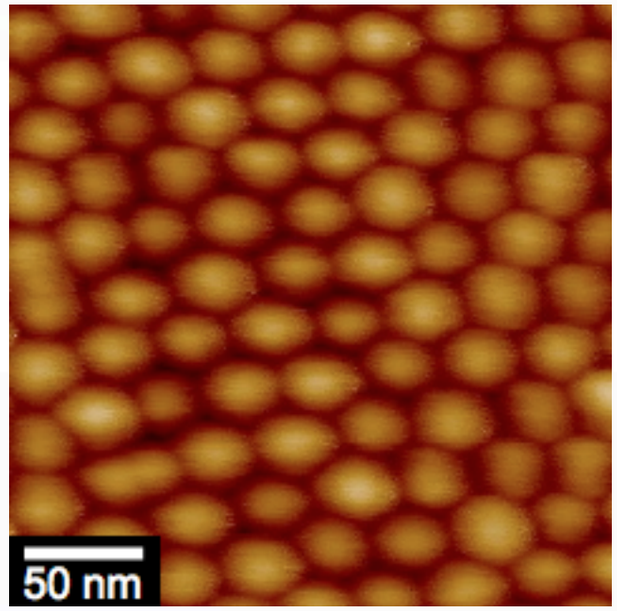
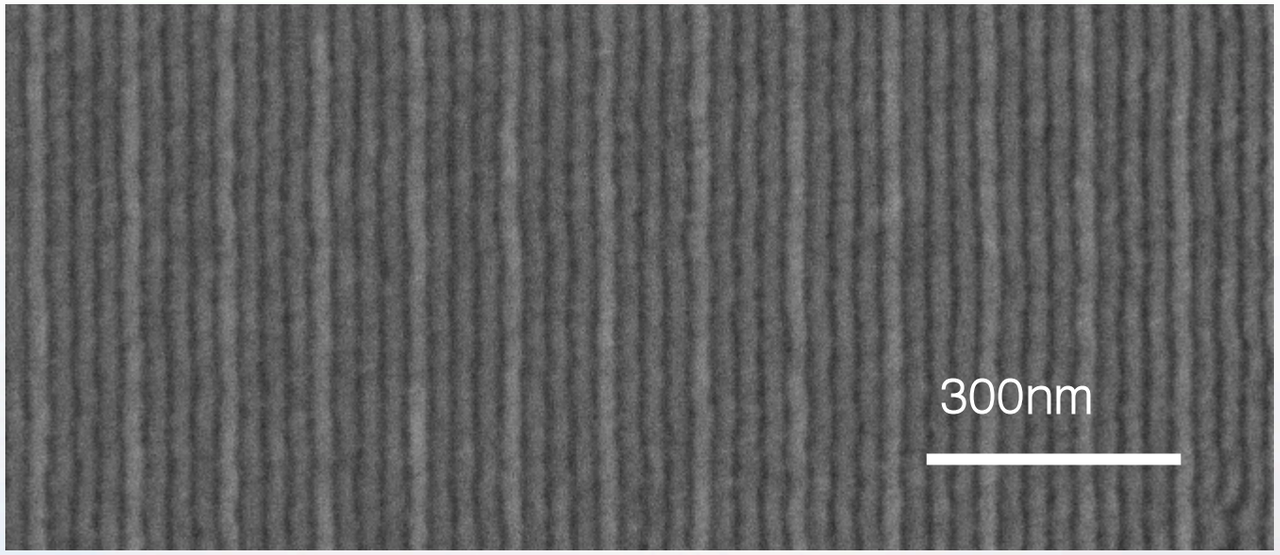
SAND2011-0176P

Patterning and Integration of Ferroelectrics and other Functional Nanostructures





Geoff Brennecka
Sandia National Laboratories

National Laboratories and Production Sites

Pacific Northwest

Idaho

National Renewable Energy

Fermi

Ames

Argonne

National Energy Technology

Brookhaven

Princeton

Thomas Jefferson

Lawrence Berkeley

Lawrence Livermore

Sandia

Stanford Linear Accelerator Center

KCP

Los Alamos

Sandia

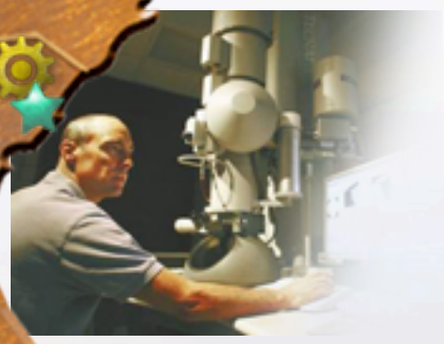
Pantex

Y-12

Oak Ridge

SRP

Savannah River



KEY:

- = Production Sites
- = NNSA Labs
- = Science
- = Nuclear Energy
- = Environmental Management
- = Fossil Energy
- = Energy Efficiency and Renewable

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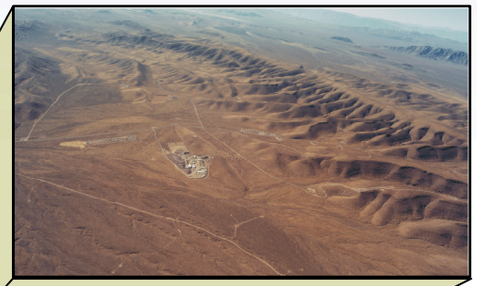

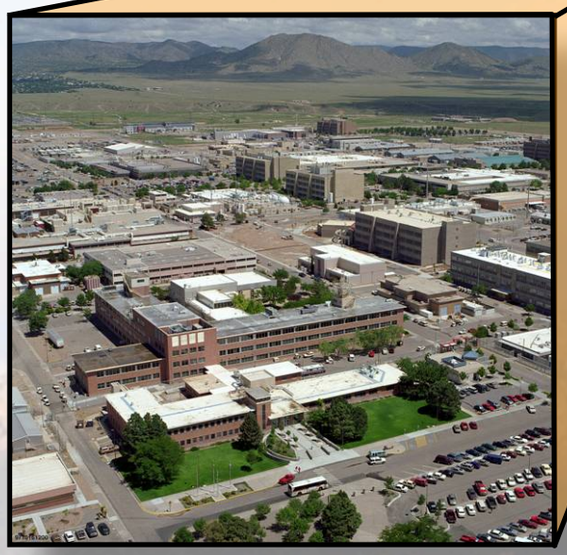

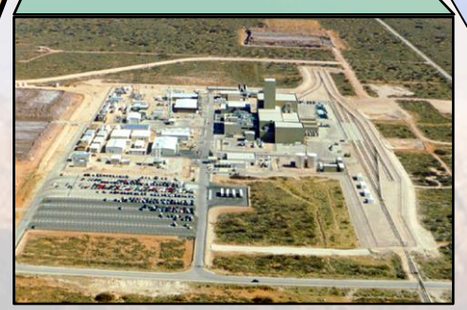

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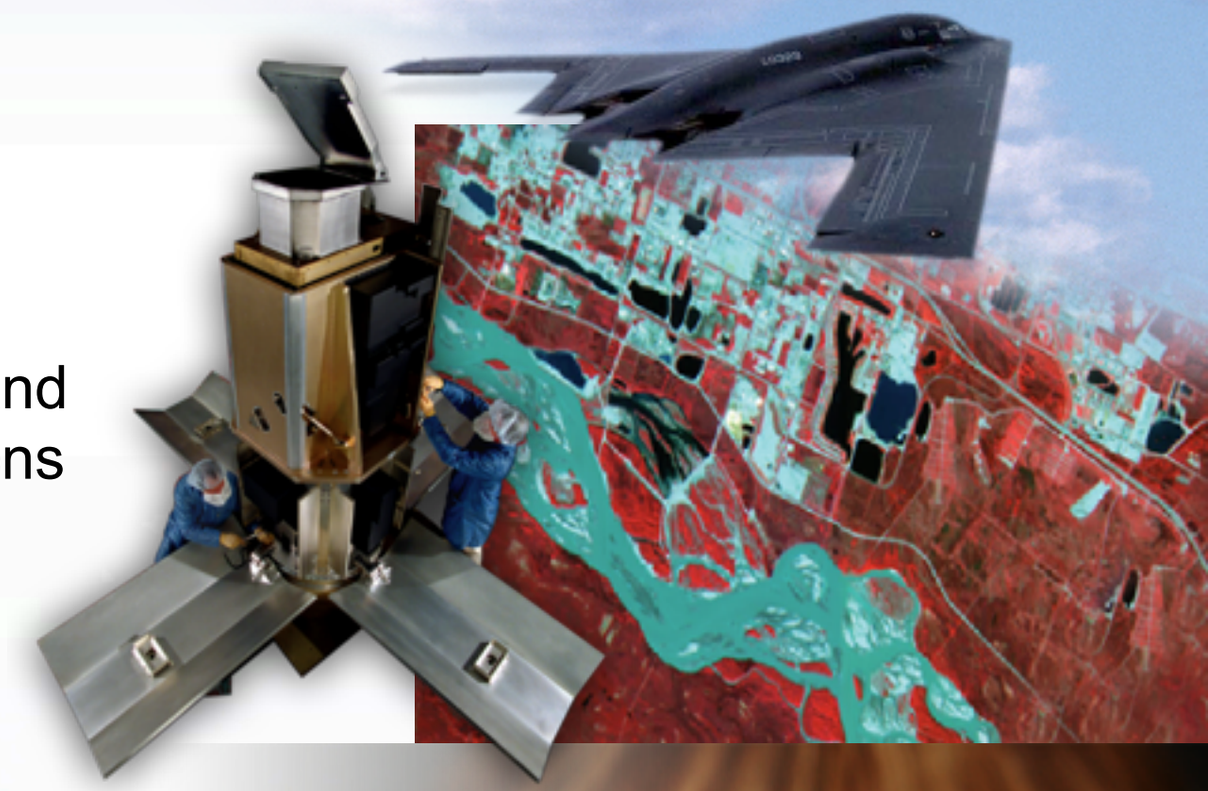
Sandia National Laboratories:
60 Years of Exceptional Service in the National Interest

- National Security Laboratory
- Broad mission in developing science and technology applications to meet our rapidly changing, complex national security challenges
- Safety, security and reliability of our nation's nuclear weapon stockpile



Sandia is #1 in total citations of energy and fuels research and 3 in papers cited in photonics research.

Sandia National Laboratories

We're Hiring...

- ~8000 full time employees
- ~2500 retirements in FY09-11
- Average tenure ~23 years

- ~200 MatSE hires expected in 2011-2012

US citizenship required for most (not all!) positions

SNL is the largest employer of Illini outside of the state of Illinois

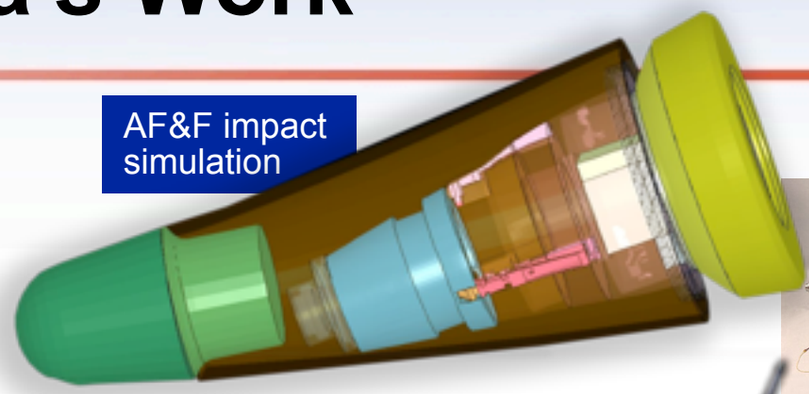
Sandia's Work

Shuttle Orbital Inspection System

4 Mission Areas

- Nuclear Weapons
- Defense Systems and Assessments
- Energy, Resources, and Nonproliferation
- Homeland Security and Defense

AF&F impact simulation



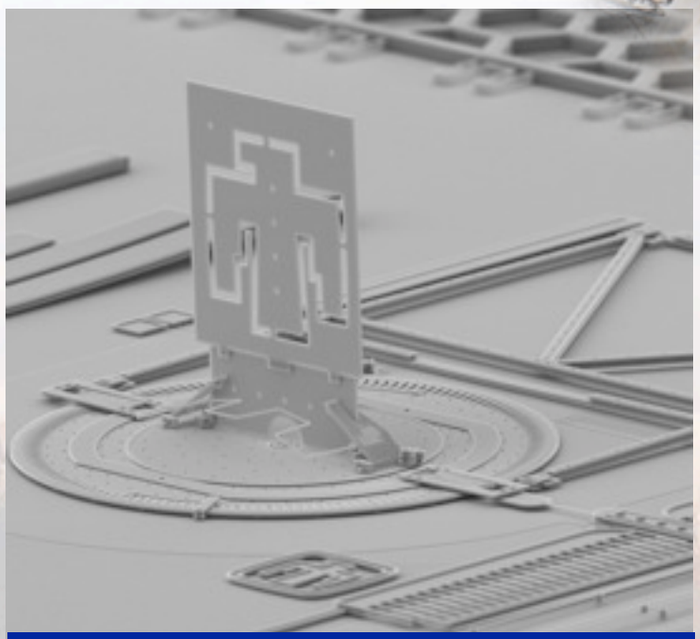
96% of total NW parts

Predator UAV with SAR

Small robotic vehicles

Renewable and alternative energy

µChemLab

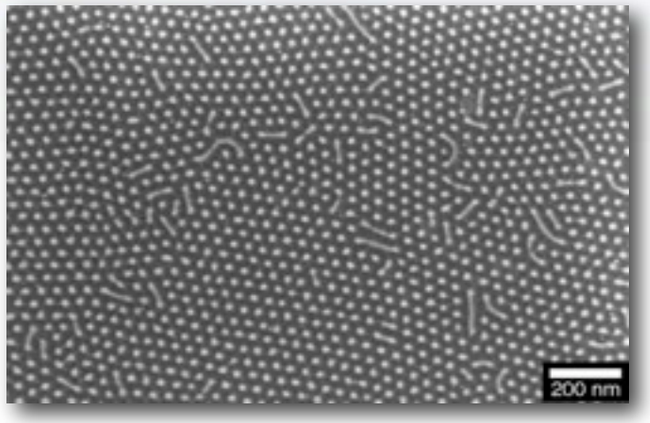


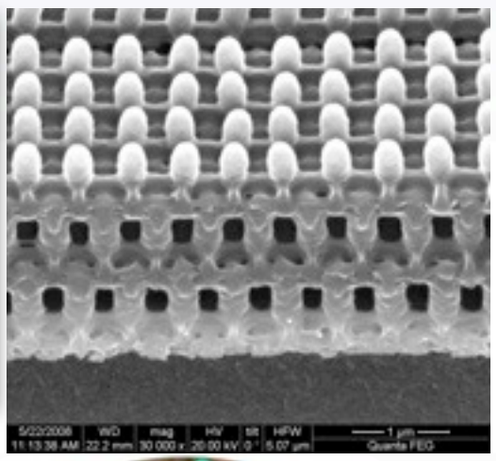
Clean room invented at SNL in 1963

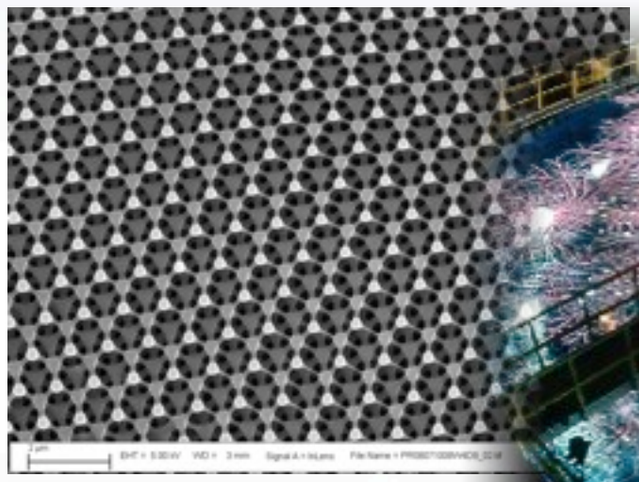
UGS

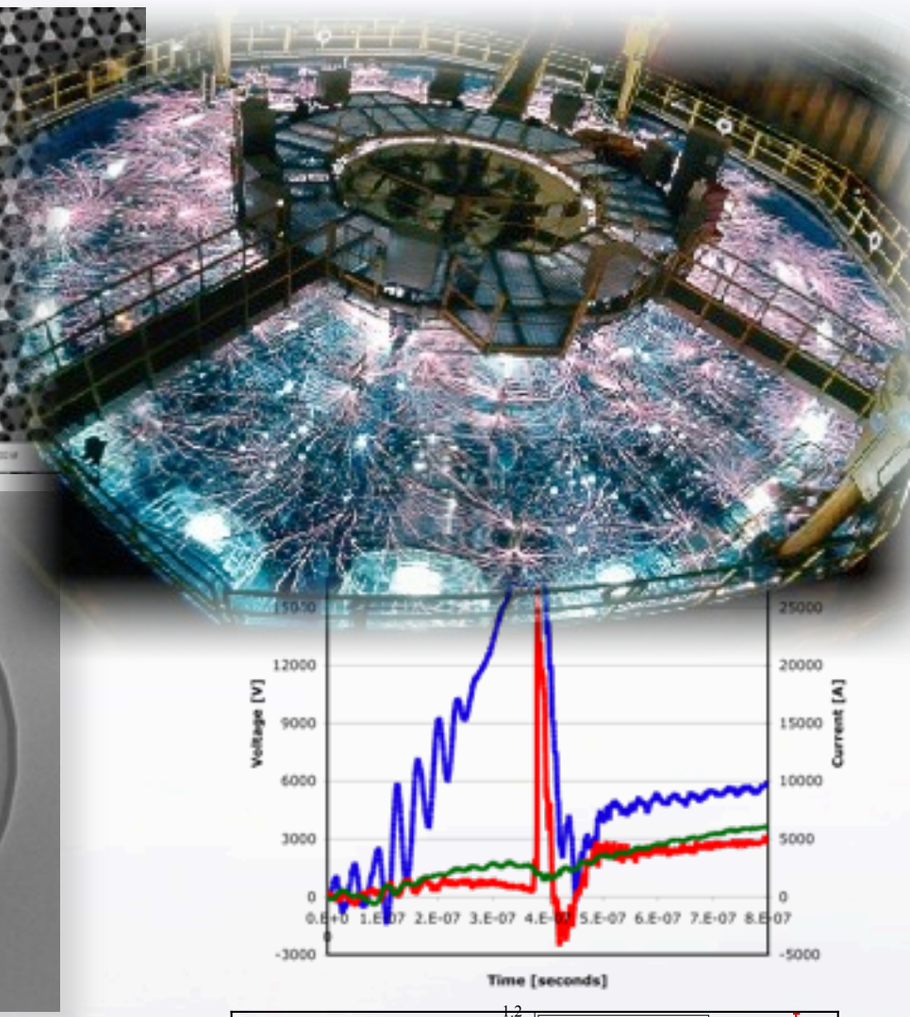
Z machine:
the world's most powerful X-ray source

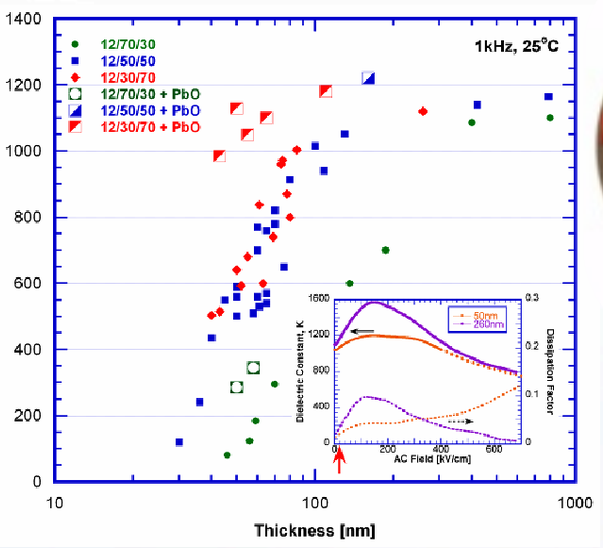
Project Sampler

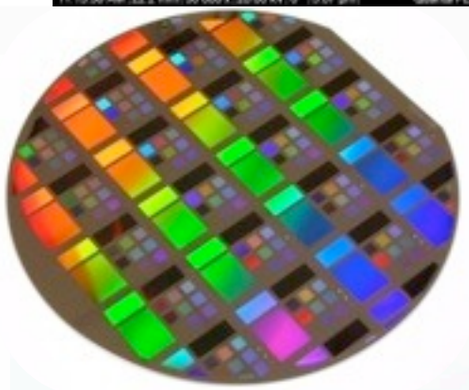


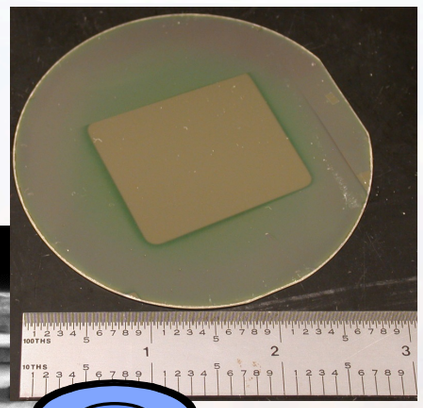


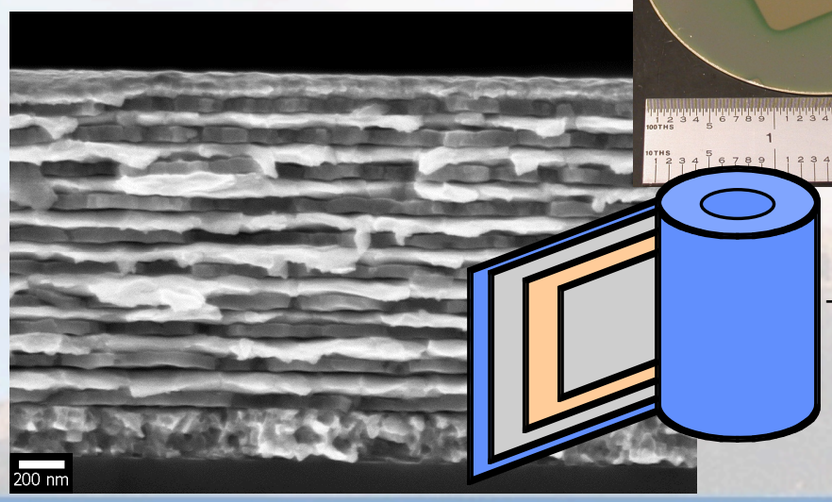


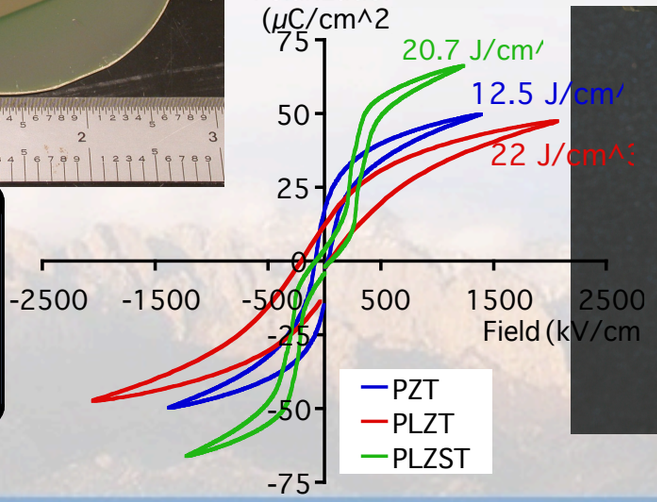


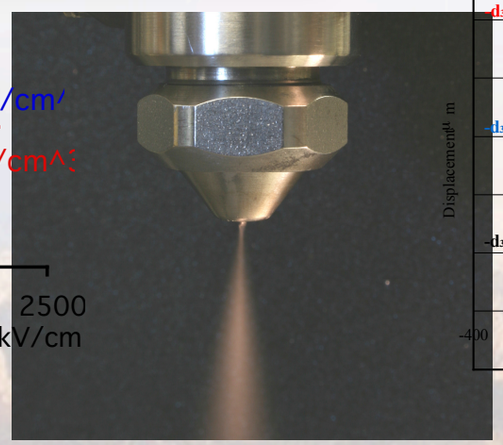


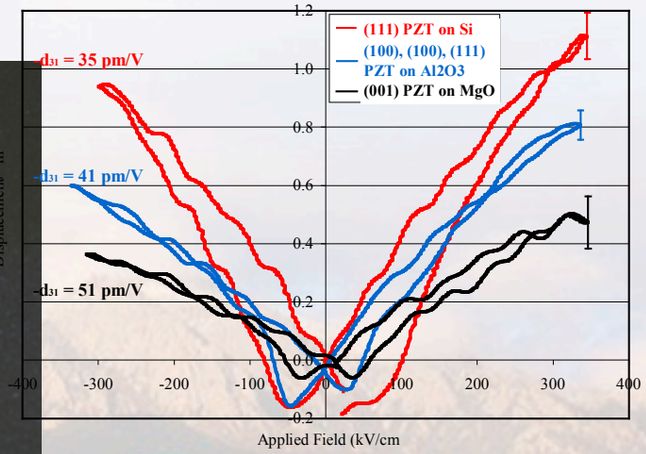












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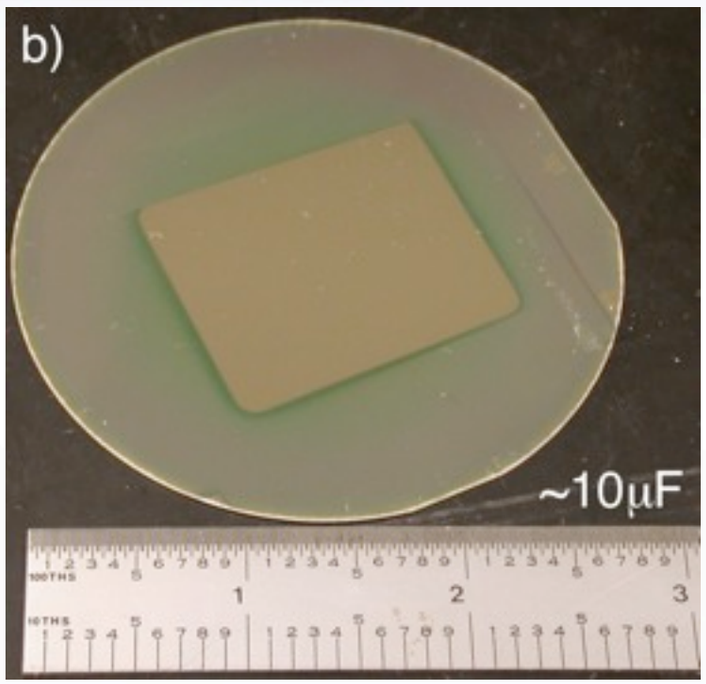
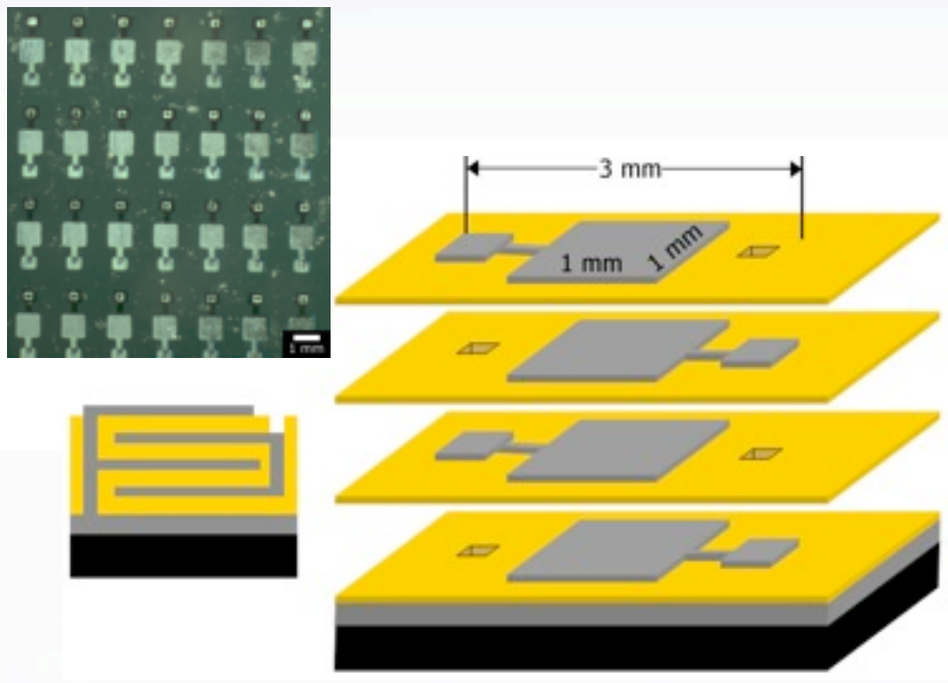
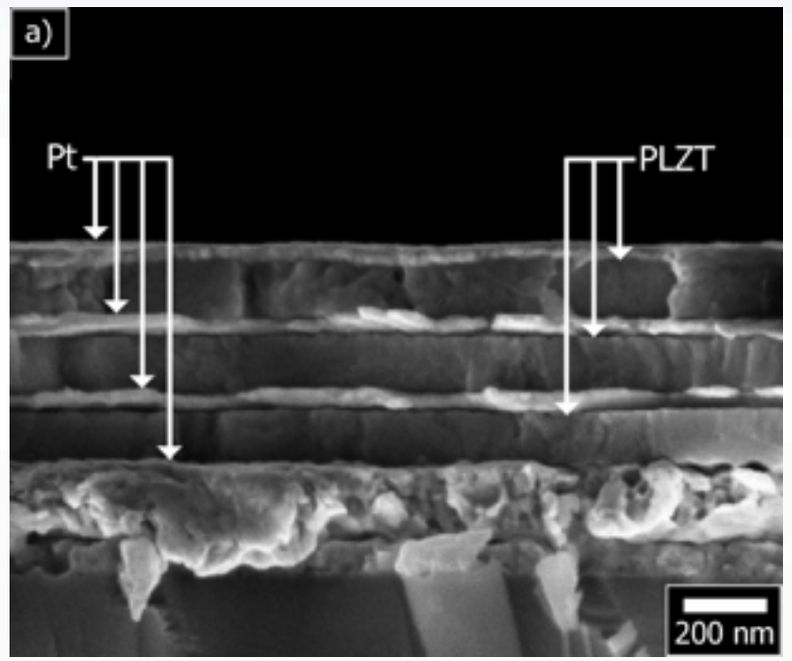
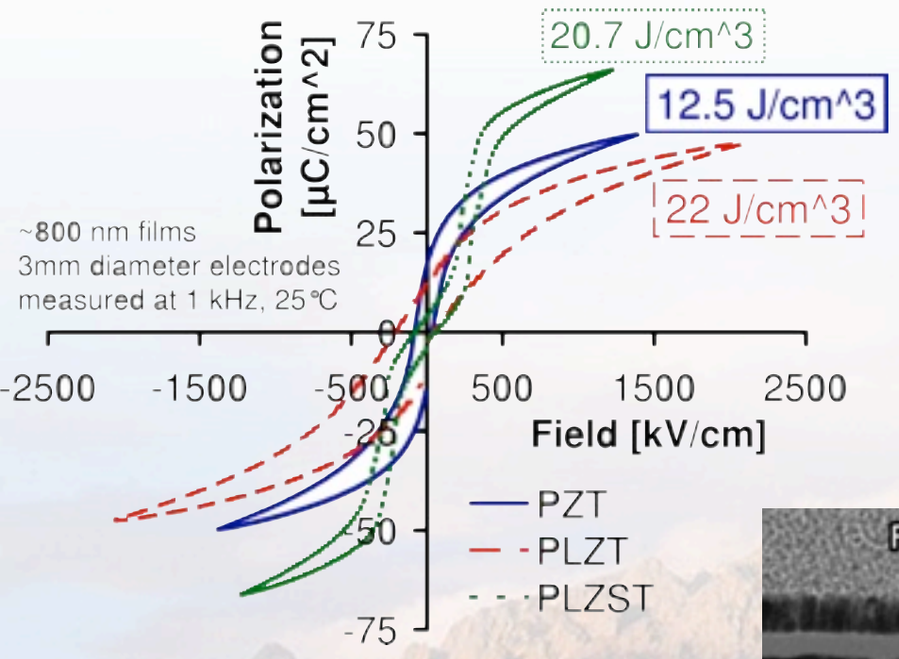
Functional Ferroelectric Thin Films





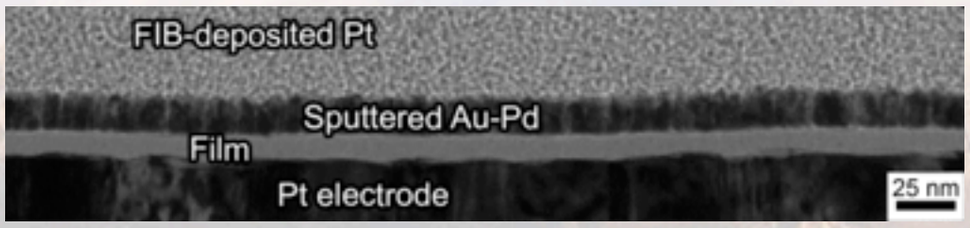


3 layers, ~120nm

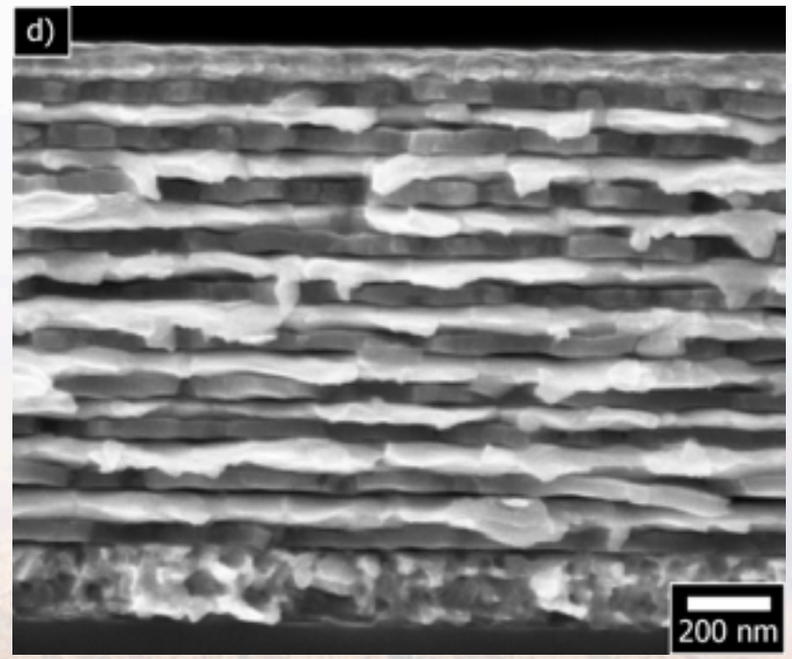


Brennecka, et al., **J. Mater. Res.** (2008), **J. Am. Ceram. Soc.** (2008, 2010)

Ultimate thickness is limited by wetting/islanding behavior during deposition and crystallization



Continuous single-phase films as thin as 9nm



10 layers, ~50nm

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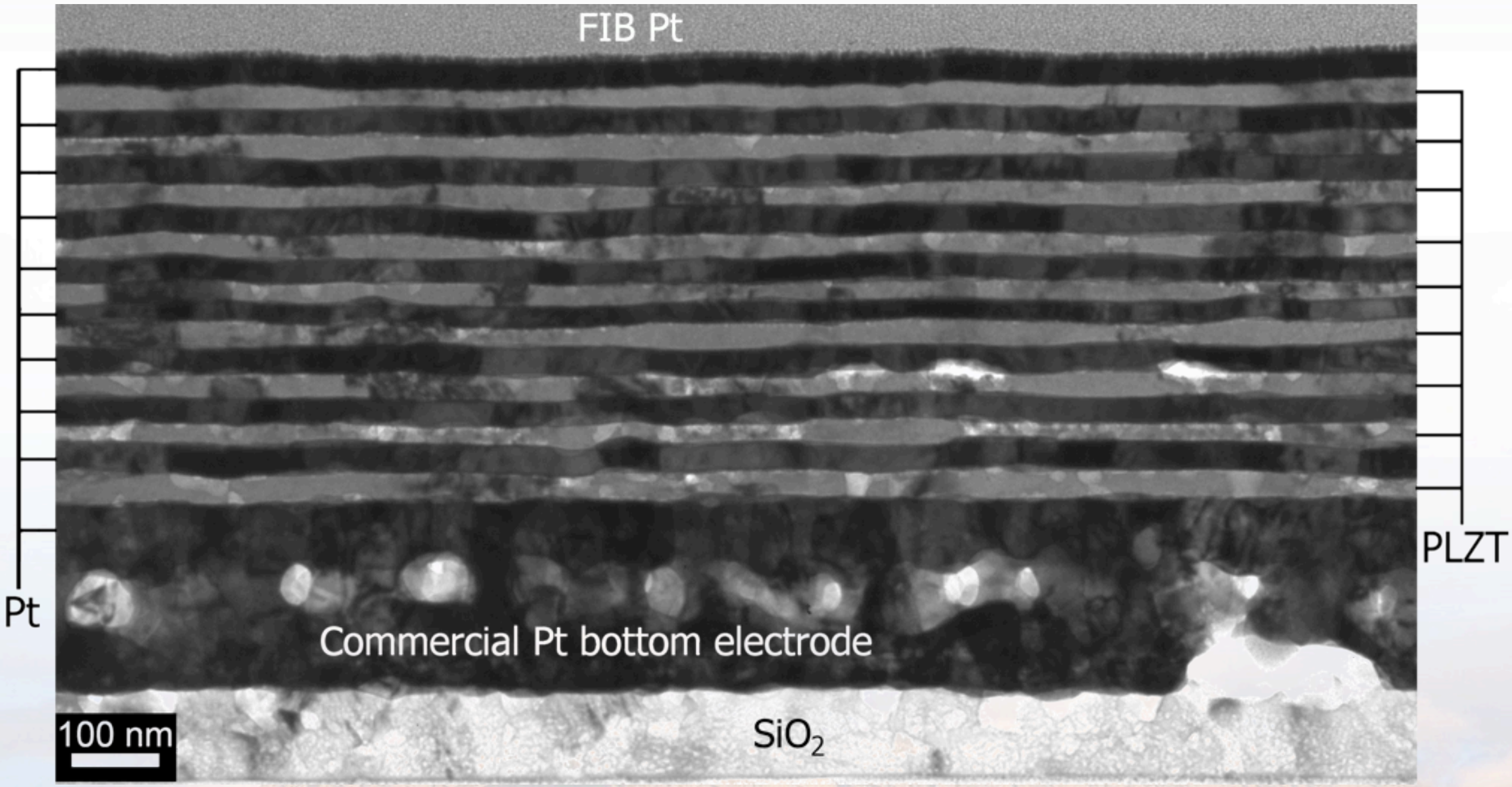
9 Dielectric Layers, ~20nm



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

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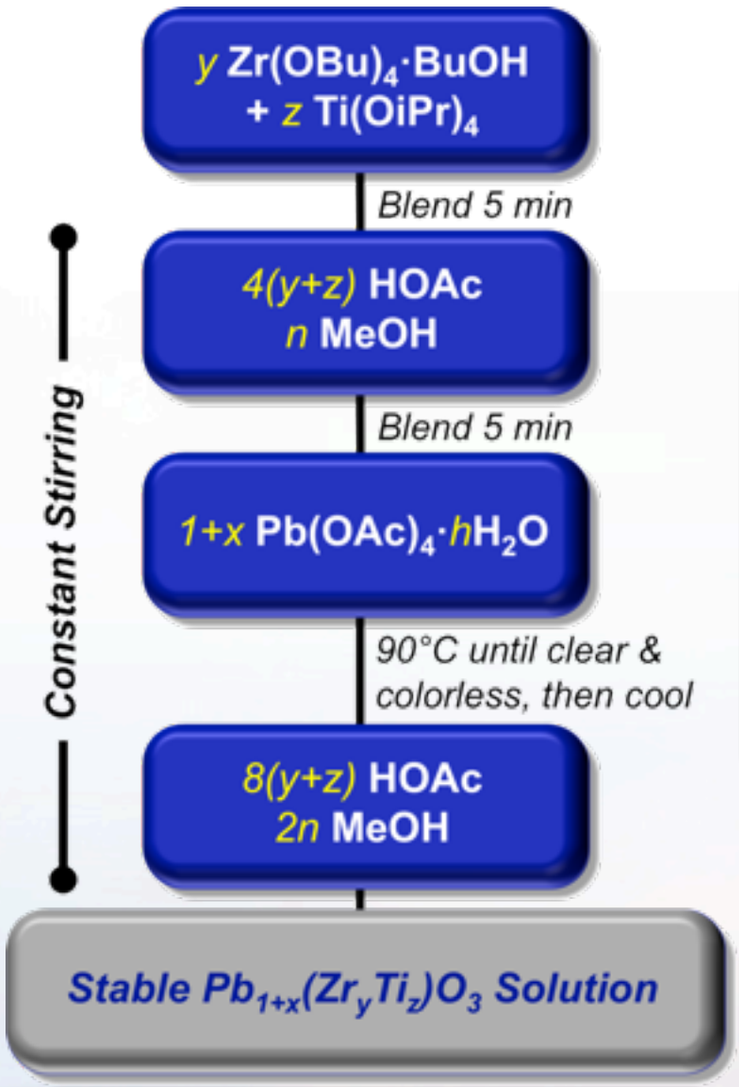
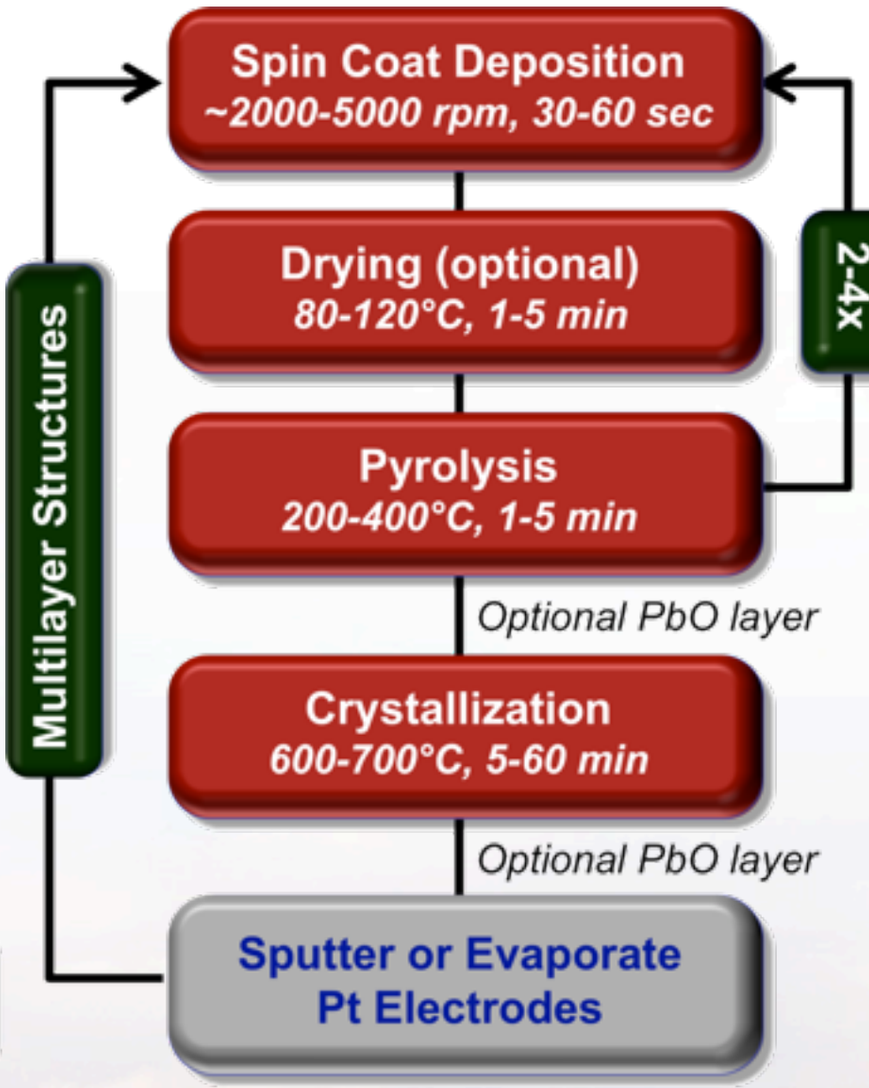
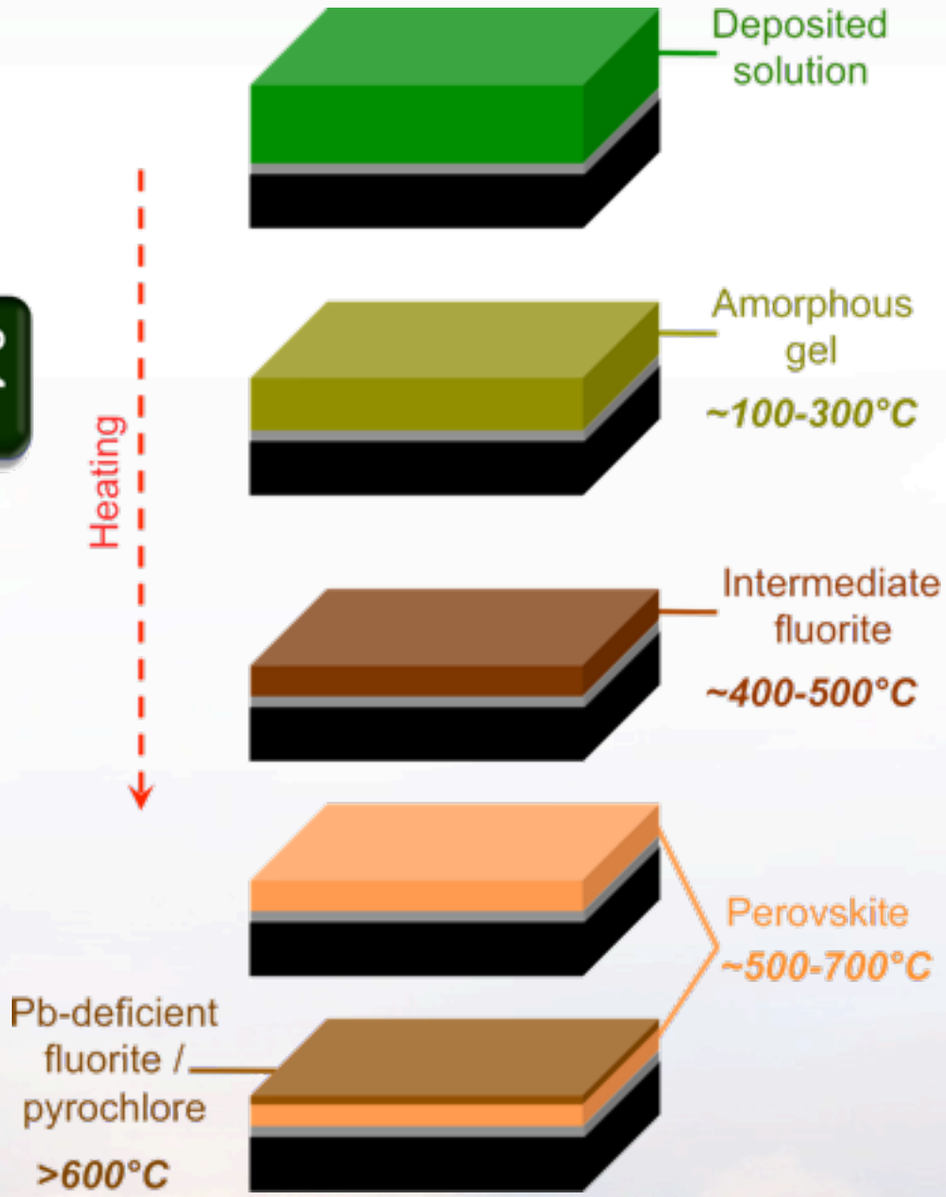
SNL IMO-based Solution Route







R.A. Assink and R.W. Schwartz; **Chem. Mater.** (1993)
G. Yi and M. Sayer; **J. Appl. Phys.** (1988)
Brennecka et al., **J. Am. Ceram. Soc**. *feature article* (2010)

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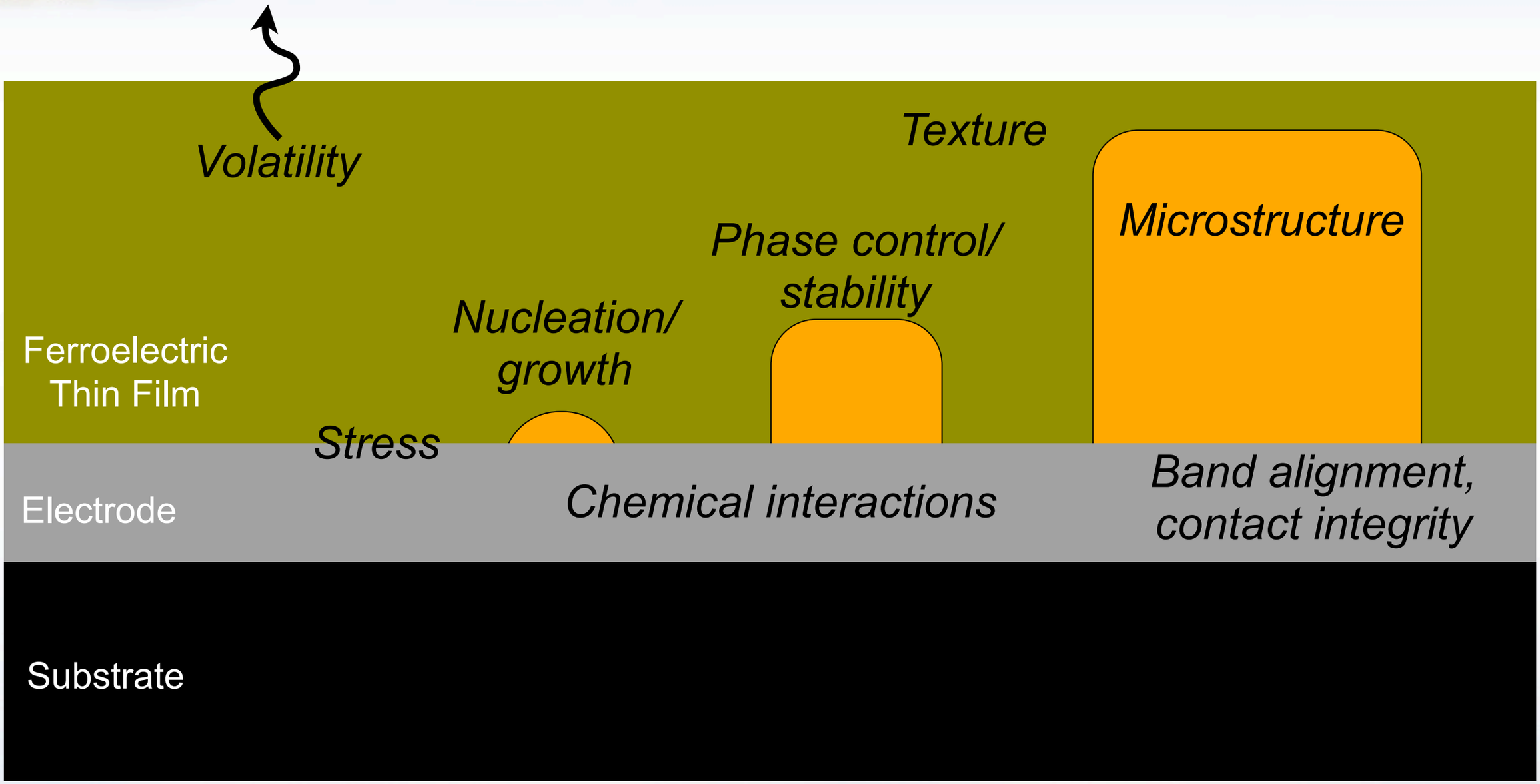
Understanding (and Control) of Processing/ Structure/Property Relationships



Temperature, Time

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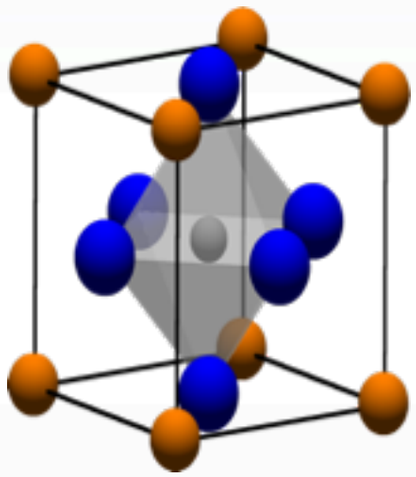
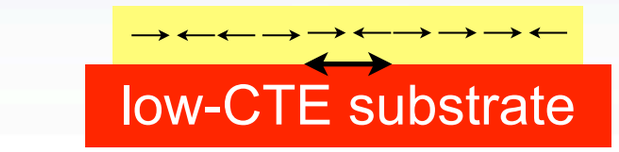
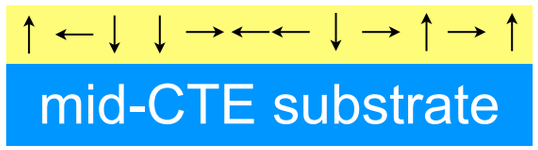
Film Texture for Tailored Properties

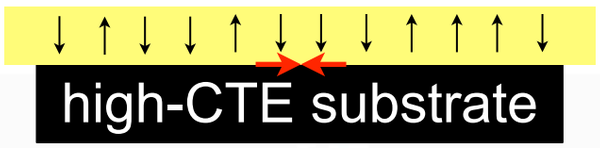
maximum polarization, minimum permittivity



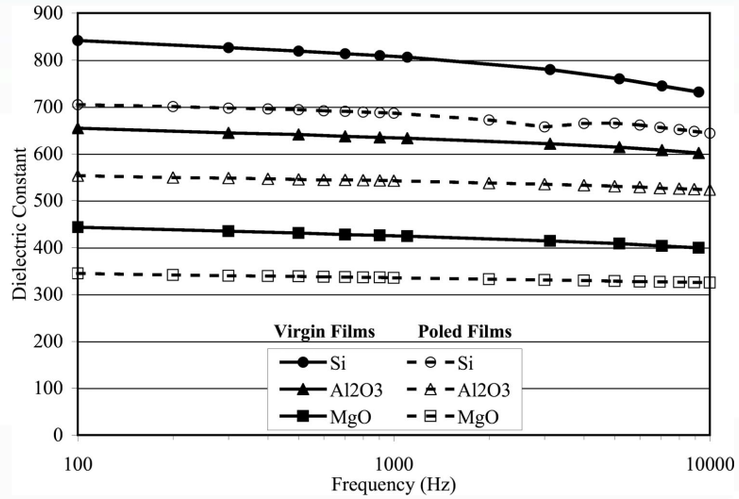
minimum polarization, maximum permittivity

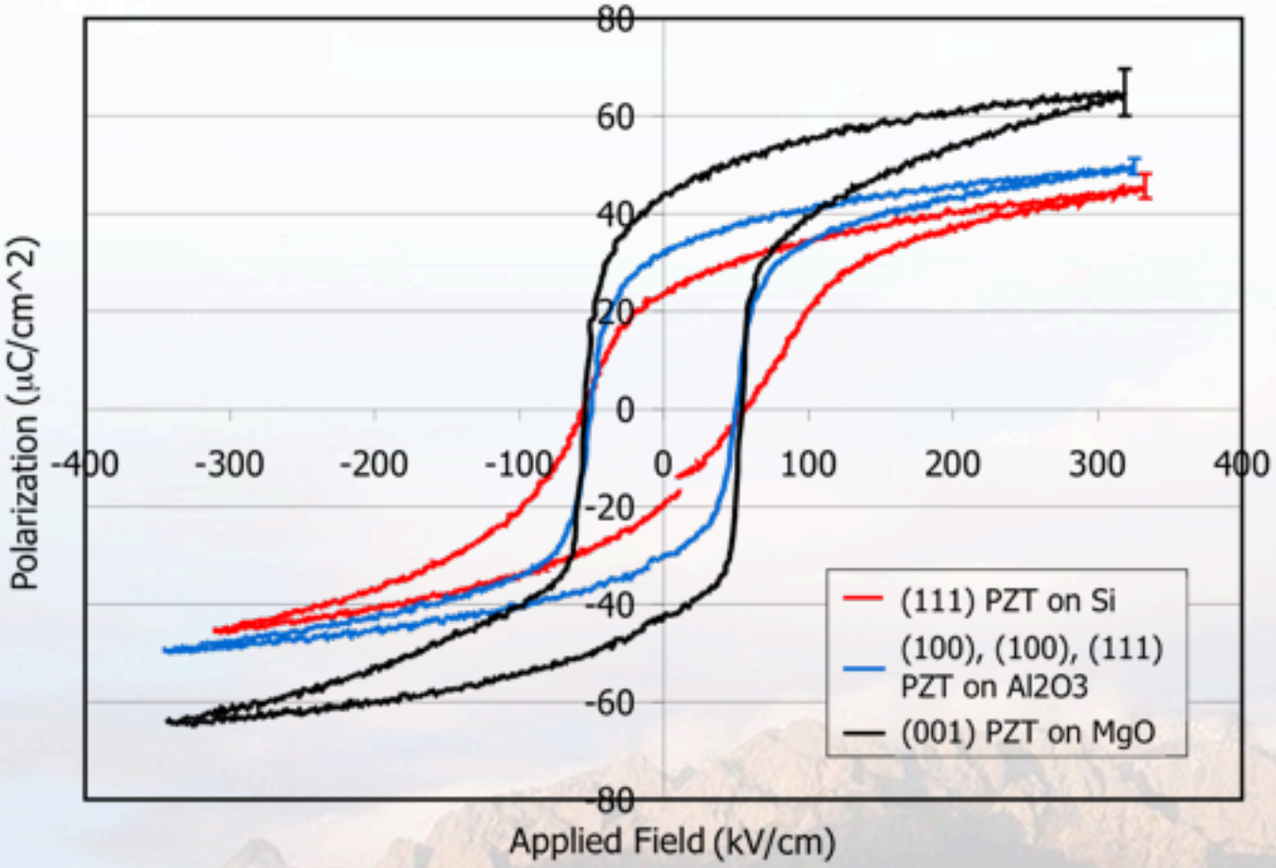


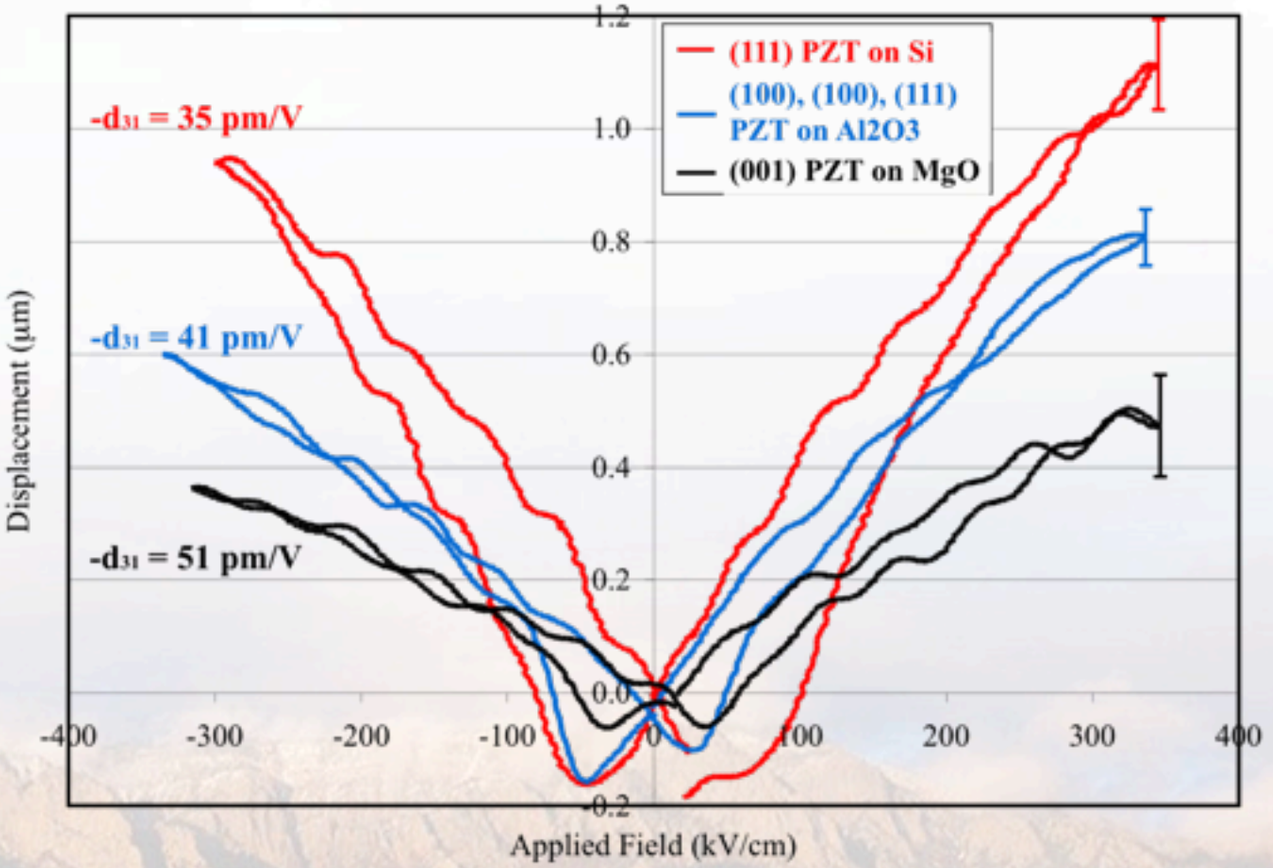




PZT 40/60 thin films







Brennecka, et al., **J. Am. Ceram. Soc.** (2002)

see also Funakubo et al.

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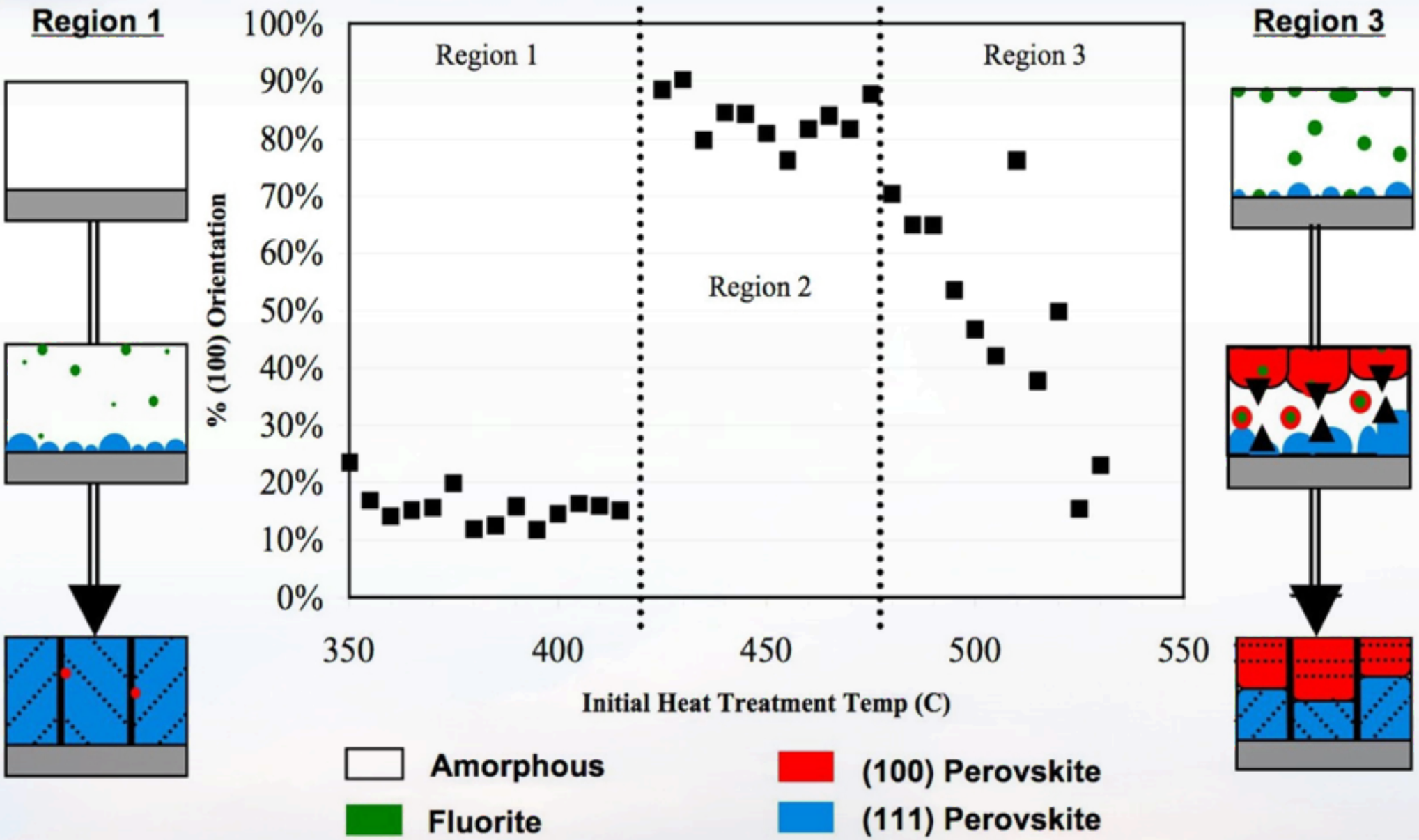
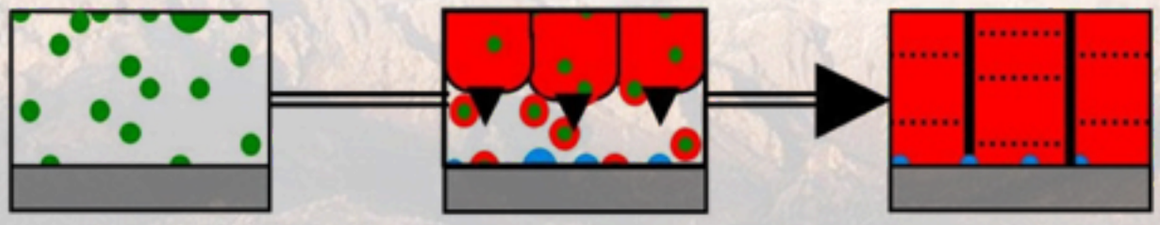
Control of Texture via Nucleation and Growth



PZT 40/60 thin films

Region 2



Brennecka et al., **J. Am. Ceram. Soc.** (2010)

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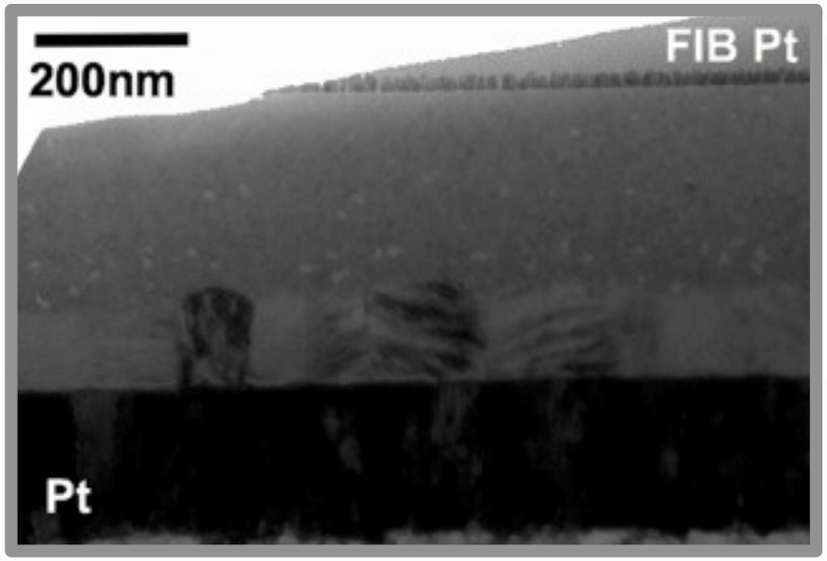
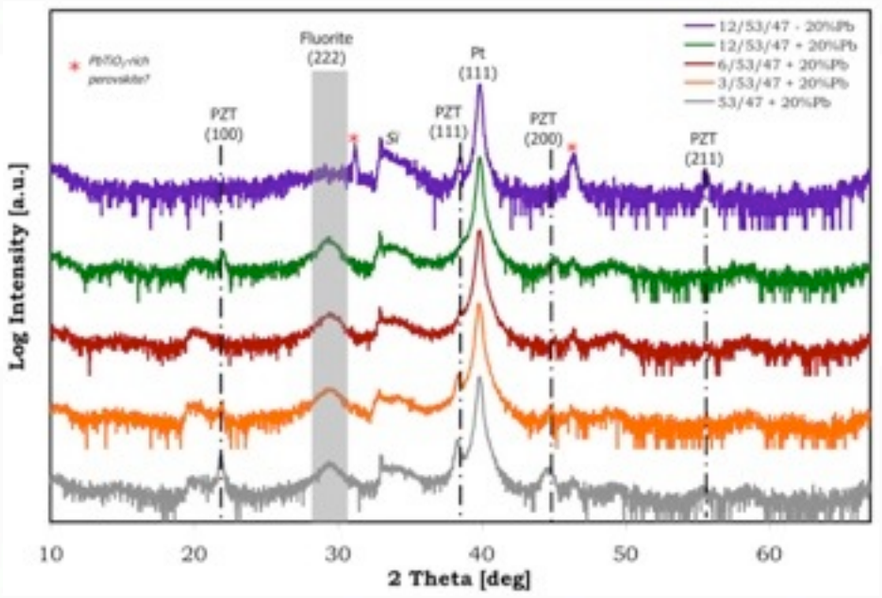
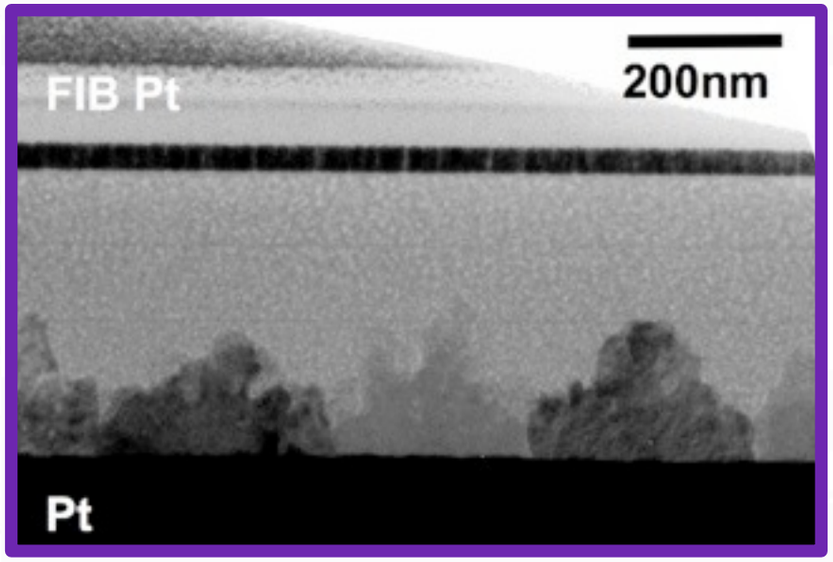
A-site cation effects on nucleation

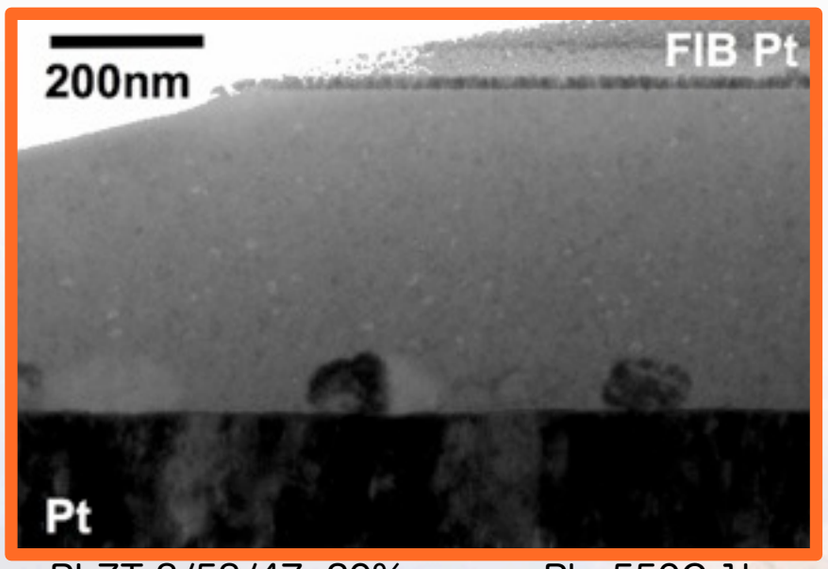


PZT 53/47, 20% excess Pb, 550C 1hr

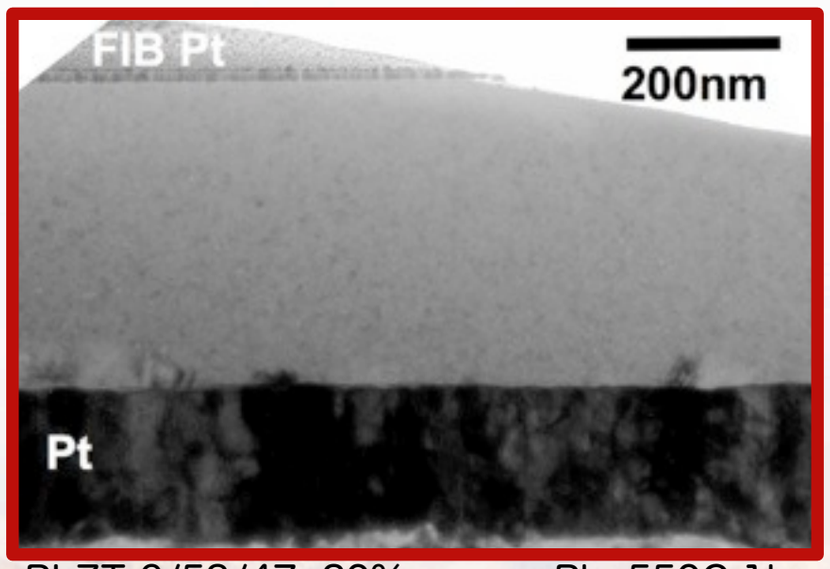




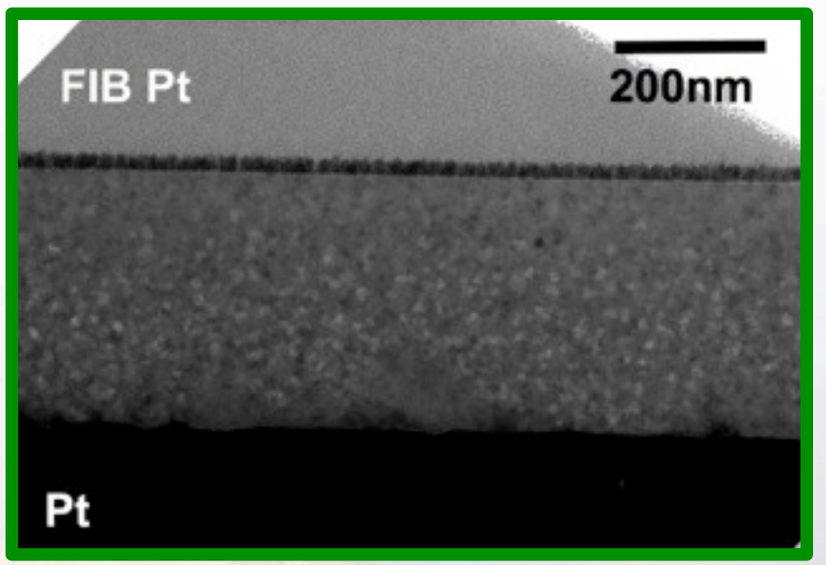
PLZT 12/53/47, 20% Pb deficient, 550C 1hr



PLZT 3/53/47, 20% excess Pb, 550C 1hr



PLZT 6/53/47, 20% excess Pb, 550C 1hr



PLZT 12/53/47, 20% excess Pb, 550C 1hr

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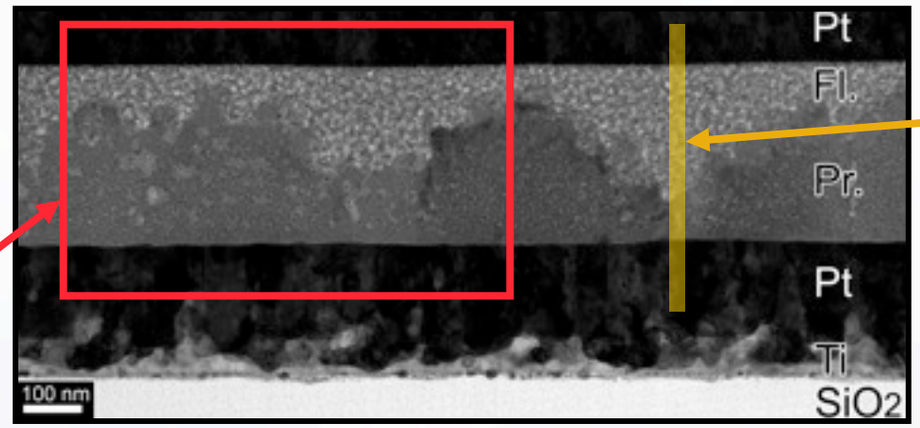
Quantitative Cation Mapping in PLZT Films

SIMS, XPS, AES depth profiling
~several 10s of microns
≠ feature size

Feature size
~hundreds of nms

Used STEM-EDS SIs to sample this scale



EDS linescan sampling
~several nanometers
≠ feature size

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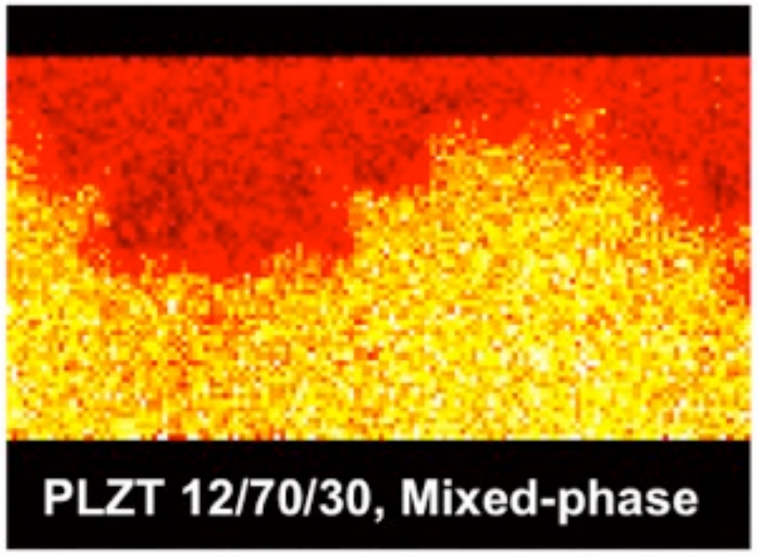
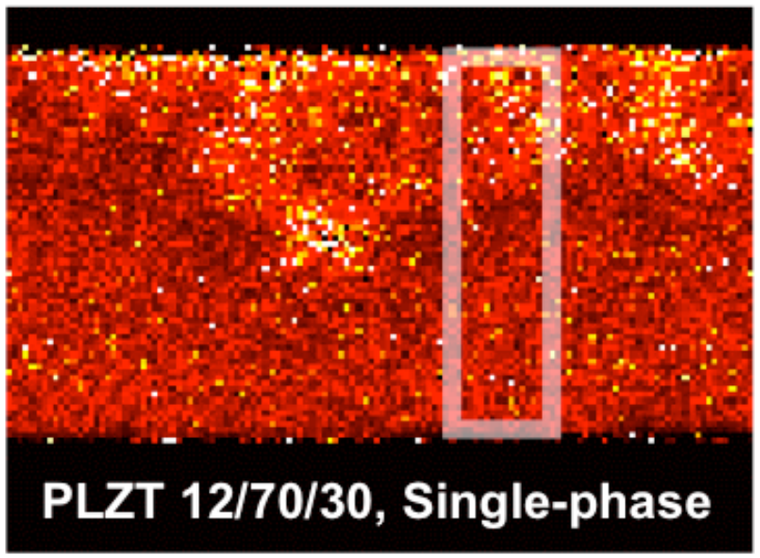
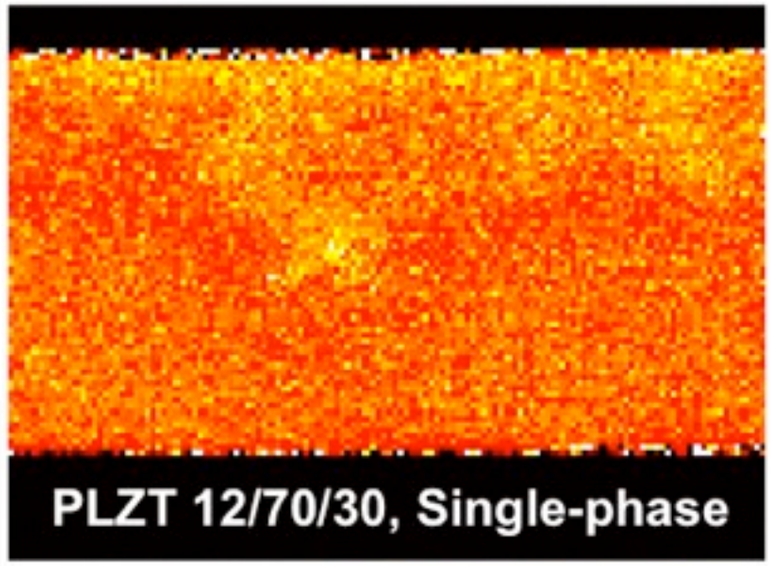
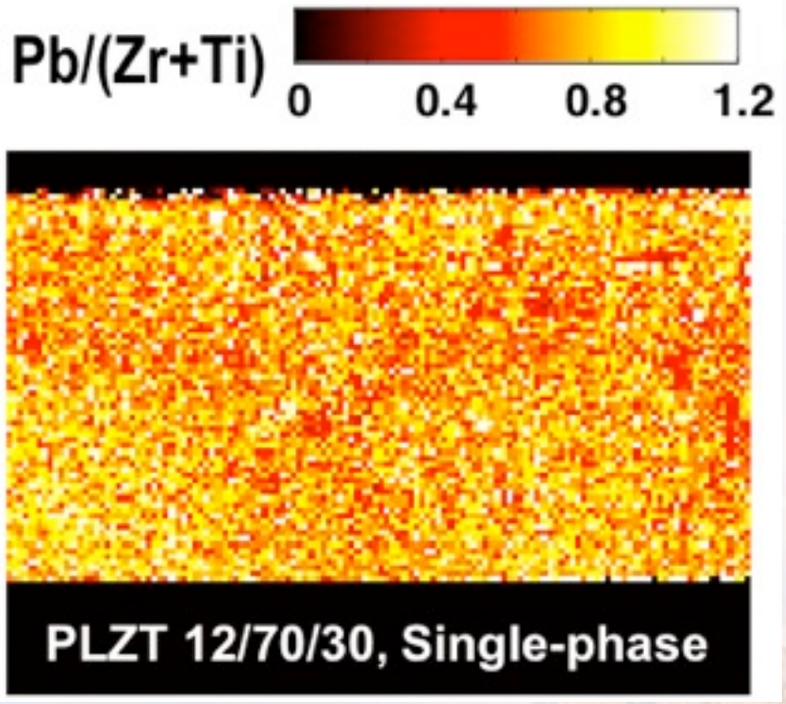
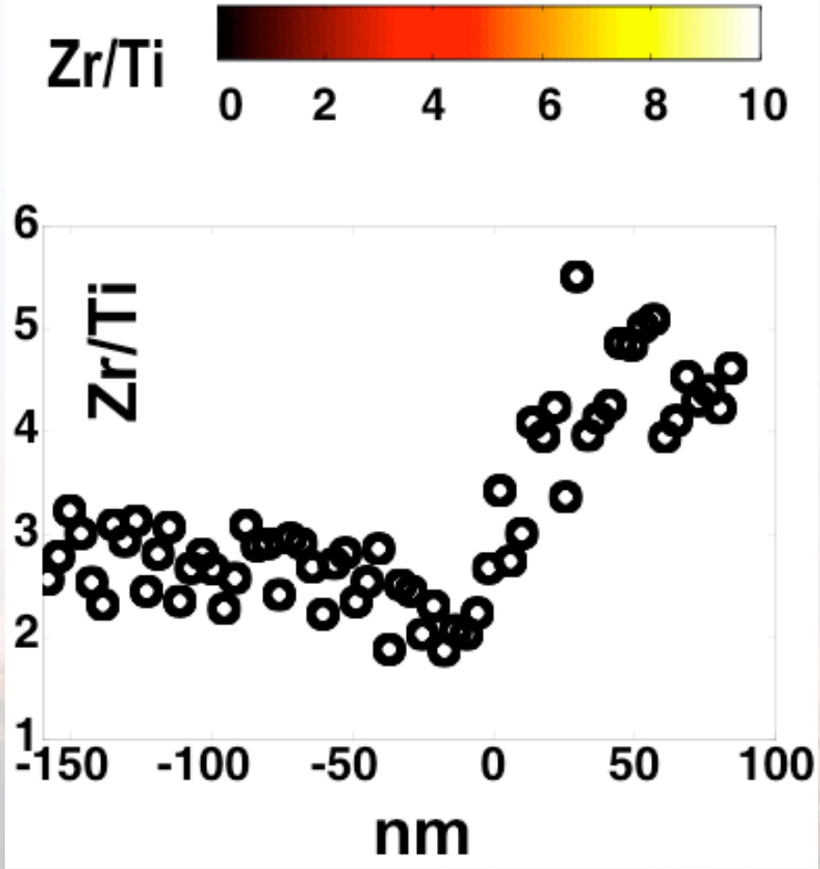
Quantitative Cation Mapping in PLZT Films











- Pb stoichiometry and homogeneity can be restored through Pb-rich annealing step
- B-site heterogeneities remain
- Evidence for co-segregation of La and Zr
- No Zr/Ti segregation observed for rapidly-crystallized PZT

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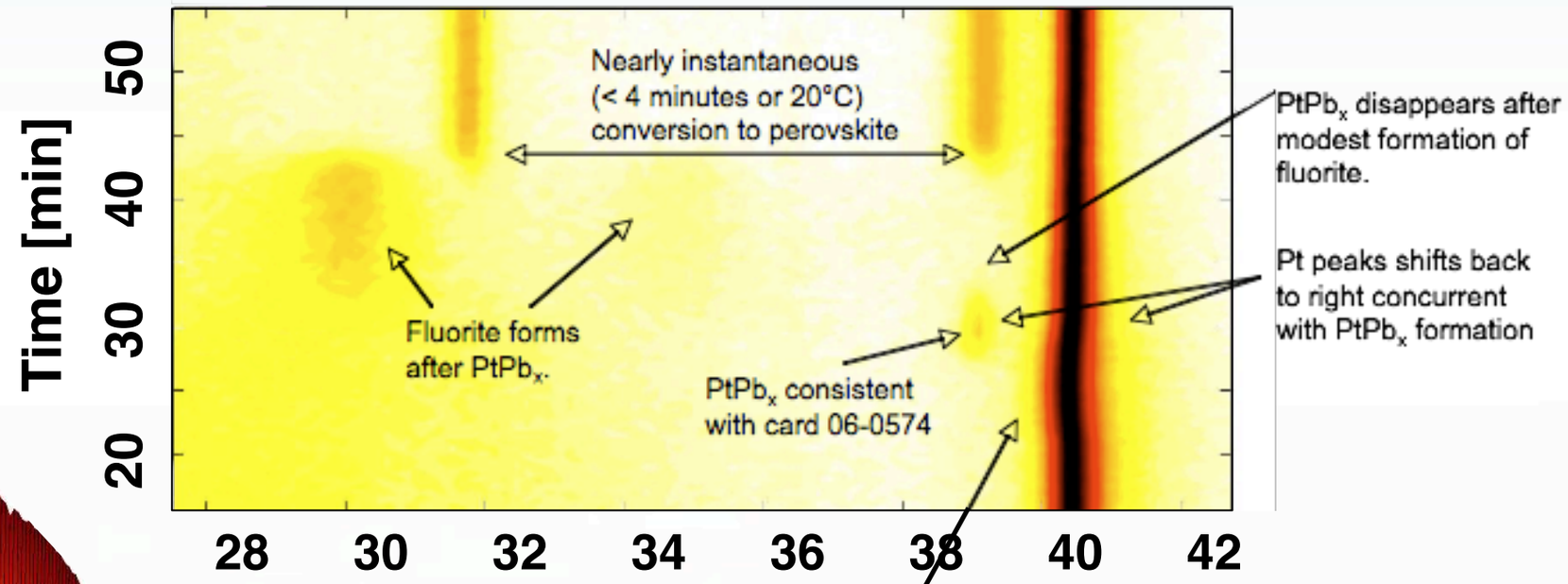
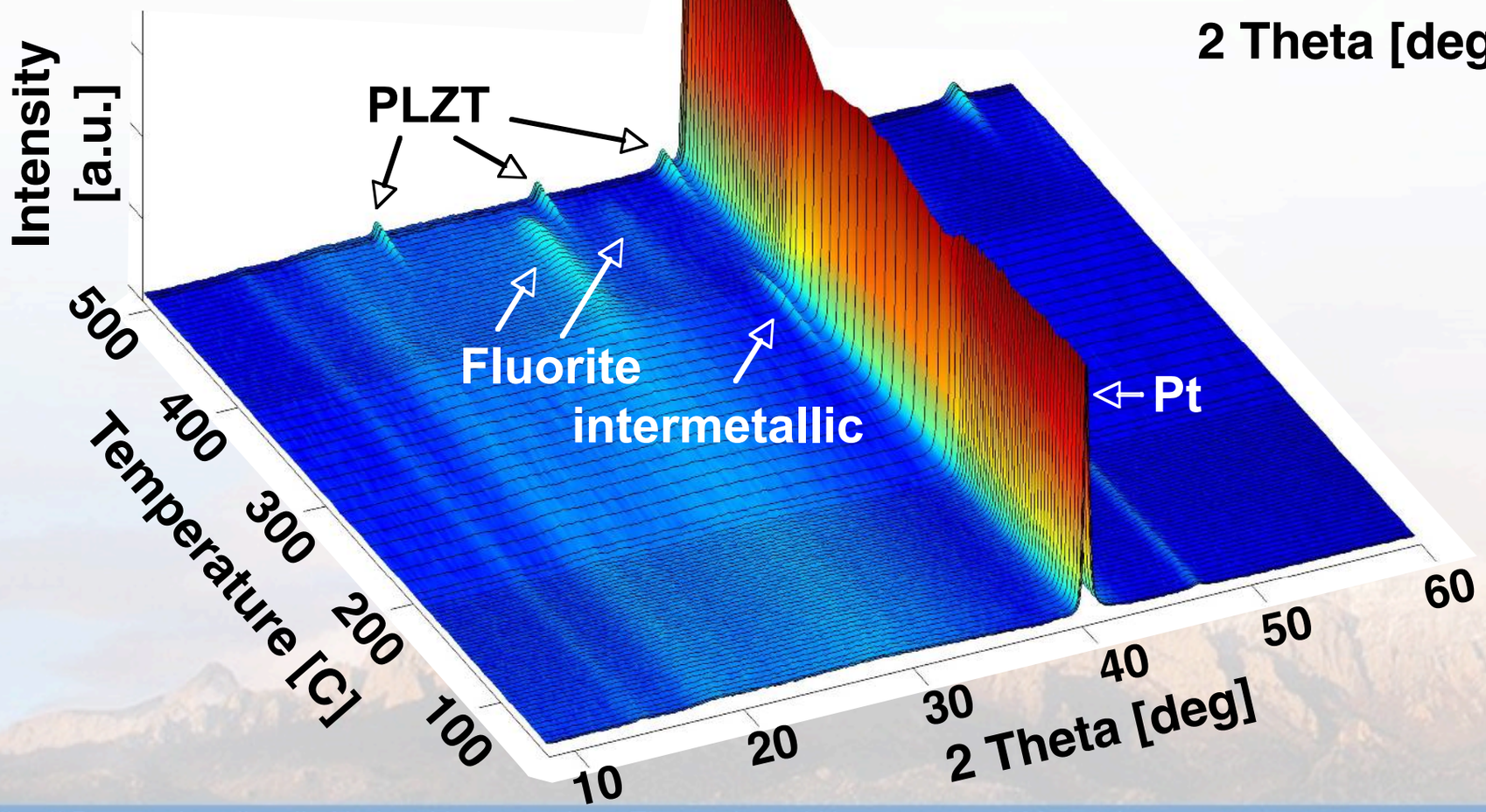
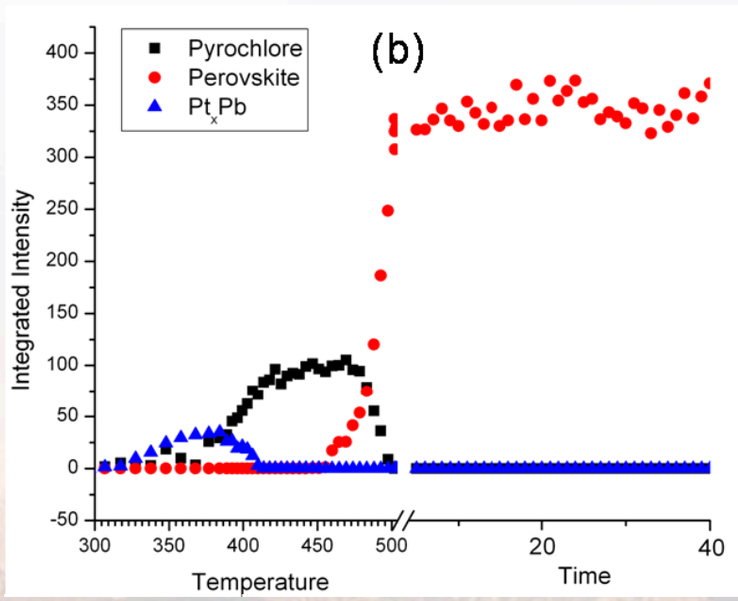
in-situ X-Ray Diffraction

in collaboration with Jacob Jones and Krishna Nittala, University of Florida

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







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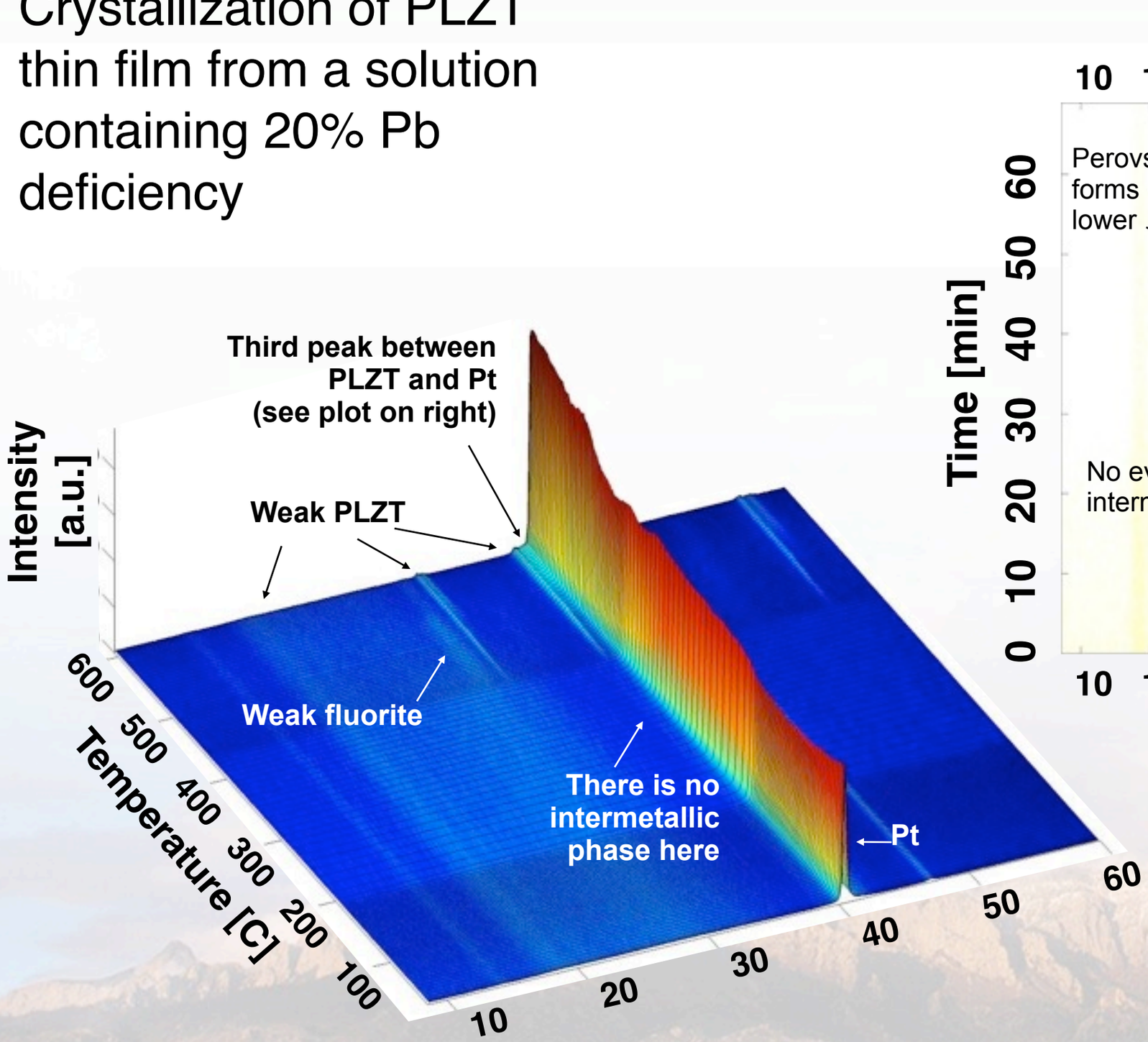
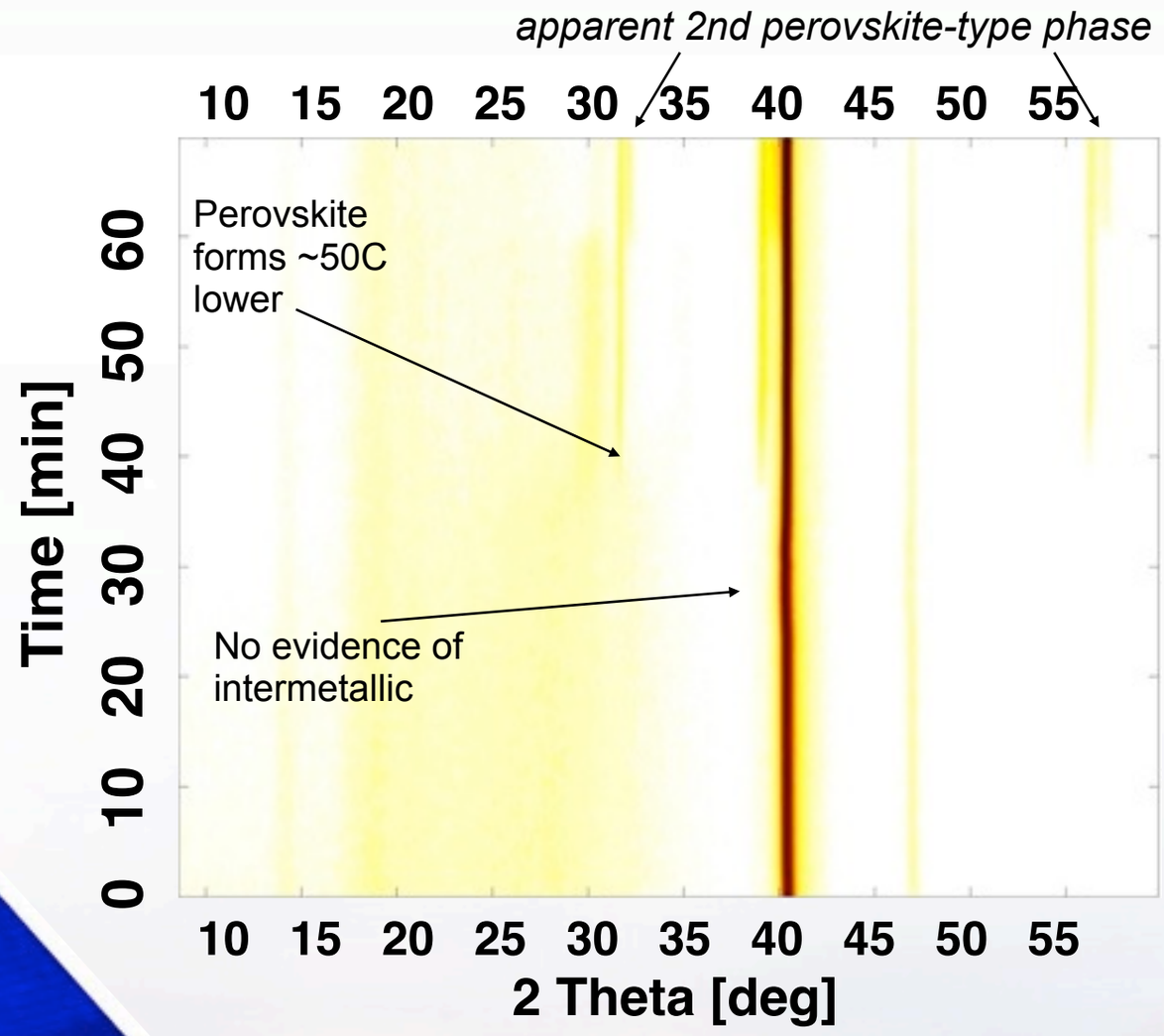
in-situ X-Ray Diffraction

in collaboration with Jacob Jones and Krishna Nittala, University of Florida

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





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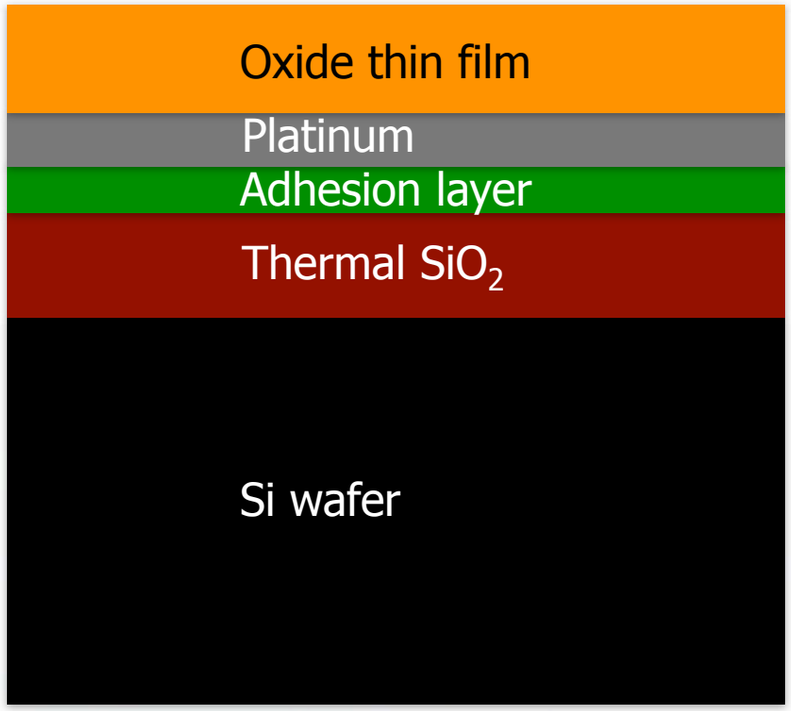
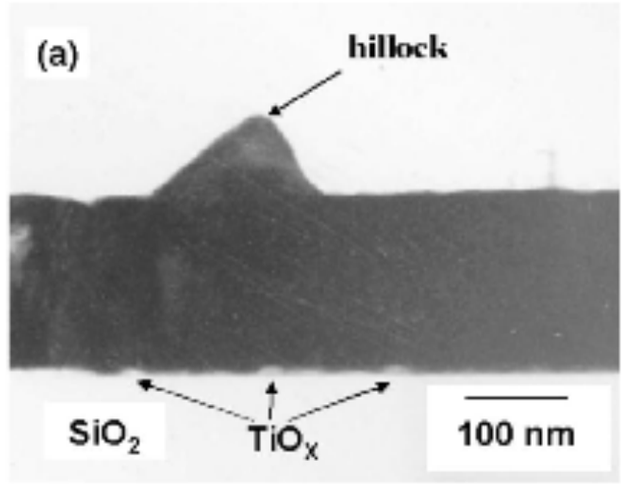
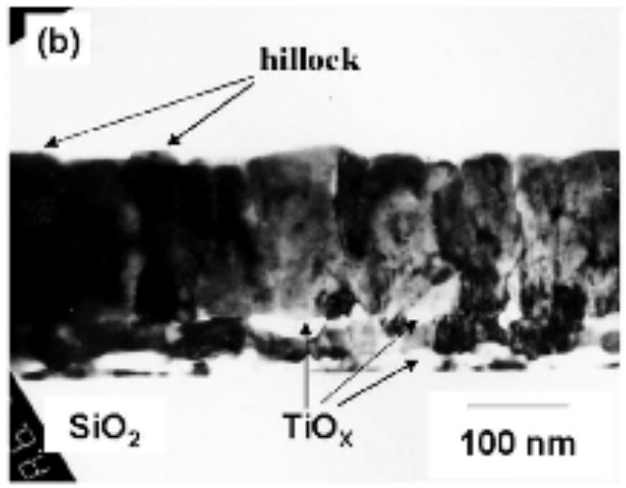
Electrode Adhesion Layer

- Platinized Si is common substrate
  - 400 – 500 nm thermal SiO_2
  - 20 – 40 nm adhesion layer: typically Ti or TiO_2
  - 100 – 200 nm Pt

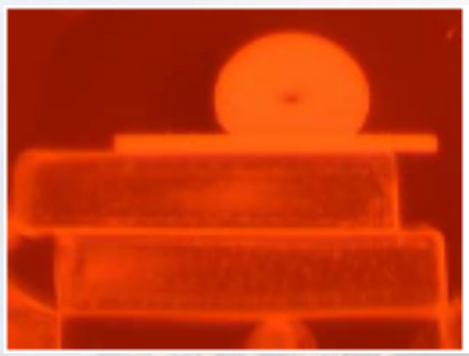
- Other adhesion layers:
  - Zr, ZrO_2 (Al Shareef et al., 1997, Zohni et al., 2008)
  - Ta (Kissurska et al., 1995)
  - Al_2O_3 (Halder et al., 2007)



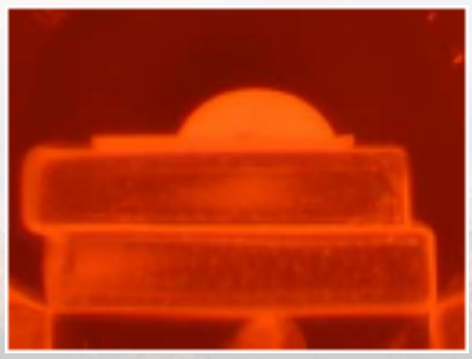




- Previous work has shown Cu wets ZnO very well:



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

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

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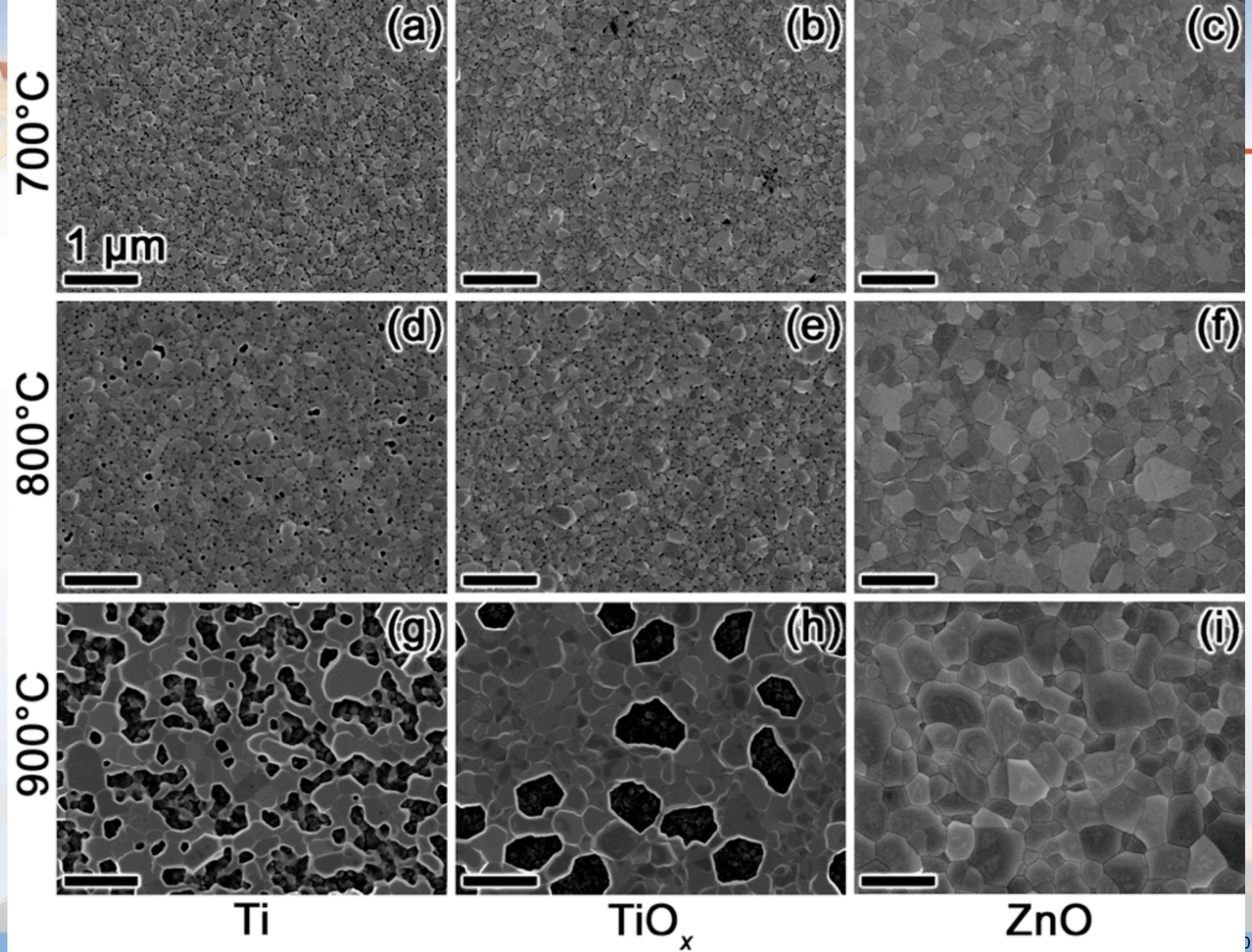
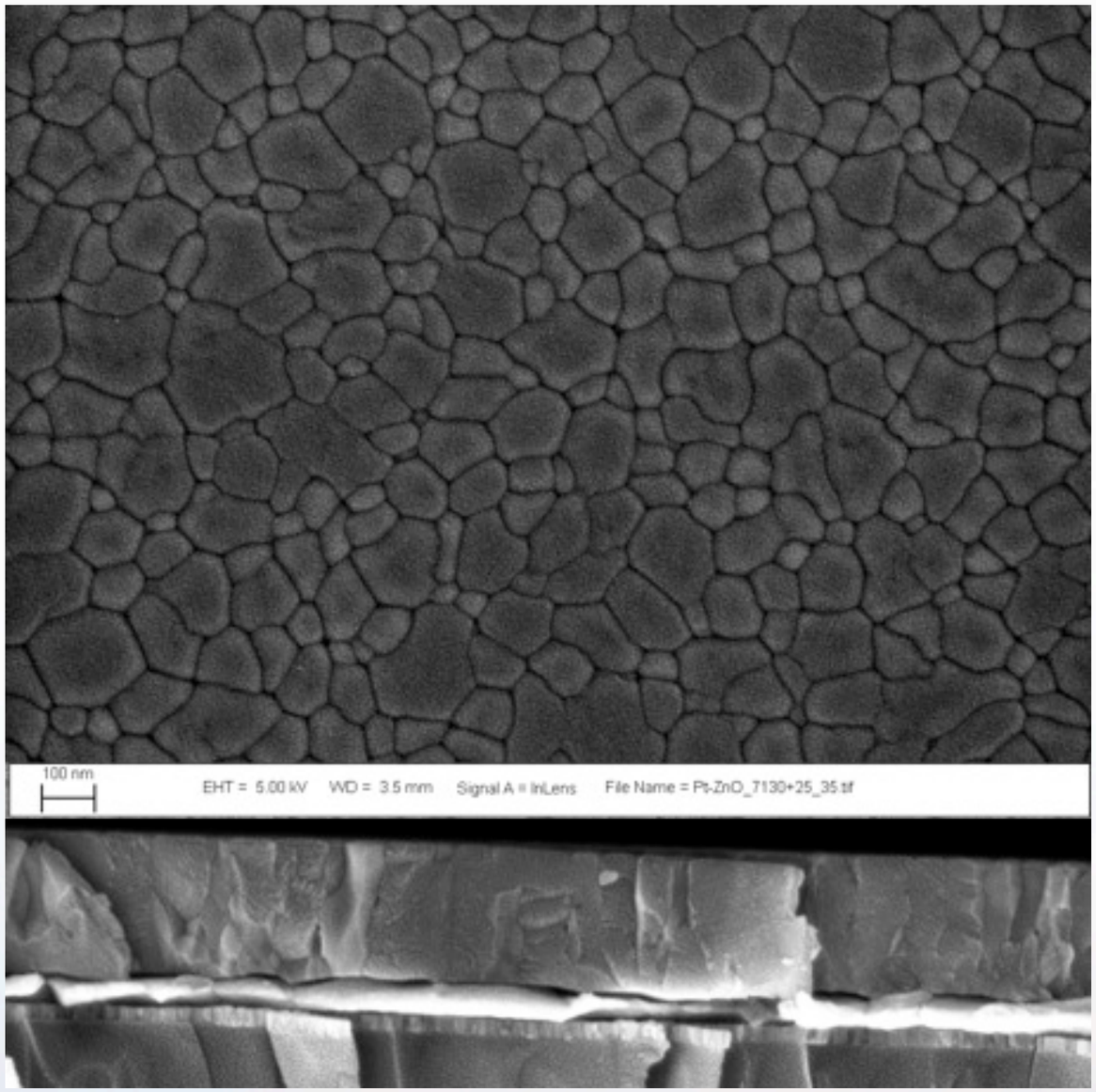
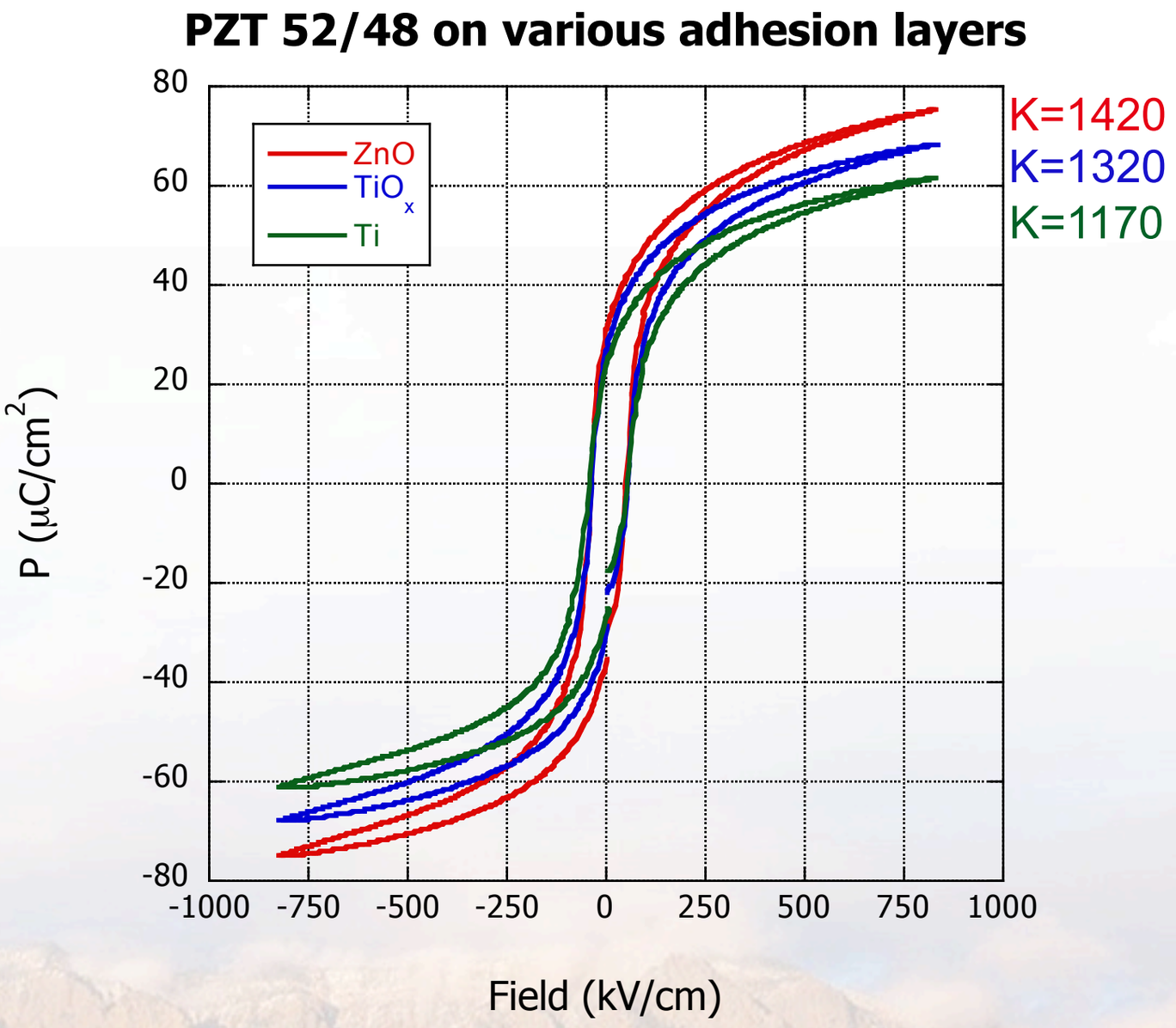

700°C
800°C
900°C
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
1 μm
Ti
TiO x
ZnO

Resulting Ferroelectric Films



PZT on Pt//ZnO//SiO_2//Si



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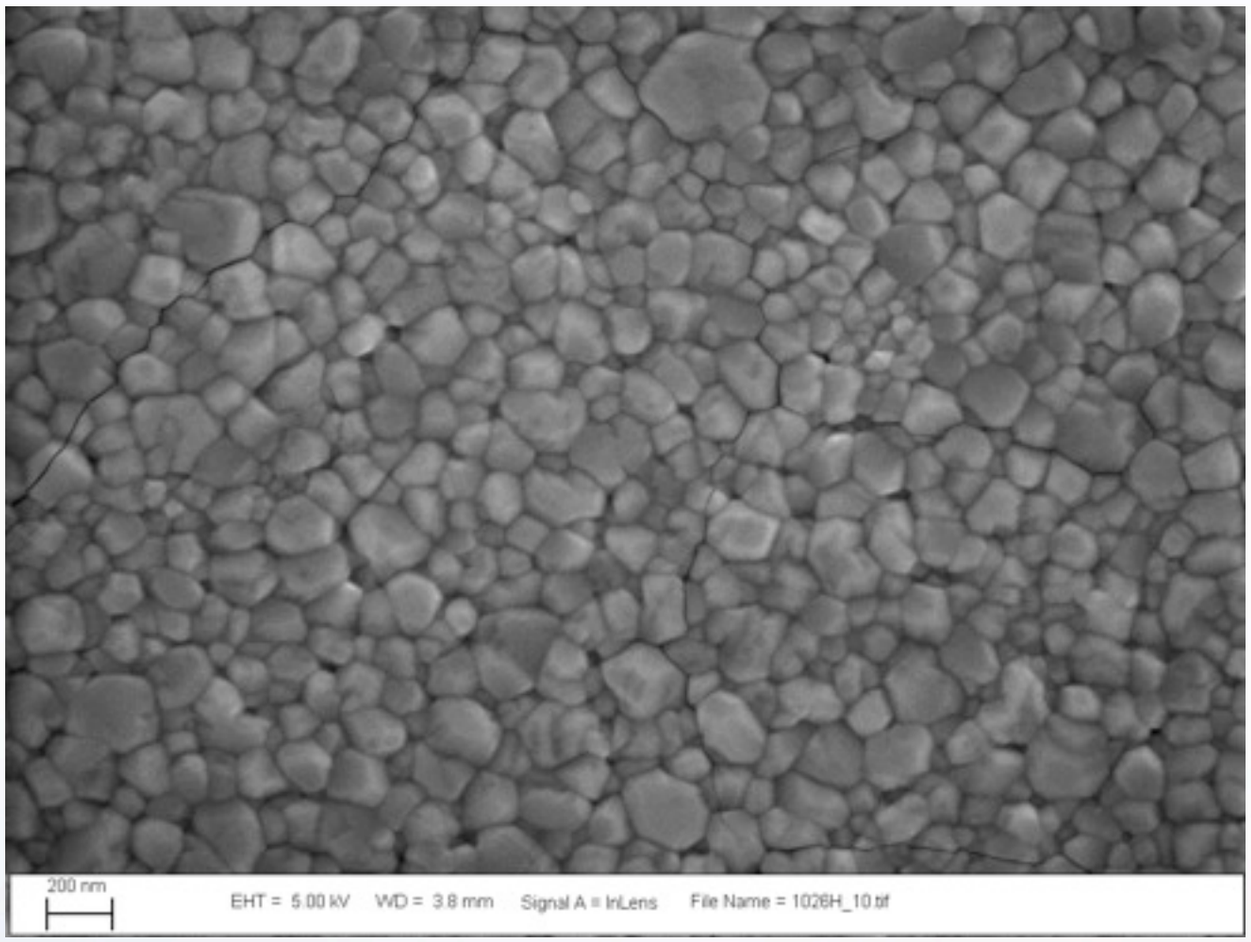
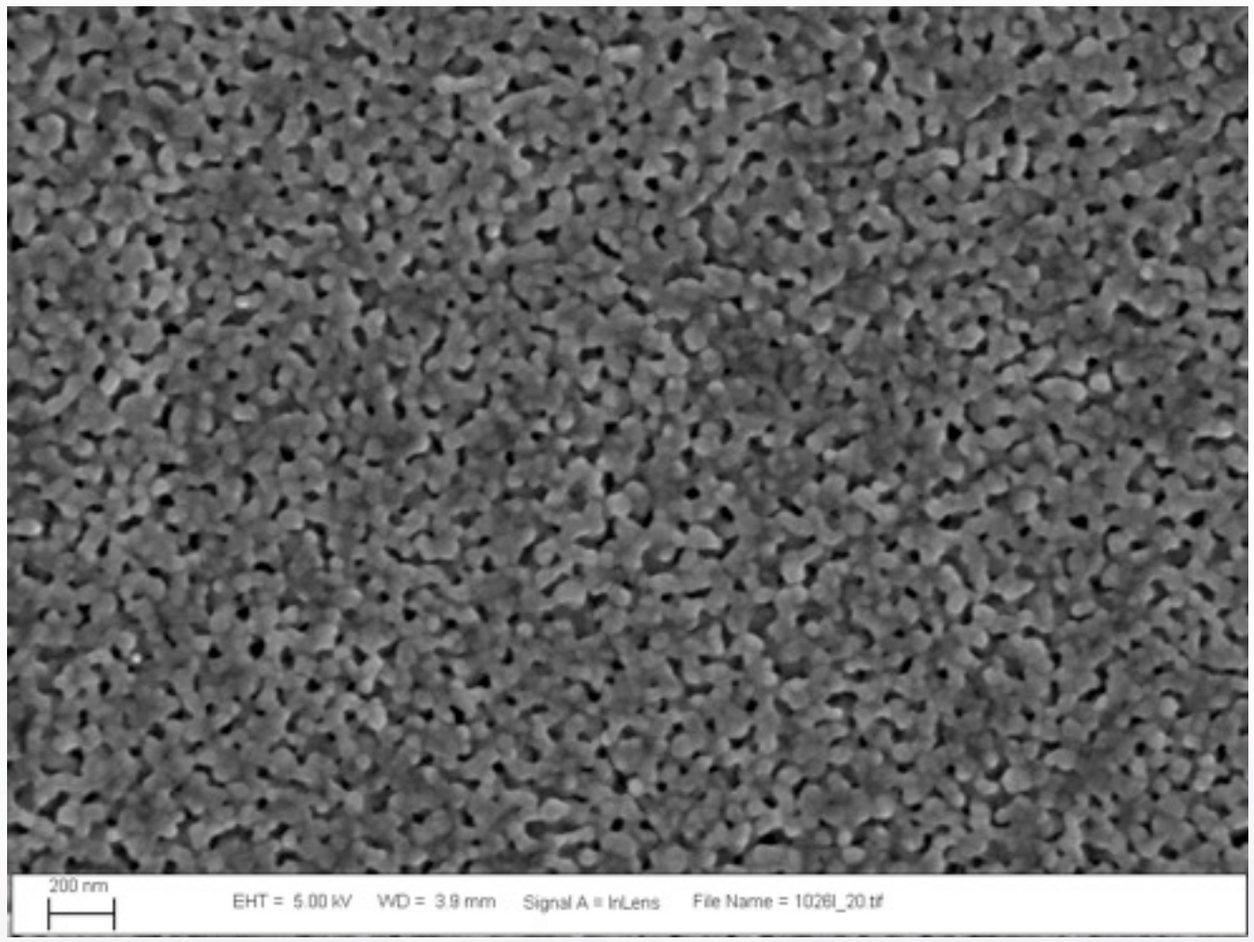
$BaTiO_3$ on Platinized Silicon



$BaTiO_3$ on $Pt//ZnO//SiO_2//Si$

K = 1800



$BaTiO_3$ on $Pt//TiO_x//SiO_2//Si$

K = 400

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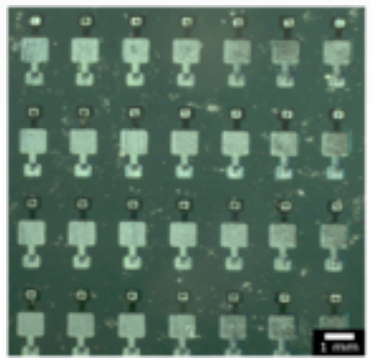
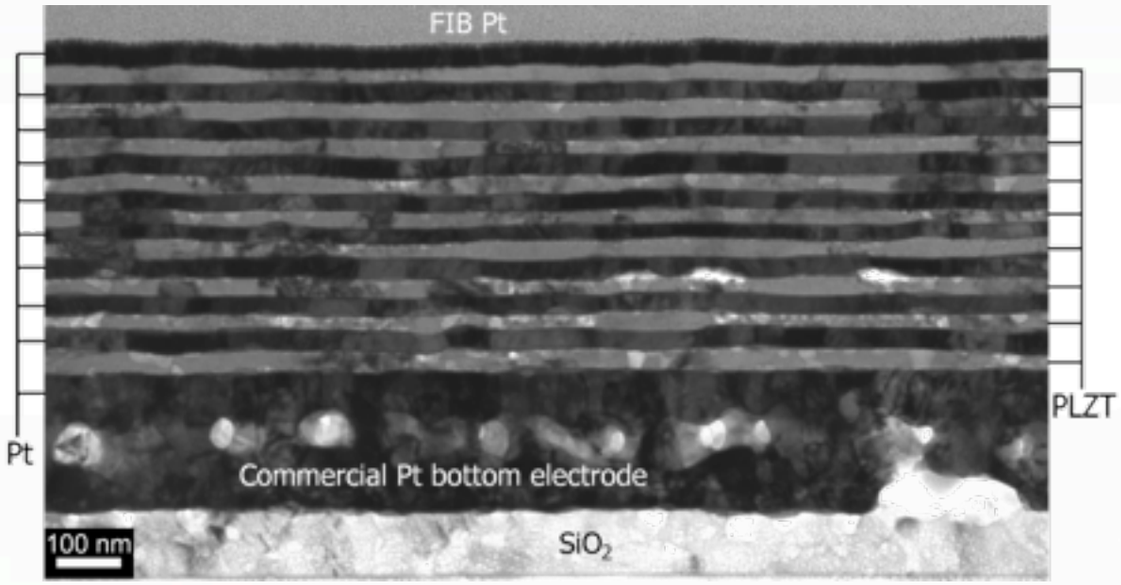
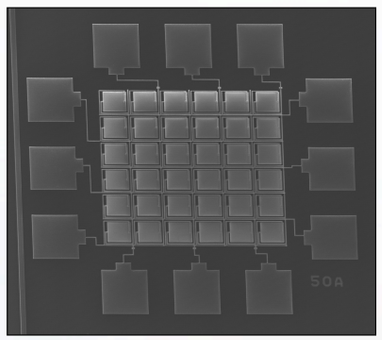
From Blanket Film to Functional Structure

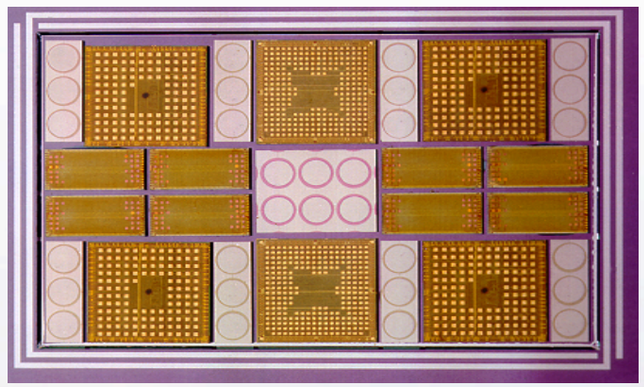


Functional PZT-based multilayer capacitor structures





Pyroelectric pixels w/aerogel insulation



Multichip module with PZT thin-film capacitor arrays

PZT-MEMs piezo cantilever beam for energy harvesting

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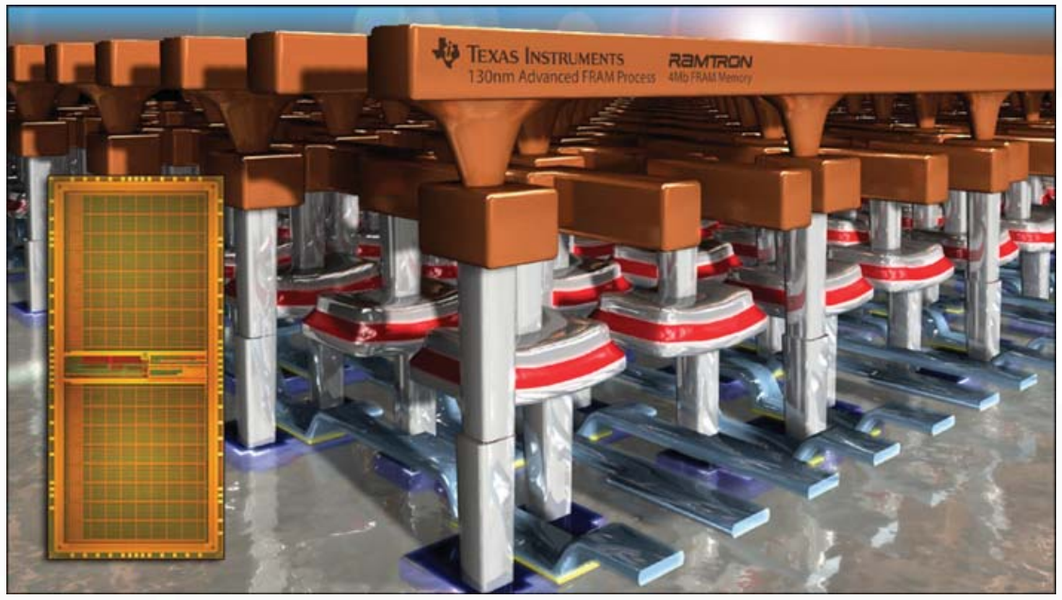
Doing More with the Same?

Integration of materials with new and/or increased functionality



From MRS Bulletin v33 (2008), originally from TI, Ramtron

General Fabrication Technique for Controlled Nanopatterning

- Any material, any substrate
- Arbitrary, addressable features/patterns
- Platform for size/interface effects studies, device development, etc.

Why Ferroelectrics?

- Demonstrate broad applicability
- Study fundamental lateral size and aspect ratio effects
- Ultrahigh density NVRAM

Target Demo Application

Information Storage (NVRAM)

- Reduce physical size
- Reduce power consumption
- Improve operation through interface control

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Doing Moore with the Same?

	First Year of IC Production	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
	DRAM ½ pitch (nm) (contacted)	52	45	40	36	32	28	25	23	20	18	16	14	13	11
	Flash ½ Pitch (nm) (un-contacted Poly)(f)	38	32	28	25	23	20	18	16	14	13	11	10	8.9	8.0
45	193 nm immersion with water														
32	193 nm Immersion Double Pattern EUV (DRAM / MPU)	Narrow Options													
22	EUV 193 nm Immersion Double / Multiple Pattern ML2 Imprint				Narrow Option										
	No proven optical solution below this line														
16	EUV Innovative 193nm immersion Multiple Pattern ML2 Imprint Directed Self Assembly Interference Lithography						Narrow Option								
11	EUV ML2 Imprint Directed Self Assembly Interference Lithography									Narrow Option					

MPU / DRAM time line

Flash Time Line

This legend indicates the time during which research, development, and qualification/pre-production should be taking place for the solution

Research Required

Development Underway

Qualification / Pre-Production

Continuous Improvement

ITRS 2009

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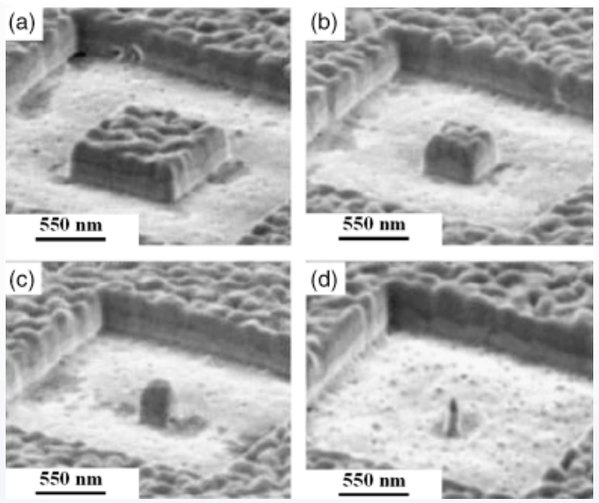
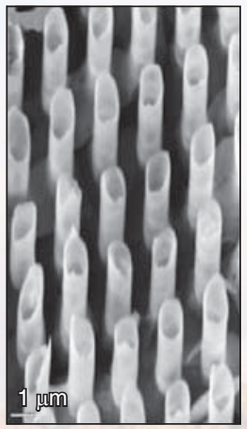
Micro-, Nano-Patterning of Arbitrary Materials

- **Challenges of expanding beyond ‘standard’ materials**

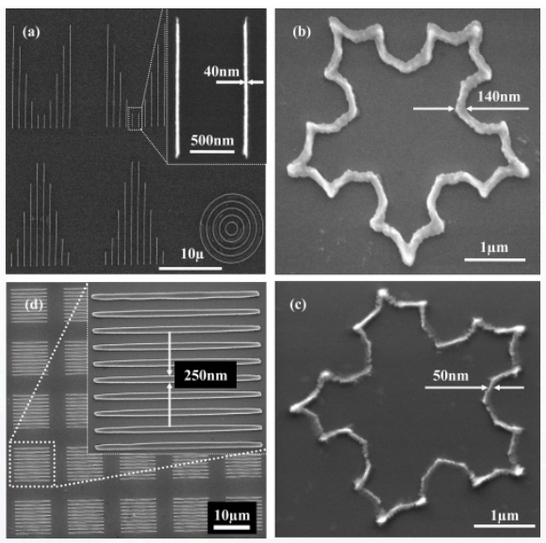
Fabrication | Patterning | Integration | Performance



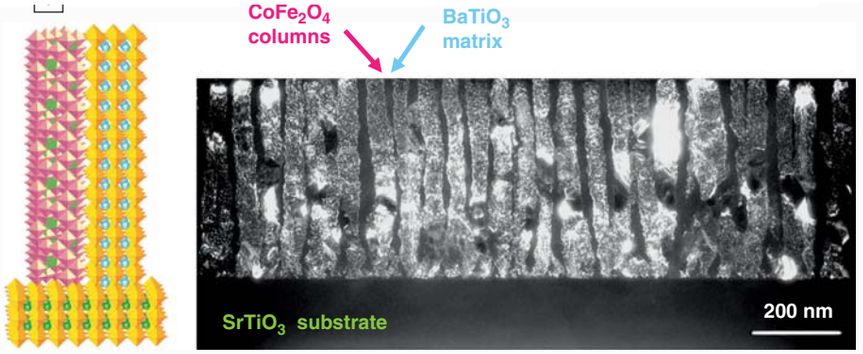
Ganpule et al., MRS Proc. (2001)



Scott et al.,
Nano Lett. (2008)



Donthu et al., Nano Lett. (2005)



Zheng et al., Science (2004)

- Need functional crystalline nanostructures without needing to develop new etching / integration approaches for each new material(s)
- **Extreme limitations on use of fab tools**

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Overview of Our Approach

- Goal: Combine flexibility and functionality of chemical solution deposition with use of e-beam and BCP patterning capabilities

Solution Deposition

Fabrication

Patterning

Integration

Performance

DSA-BCP

Fabrication

Patterning

Integration

Performance

Challenges:

- Avoid etching functional materials
- Avoid any fab-based processes during/ after deposition of functional materials
- Maintain feature integrity after thermal treatment(s)
- Retain function in nanoscale features

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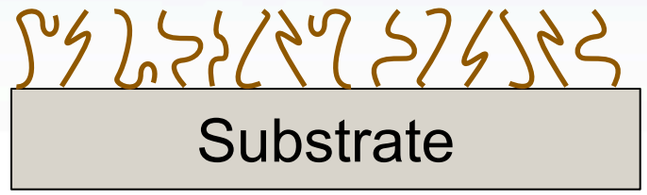
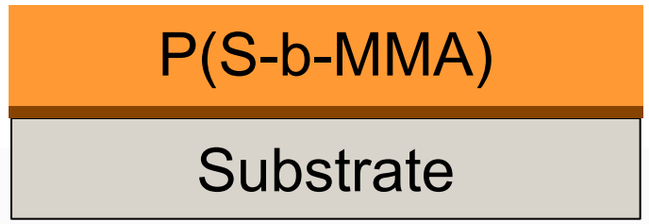
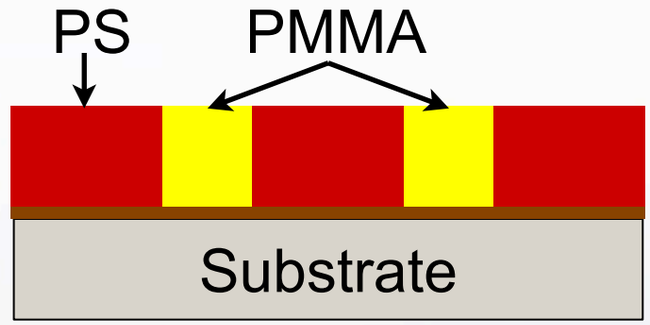
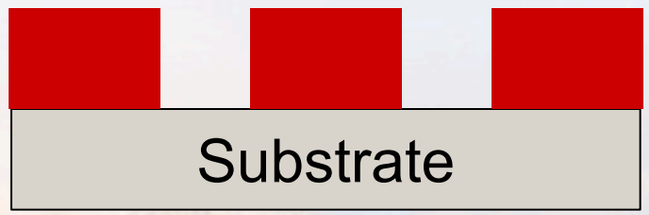
Patterning

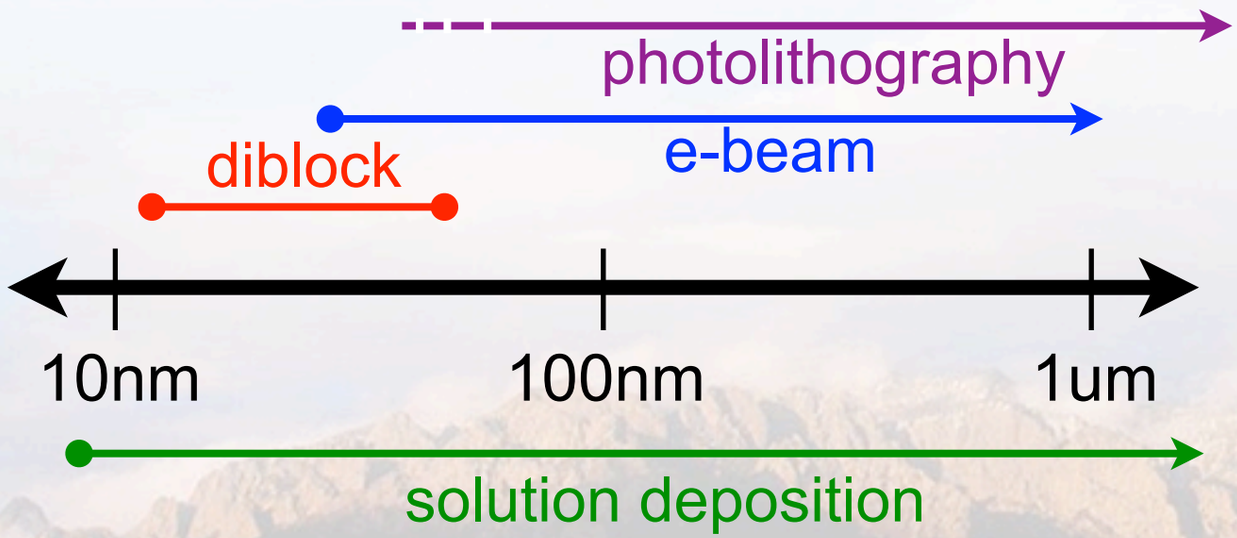
- **Continuous films are very limited in function**
- **Difficulties of etching PZT-based films**
  - Access to tools...
  - Property/reliability degradation
- **Alternative approaches to patterning/integration**
  - Direct write
  - Microcontact printing
  - Various transfer techniques
  - PZT-friendly lithography











Guarini, K W, et. al., *J. Vac. Sci. & Tech. B*, 2001, **19** (6), 2784-2788

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Sub-22nm Lithographic Options

Extreme Ultraviolet Lithography (EUVL)

13.2 nm soft x-ray source power

(+) high-resolution resist development
(-) poor Line Edge Roughness (LER)
(-) complex, ***costly***

Mask-less Lithography (ML2)

(+) high resolution electron-beam, ion-beam
(-) slow serial process, ***costly, charge build-up***

Interference Lithography (IL)

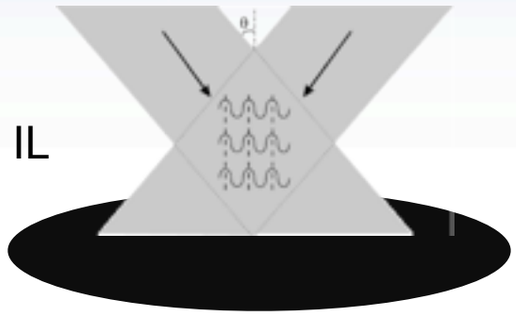
(+) rapid, large area, parallel process
(+) **low cost** (rapid, large area, maskless)
(+) tunable symmetry, period, motif
(-) layer alignment & spatial pattern variation difficult

Directed Self-assembly (DSA)

(+) alignment to pre-pattern gives long-range order periodicity set by size of blocks
(+) pattern rectification and density multiplication
(-) slow process with many steps

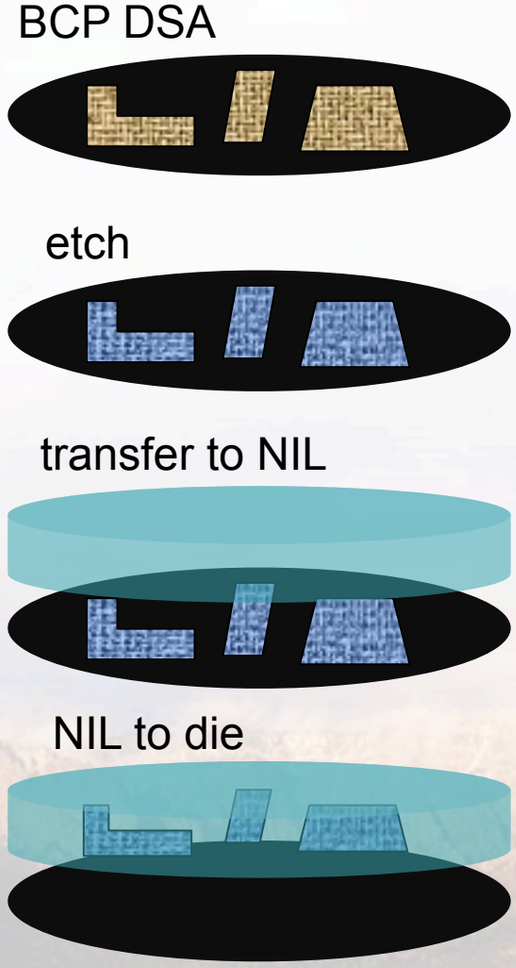
Nano-Imprint Lithography (NIL)

(+) long-range order set by master
(-) overlay can be difficult
(+) high resolution
(+) **low cost**



IL-defined chemical pre-patterns

– 60-90 nm pitch, ~4 cm^2 areas



BCP Directed Self Assembly

– 20-30 nm pitch device patterns
– 10-50 nm CDs
– Half-pitch to ~11 nm over ~4 cm^2 areas

Pattern transfer to create Nano-Imprint lithography (NIL) device masters

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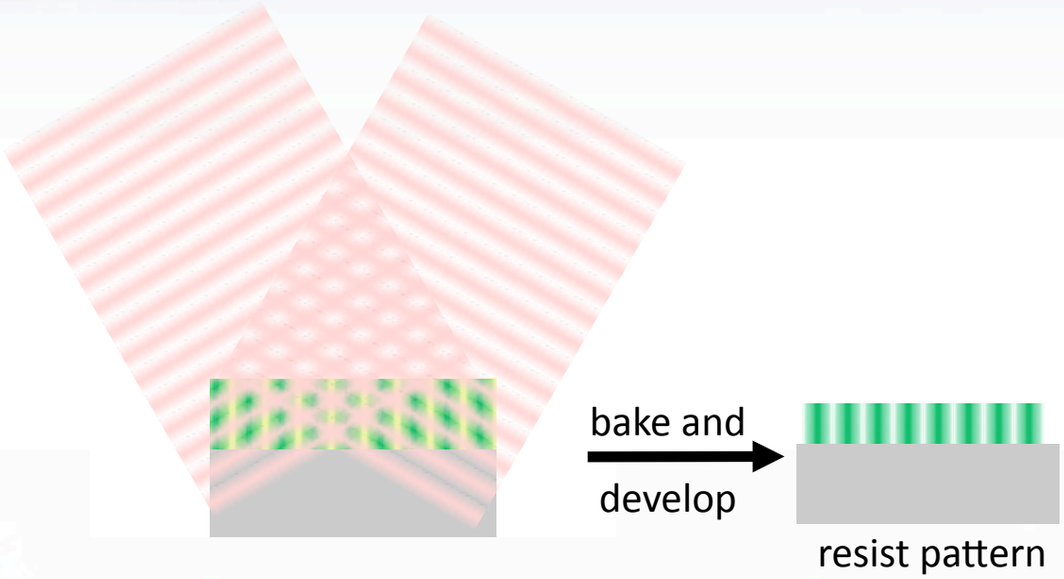
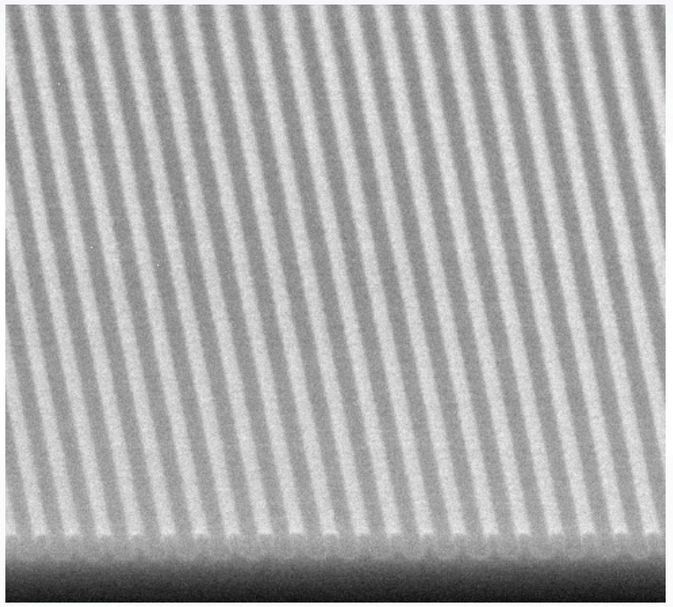
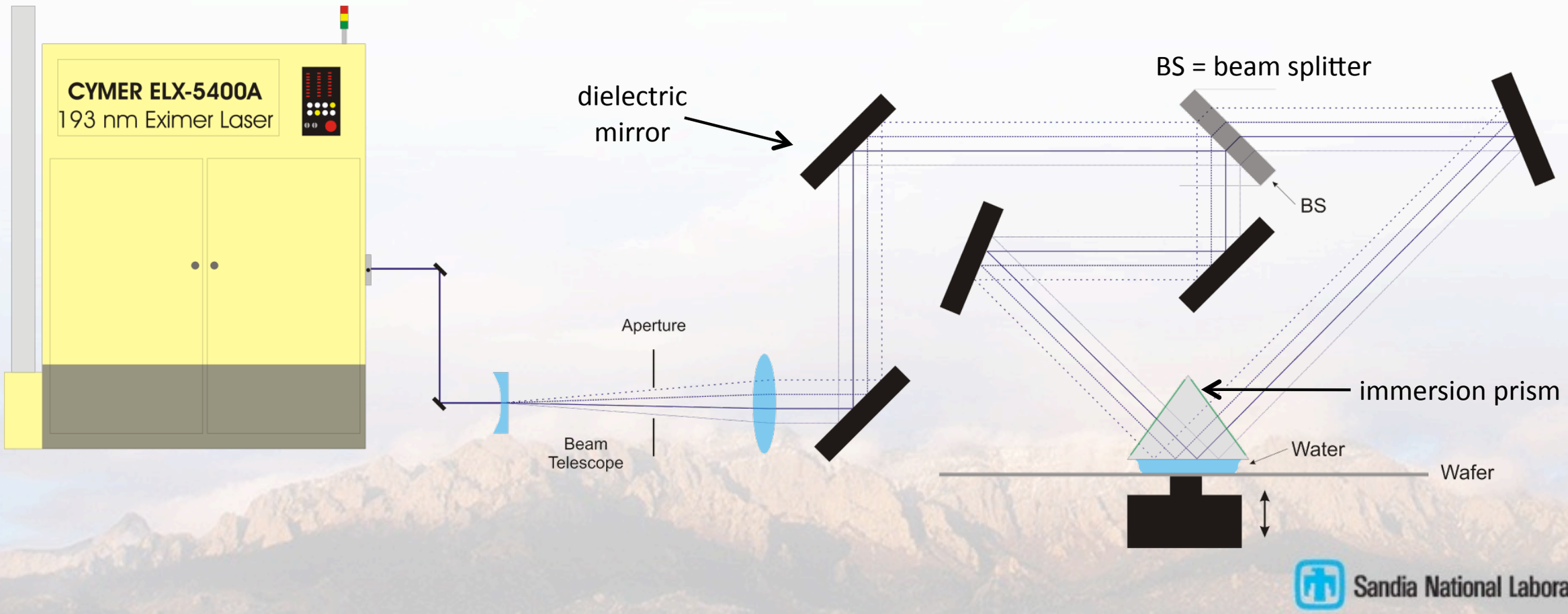
Optical Interference Lithography

with Prof. Steve Brueck





Critical dimensions ~70 nm
Patterned areas ~4cm^2



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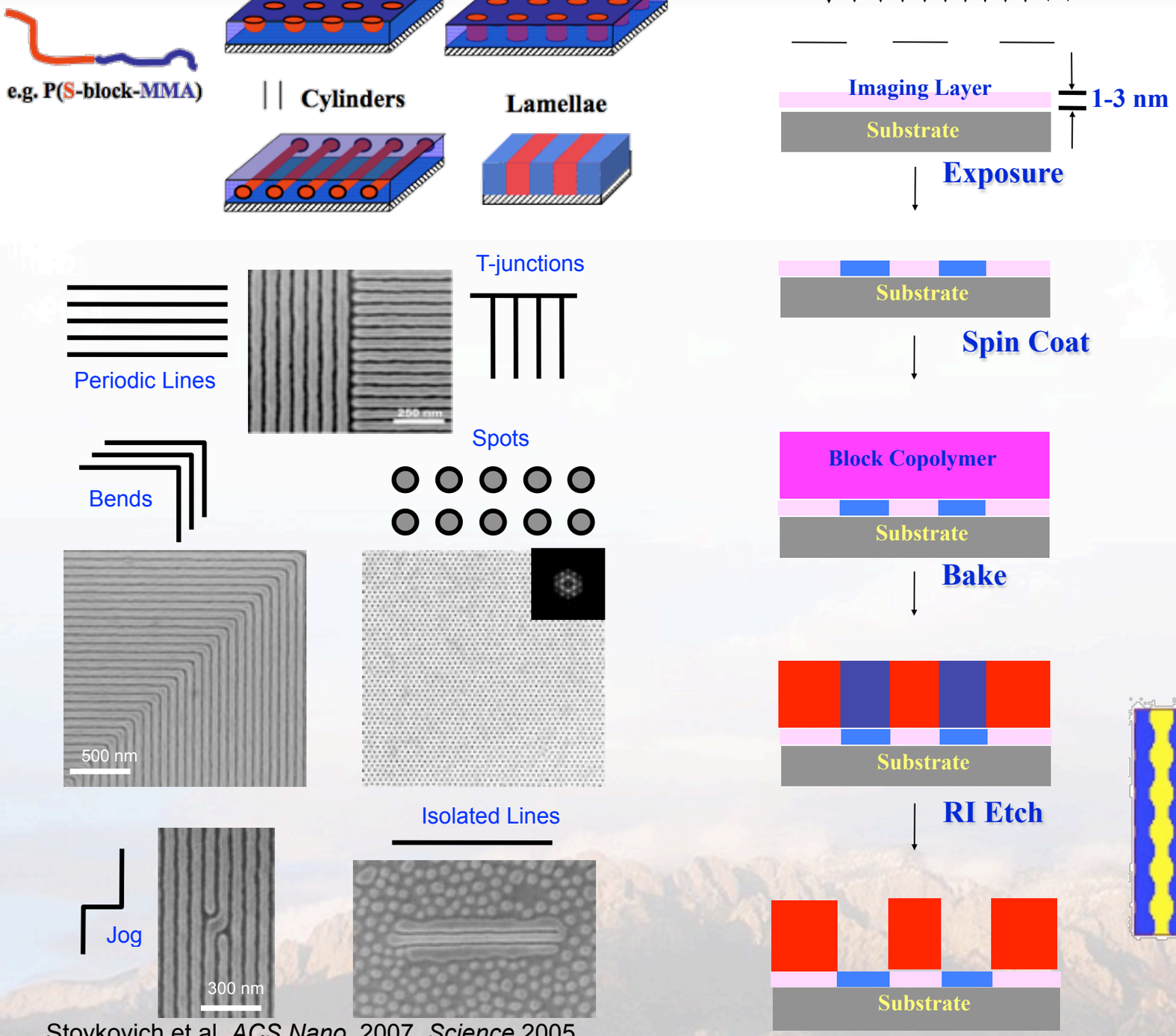
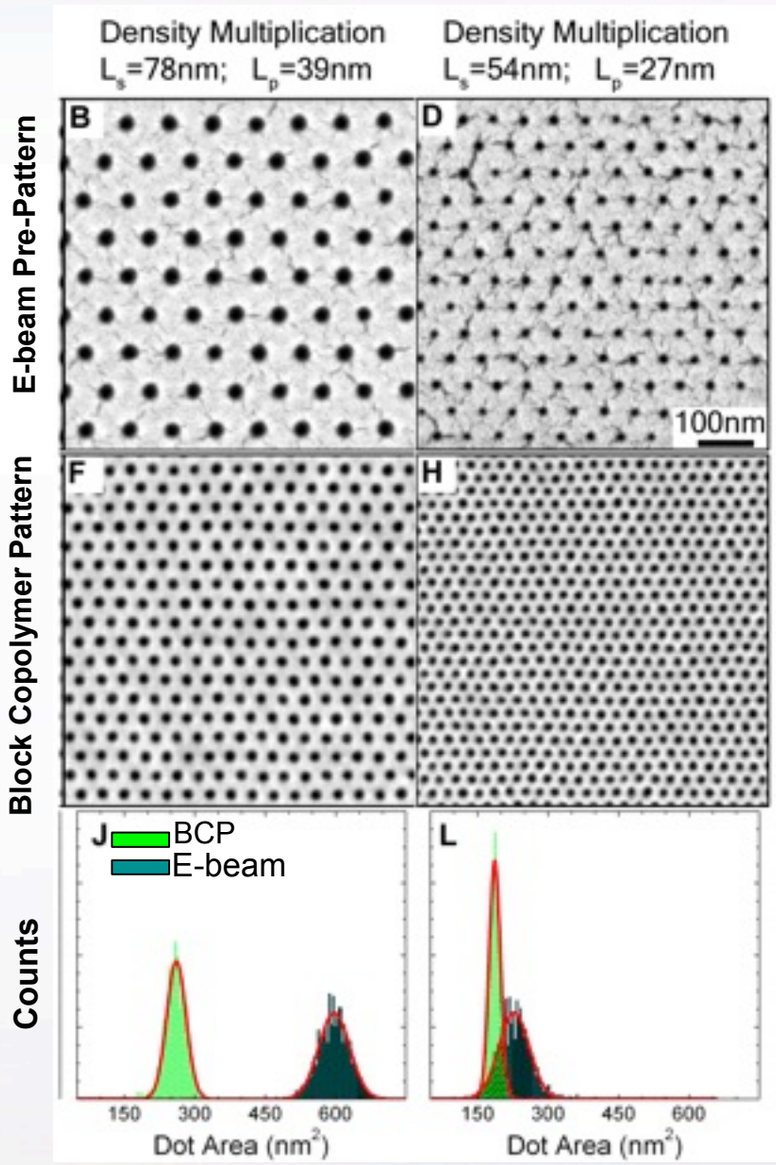
Block-Copolymer Directed Self Assembly

with Profs. Paul Nealey and Juan de Pablo

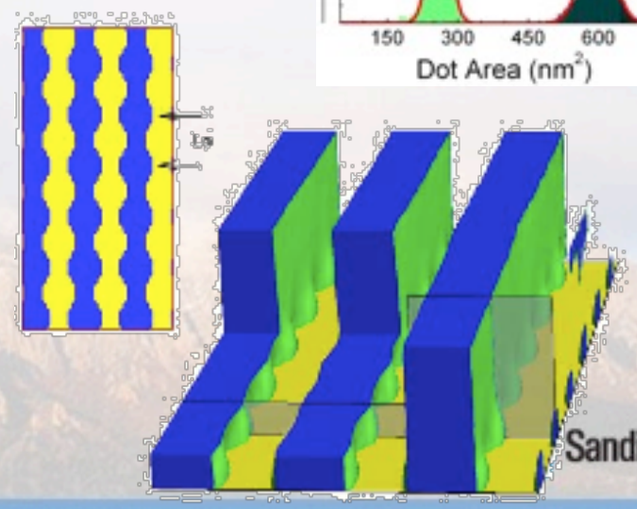
THE UNIVERSITY of WISCONSIN MADISON



Stoykovich et al. *ACS Nano*, 2007, *Science* 2005



Ruiz, Nealey, de Pablo et al. *Science*, 2008



Daoulas et al., Langmuir, 2008

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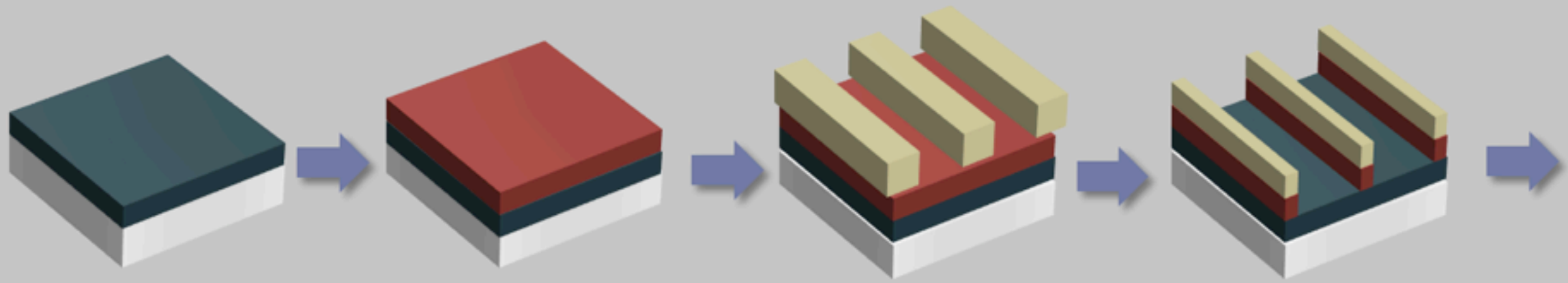
Density Multiplication

Process flow with ARC and 193i

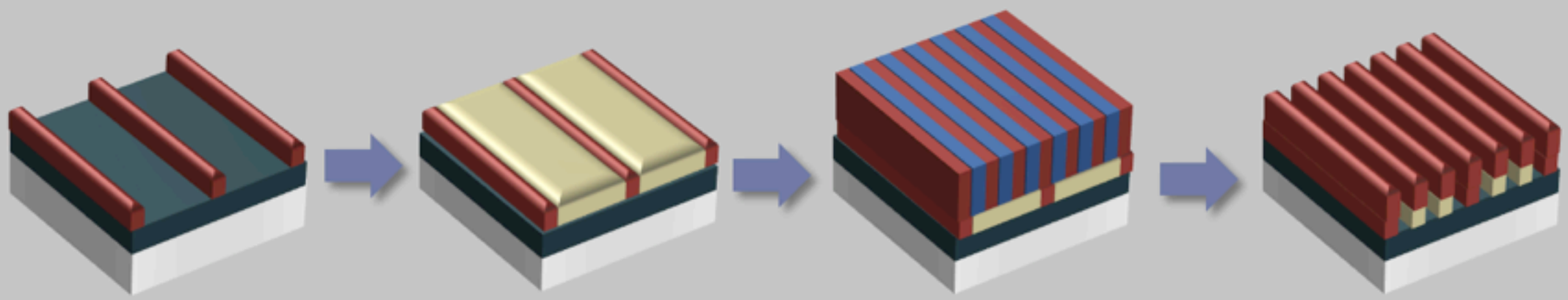


Inorganic ARC deposition

X-PS cross-linking

193i interference lithography

O_2 plasma etching (breakthrough and trim)



PR strip with solvent

random-OH brush deposition

BCP directed-assembly

PMMA removal

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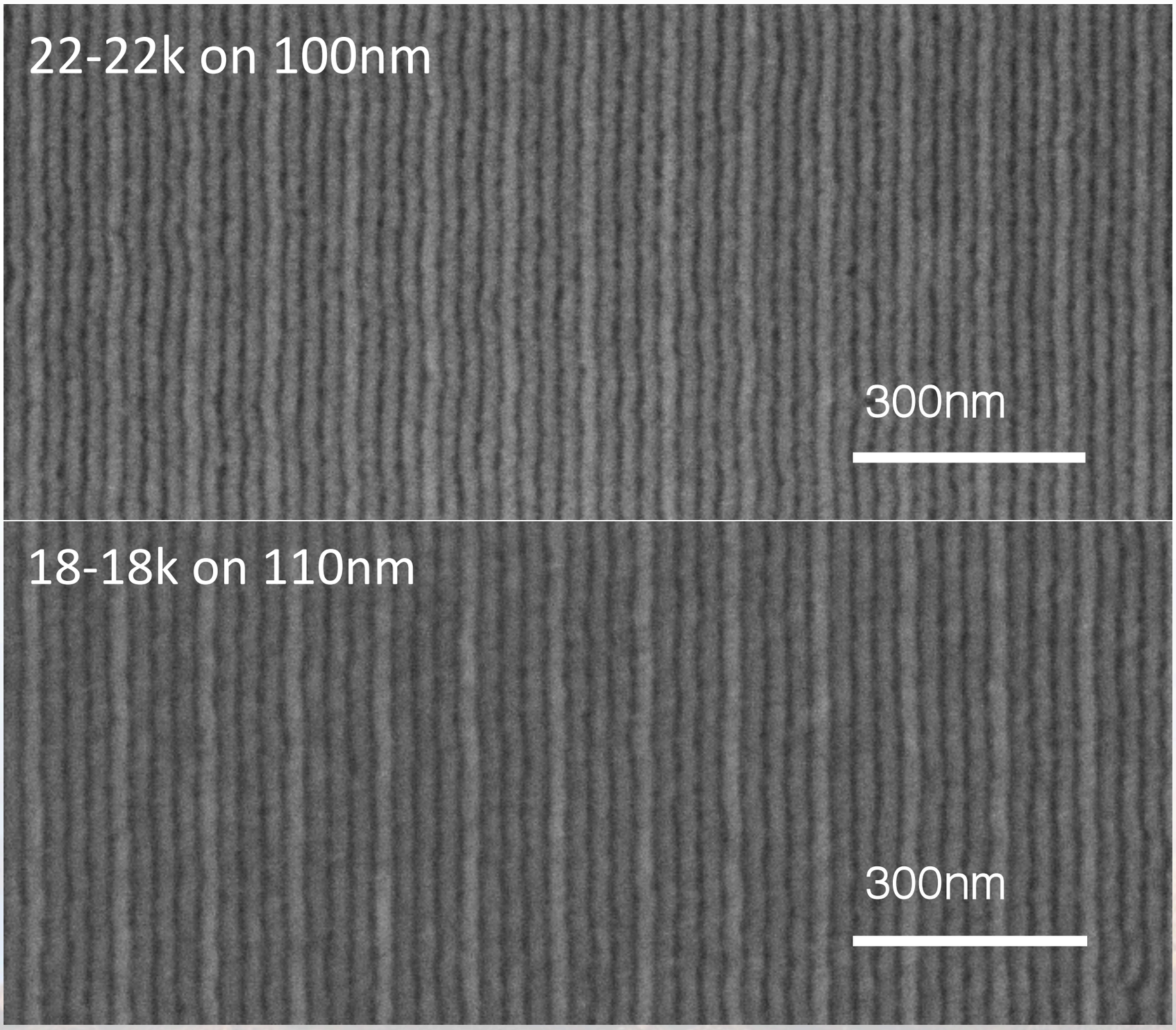
3x density multiplication
30nm features in 90nm IL pattern
over mm^2 areas

Density Multiplication



4X Multiplication

Molecular weight inaccuracies, inconsistencies, and distributions limit continued multiplication factors

Surface interactions are crucial

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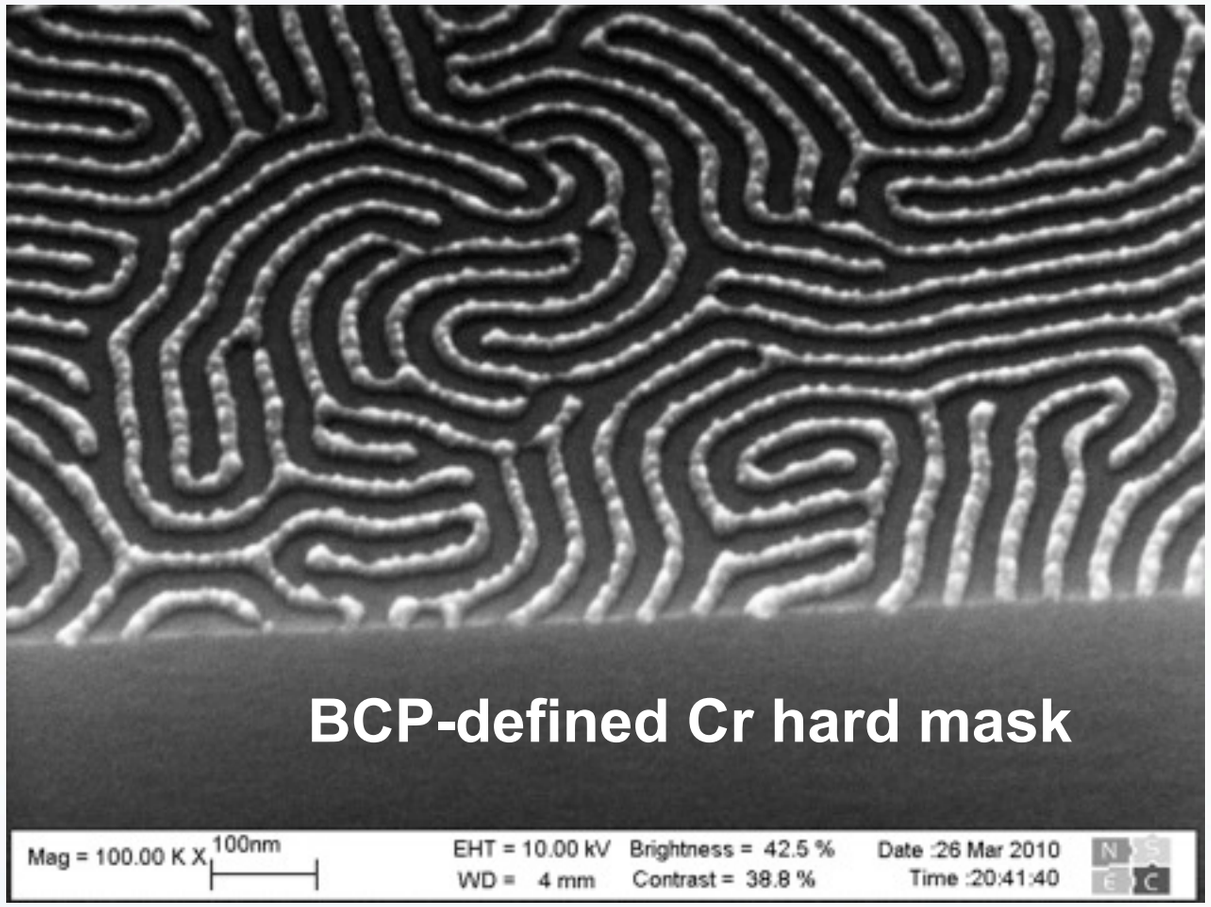
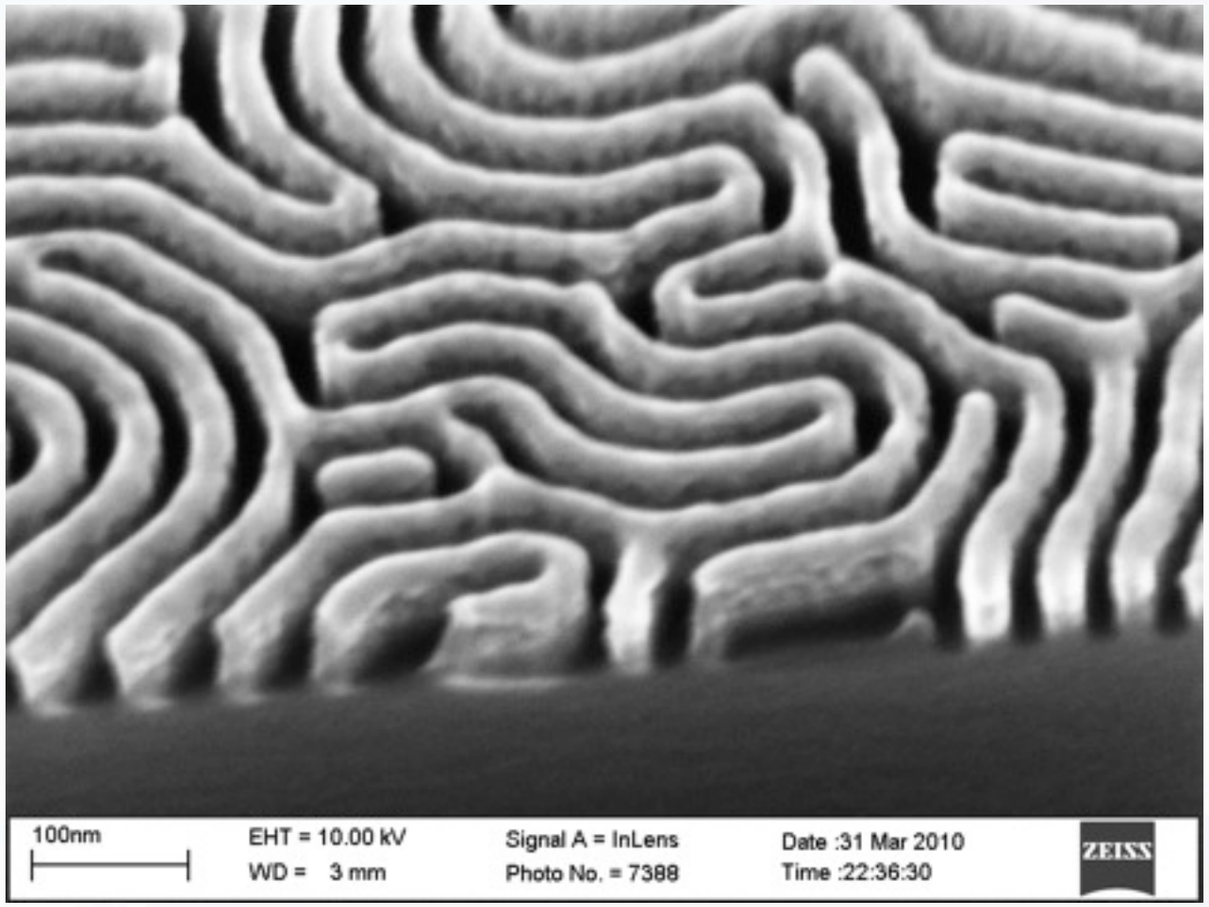
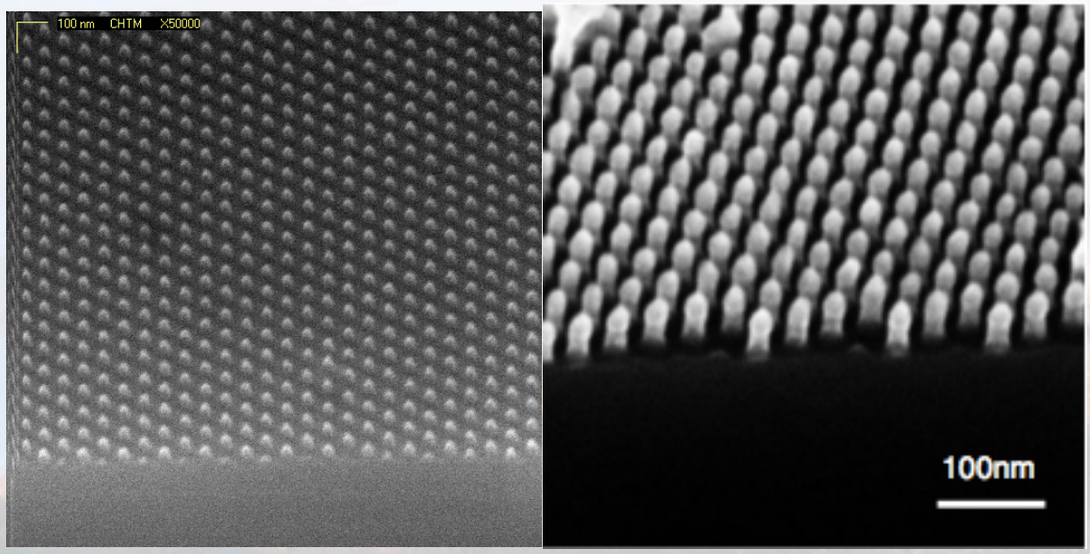
Pattern Transfer

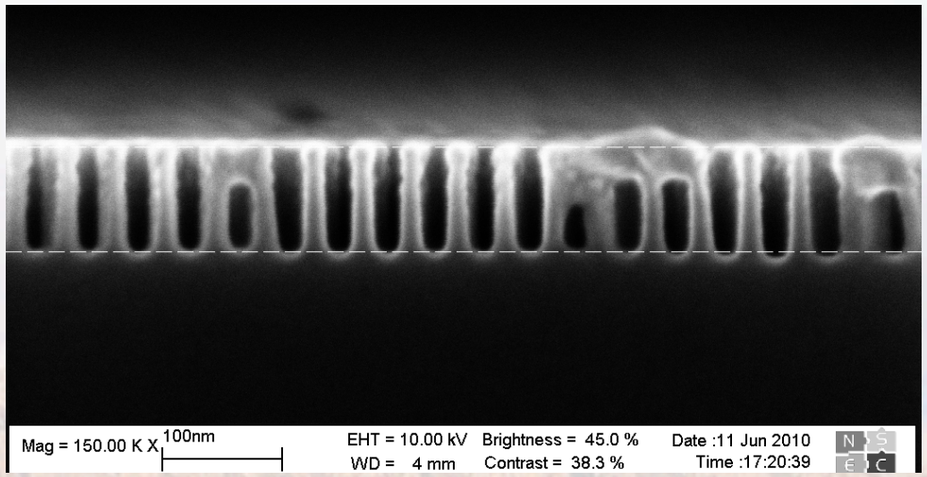






Si pillars defined by BCP for NIL master

Si etched through Cr mask



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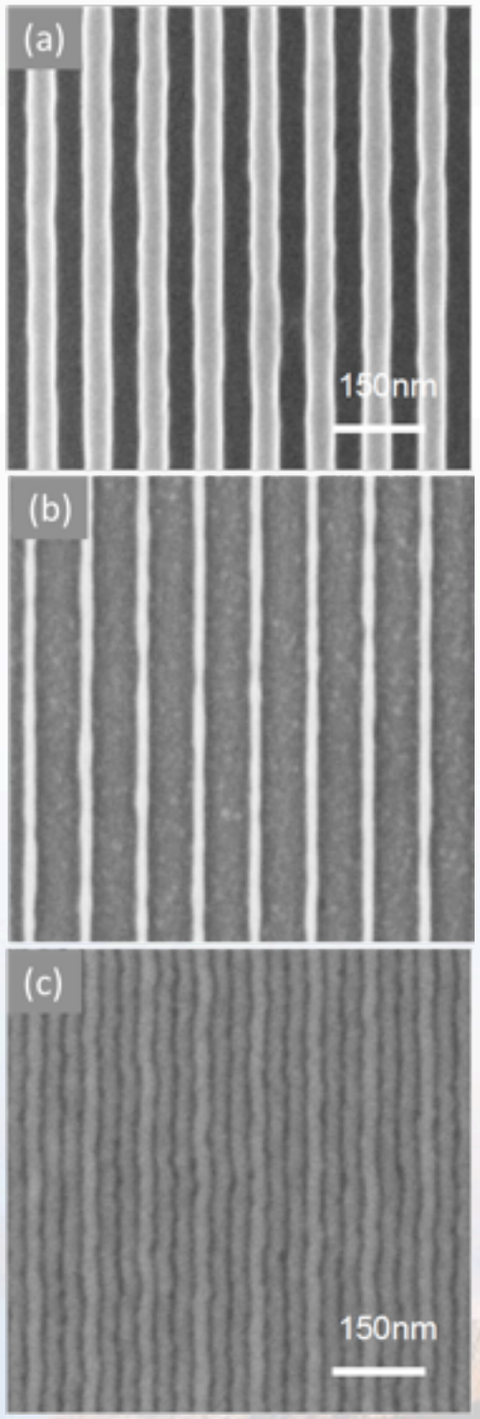
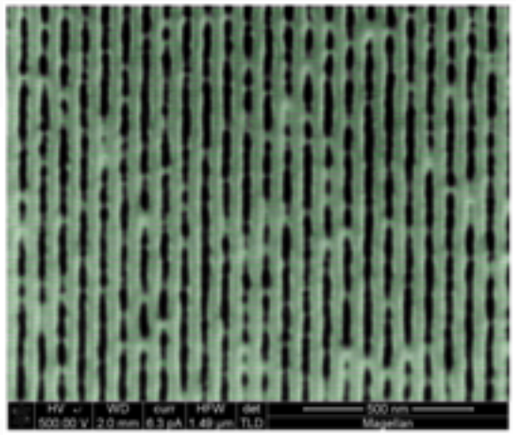
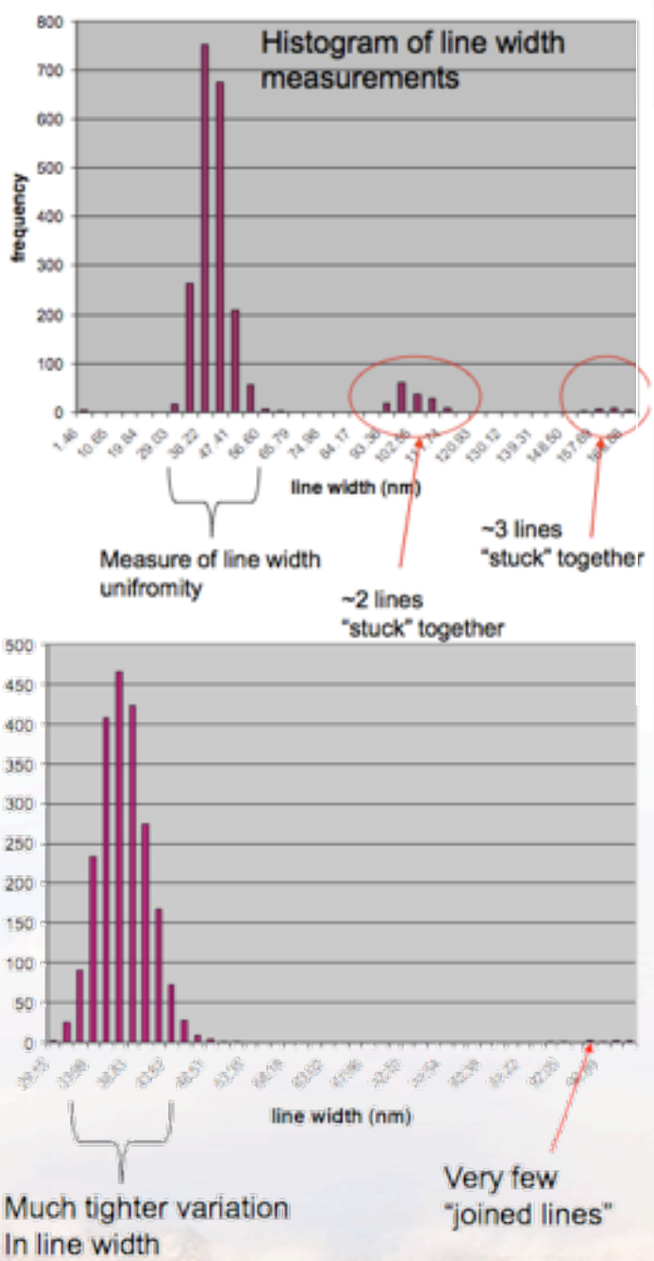
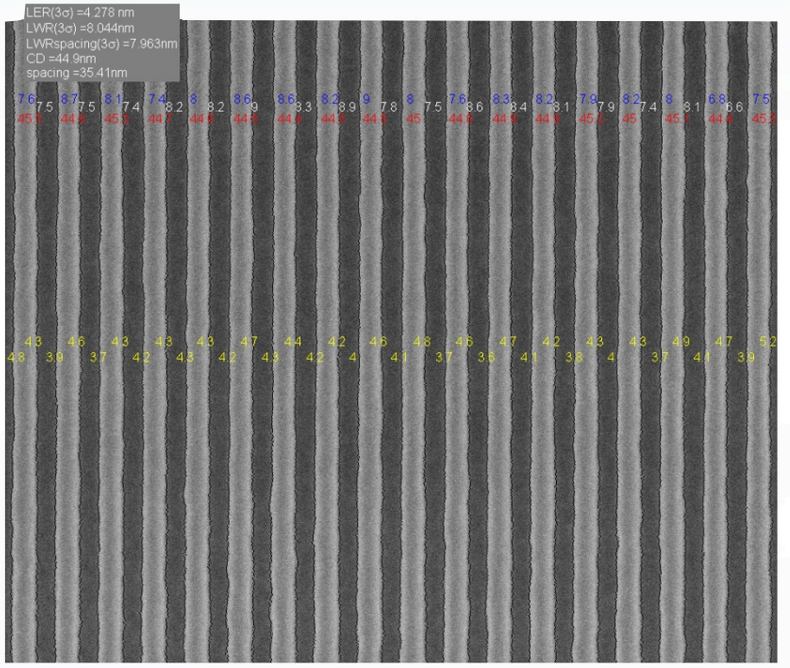
Metrology





After insertion of 100 grid lines and BOOLEAN combination





Line Edge Roughness (LER)
3σ deviation of a line edge from best-fit straight line
target LER < 5 %

Intel-blessed standard, quantitative, non-destructive feature/defect analysis at each stage of process

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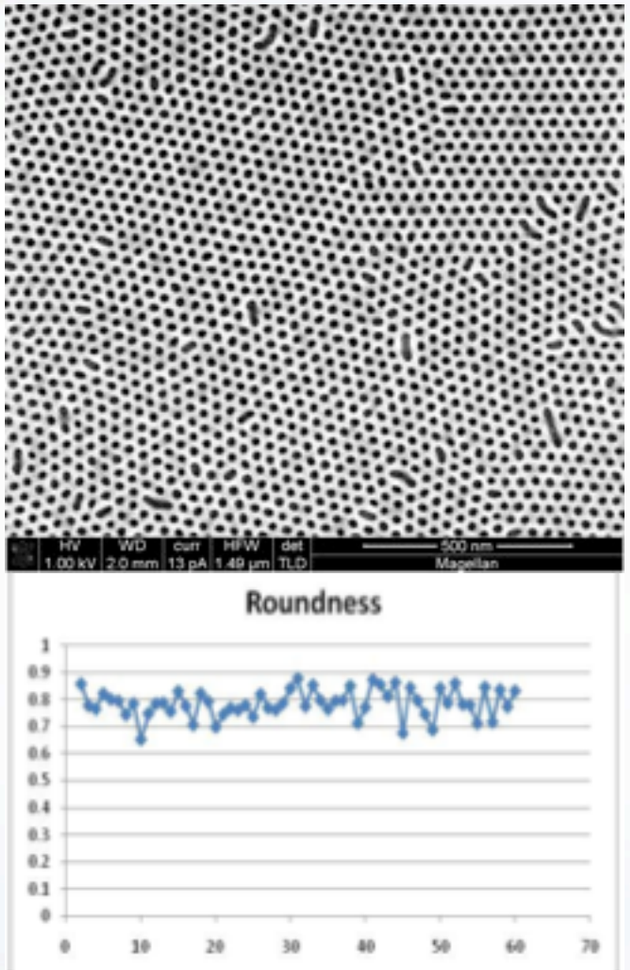
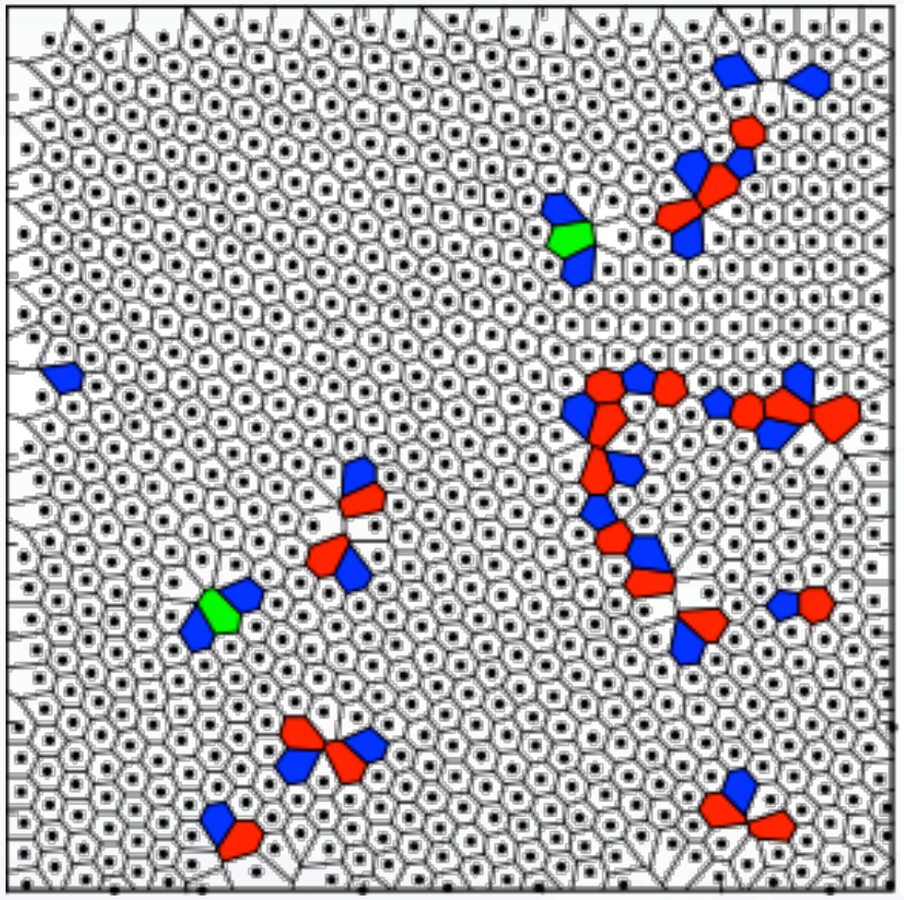
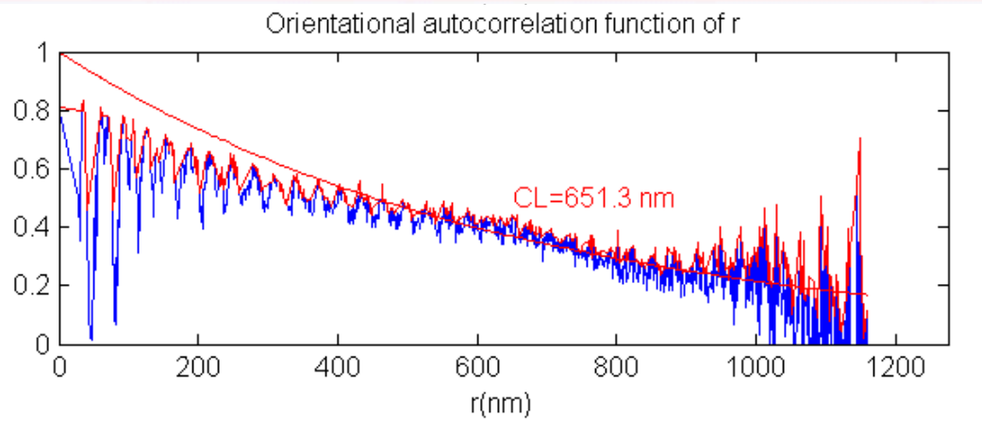
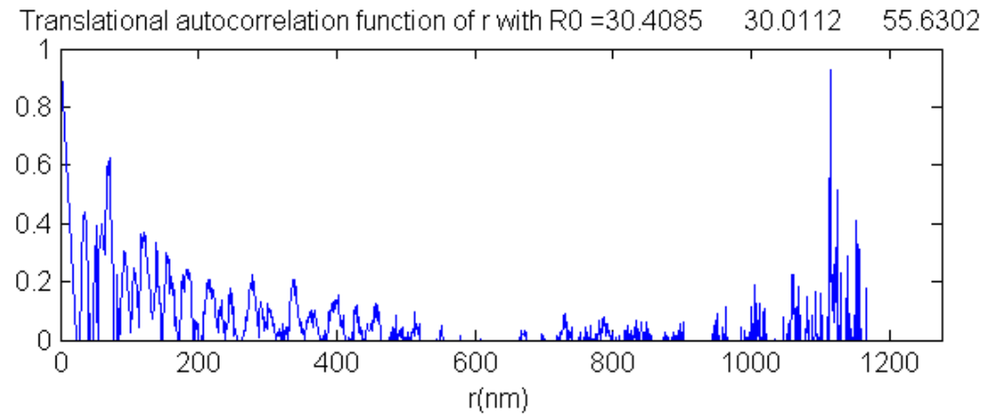
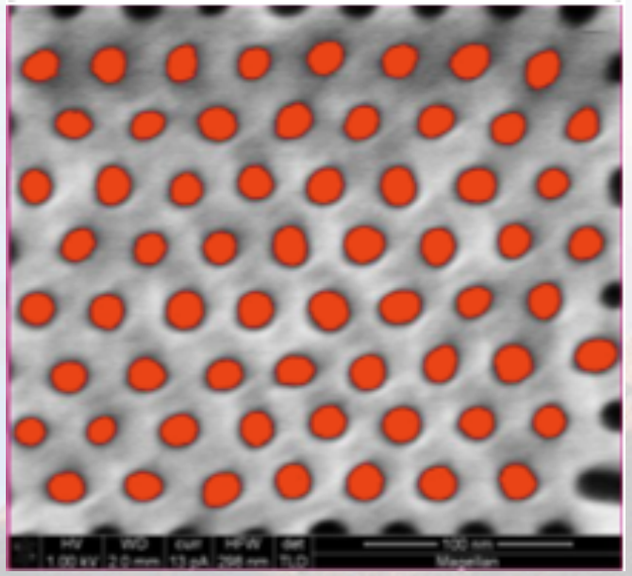
Metrology











All made possible by FEI Magellan SEM:
quantitative sub-nm measurements from
uncoated samples

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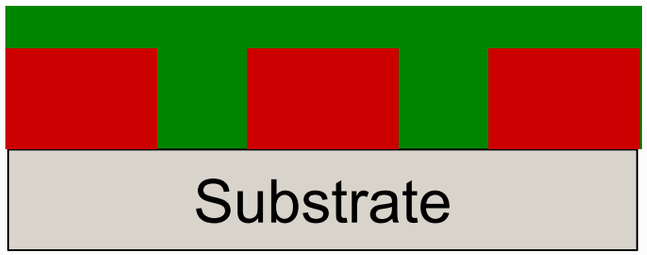
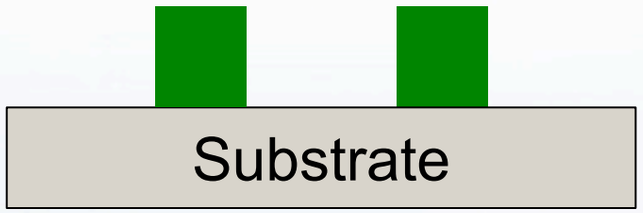
Additive Fabrication of Patterned Electronic Oxides

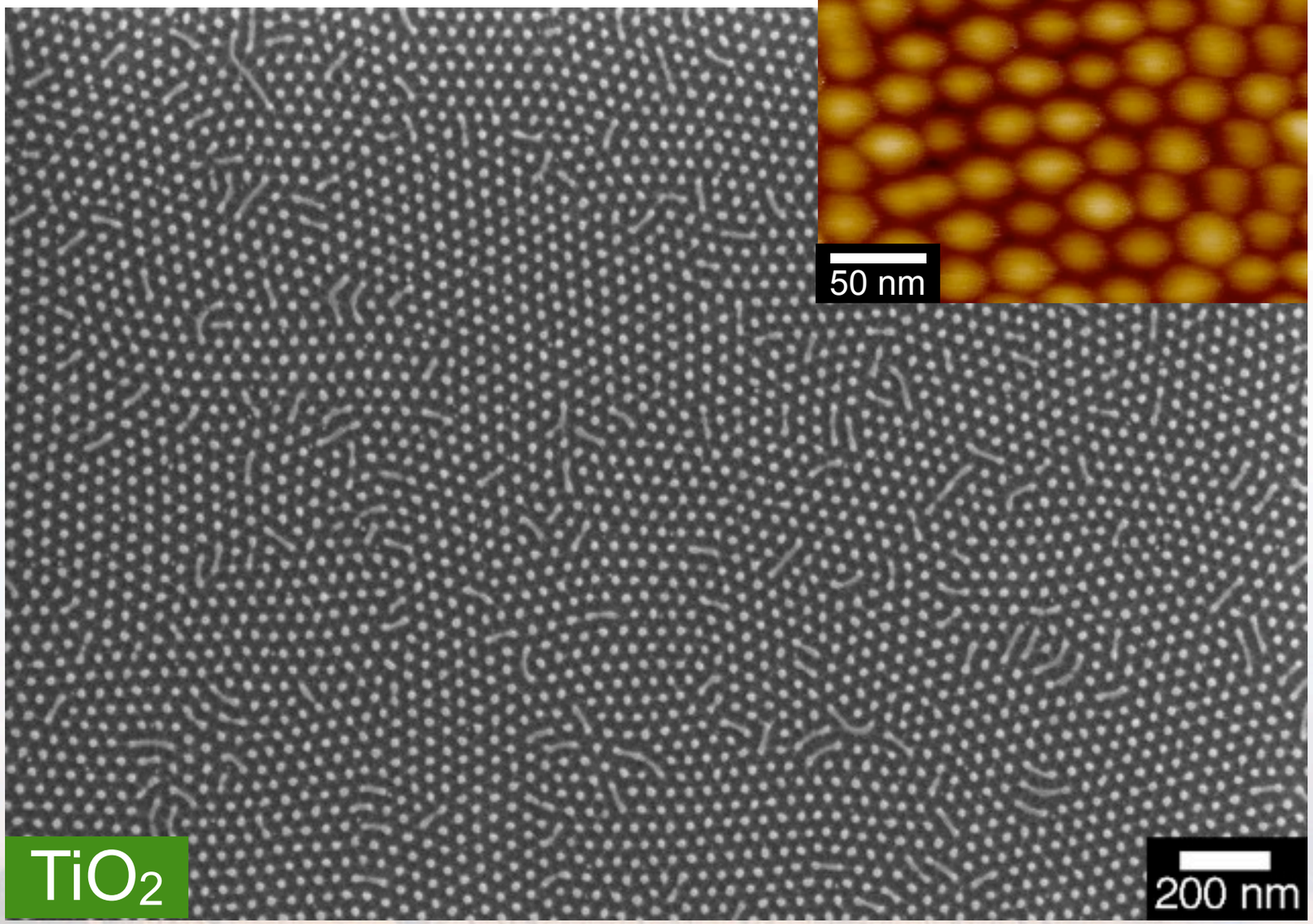


Fill, Gel



Remove Mask

$CHF_3 + O_2$



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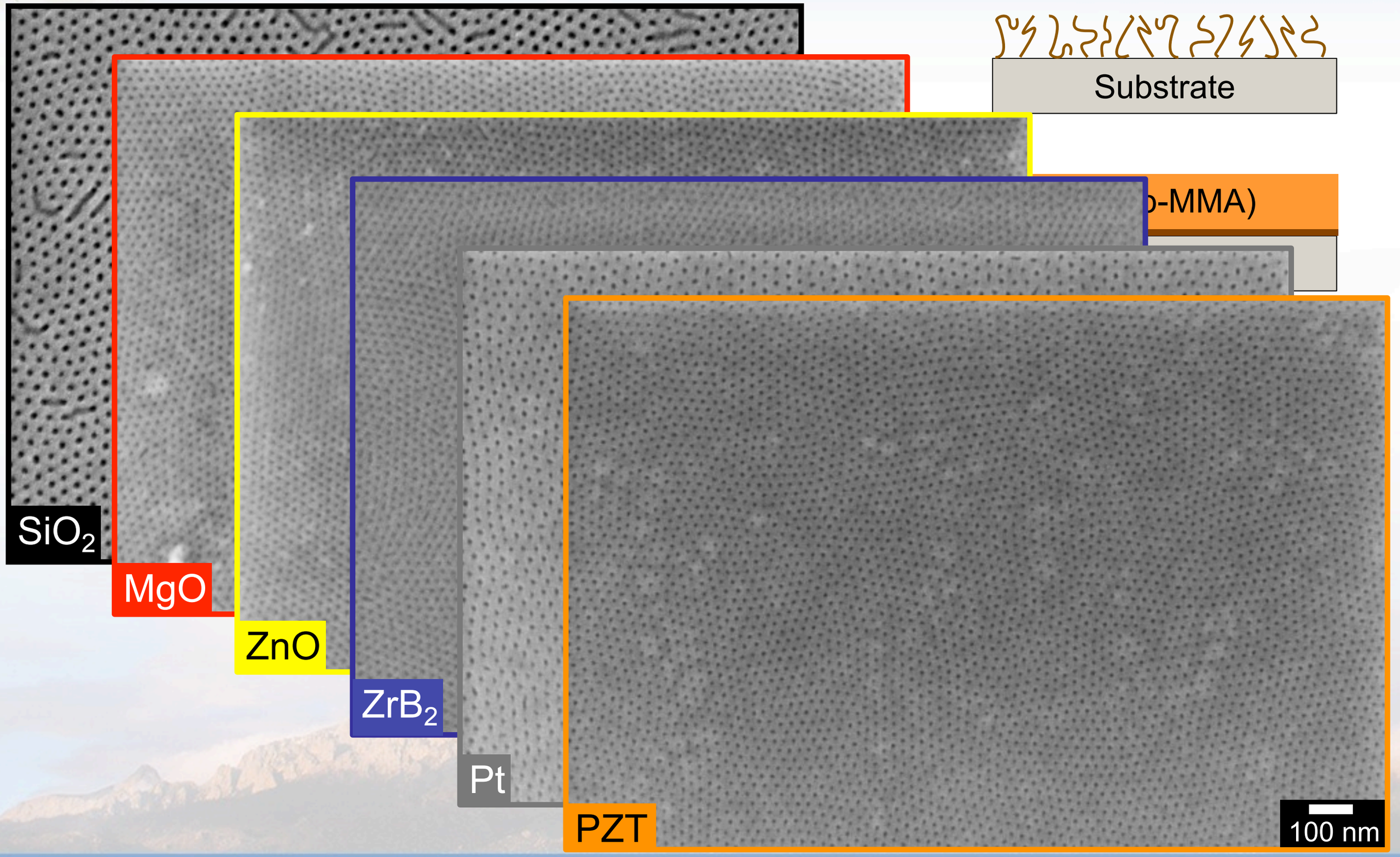
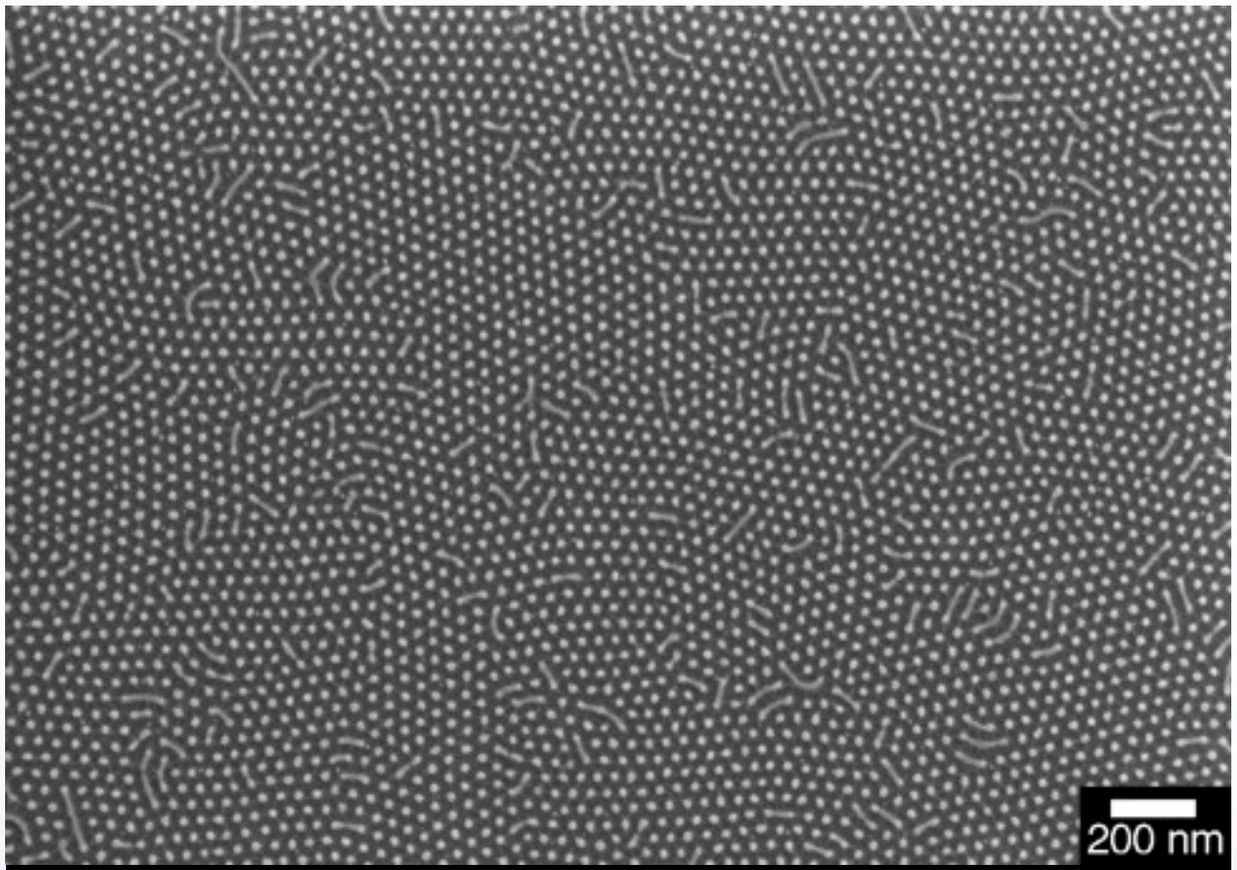
Diblock Assembly on Various Substrates

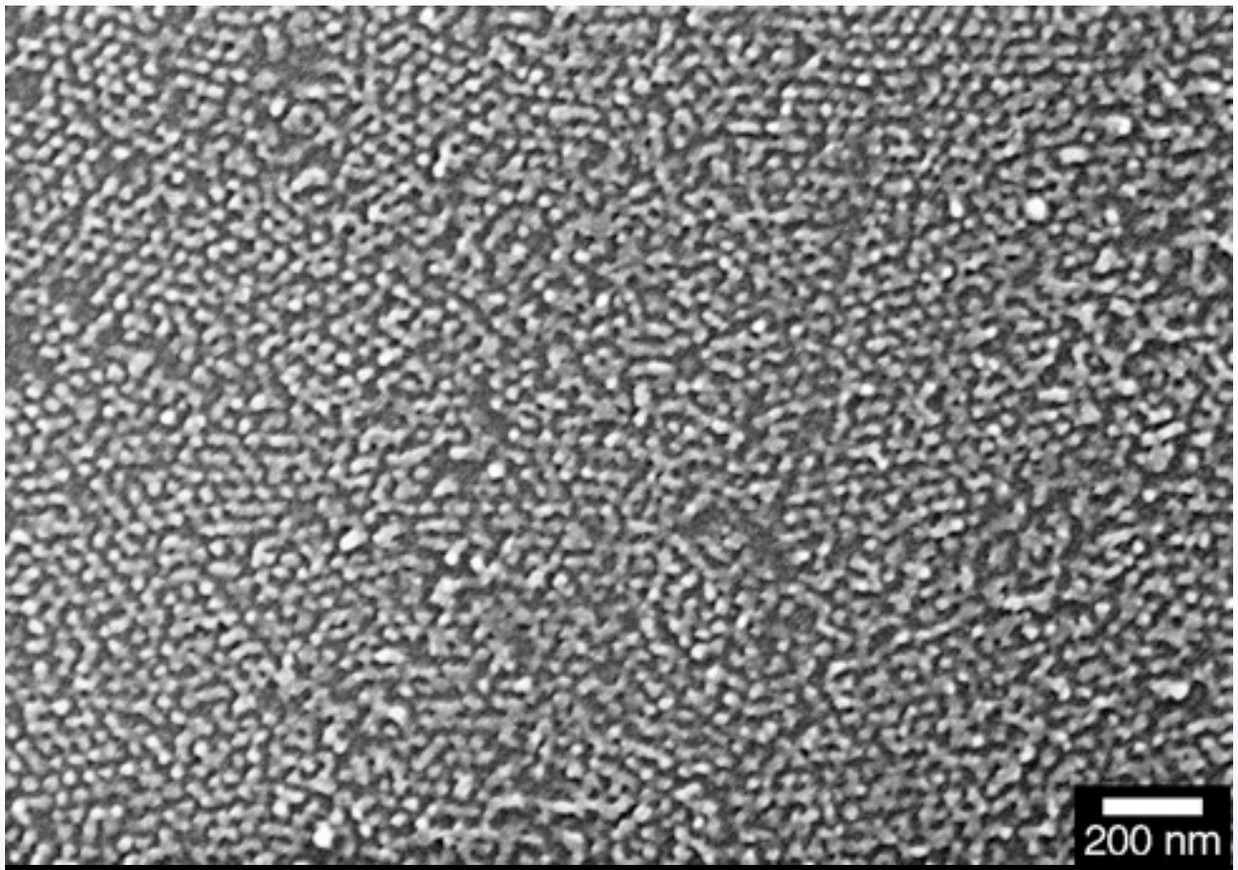


Crystallization Destroys Freestanding Nanofeatures

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



Amorphous TiO_2



Crystalline TiO_2 (Anatase)

Still lacking:

- Controlled long-range order for addressability
- Crystallization before patterning or within inert and removable mask

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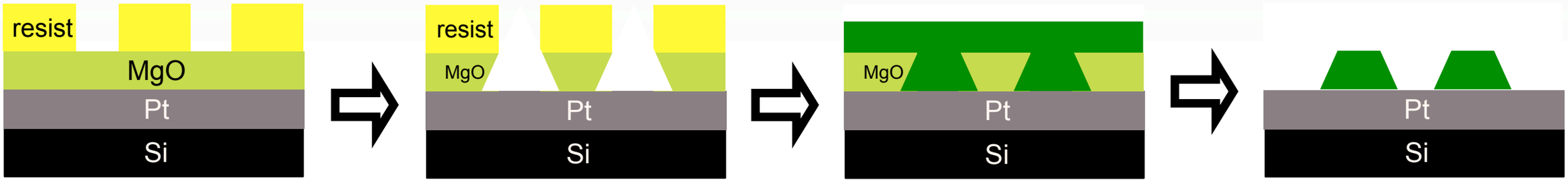
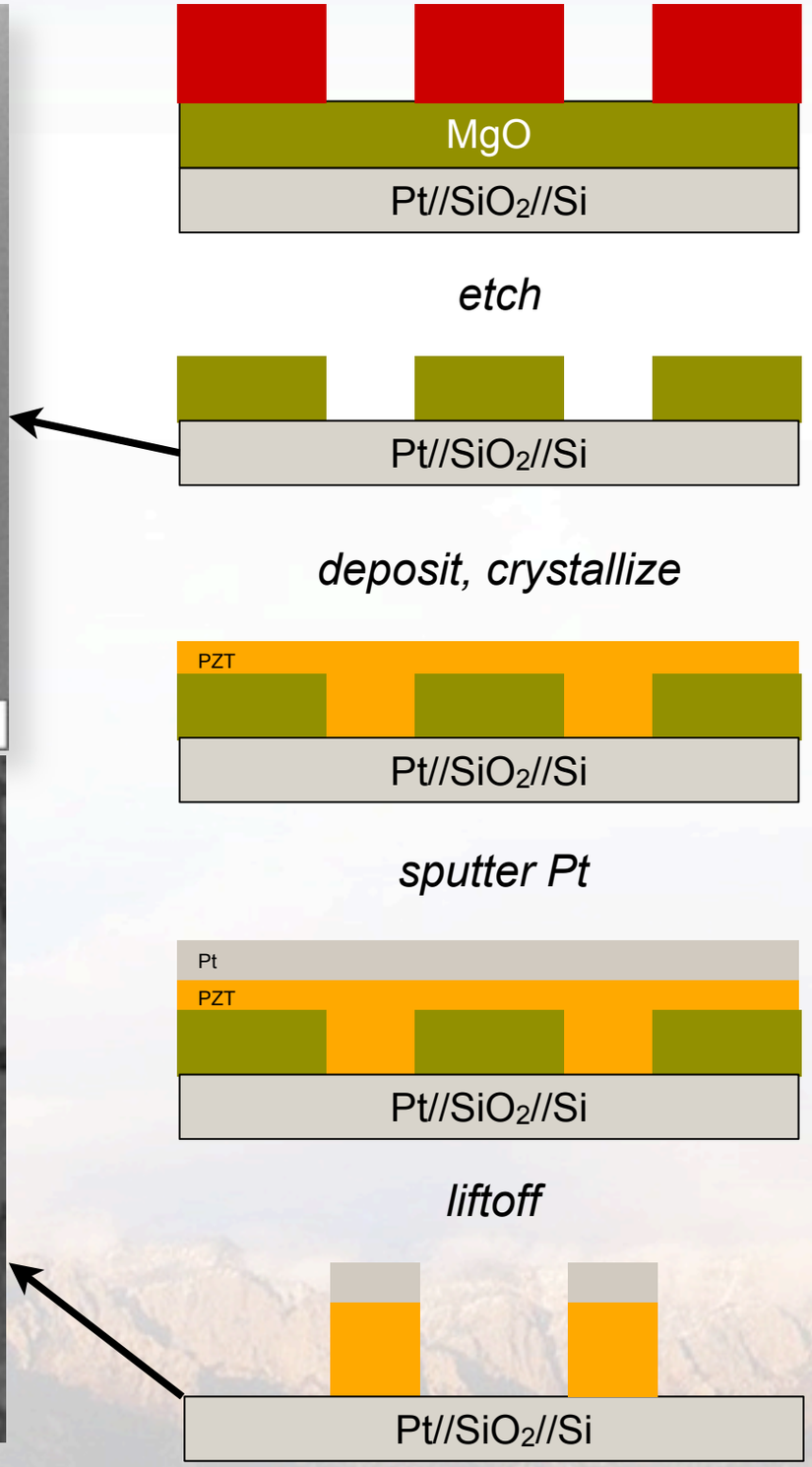
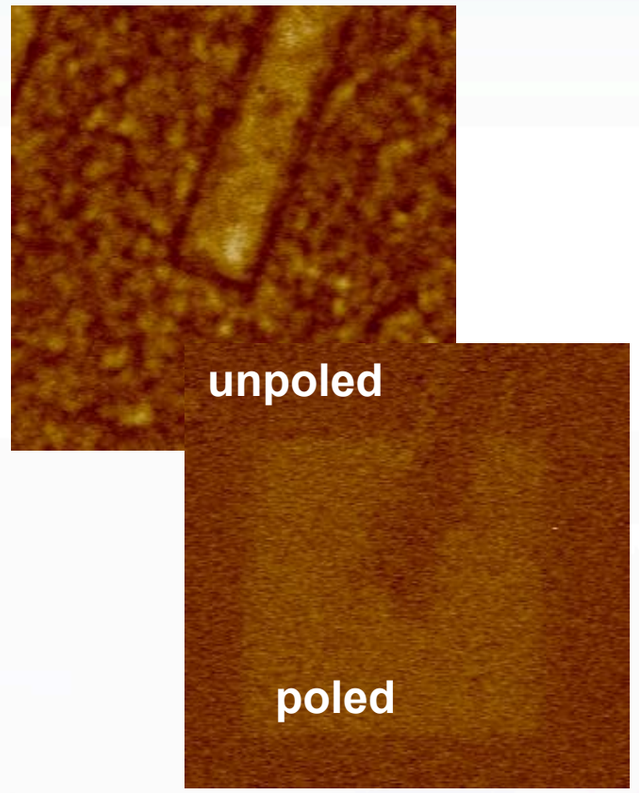
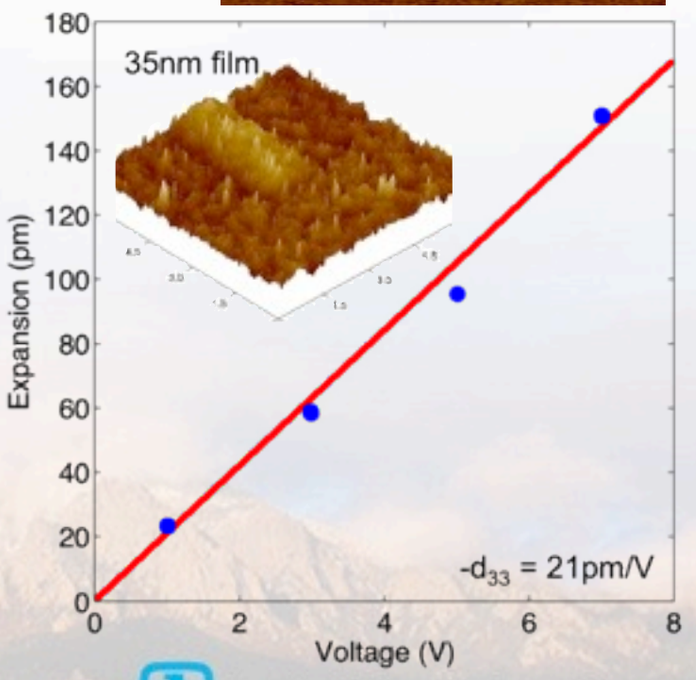
Maintaining Pattern Fidelity through Thermal Processing (>600°C)



Alternate Microscale Patterning







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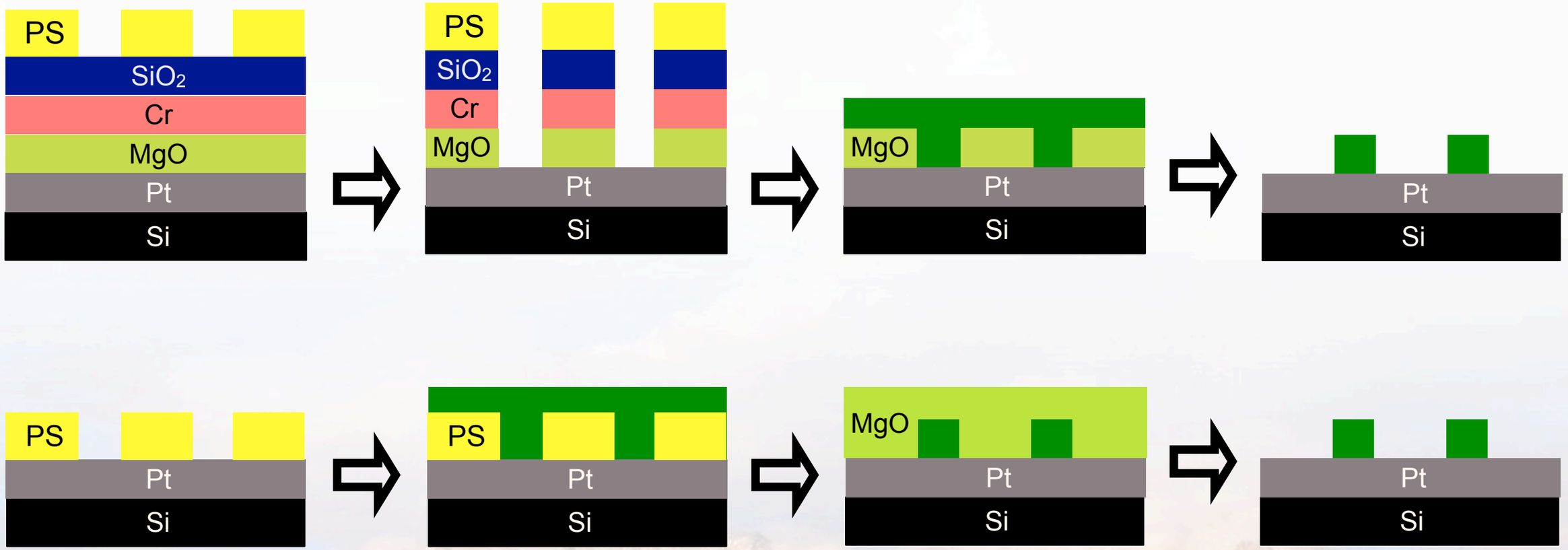
Maintaining Pattern Fidelity through Thermal Processing (>600°C)

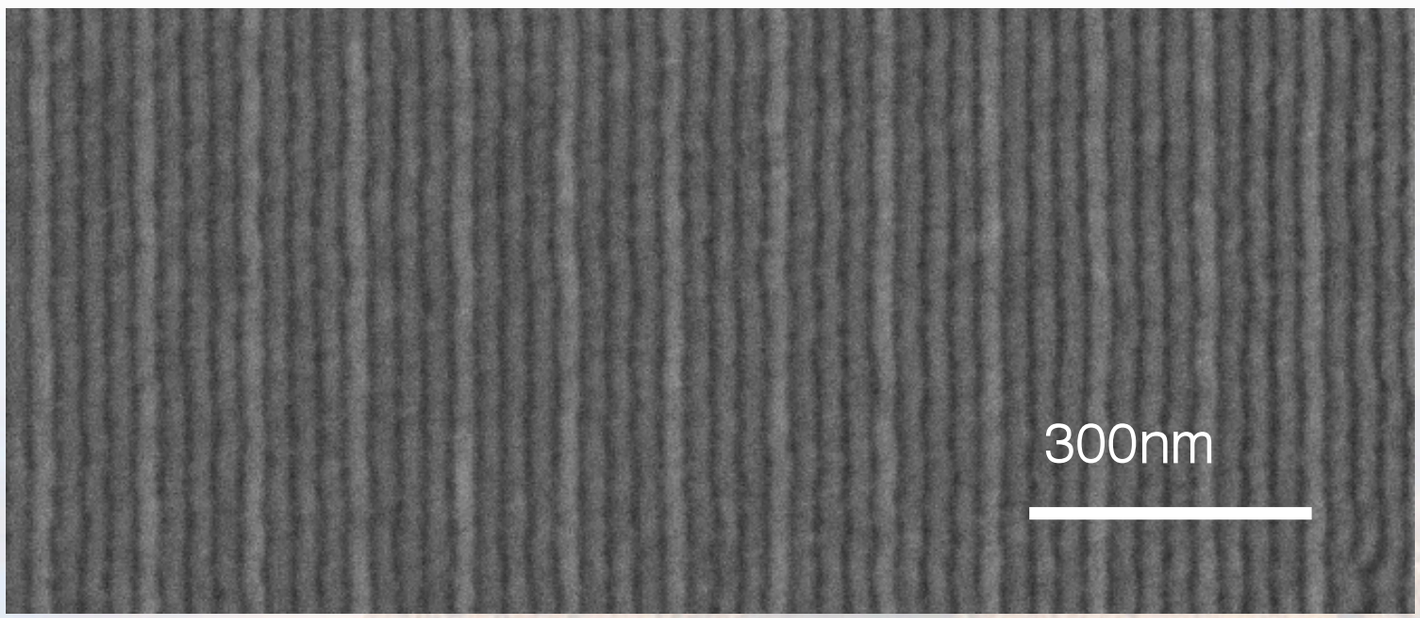
Wet Etch Limits to Microscale

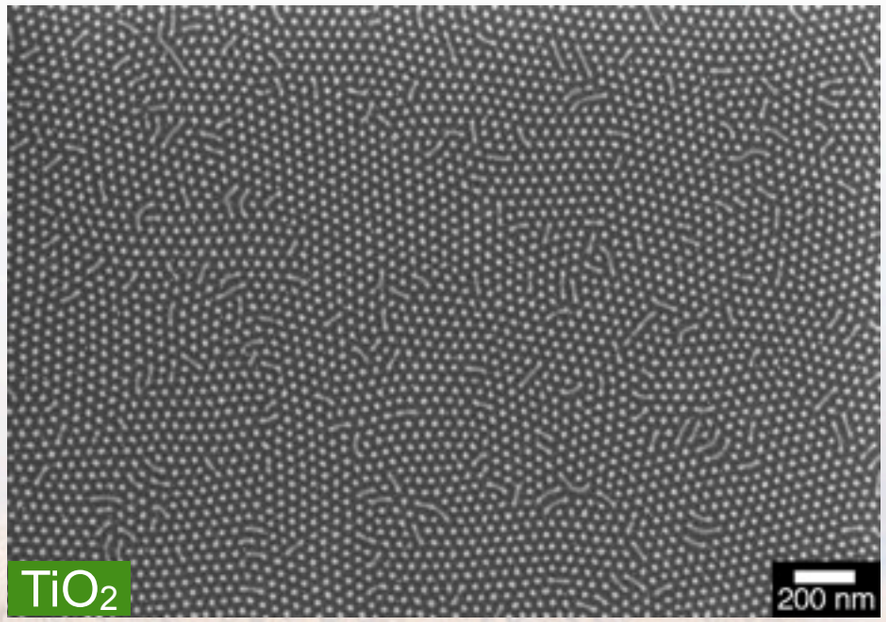
Maintaining Pattern Fidelity through Thermal Processing (>600°C)



Summary

- Solution deposition of ferroelectrics is alive and well
- Up to 4x density multiplication with DSA-BCP over mm^2 areas
- Extended BCP-based patterning to wide variety of materials (substrates and solution-derived features)
- Initial work on extending functional solution-derived ferroelectrics to etch-free 2+ dimensions





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Acknowledgments

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- Jon Ihlefeld
- Matt George
- Bruce Tuttle
- Chris Shelton
- Kelsey Meyer
- Mark Rodriguez
- Aaron Gin
- David Scrymgeour
- Bonnie McKenzie
- Dick Grant
- Michael Rye
- Jeff Stevens

External Collaborators

- University of Wisconsin
  - Profs. Paul Nealey and Juan de Pablo
  - Shengxiang Ji
  - Charlie Liu
  - Lance Williamson
  - Brandon Peters
- University of Texas-Austin
  - Prof. John Ekerdt
  - Wes Ahearn
  - Wyatt Winkenwerder
  - Ryan Fitzpatrick
- University of Florida
  - Prof. Jacob Jones
  - Krishna Nittala
- Missouri S&T
  - Prof. Bill Fahrenholtz
  - Harlan Brown-Shaklee
- Intel
  - Todd Younkin
  - Mike Garner
  - David Shykind
  - Steve Putna
- ExxonMobil
  - Mark Disko
  - Amy Herhold

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