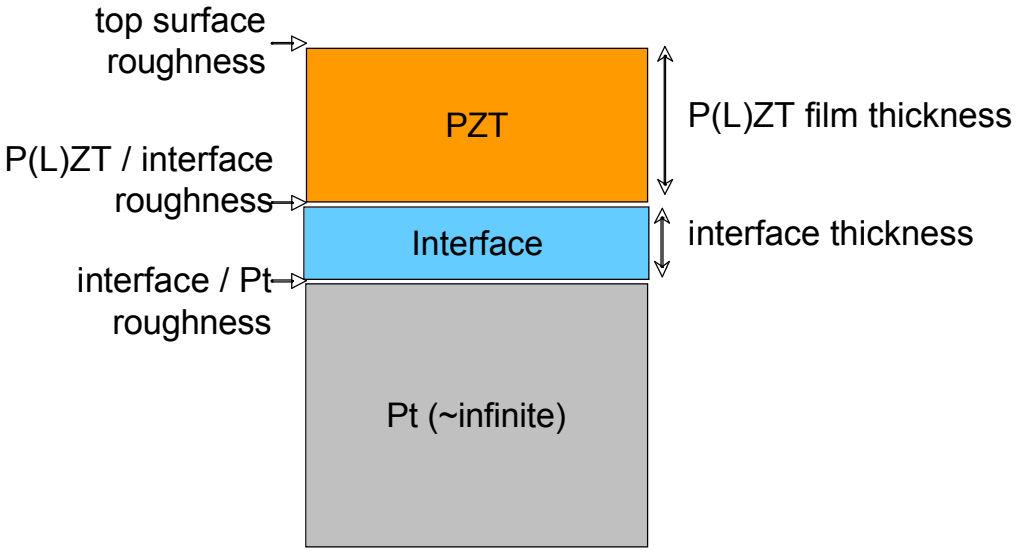
Properties are severely compromised below ~50nm

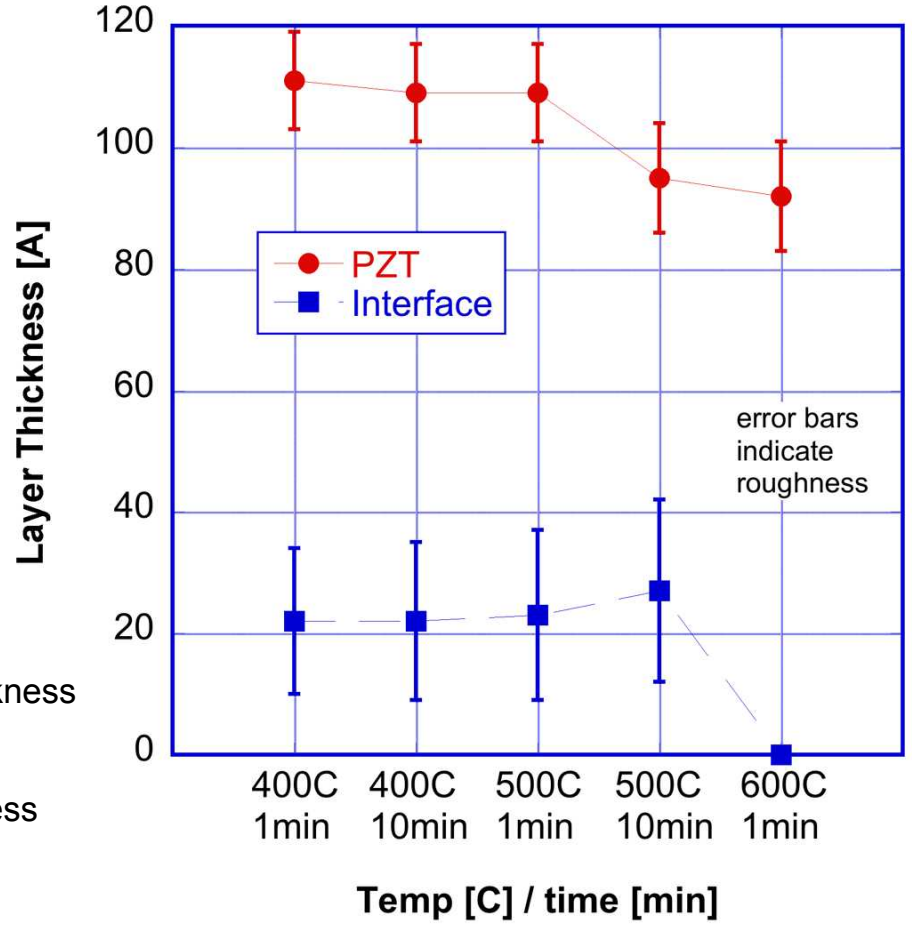




PLZT-Pt Interactions







Brennecka, et al., ***Proc. ISAF*** *(2008)*

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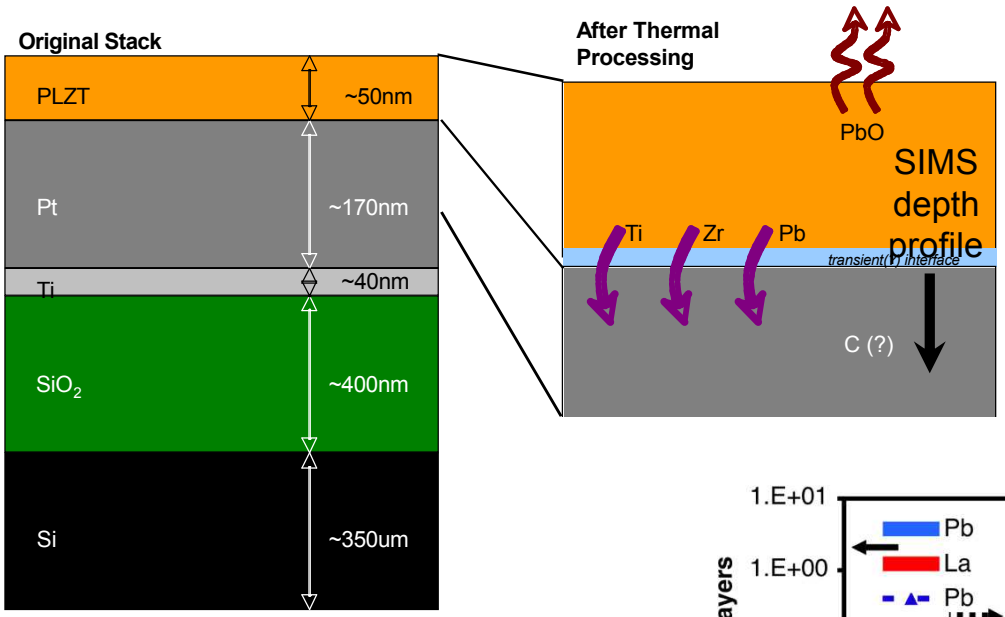
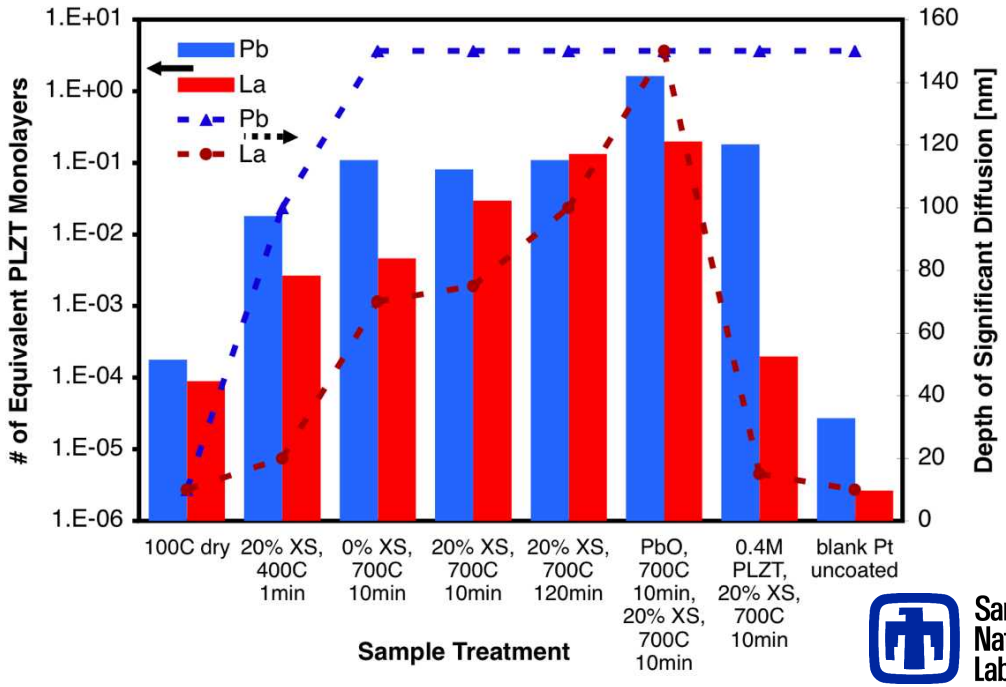
PLZT-Pt Interactions





Brennecka, et al., ***Proc. ISAF*** *(2008)*

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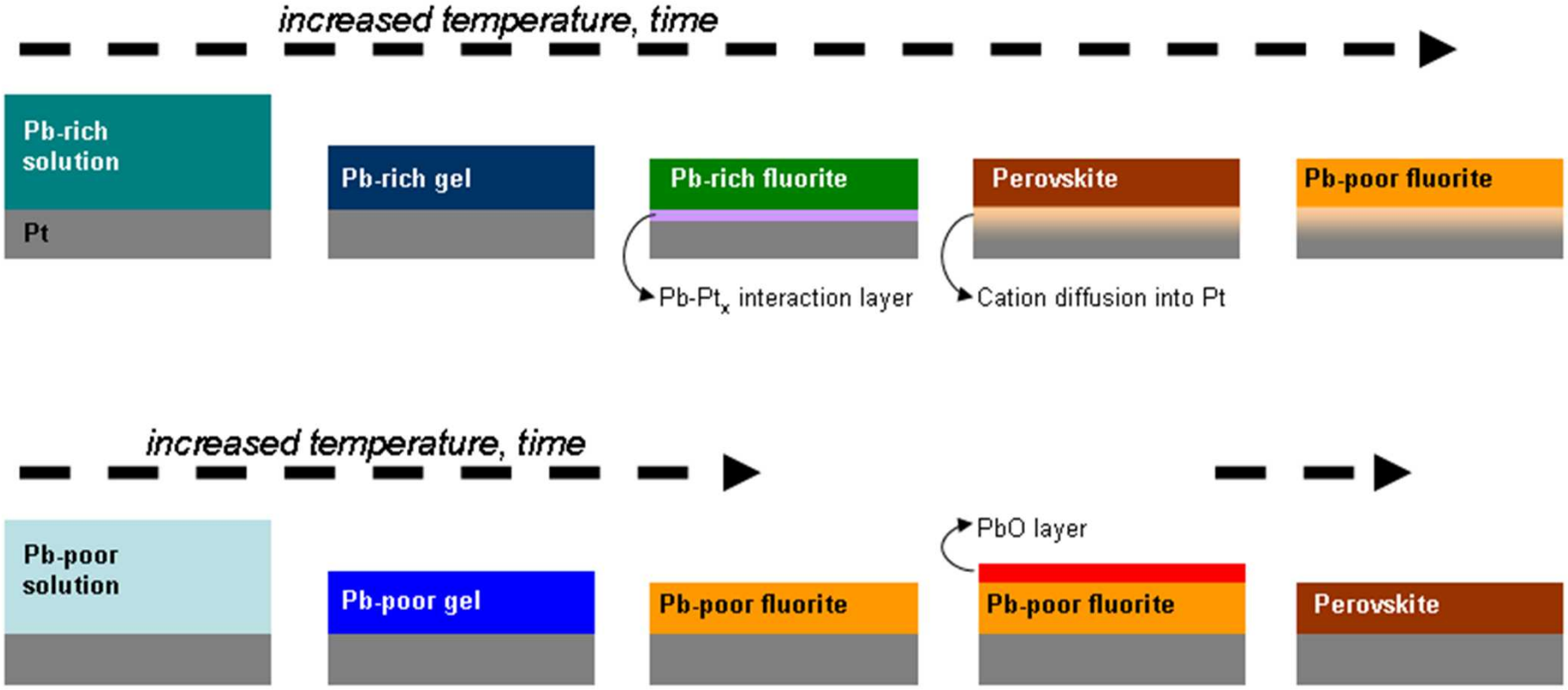
Fluorite ⇔ Perovskite Reversibility

Traditional processing



Pb-deficient followed by conversion

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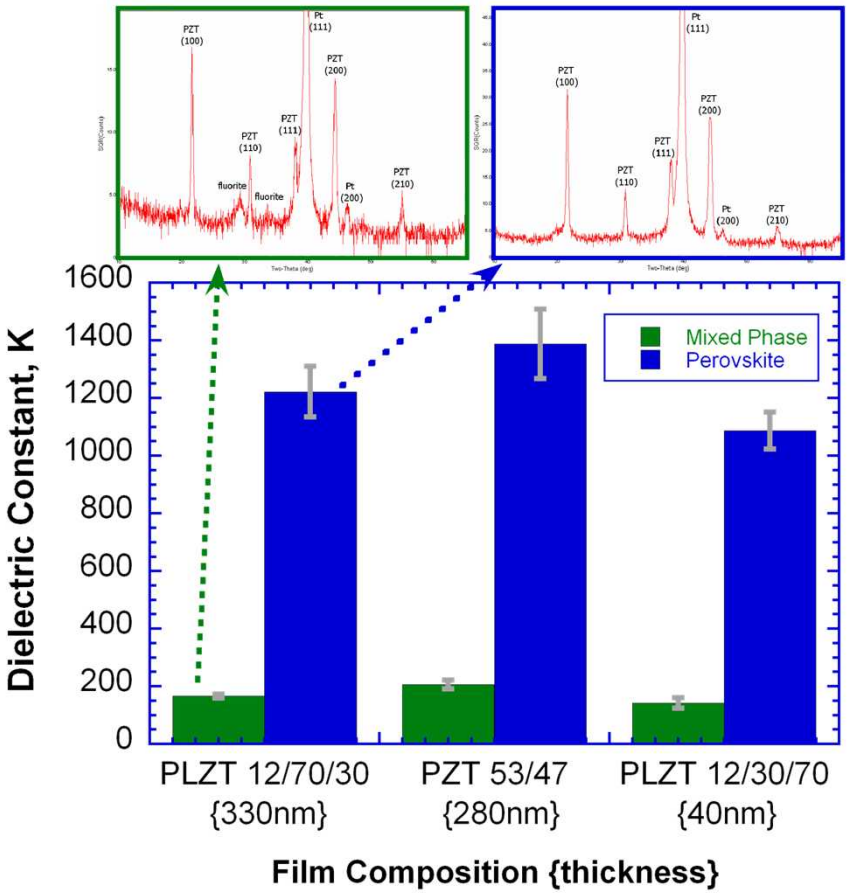
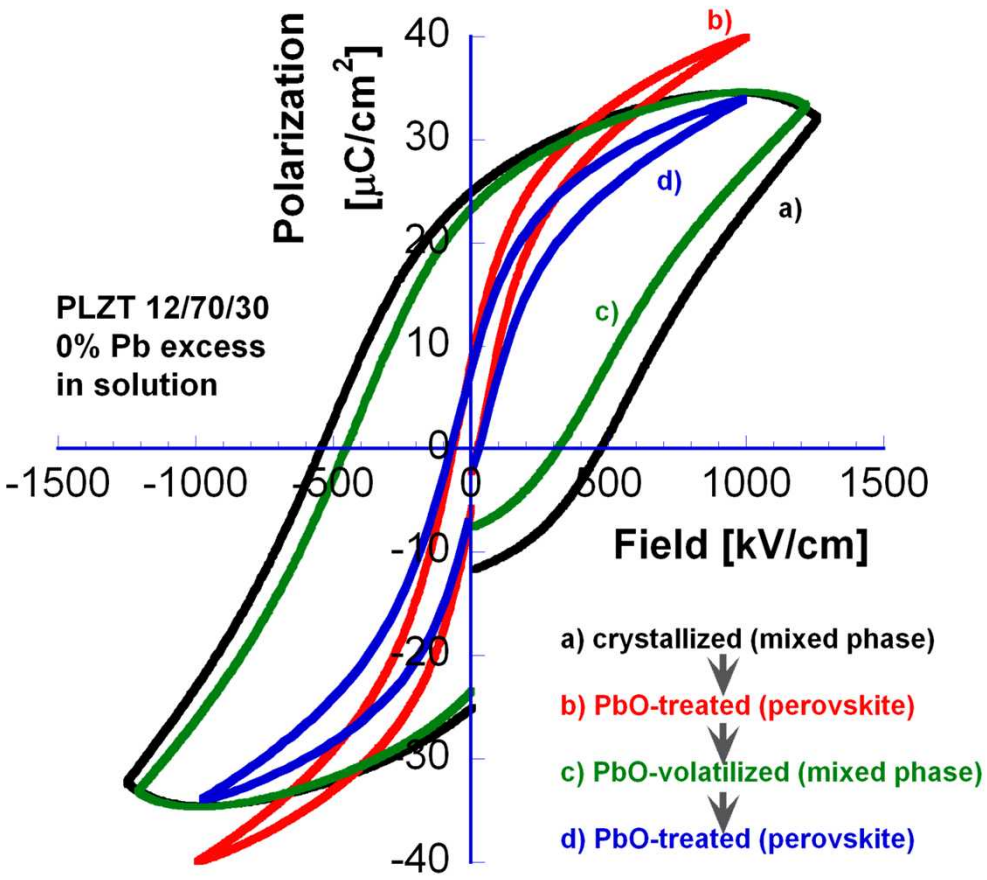
Fluorite ⇔ Perovskite Reversibility





Brennecka, et al., ***Adv. Mater.*** *(2008)*

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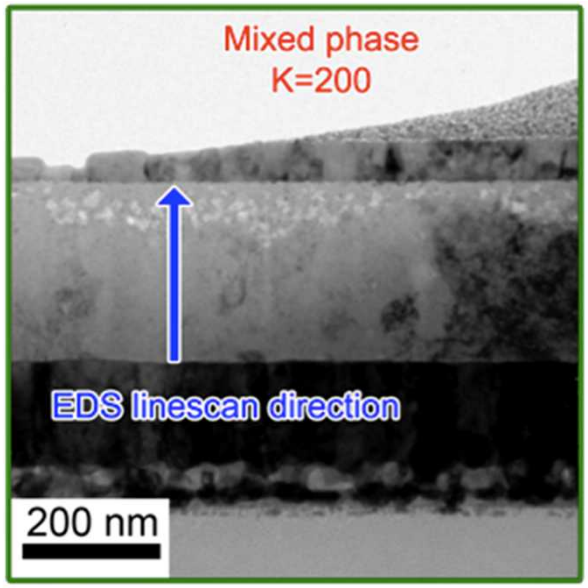
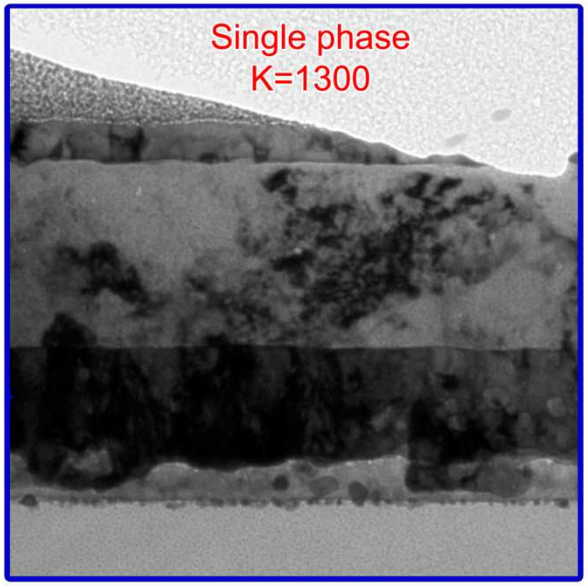
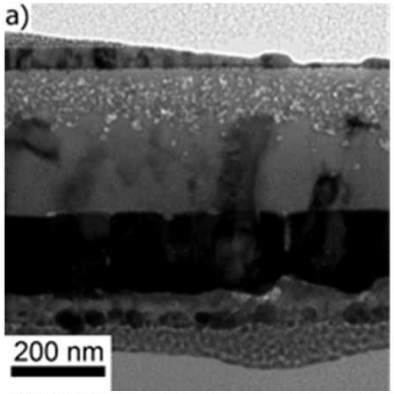
Fluorite ⇔ Perovskite Reversibility

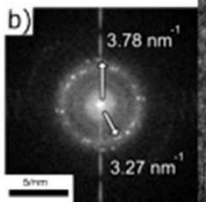


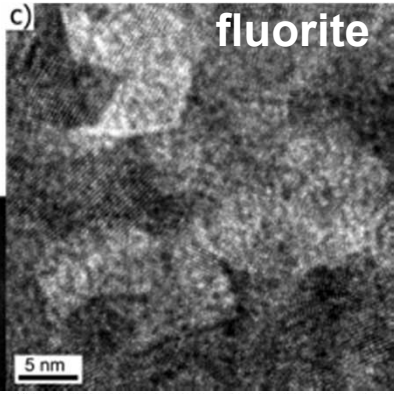
FIB Pt
Pt
PZT
Pt
TiO_x
SiO_2

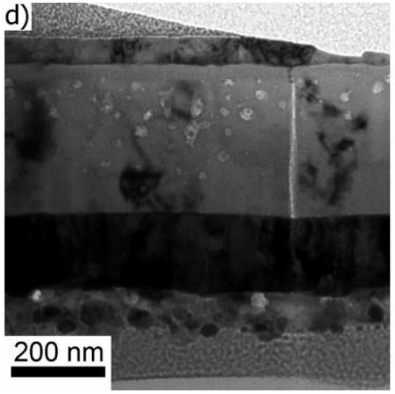




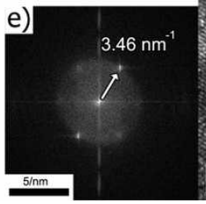
Near top of film

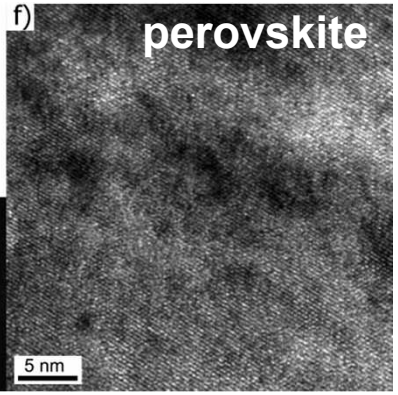




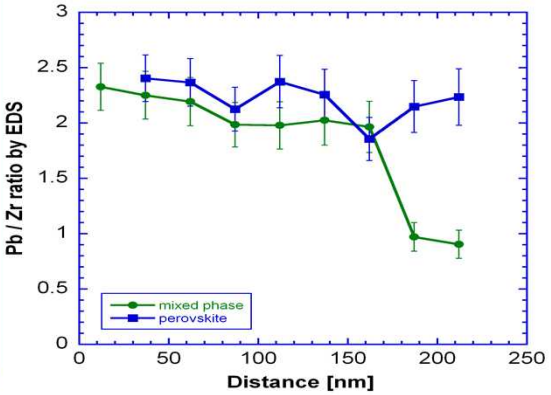


Near top of film





PLZT 12/70/30
0% Pb excess
in solution



PZT 53/47
10% Pb-deficient
solution

Brennecka, et al.,
Adv. Mater. *(2008)*

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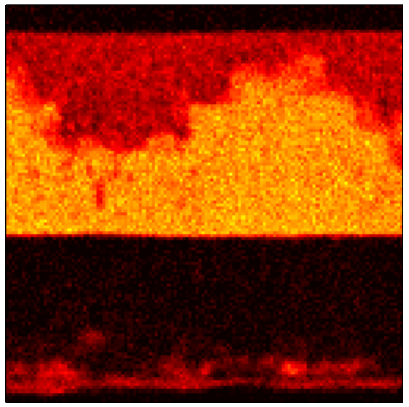
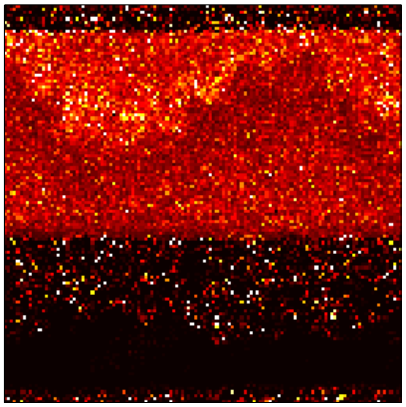
Quantitative Cation Mapping



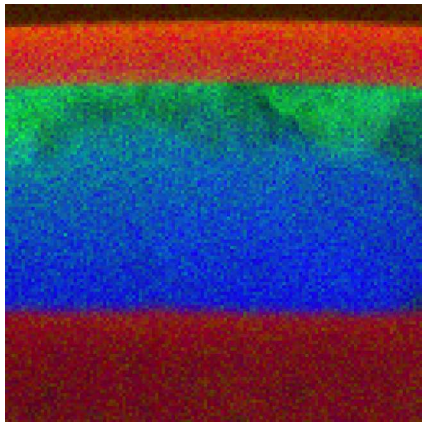
0 50 100 150 200

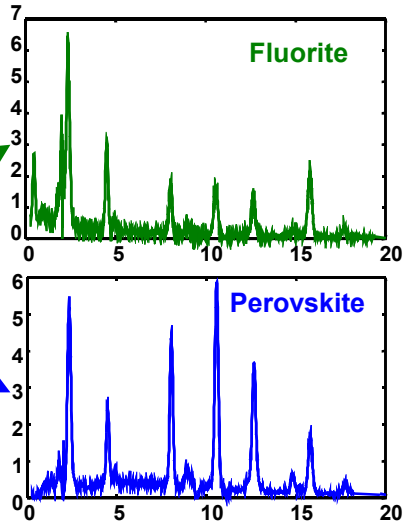
Pb content

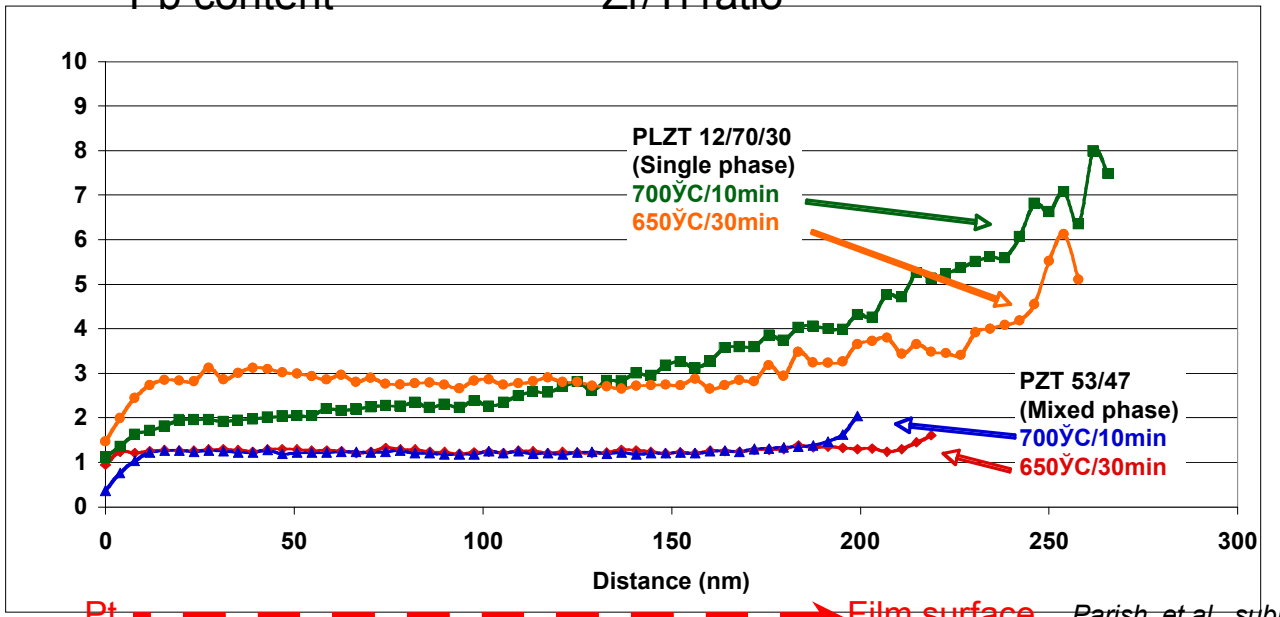


0 2 4 6 8 10

Zr/Ti ratio







Multivariate statistical analysis of TEM EDS data allows single-pixel resolution chemical and/or phase determination

Parish, et al., submitted to ***J. Am. Ceram. Soc.***

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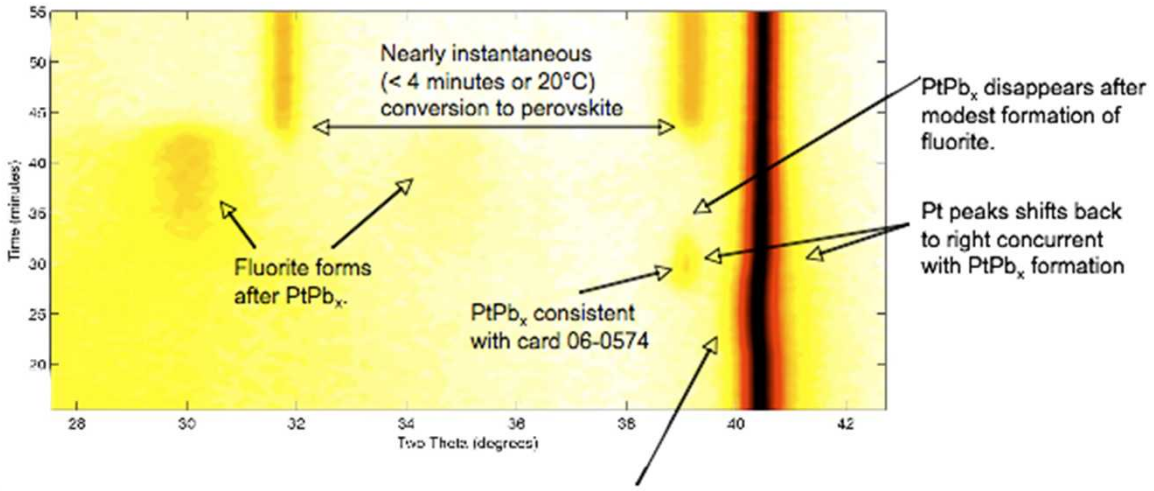
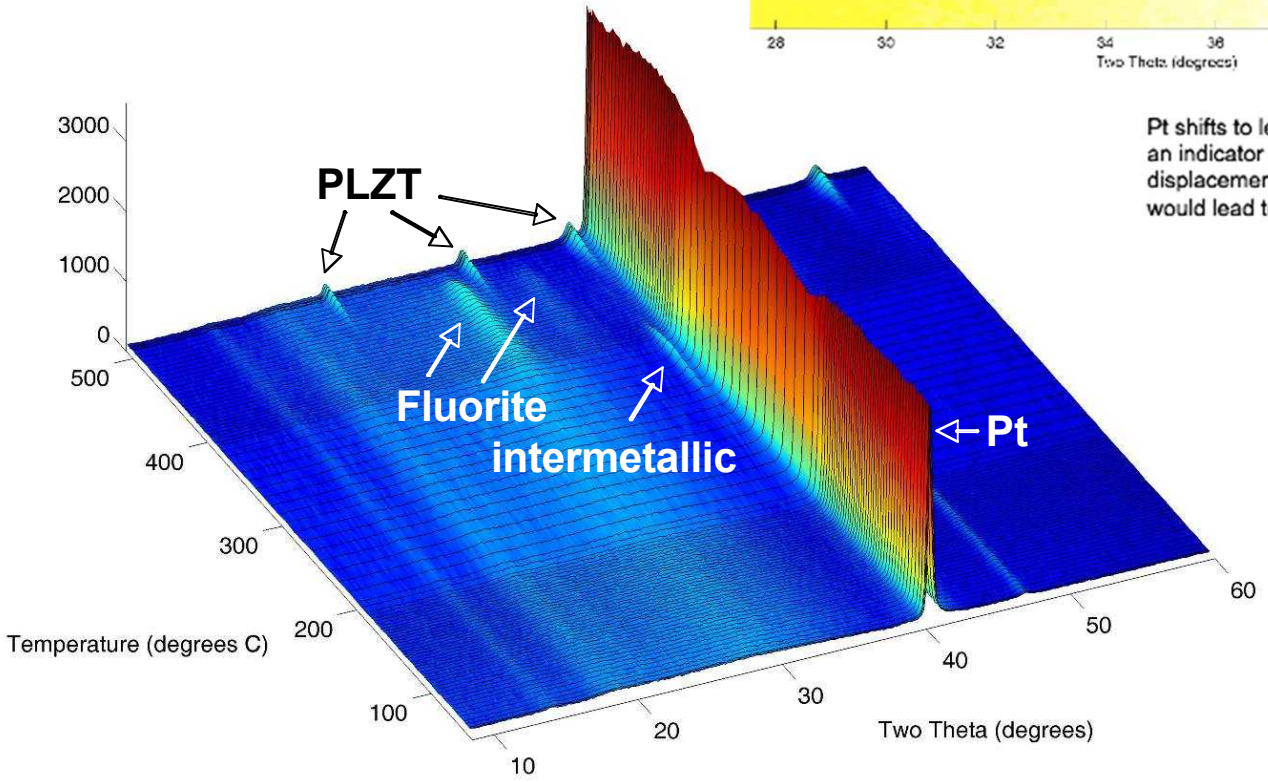
in-situ X-Ray Diffraction

Crystallization of PLZT thin film from a solution containing 20% XS Pb





in collaboration with Jacob Jones at the University of Florida

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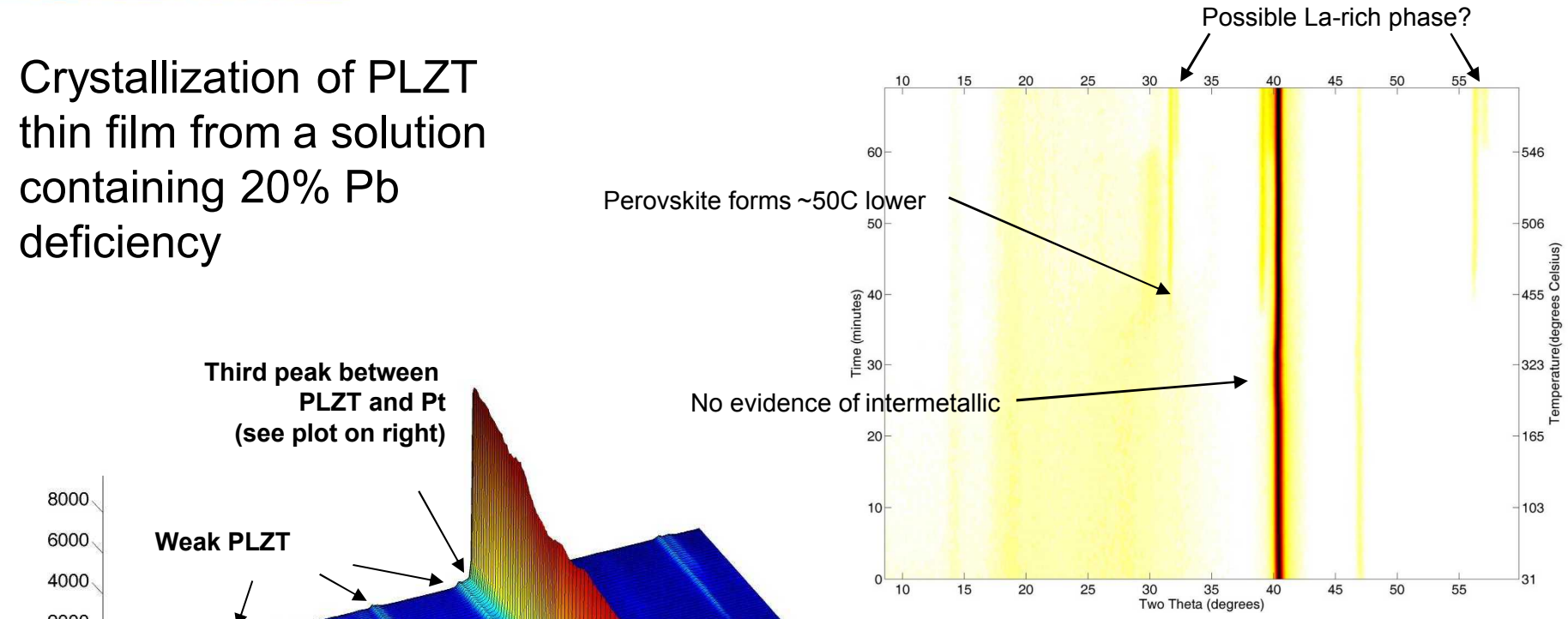
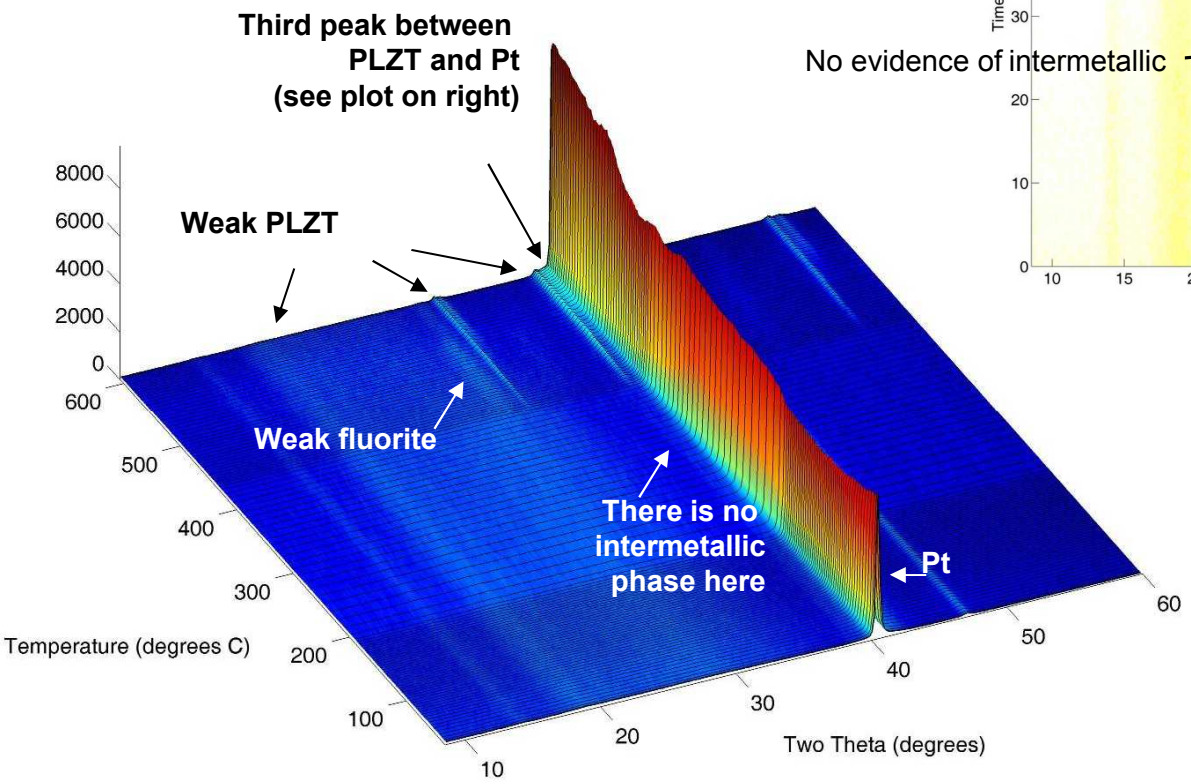
in-situ X-Ray Diffraction

Crystallization of PLZT thin film from a solution containing 20% Pb deficiency





in collaboration with Jacob Jones at the University of Florida

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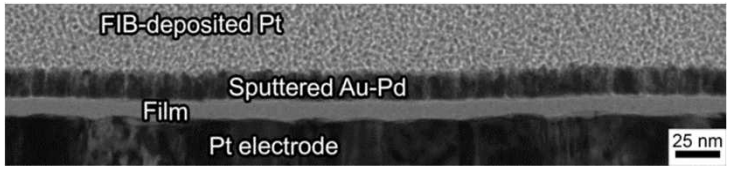
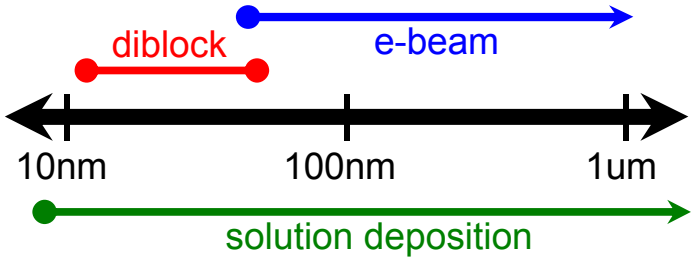
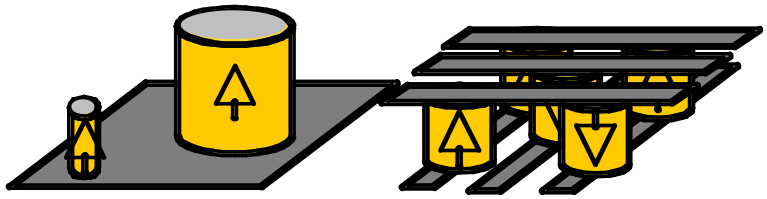
Extend Ultrathin Films into 2D Patterning

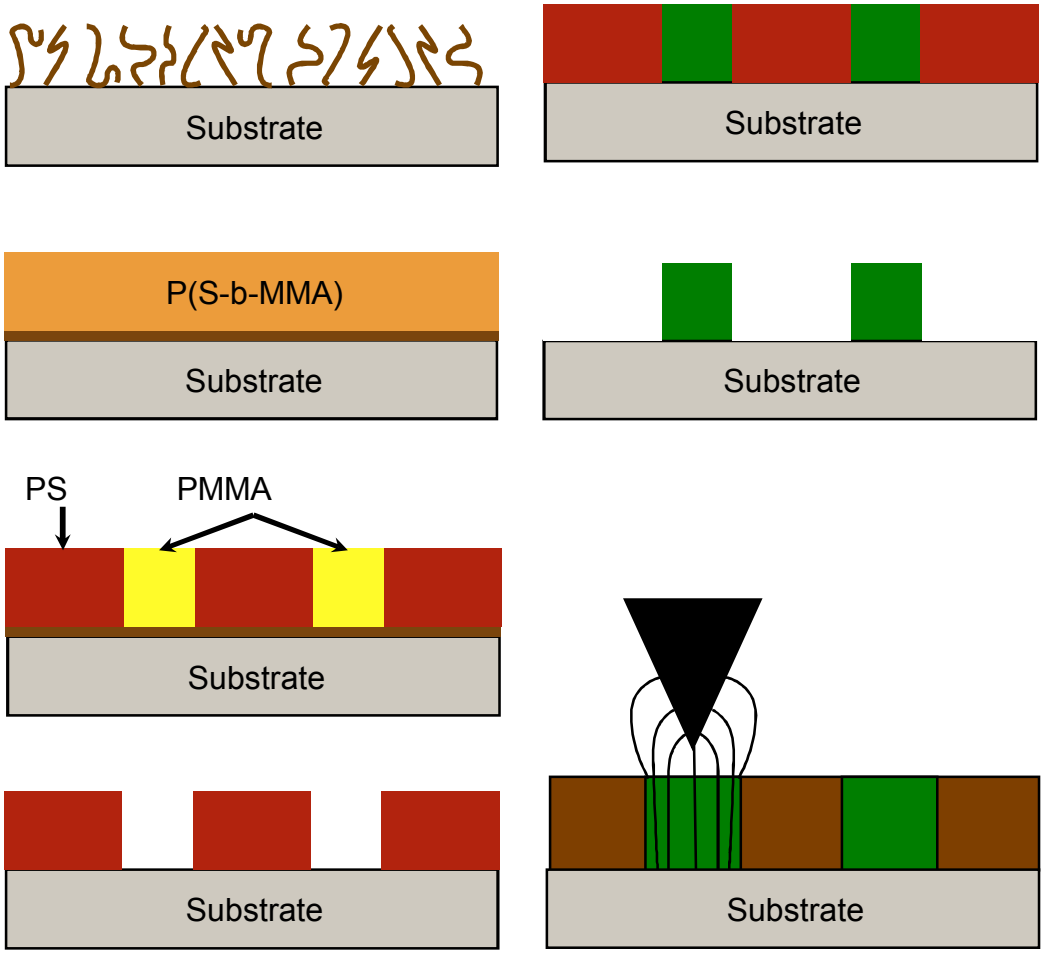


Generic platform for nanoscale studies and device fabrication

- **continuous dimension control**
- **variety of materials systems**
- studies of fundamental size, aspect ratio, and interface effects







Working with UT-A and UWisc on surface treatment and diblock orientation

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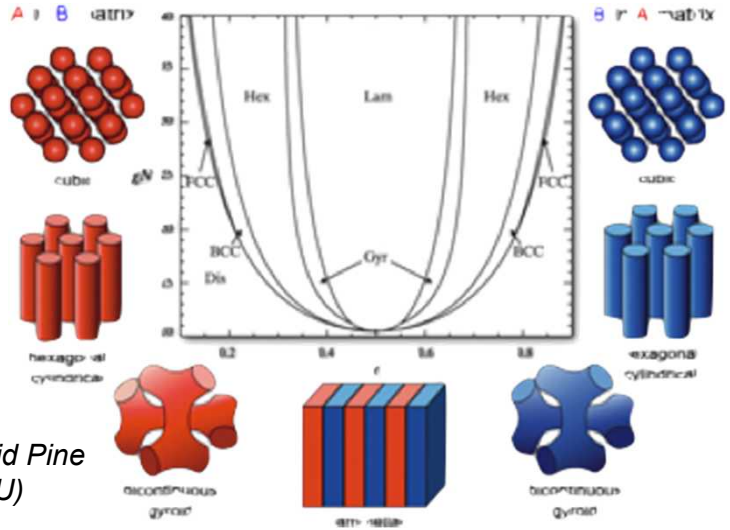
Diblock Copolymer Self-Assembly



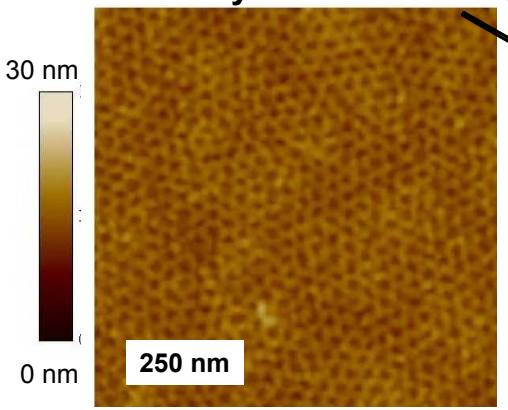
David Pine (NYU)

- Phase separation of immiscible 'blocks'
- Various morphologies are thermodynamically stable
- Choice of blocks and ratios gives (some) control over size, distribution, and morphology

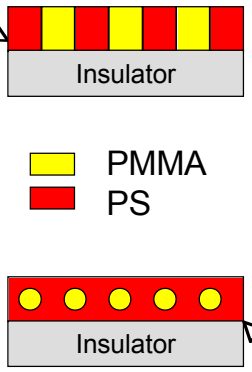
Cylinders

<u>PMMA cylinders perpendicular to surface</u>

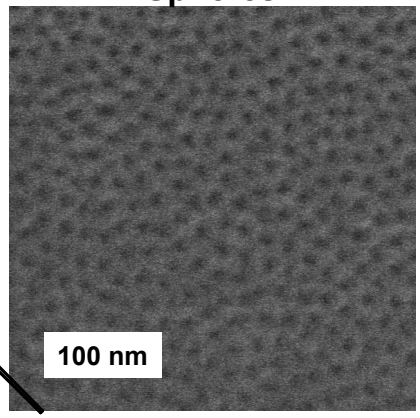
- Mn = 67000 g/mol
- 70% styrene
- 30% methyl methacrylate
- 20 nm diam pores
- ~6×10^{10} cm^{-2}



AFM image of cylindrical P(S-b-MMA) template on silicon dioxide after sputtered with gold for mechanical stability



Spheres



SEM image of spherical P(S-b-MMA) template

<u>PMMA spheres in monolayer</u>

- Mn = 78000 g/mol
- 83% styrene
- 17% methyl methacrylate
- 12 nm diam pores
- ~1.2×10^{11} cm^{-2}

Assembly done at UT-A

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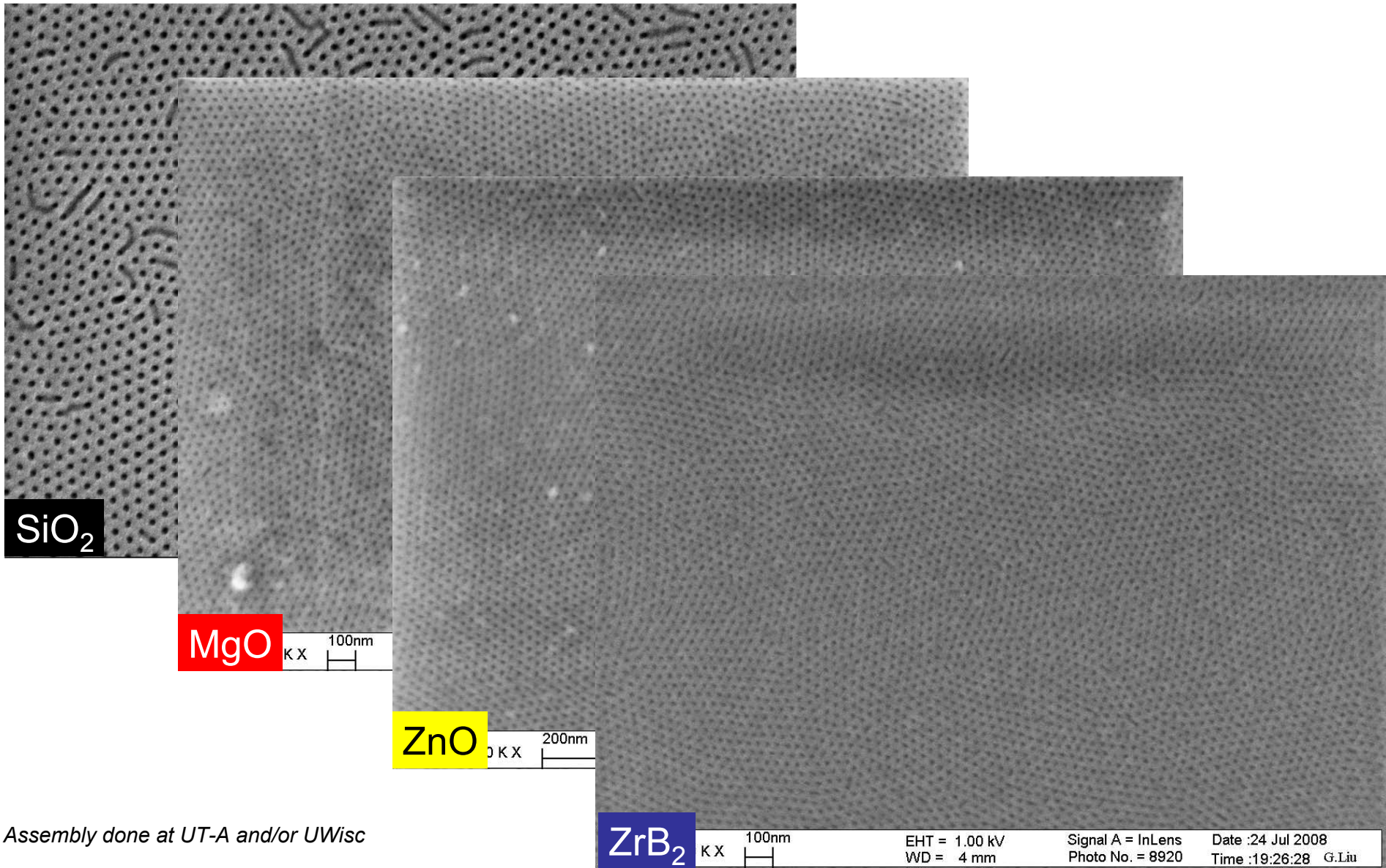
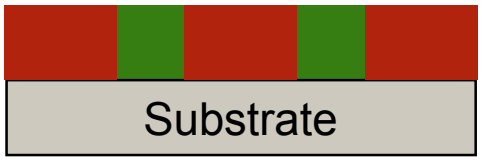
Diblock Patterning on Various Substrates

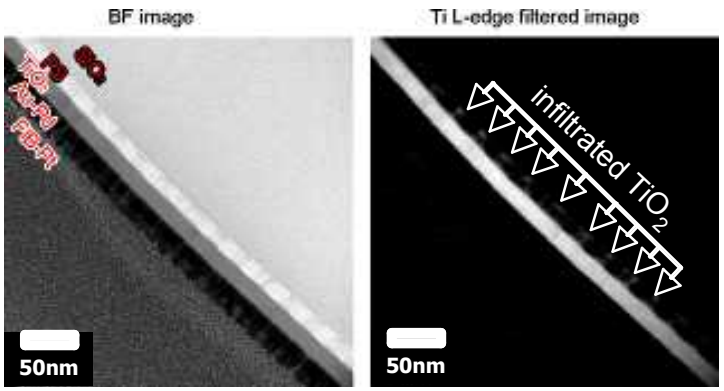


Assembly done at UT-A and/or UWisc

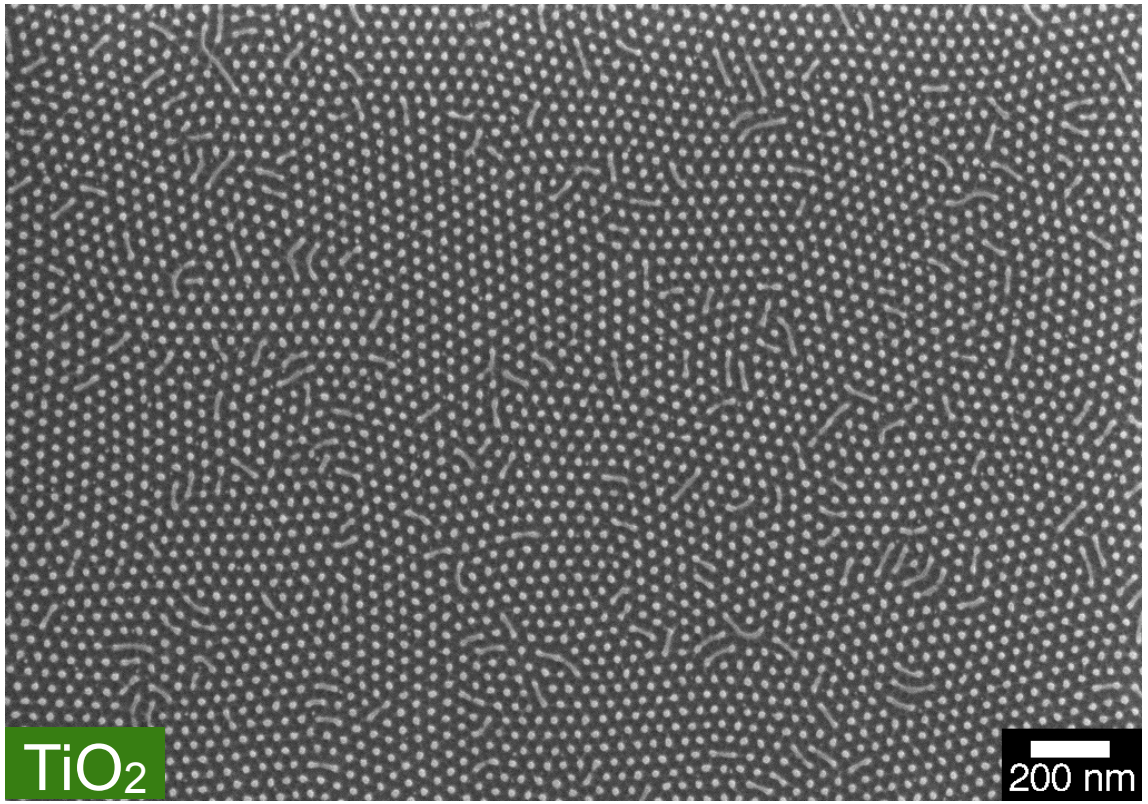
Deposition of Electronic Oxides

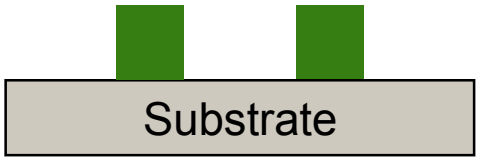


Gel



TiO_2 solution infiltrates 20nm columnar features in nanopatterned PS (also shown in HfO_2)





Remove PS

Technique also shown to be compatible with Ni, V, and Mn oxides

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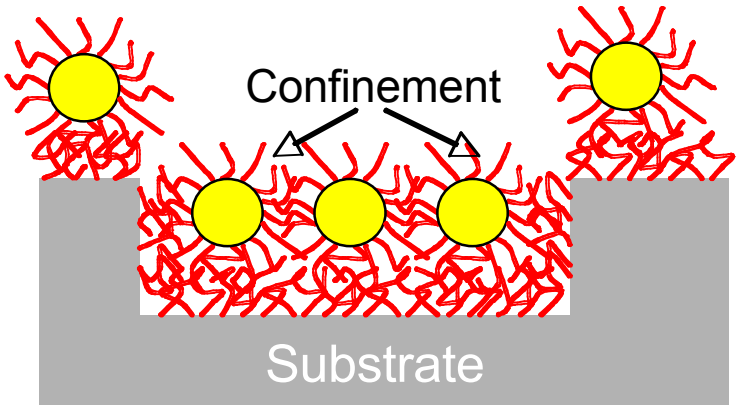
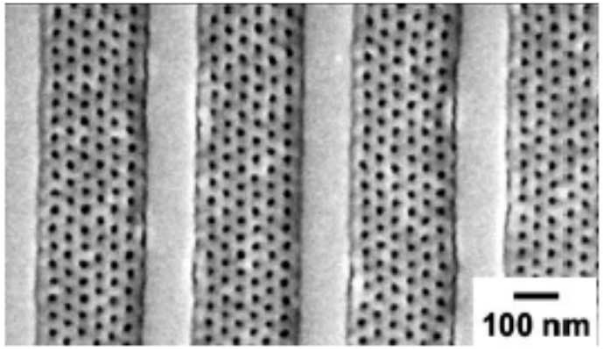
Graphoepitaxy

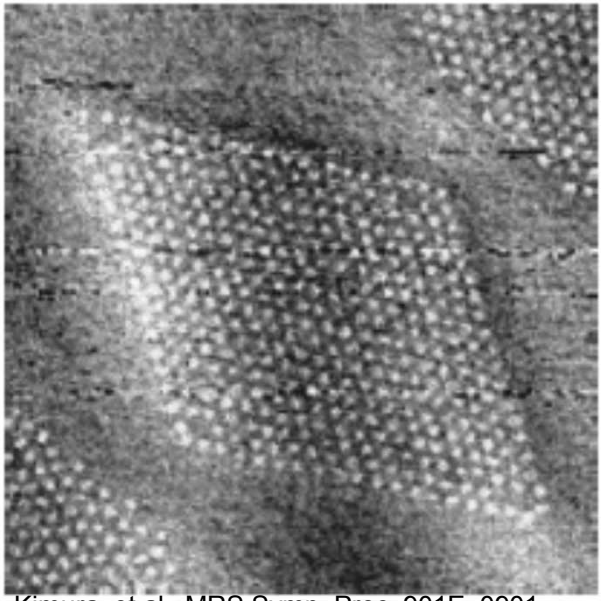
- Geometric confinement can lead to ‘crystalline’ single-domain state
- Demonstrated for Si / SiO_2 with cylindrical and spherical diblocks
- *Pre-defined pixel location*



R.A. Segalman, et al., Macromolecules, 36 4498-4506 (2003)



C. T. Black, et al., IEEE Trans. Nanotechnology 3 (5) 412-415 (2004)



Kimura, et al., MRS Symp. Proc. 901E, 0901-Ra05-05-Rb05-05.1 (2006)

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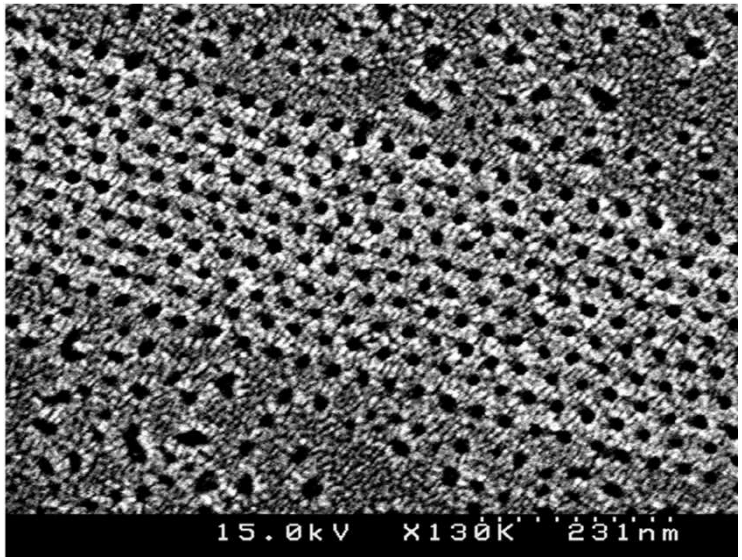
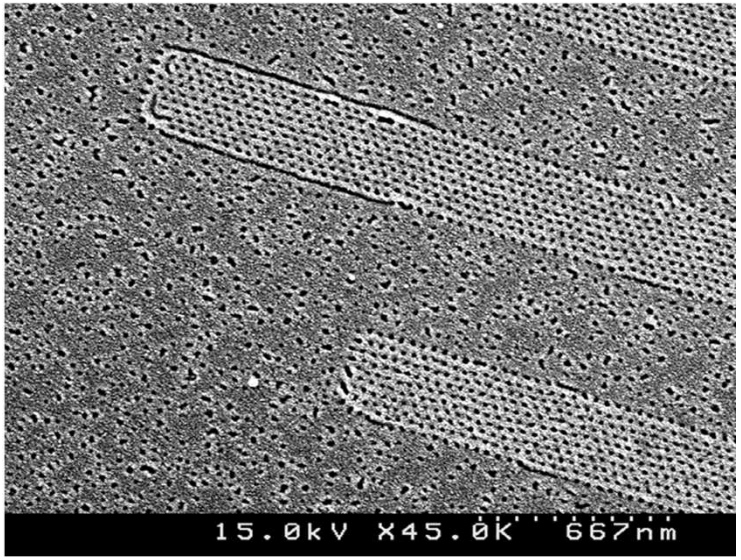
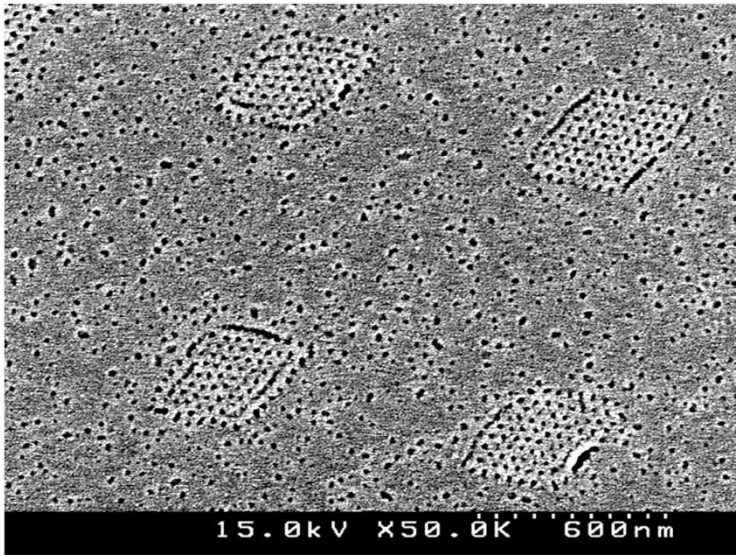
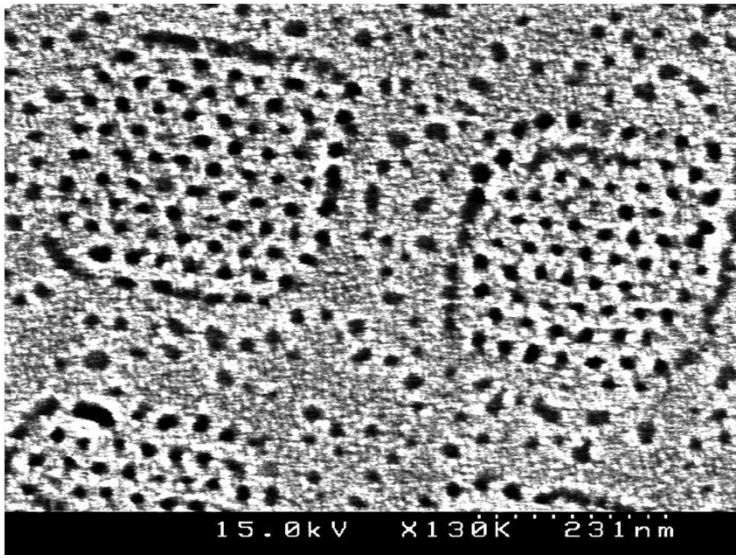
Successful Graphoepitaxy (UT-A)









(250nm wide features, 35nm thick diblock copolymer)

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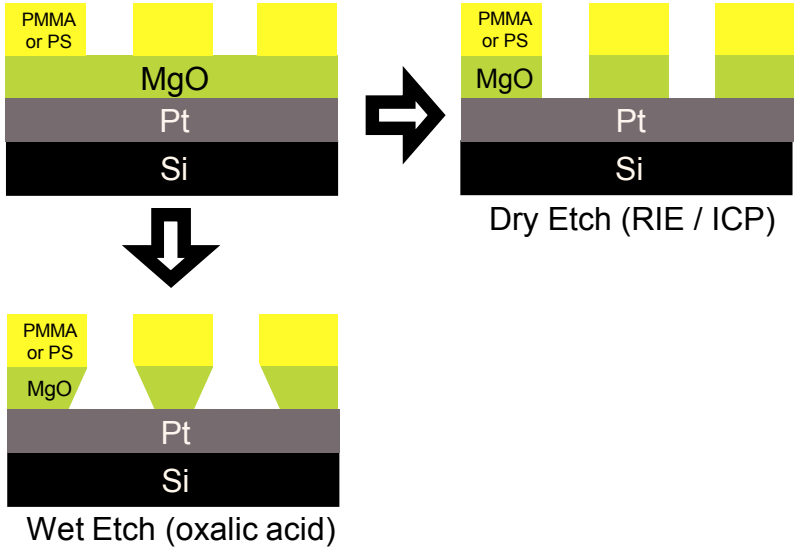
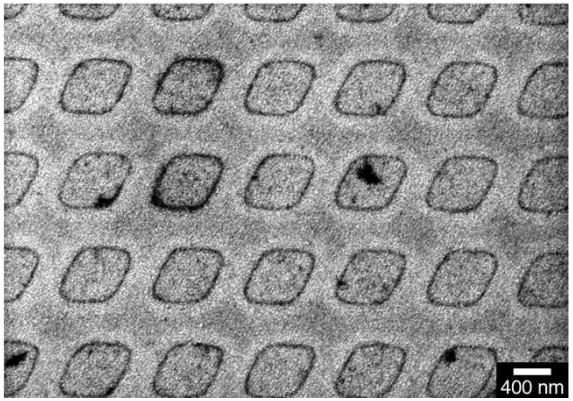
Pattern Transfer for Added Flexibility

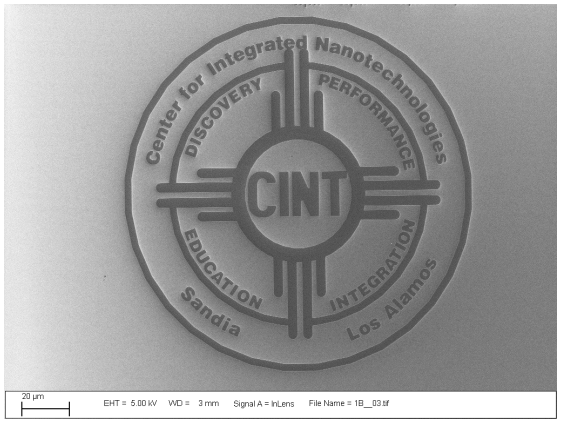


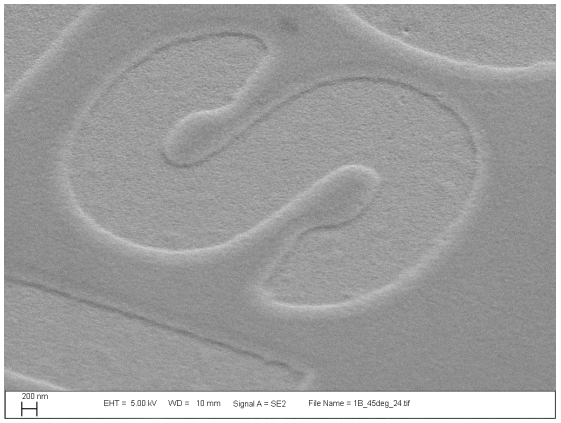
Dry Etch (RIE / ICP)

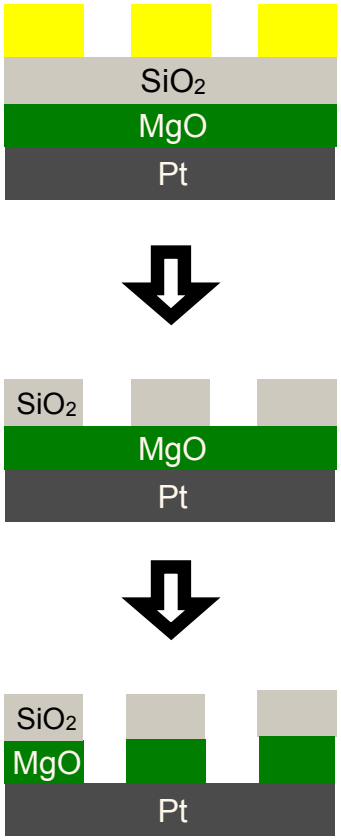
Wet Etch (oxalic acid)



Wet etch:
- high selectivity
- low edge resolution







Dry etch:
- low selectivity
- relatively high edge resolution
- attempting SiO_2 hard mask

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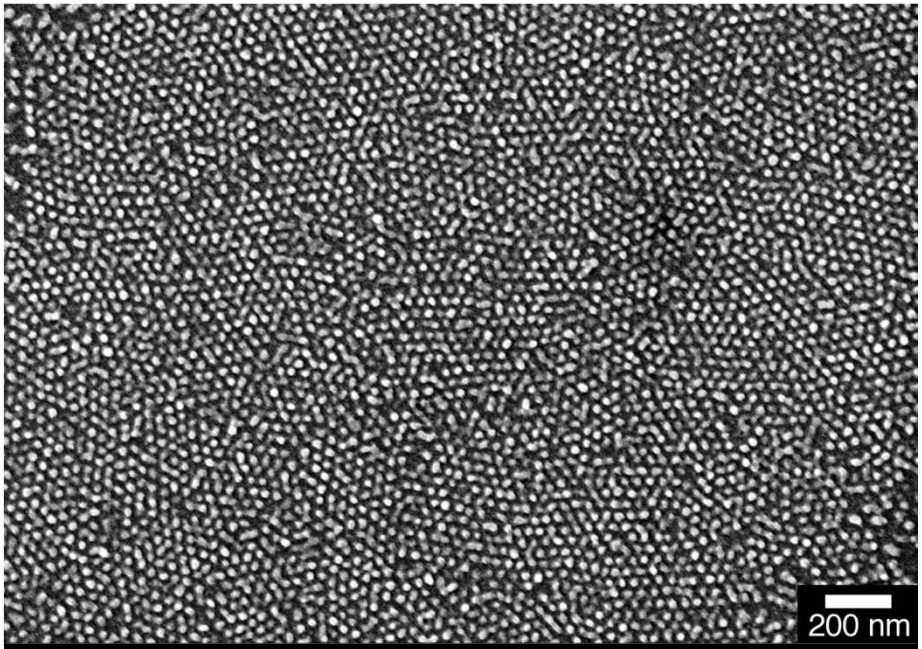
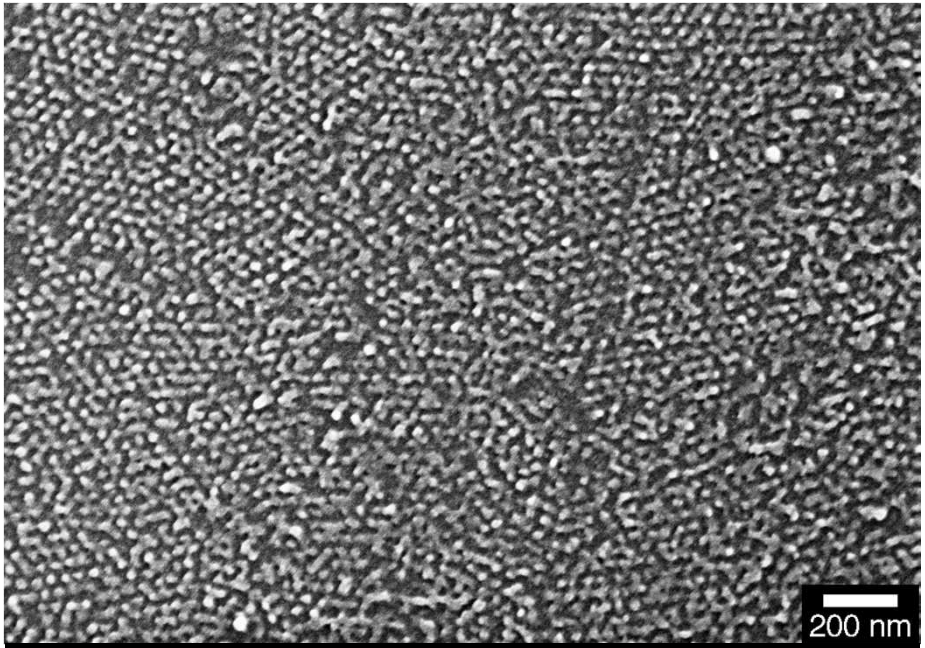
Crystallization of Freestanding Nanofeatures

After removal of PS mask, TiO_2 nanopillars were heated to 550° C for 30min to crystallize.



Amorphous TiO_2



Crystalline TiO_2 (Anatase)

Nanofeatures are still mostly discrete, but some ripening has taken place.

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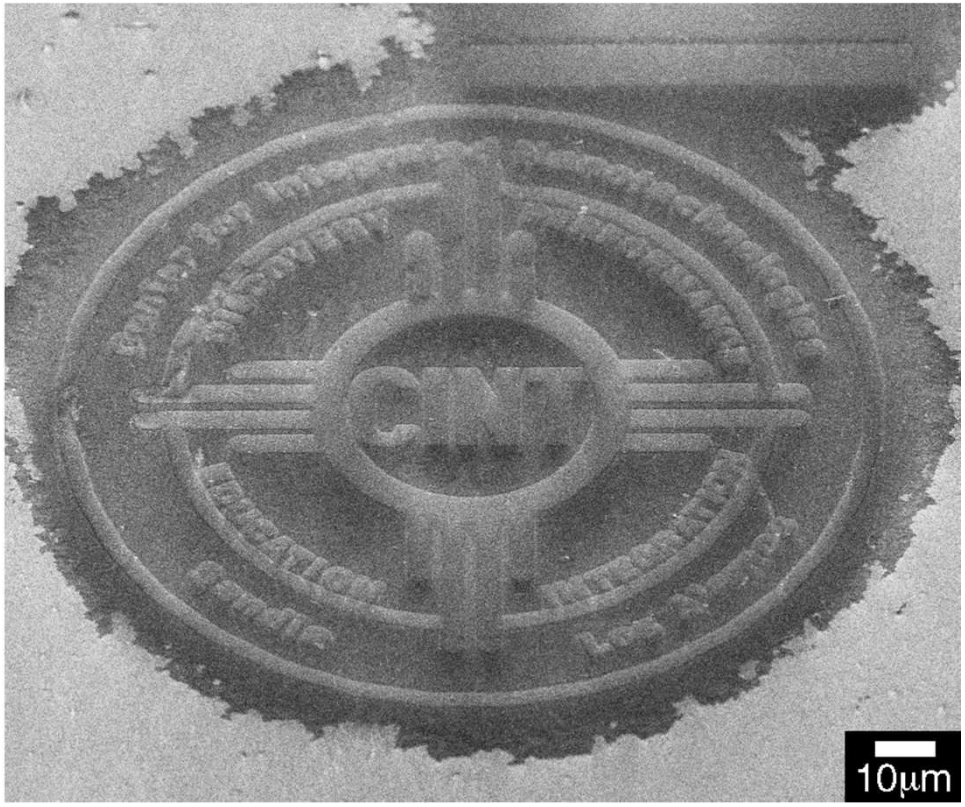
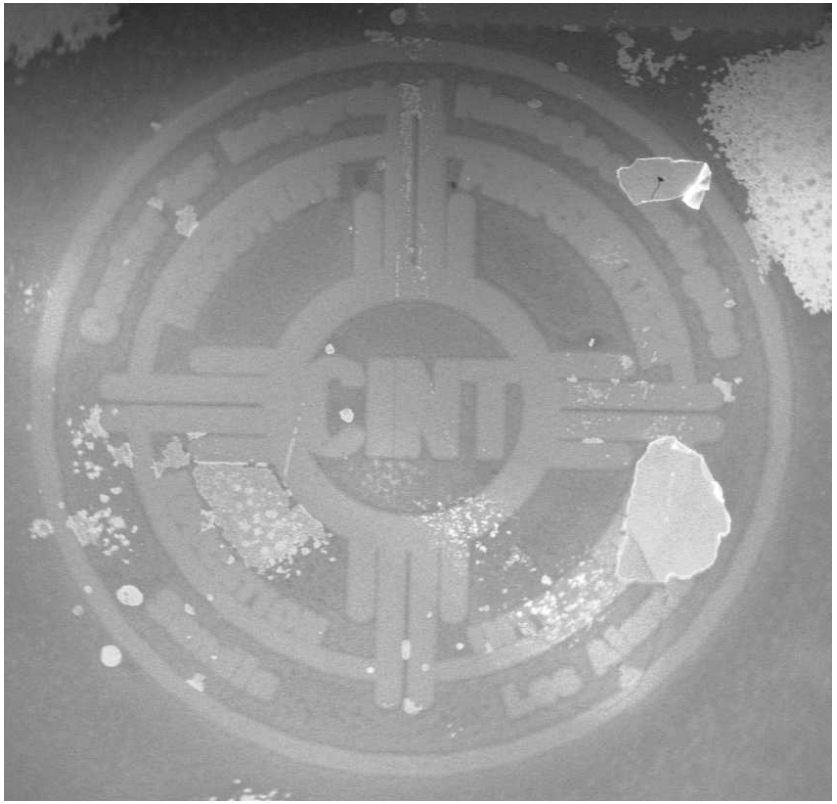
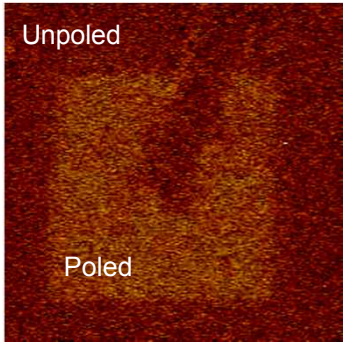
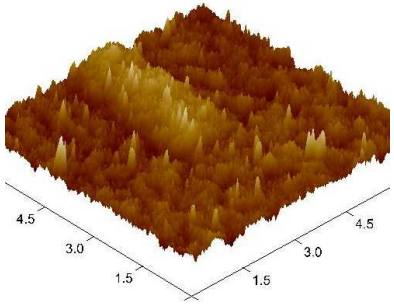
MgO-Mediated Pattern Transfer to PZT









- Pattern transfer (top left)
- Pt liftoff (top right)
- PZT is piezoelectric and appears to be ferroelectric

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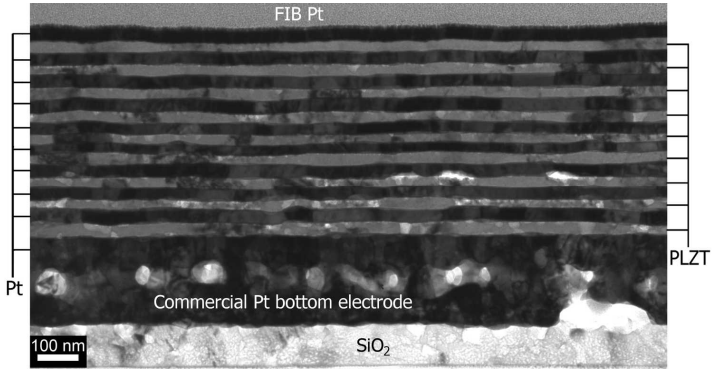
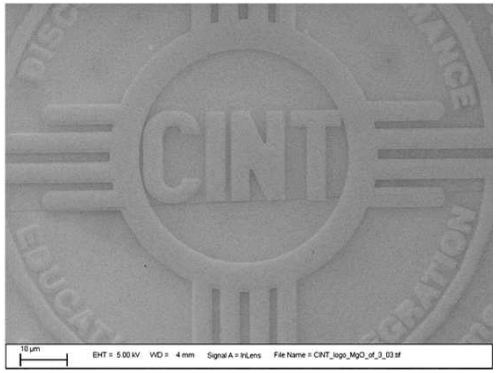
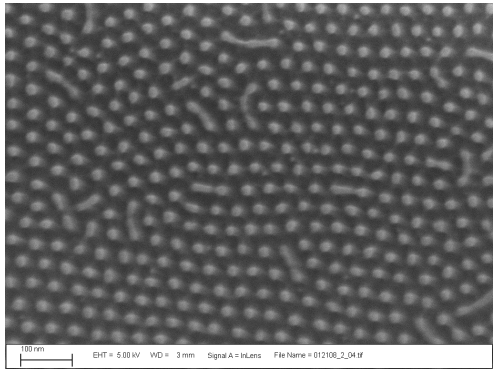
Summary

- Continuous single or multilayer films for capacitor applications
  - Optimization of film performance below ~50nm requires better control of phase / interface development







- General patterning approach
  - Useful platform for fundamental studies and devices
  - Diblock-copolymer mask for ~12-50nm feature definition
  - Graphoepitaxy (and/or chemical patterning) for bi-level pattern control
  - Etching step currently the limiting factor for breadth of materials capabilities

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