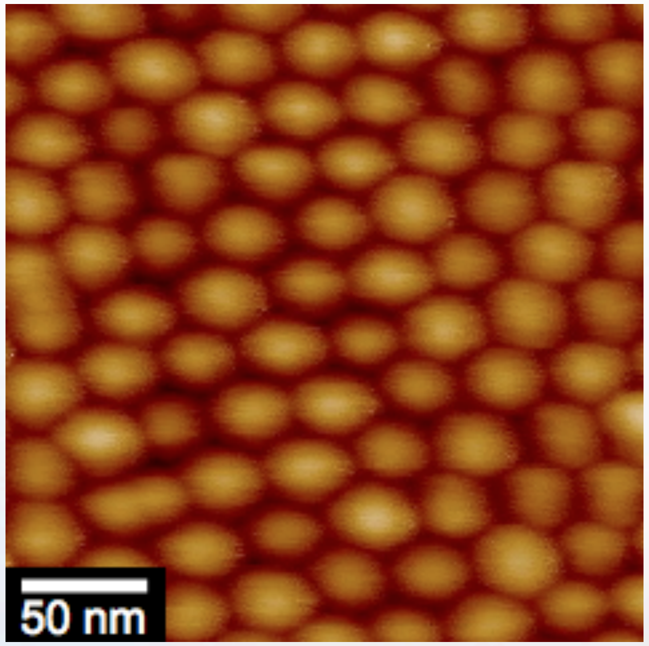
SAND2011-6647C

Chemical, Phase, and Interface Effects in Solution-Based Fabrication of Continuous and Nanopatterned Thin Film Ferroelectrics



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University of Florida, Gainesville, FL USA

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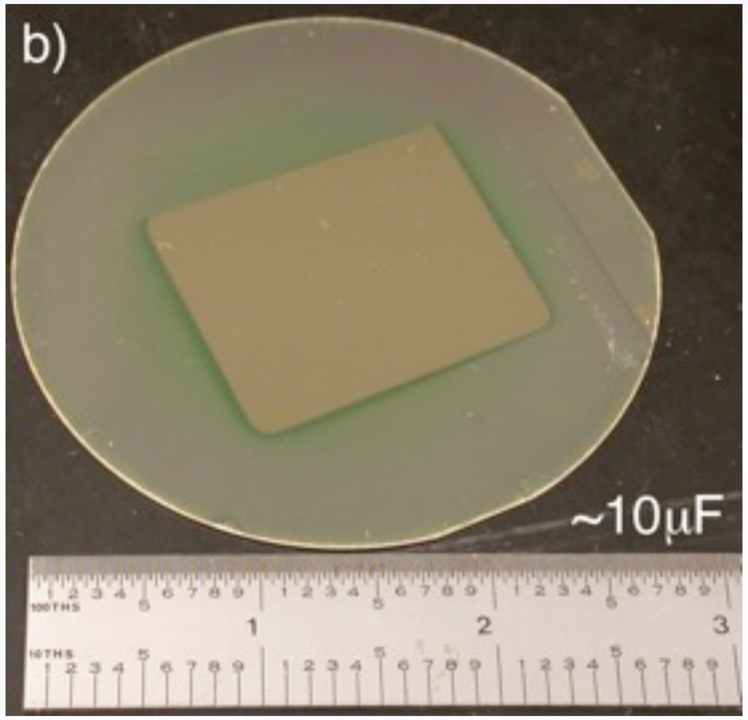
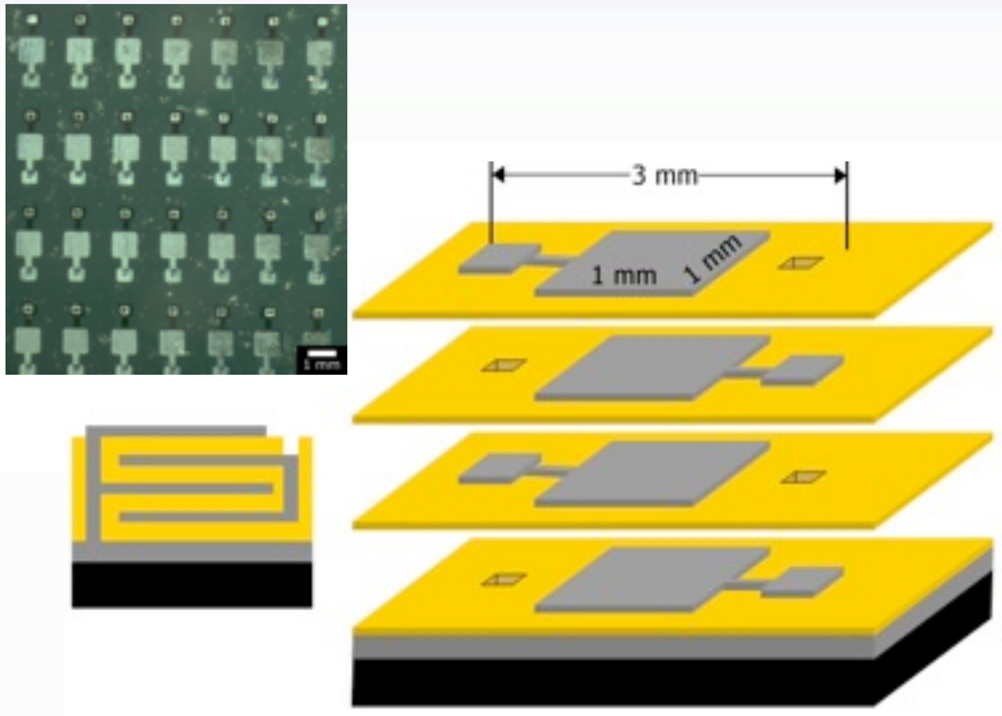
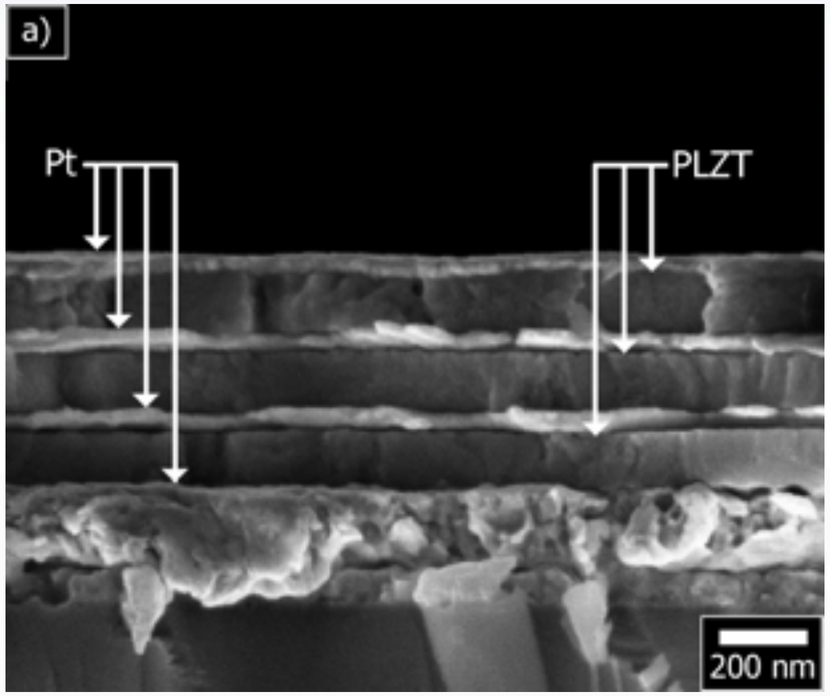
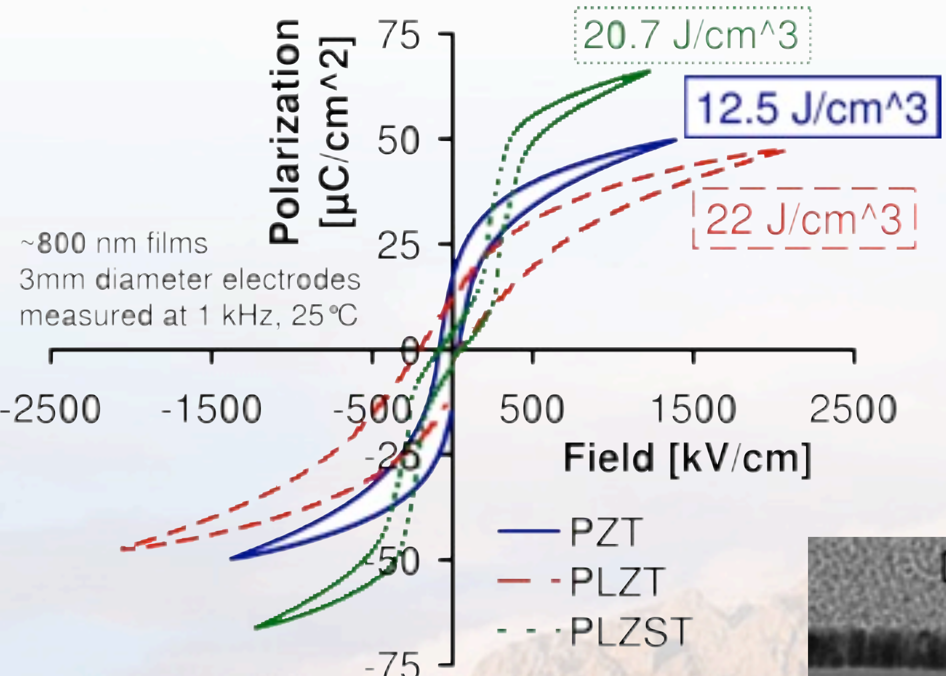
Functional Ferroelectric Thin Films



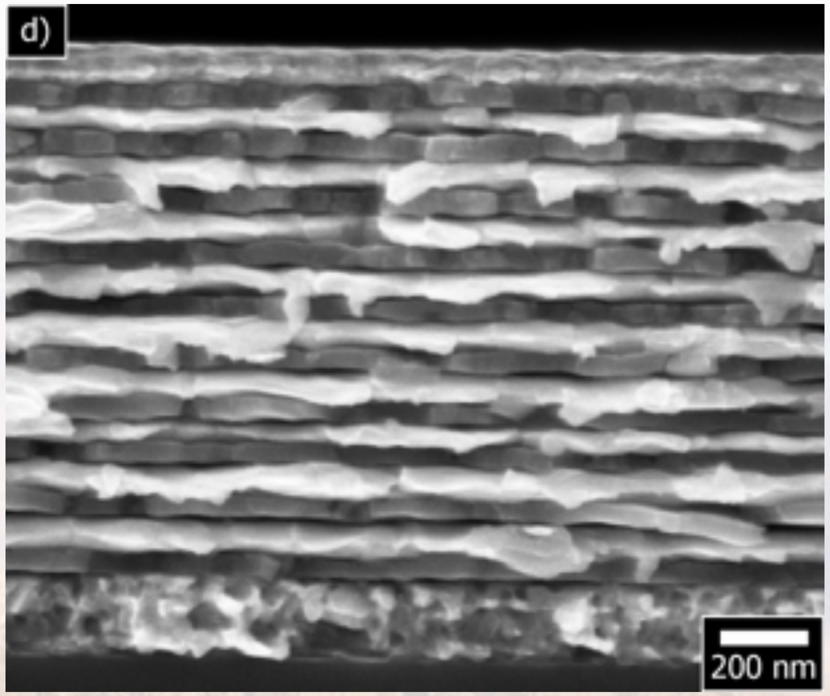




3 layers, ~120nm

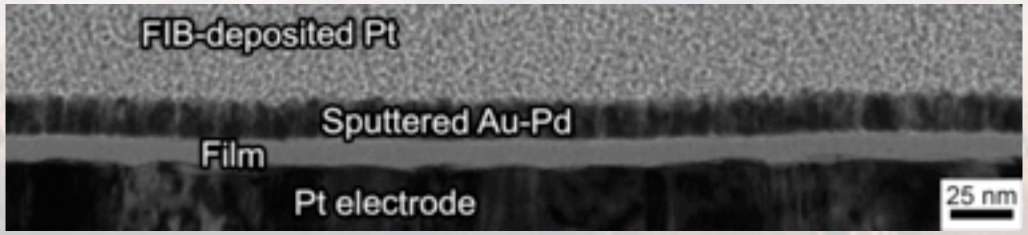


Ultimate thickness is limited by wetting/islanding behavior during deposition and crystallization



10 layers, ~50nm

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



Continuous single-phase films as thin as 9nm

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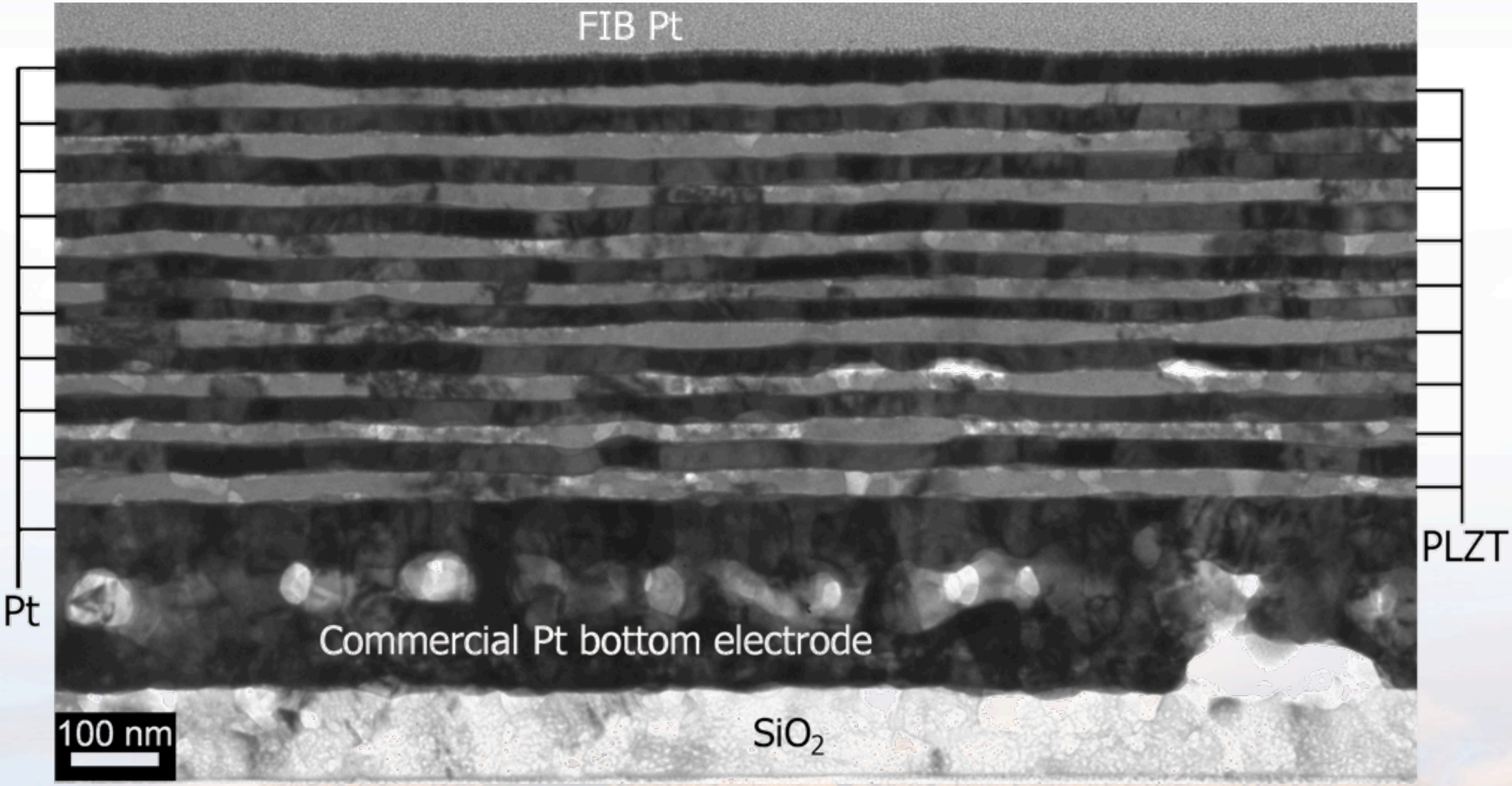
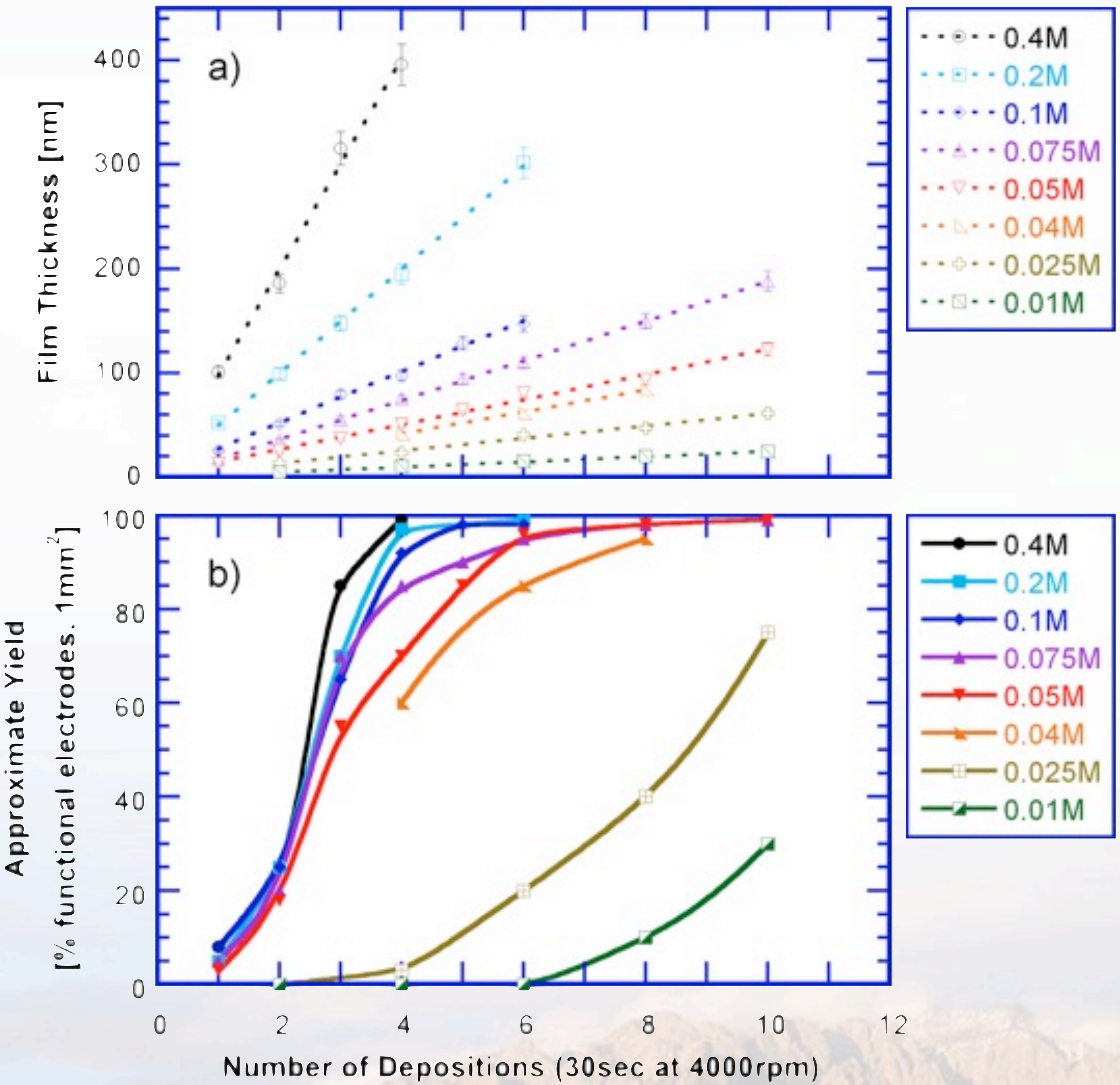
9 Dielectric Layers, ~20nm

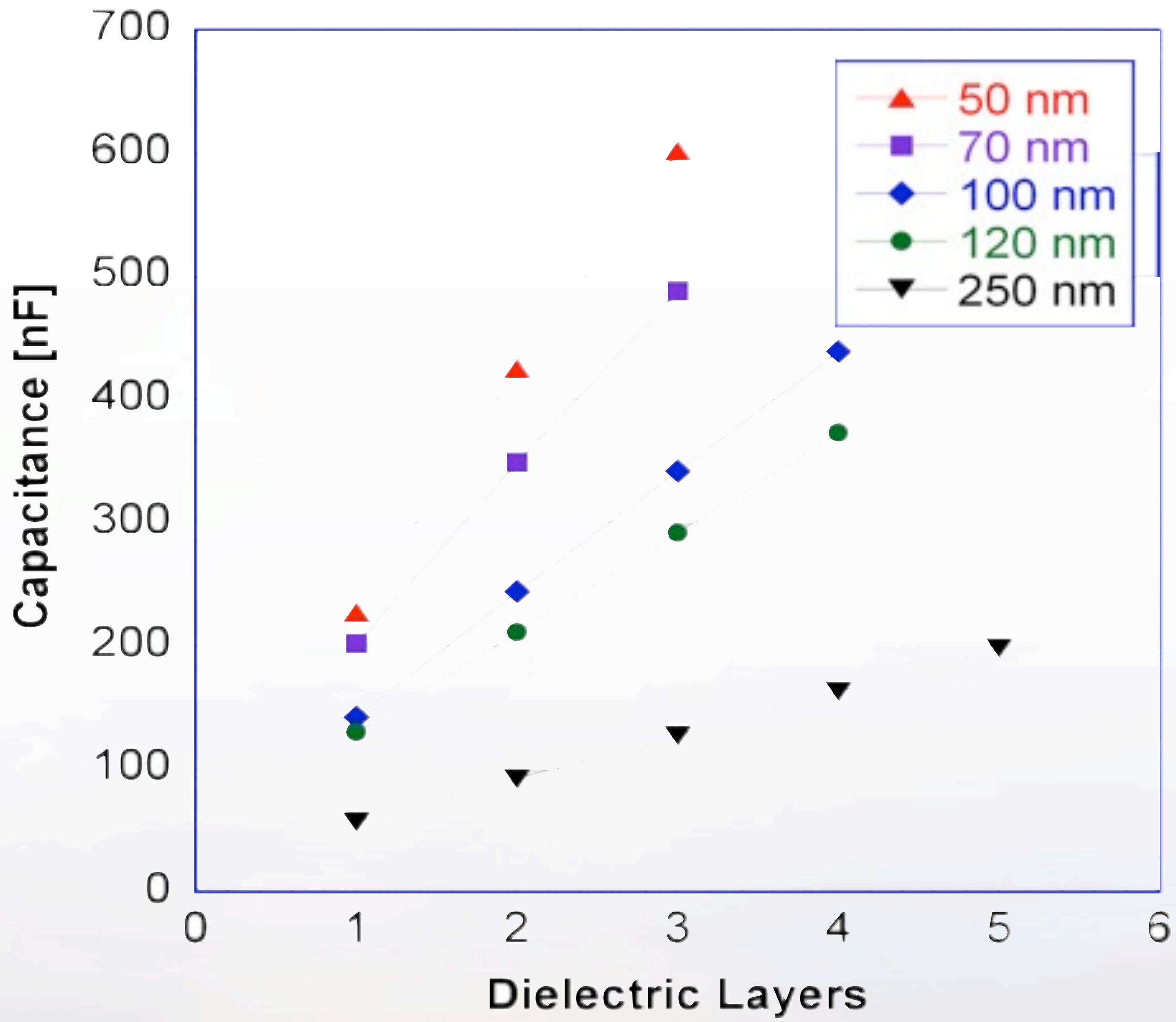


Brennecka, et al., **J. Mater. Res.** (2008)

Good News: Yield, Scaling



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



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

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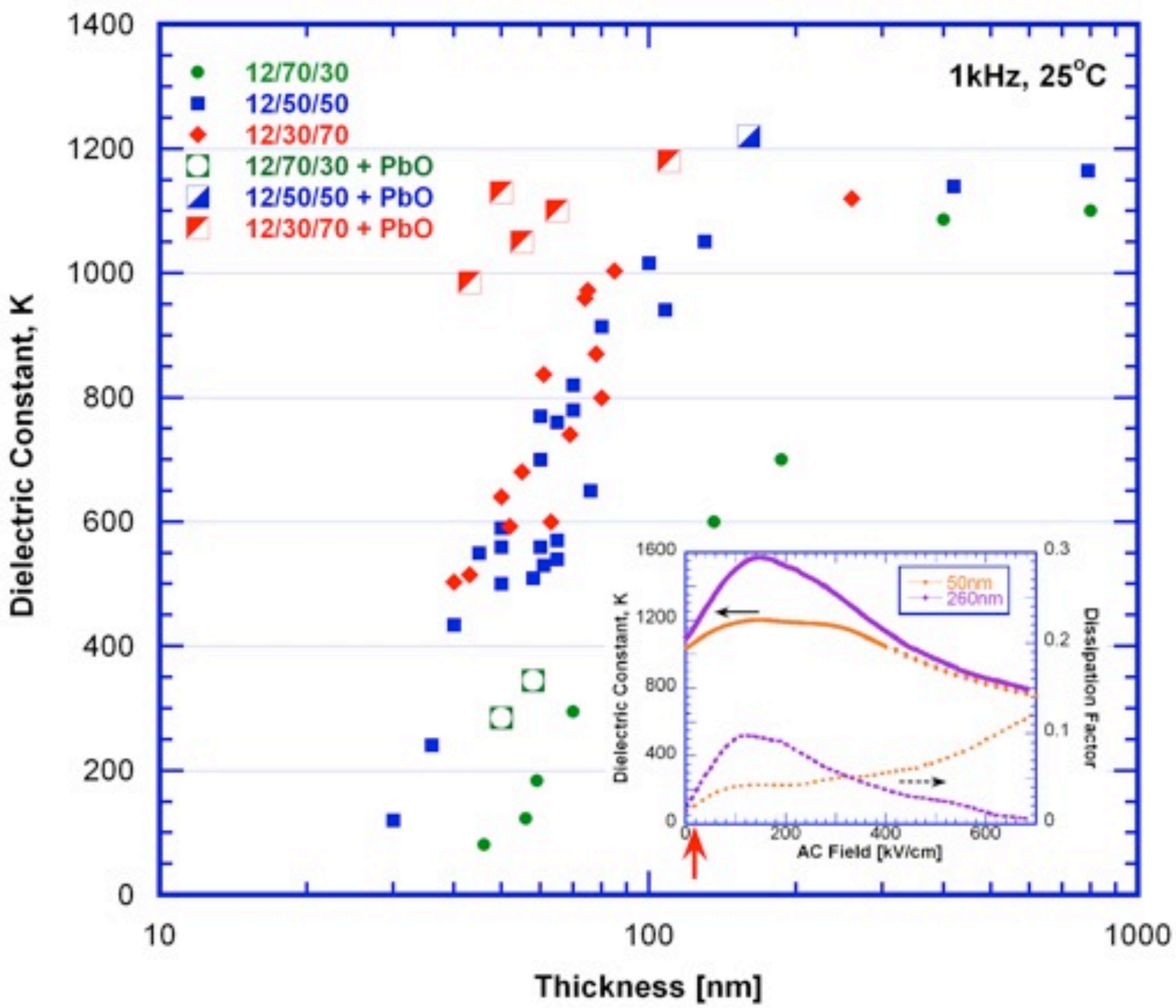
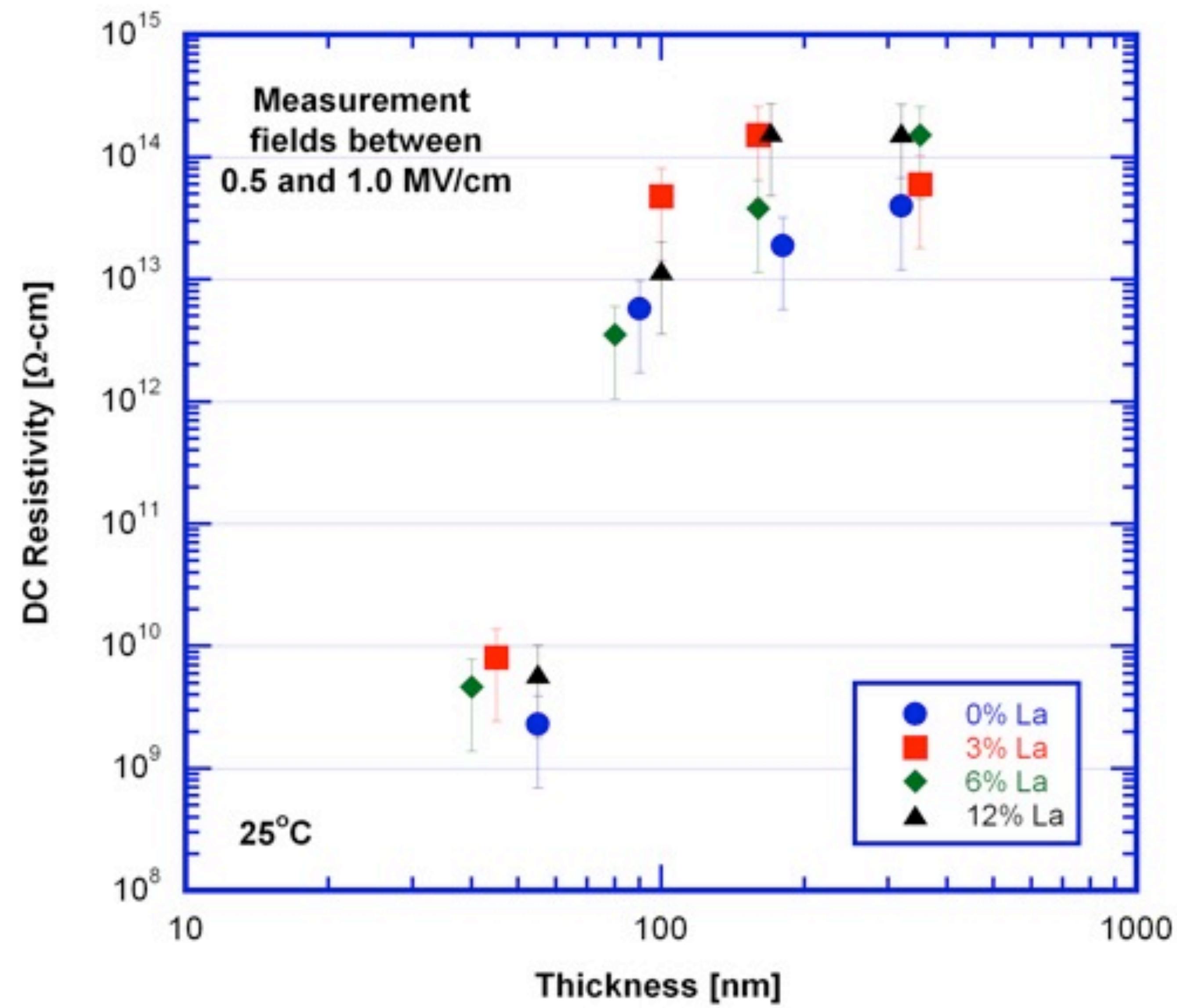
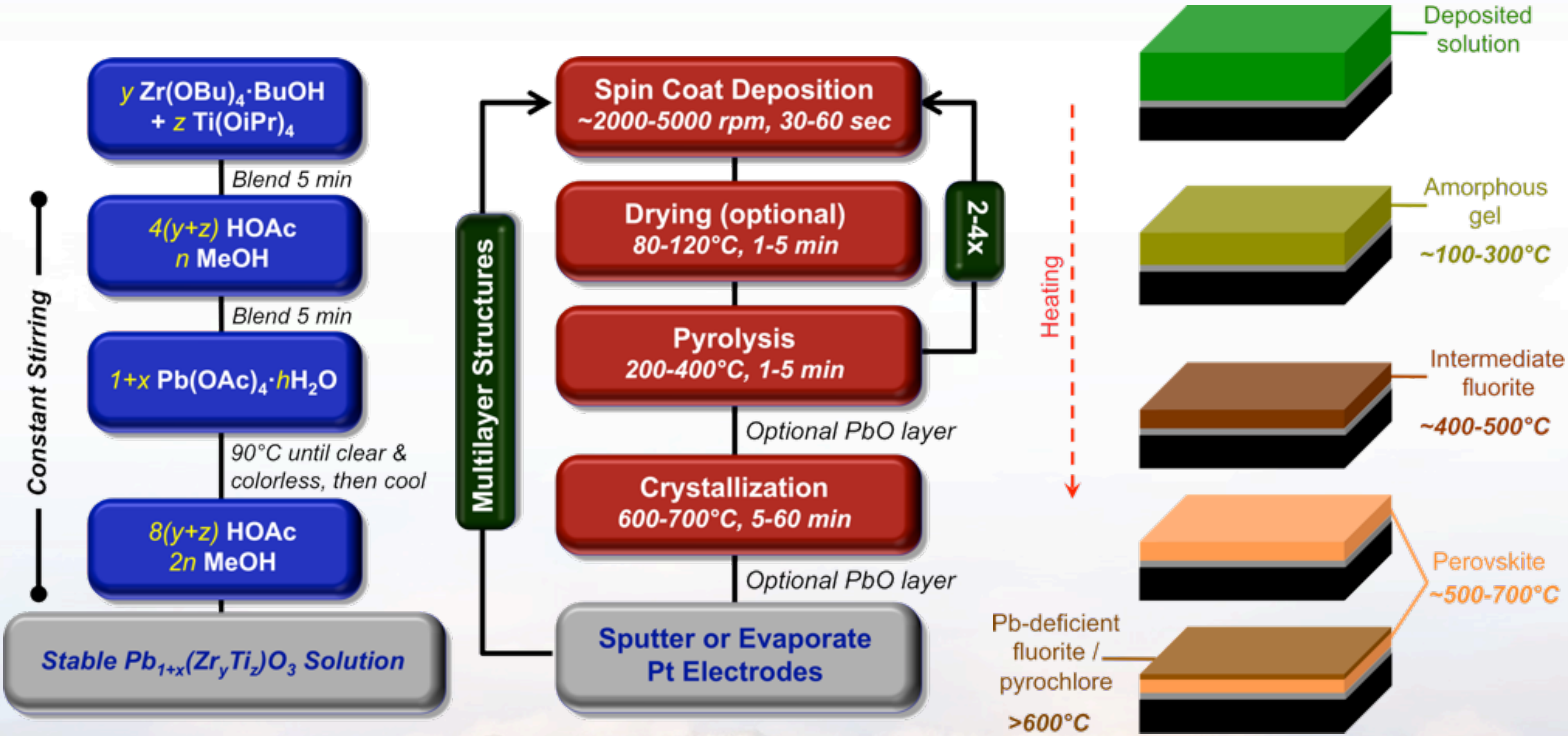
Bad News: Degradation in Thin Layers





*Brennecka and Tuttle, **J. Mater. Res.** (2007)*

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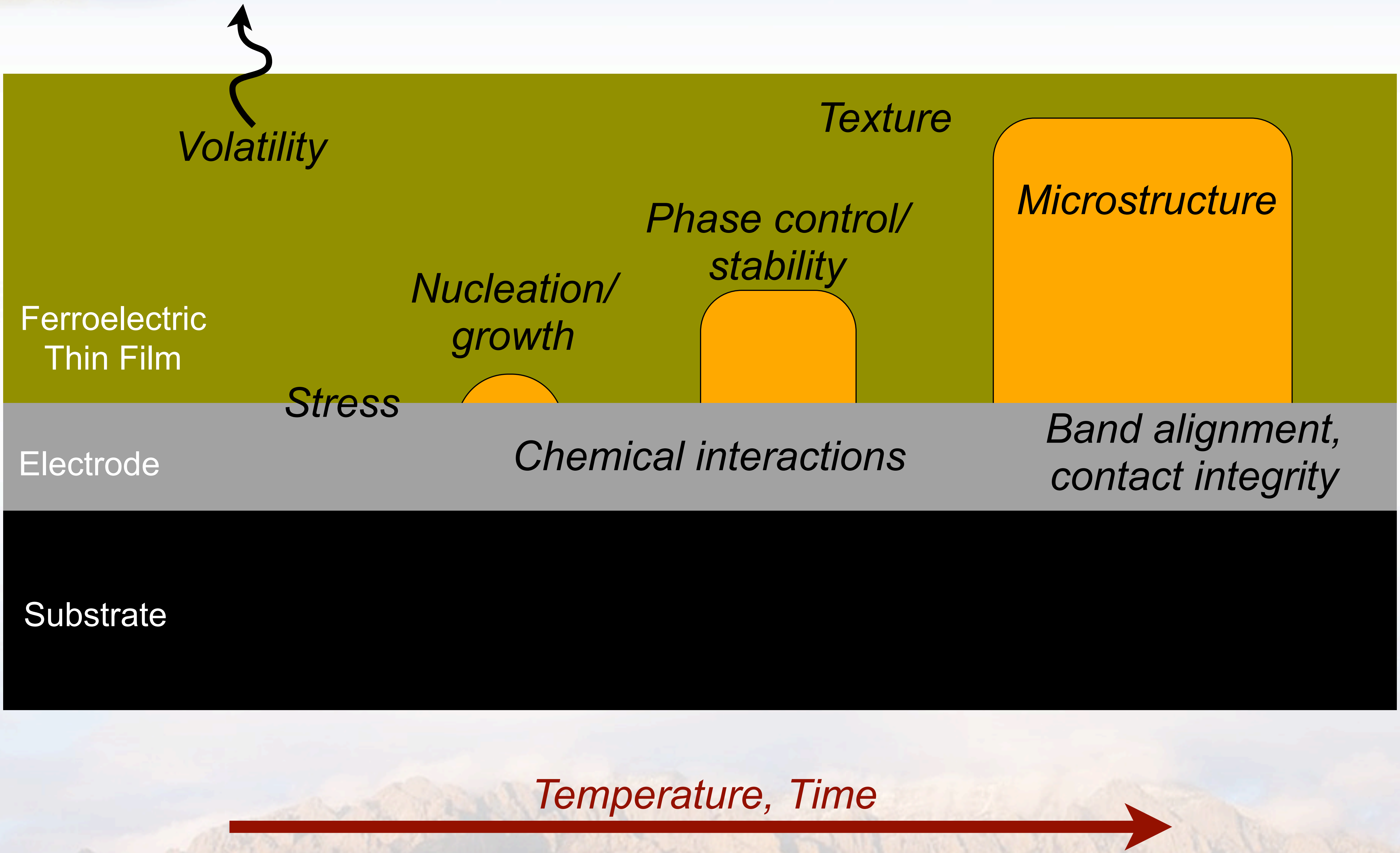
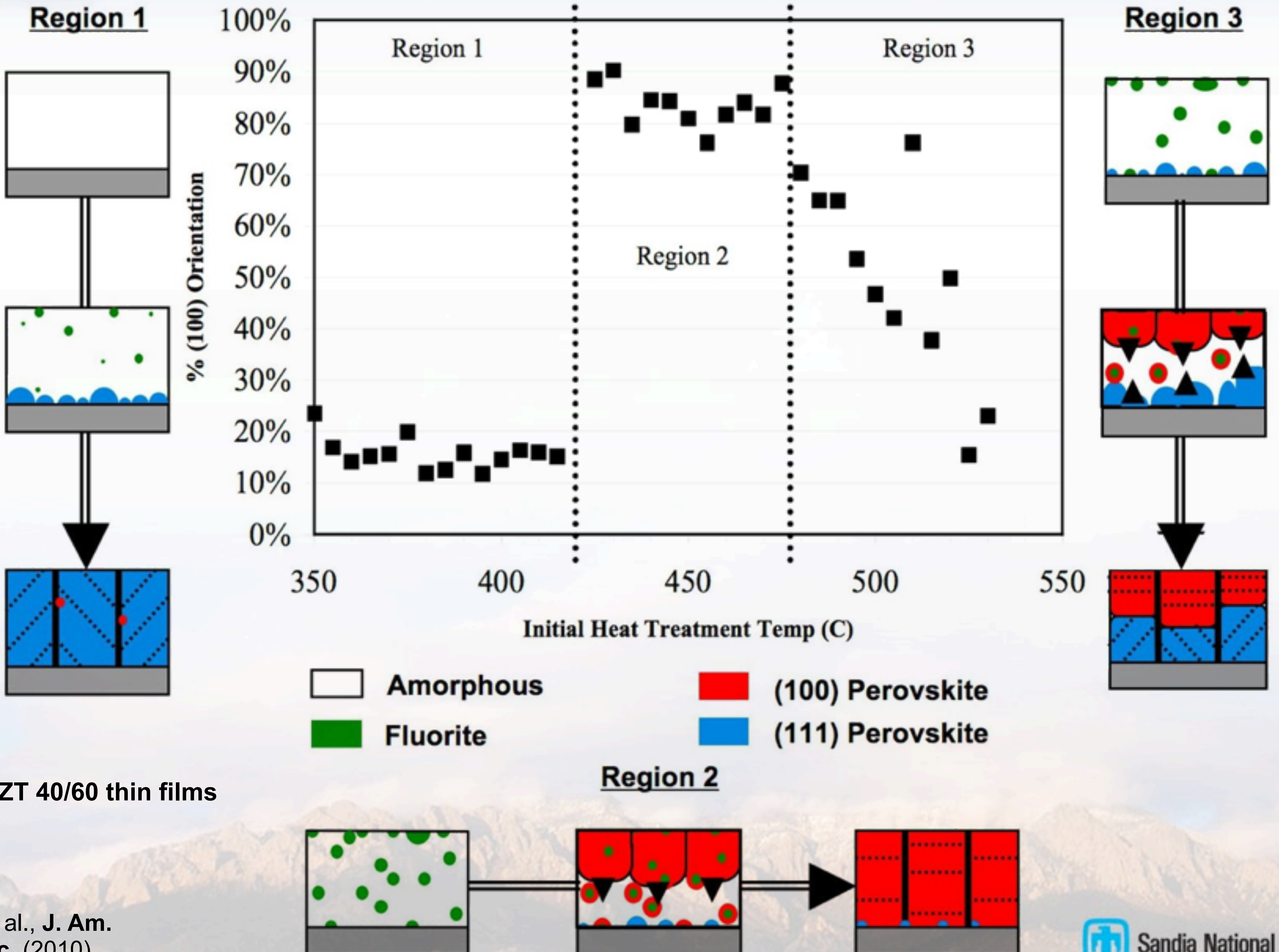
Understanding (and Control) of Processing/ Structure/Property Relationships



Control of Texture via Nucleation and Growth



PZT 40/60 thin films

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

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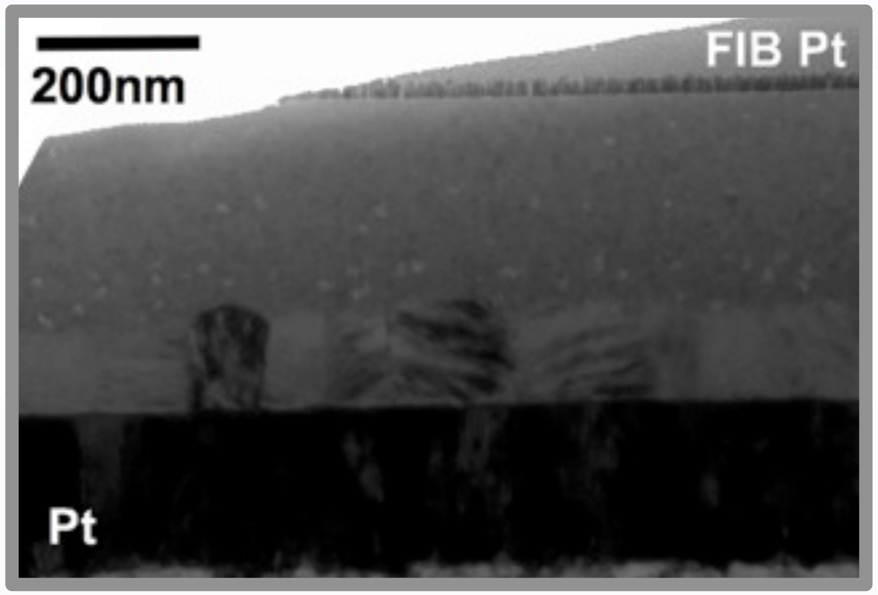
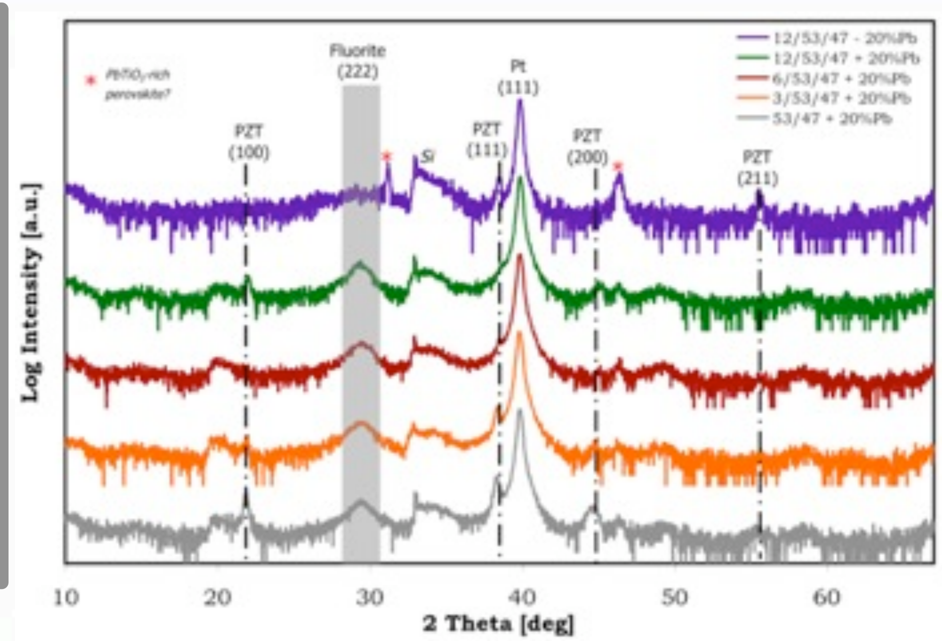
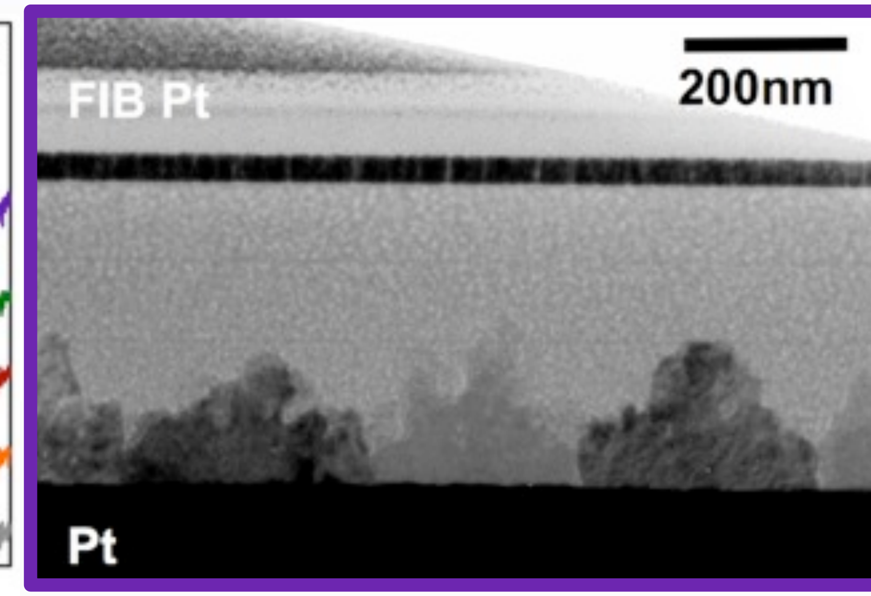
A-site cation effects on nucleation

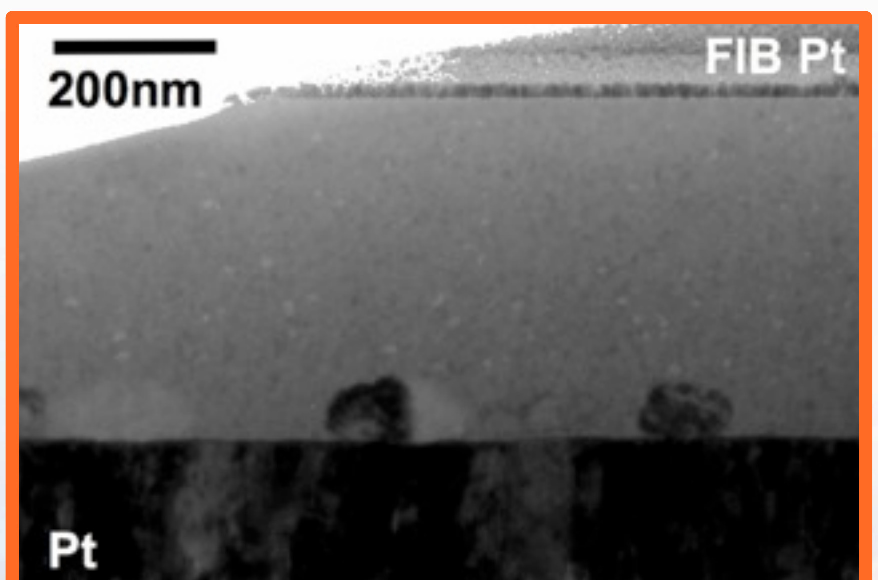


PZT 53/47, 20% excess Pb, 550C 1hr

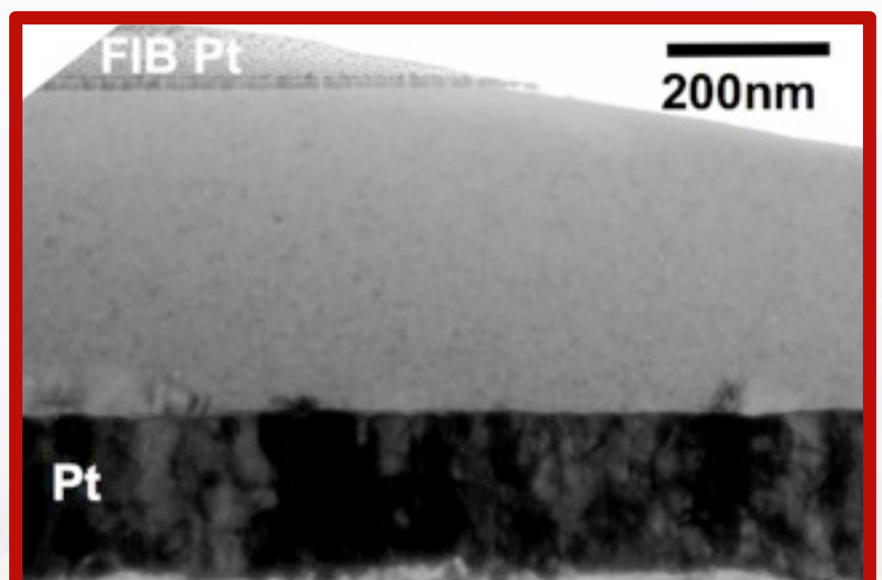




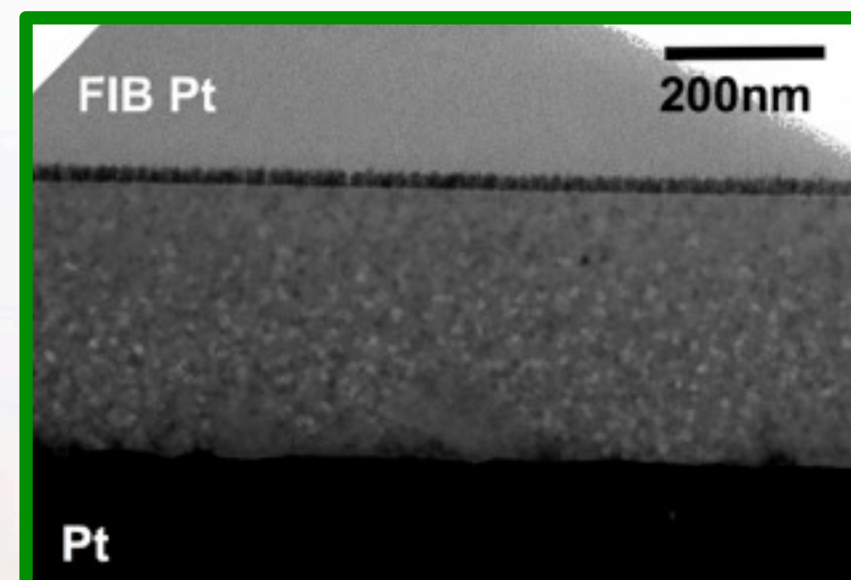
PLZT 12/53/47, 20% Pb deficient, 550C 1hr



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

fix brightness/contrast

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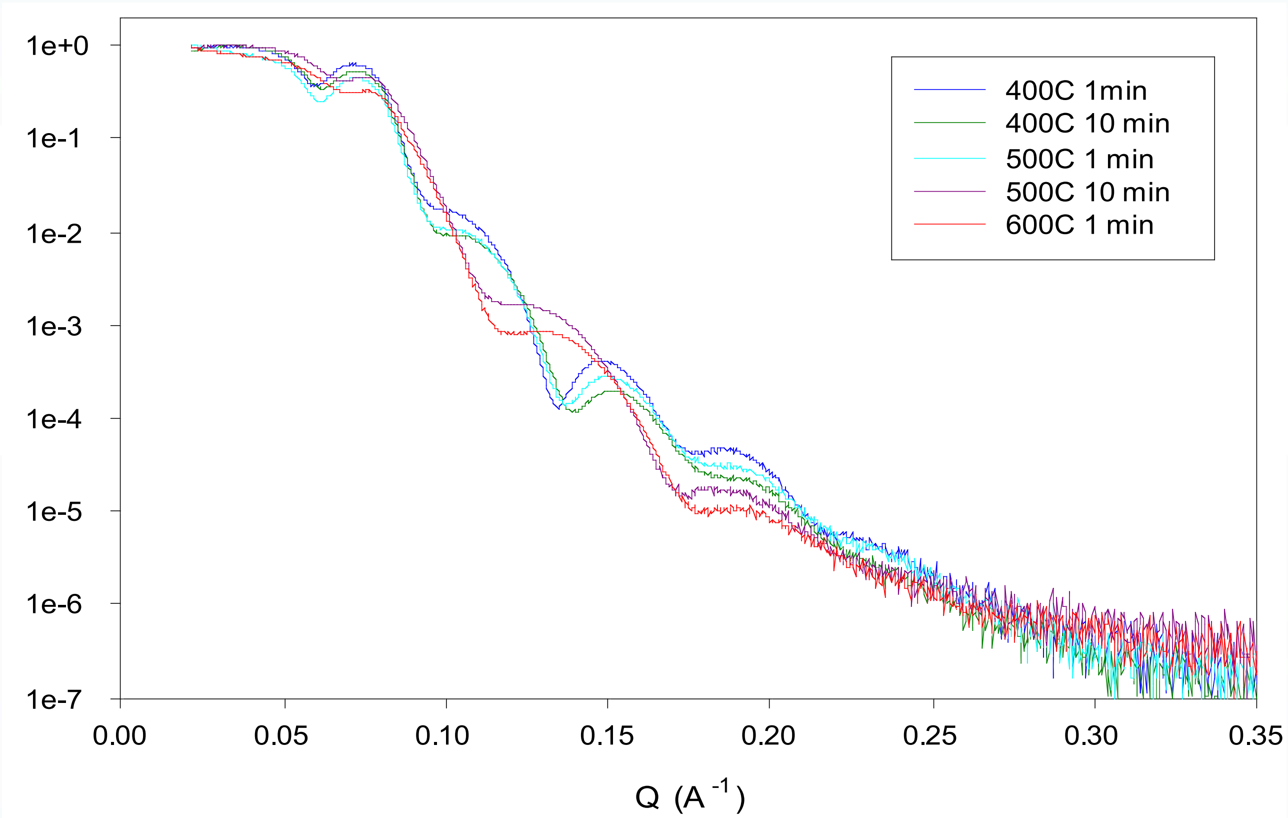
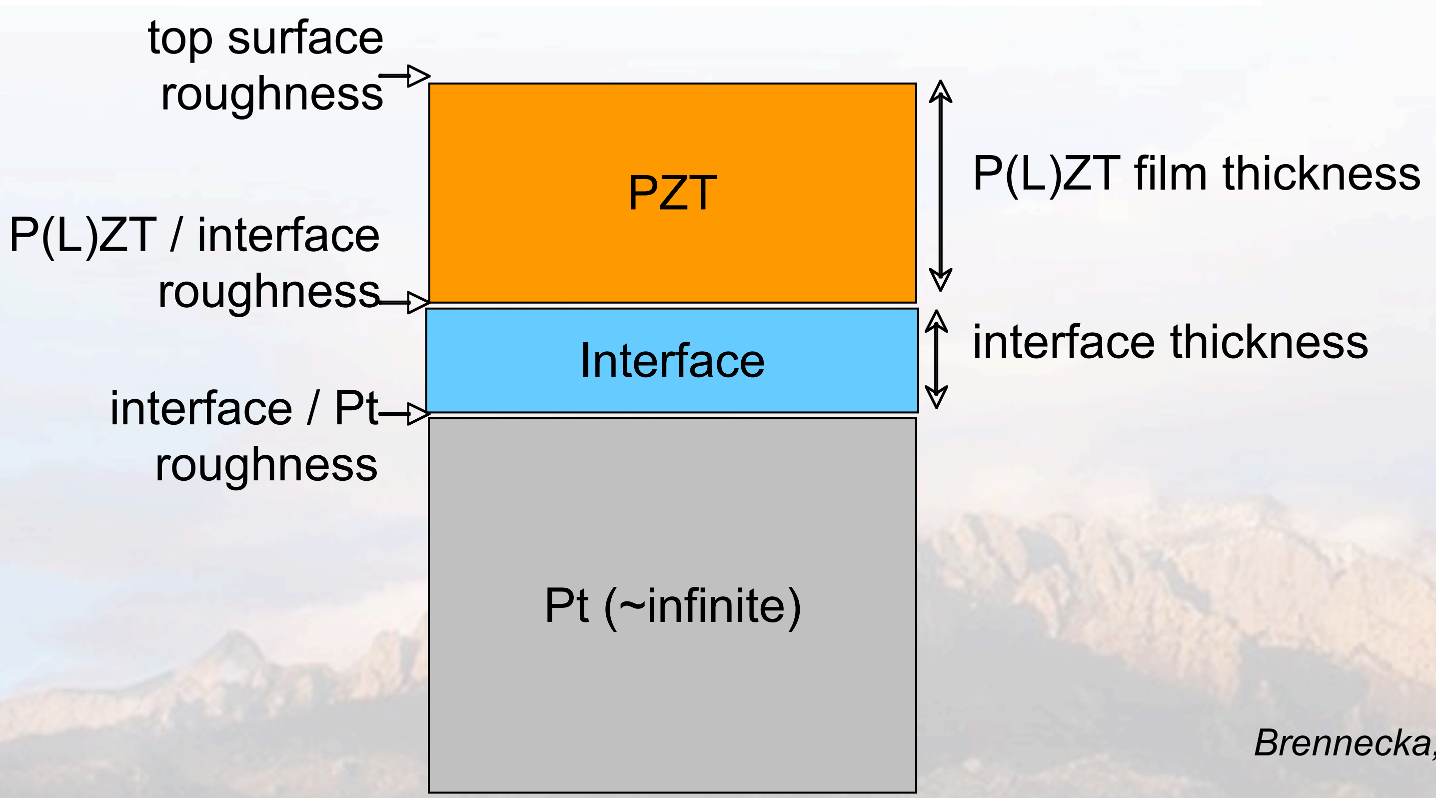
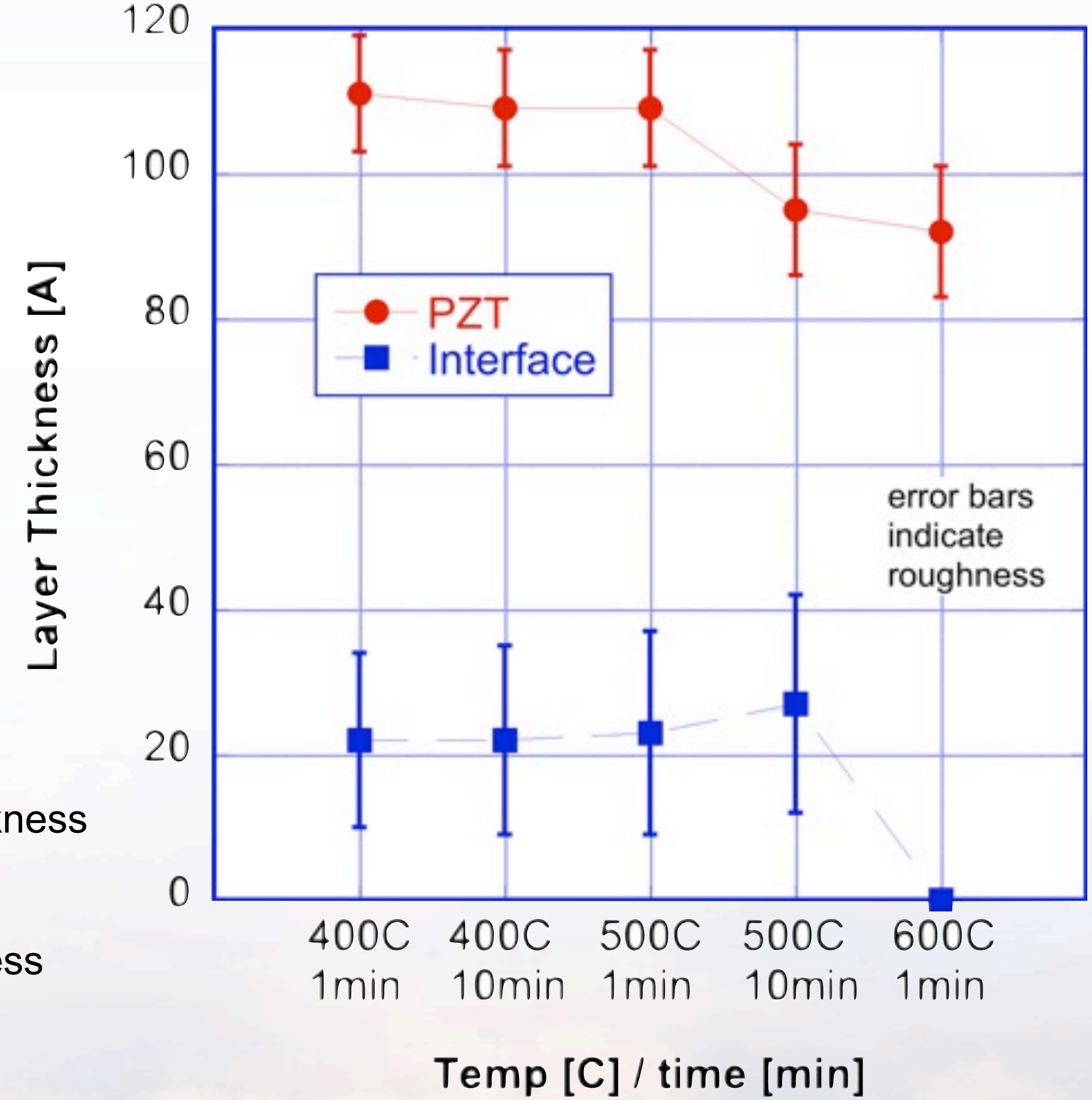
PLZT-Pt Interactions

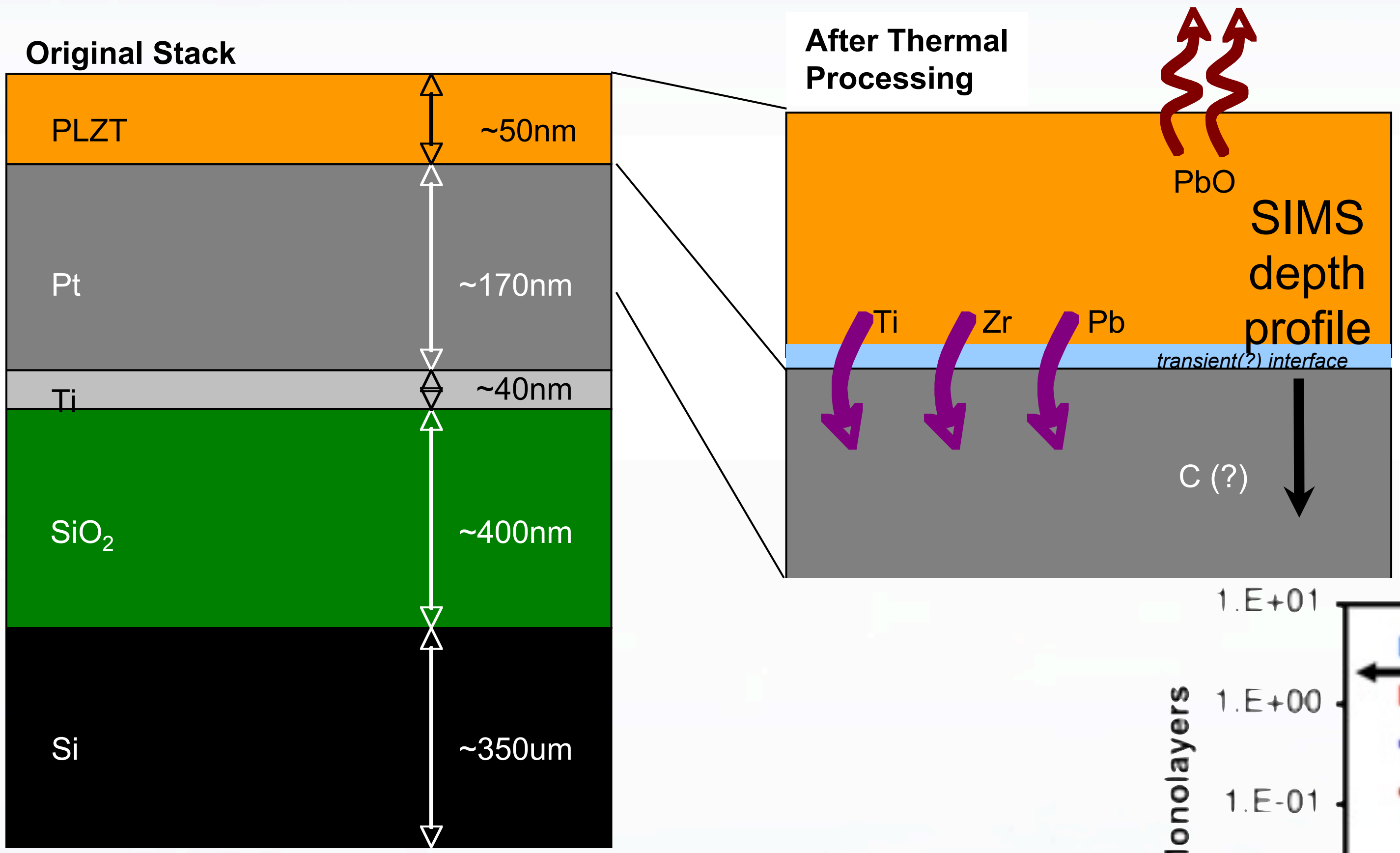


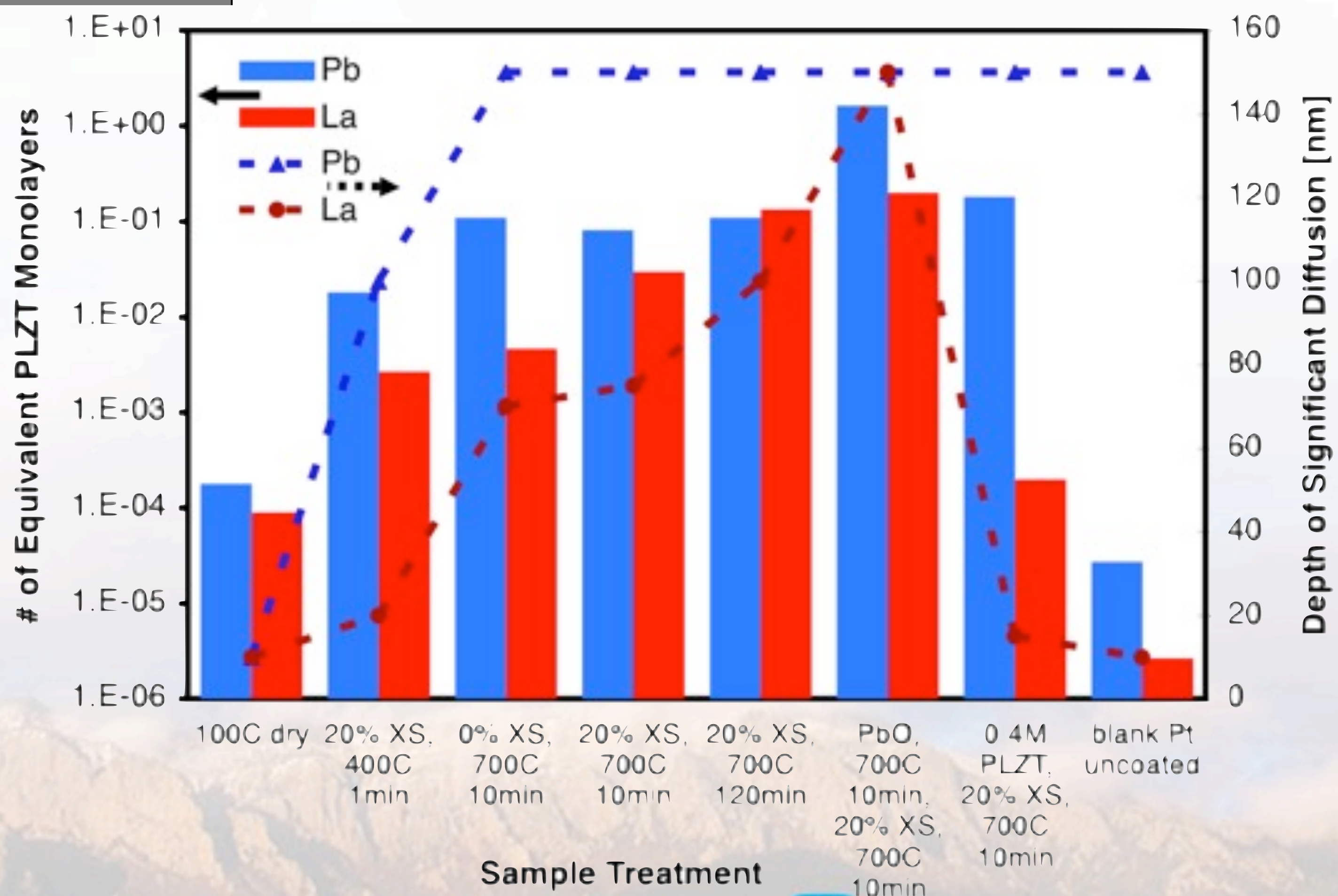




Brennecka, et al., ***Proc. ISAF*** (2008)

PLZT-Pt Interactions





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

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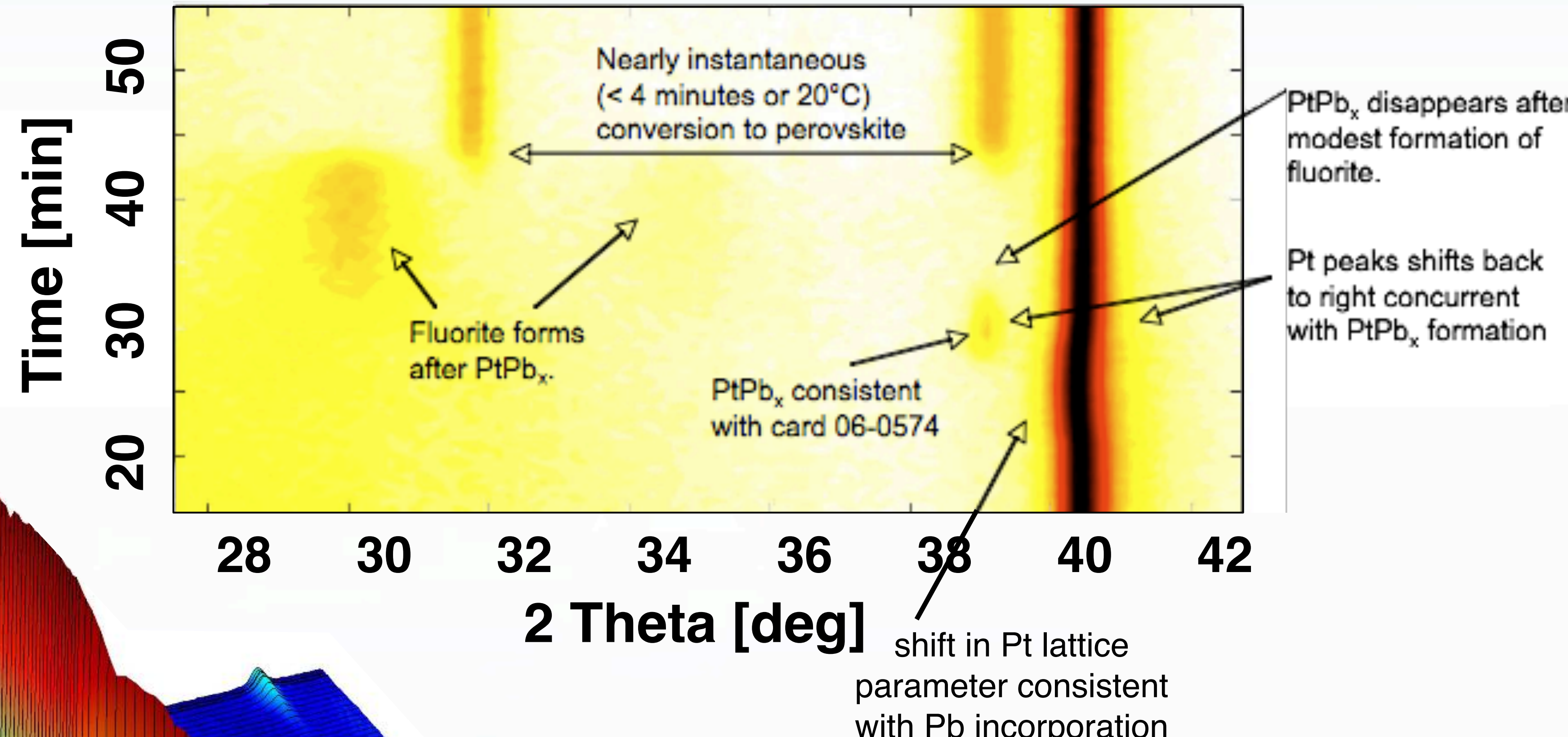
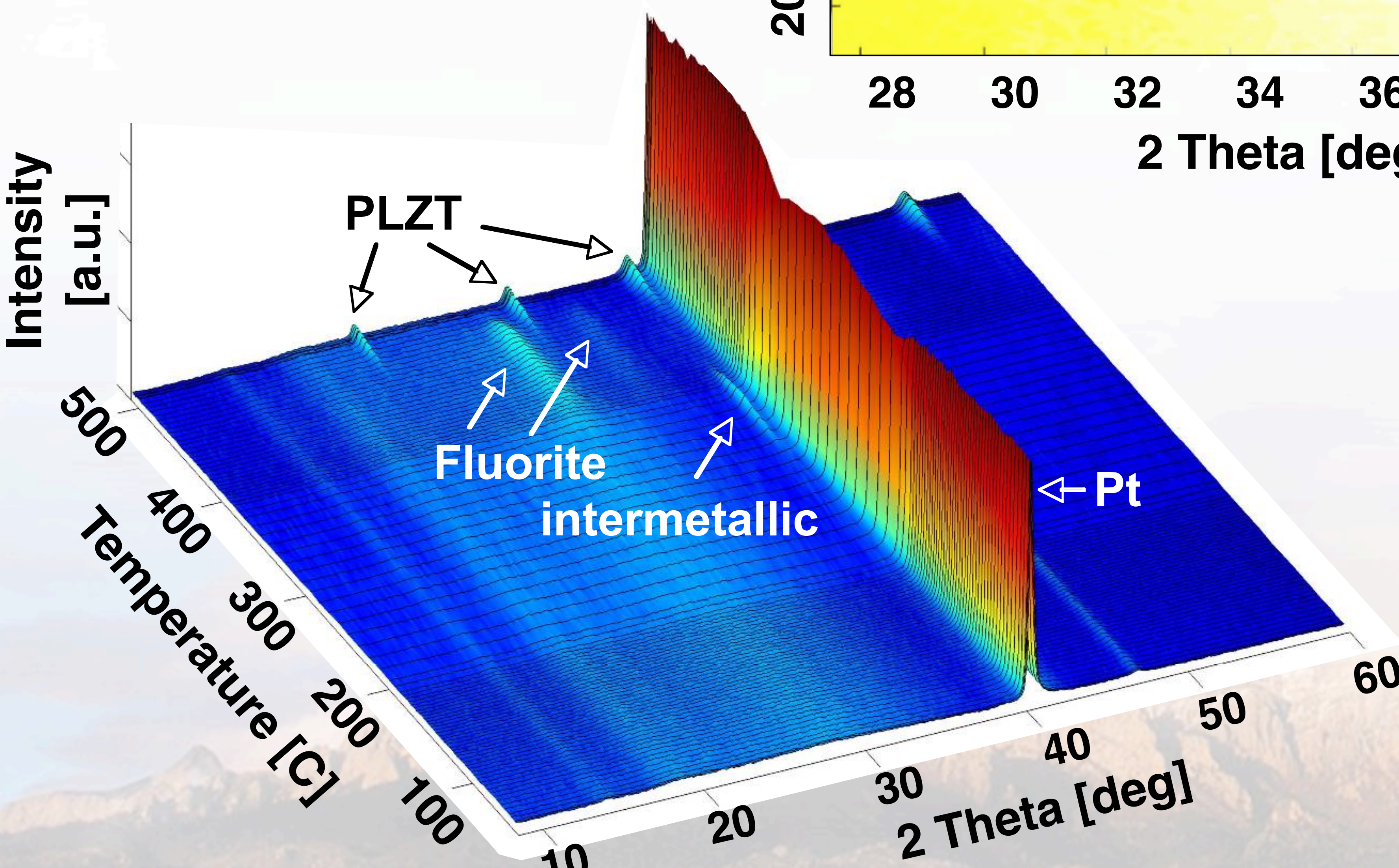
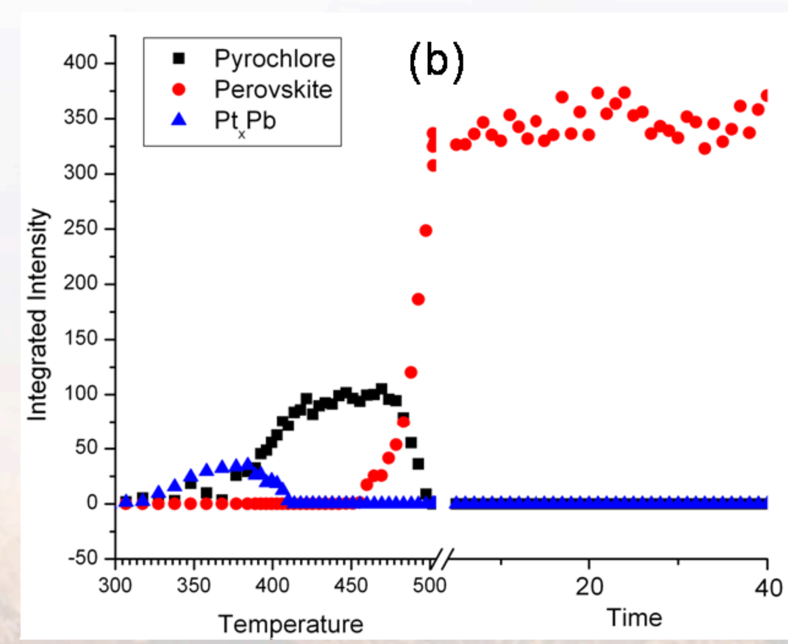
in collaboration with
Jacob Jones and
Krishna Nittala,
University of Florida

in-situ X-Ray Diffraction

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



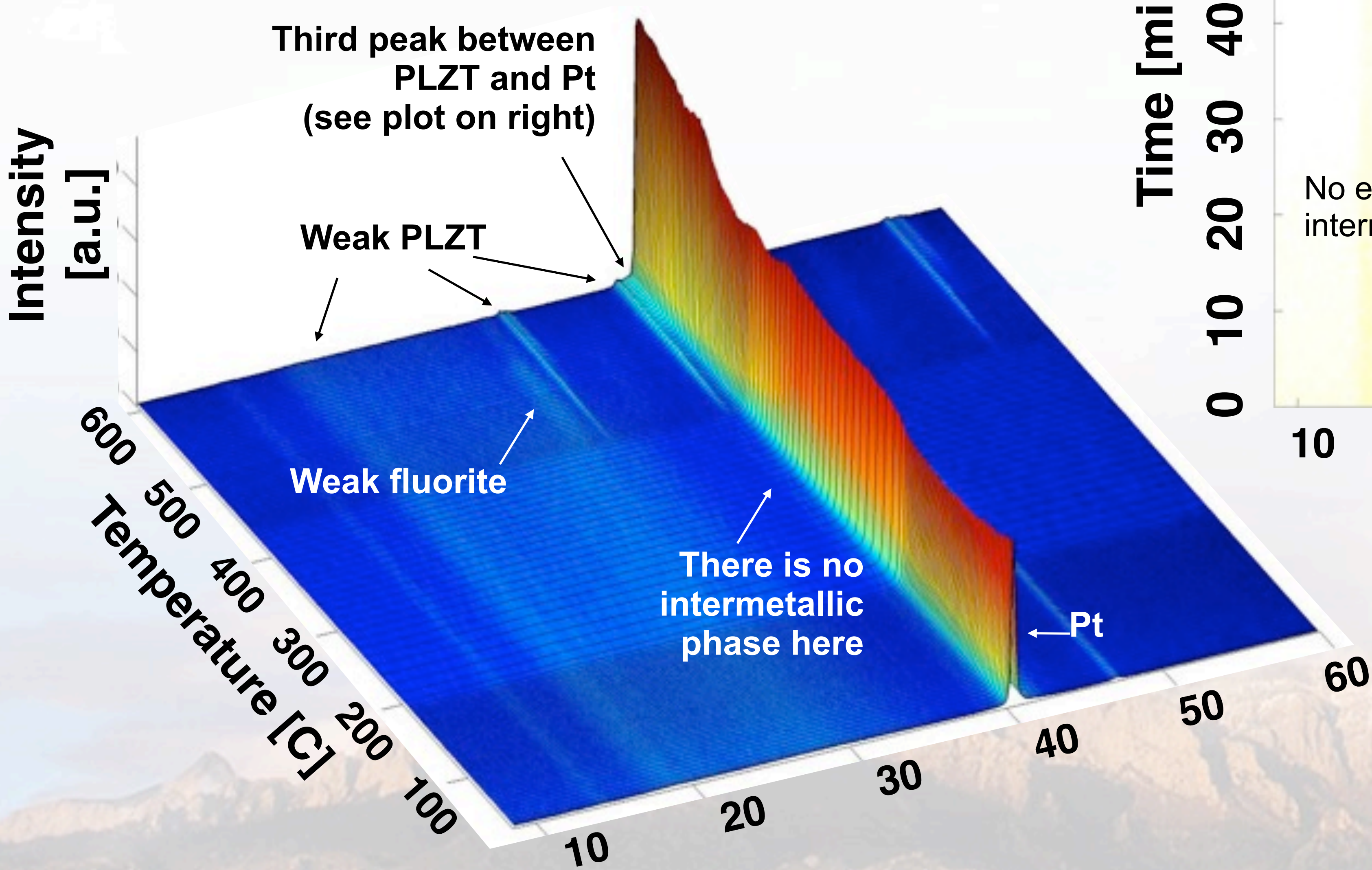


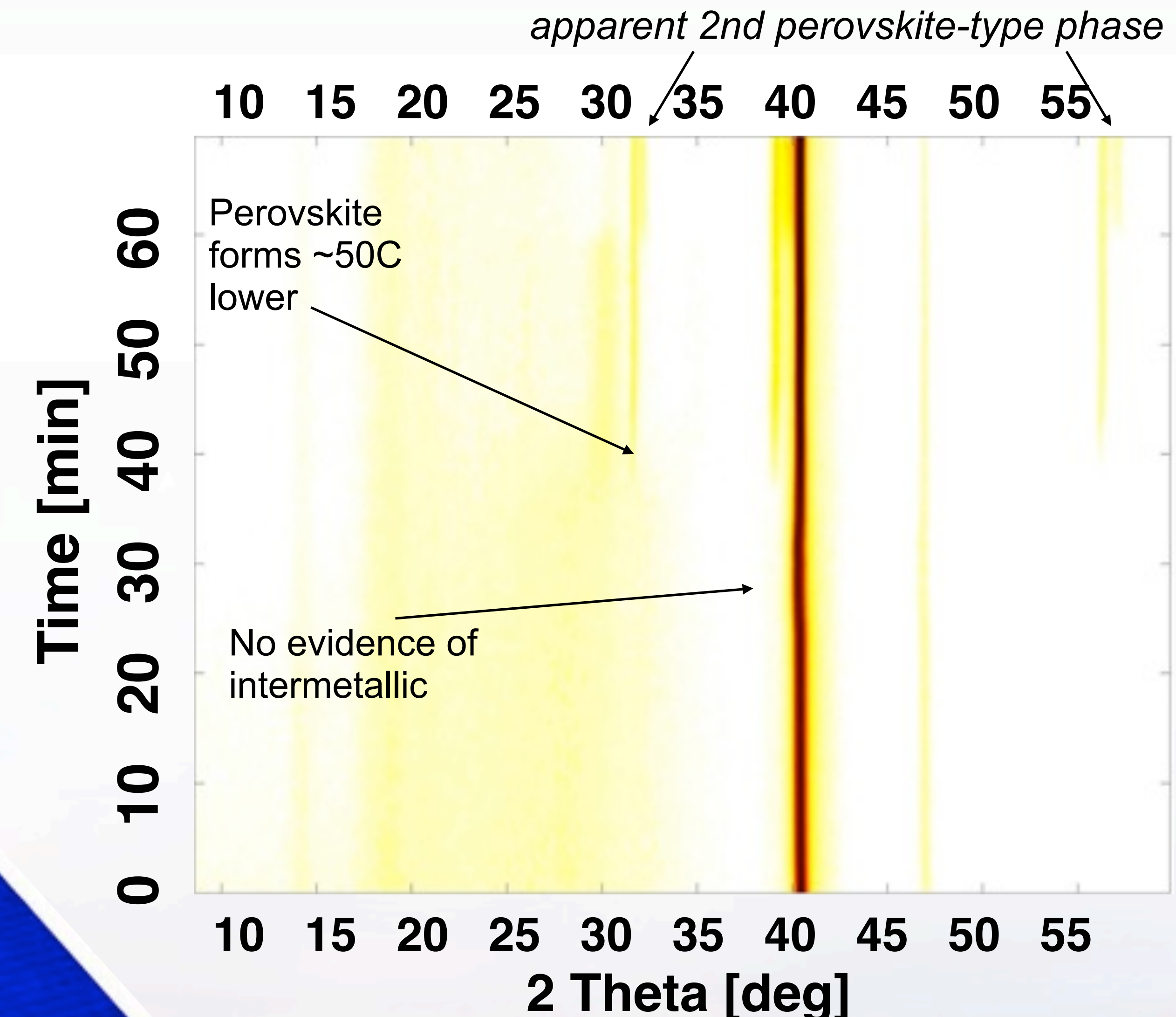


in collaboration with
Jacob Jones and
Krishna Nittala,
University of Florida

in-situ X-Ray Diffraction

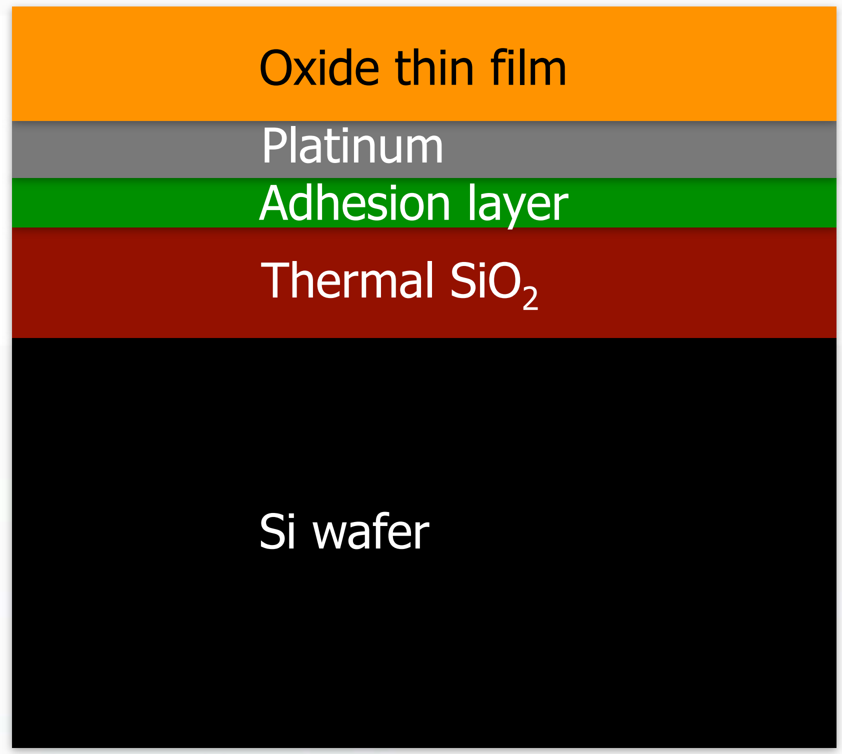
Crystallization of PLZT thin film from a solution containing 20% Pb deficiency

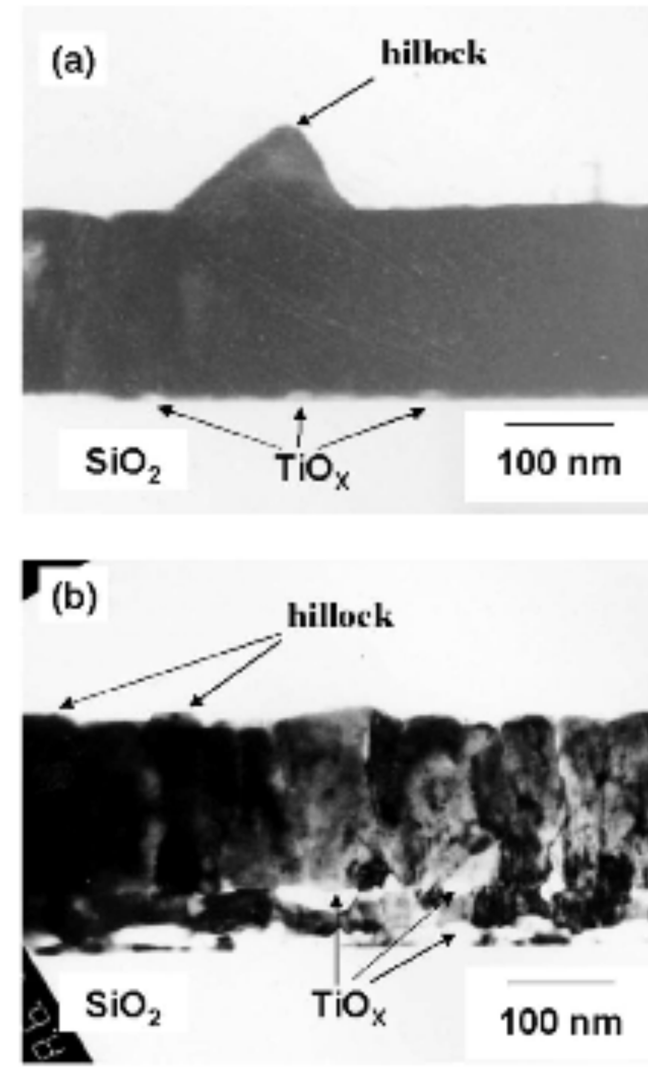




Electrode Adhesion Layer

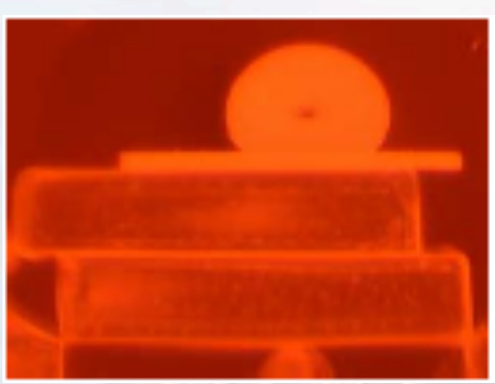
- Platinized Si is common substrate
  - 400 – 500 nm thermal SiO_2
  - 20 – 40 nm adhesion layer: typically Ti or TiO_2
  - 100 – 200 nm Pt



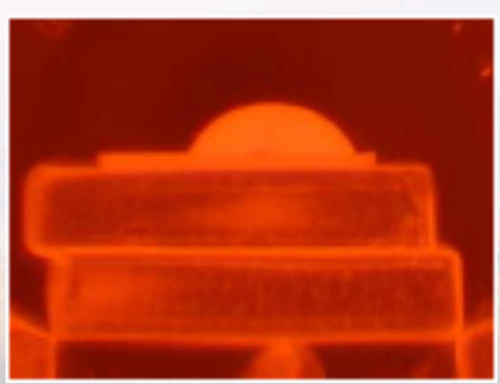


- Other adhesion layers:
  - Zr, ZrO_2 (Al Shareef et al., 1997, Zohni et al., 2008)
  - Ta (Kissurska et al., 1995)
  - Al_2O_3 (Halder et al., 2007)

- 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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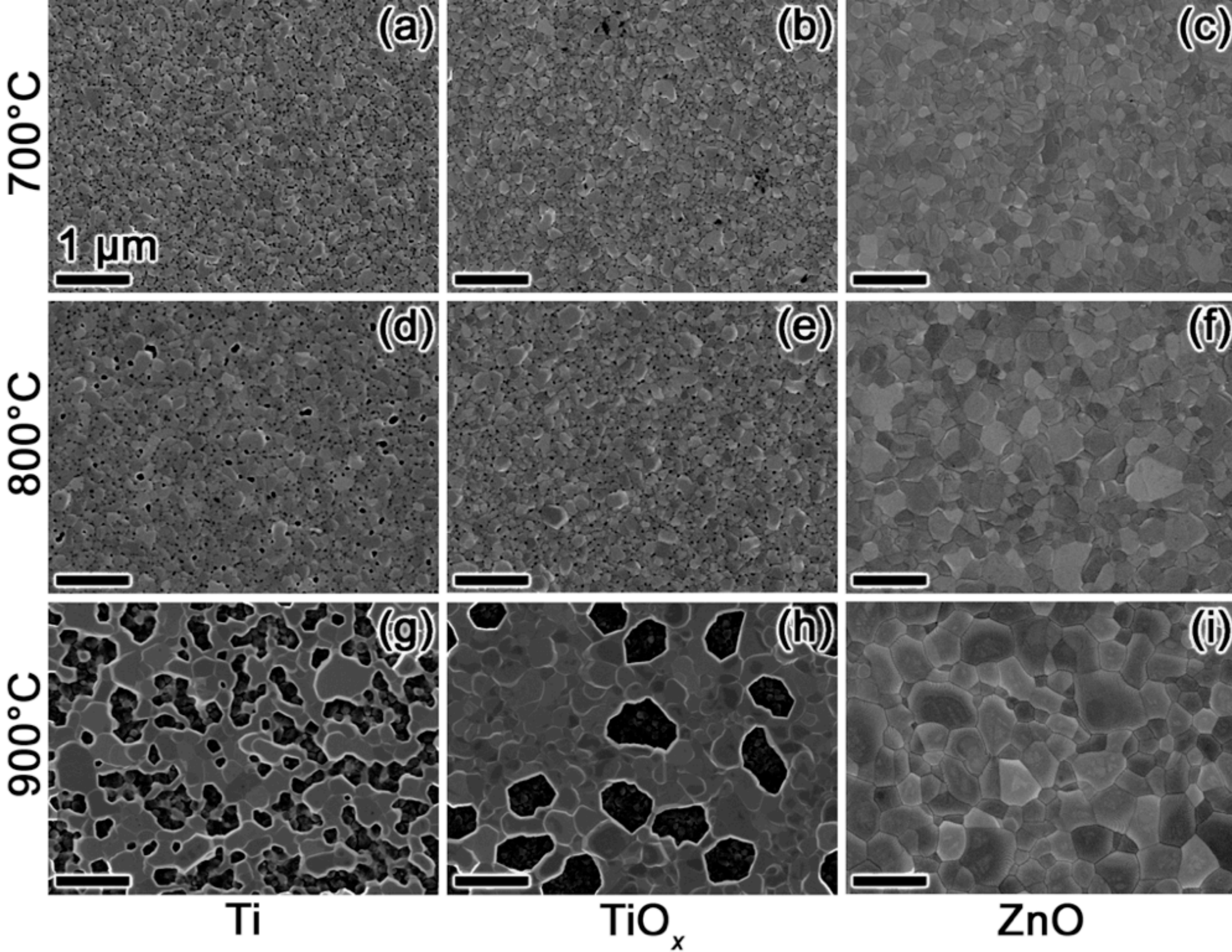
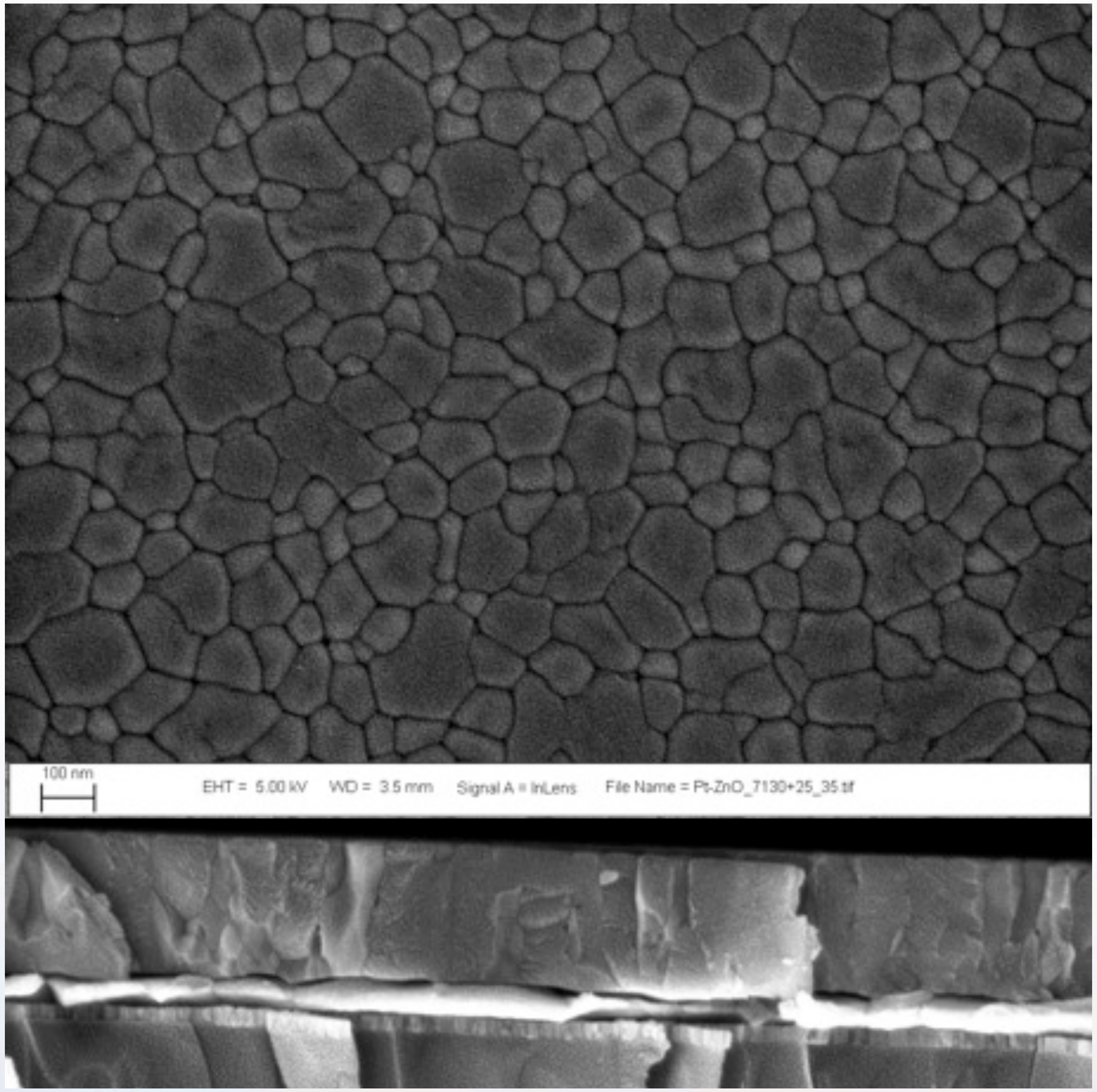
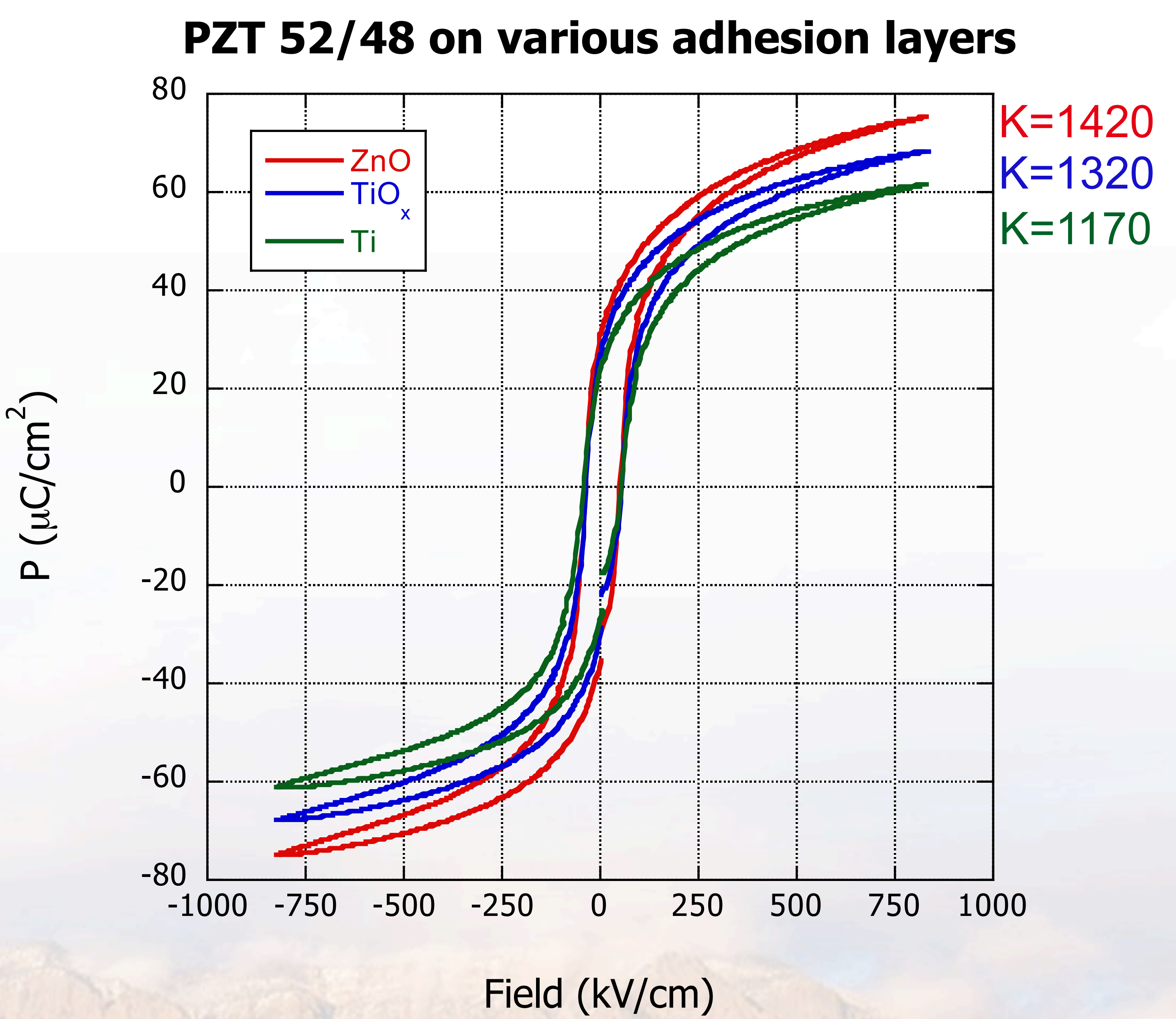


700°C
800°C
900°C
(a)
(b)
(c)
(d)
(e)
(f)
(g)
(h)
(i)
1 μm
Ti
TiO$_x$
ZnO

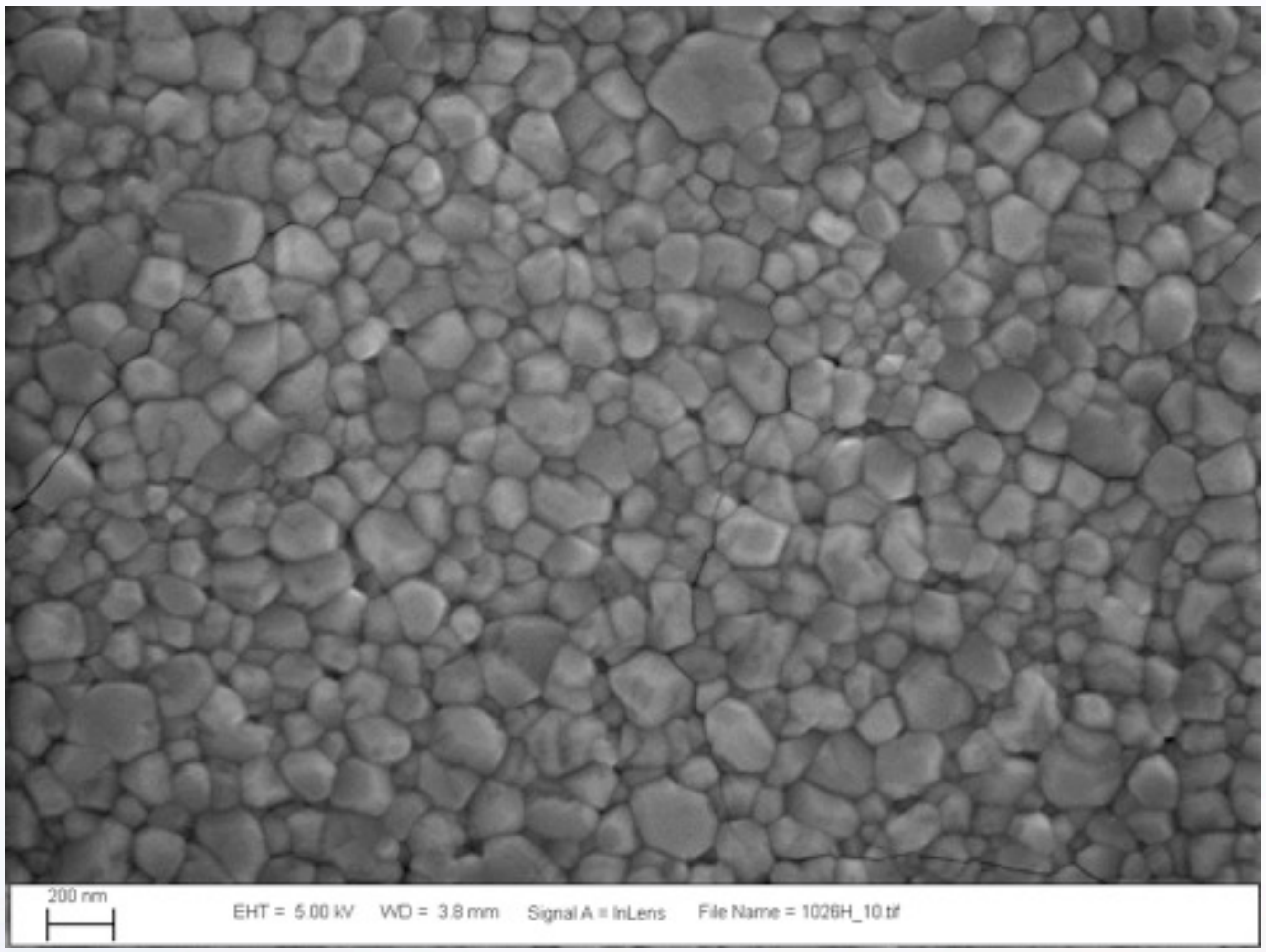
Resulting Ferroelectric Films



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

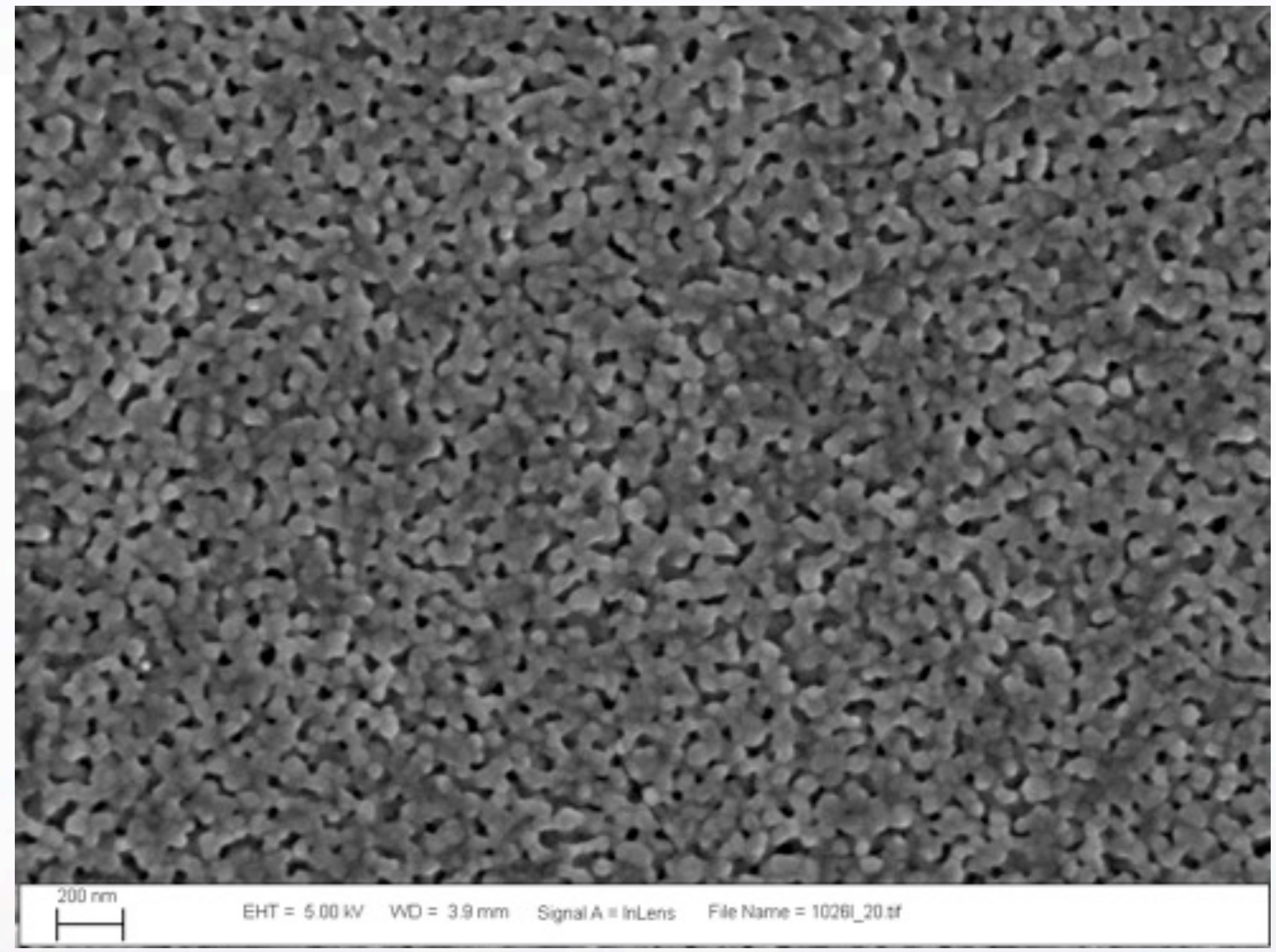


$BaTiO_3$ on Platinized Silicon



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

K = 1350



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

K = 400

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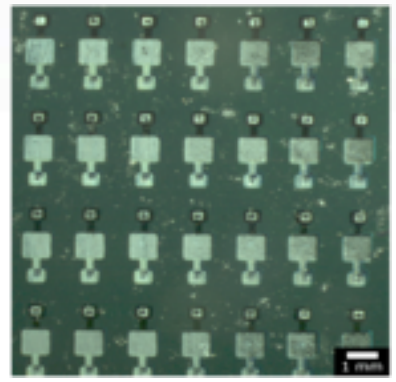
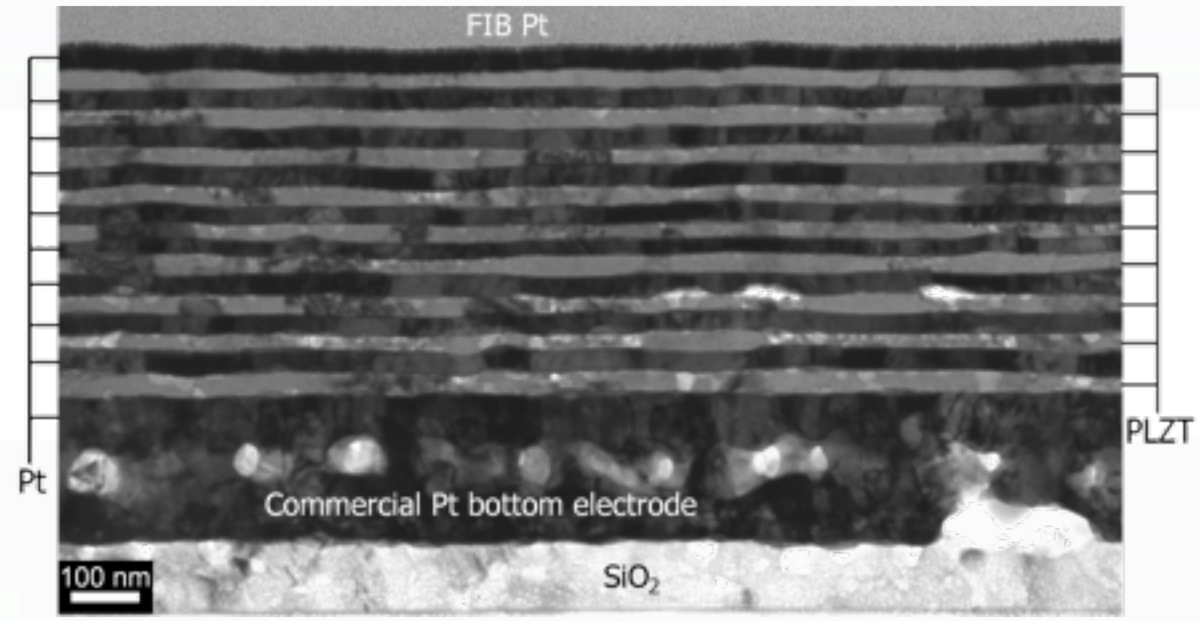
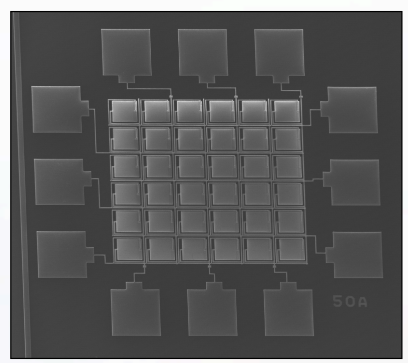
From Blanket Film to Functional Structure

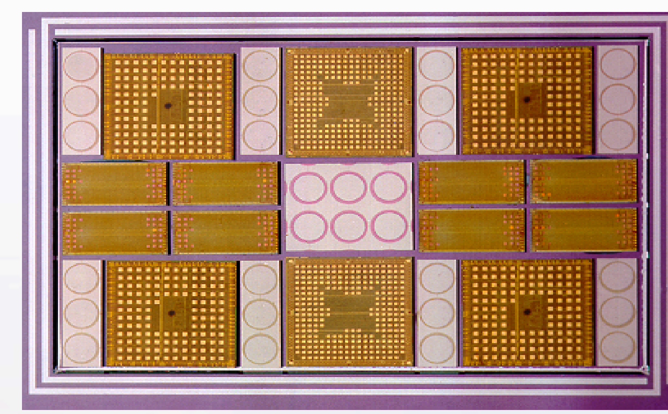


Functional PZT-based multilayer capacitor structures





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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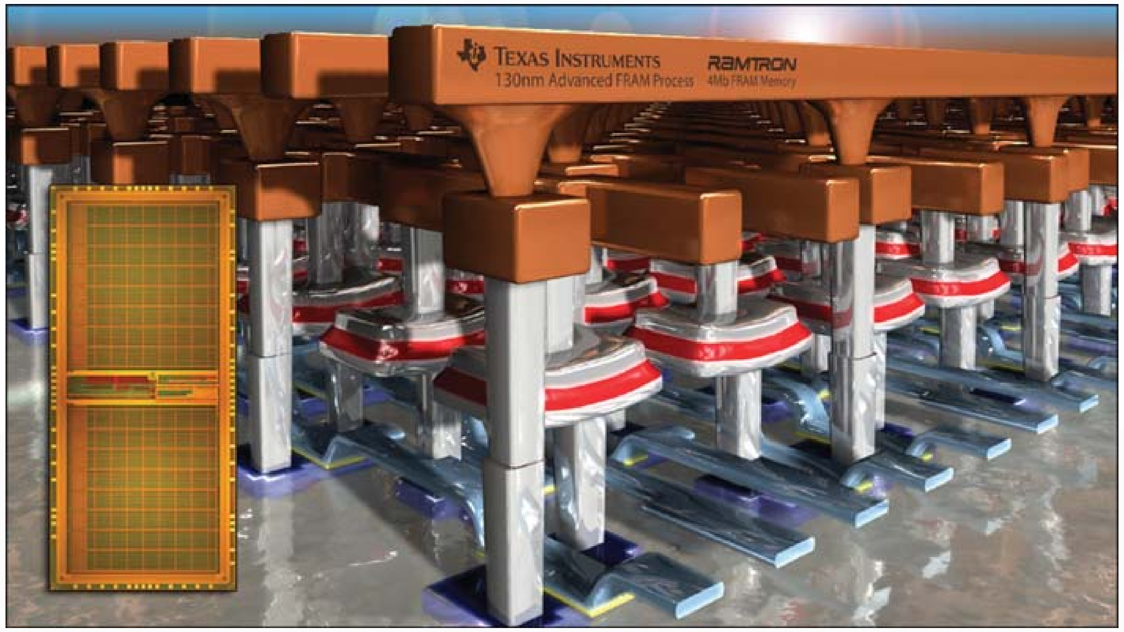
Doing More with the Same?

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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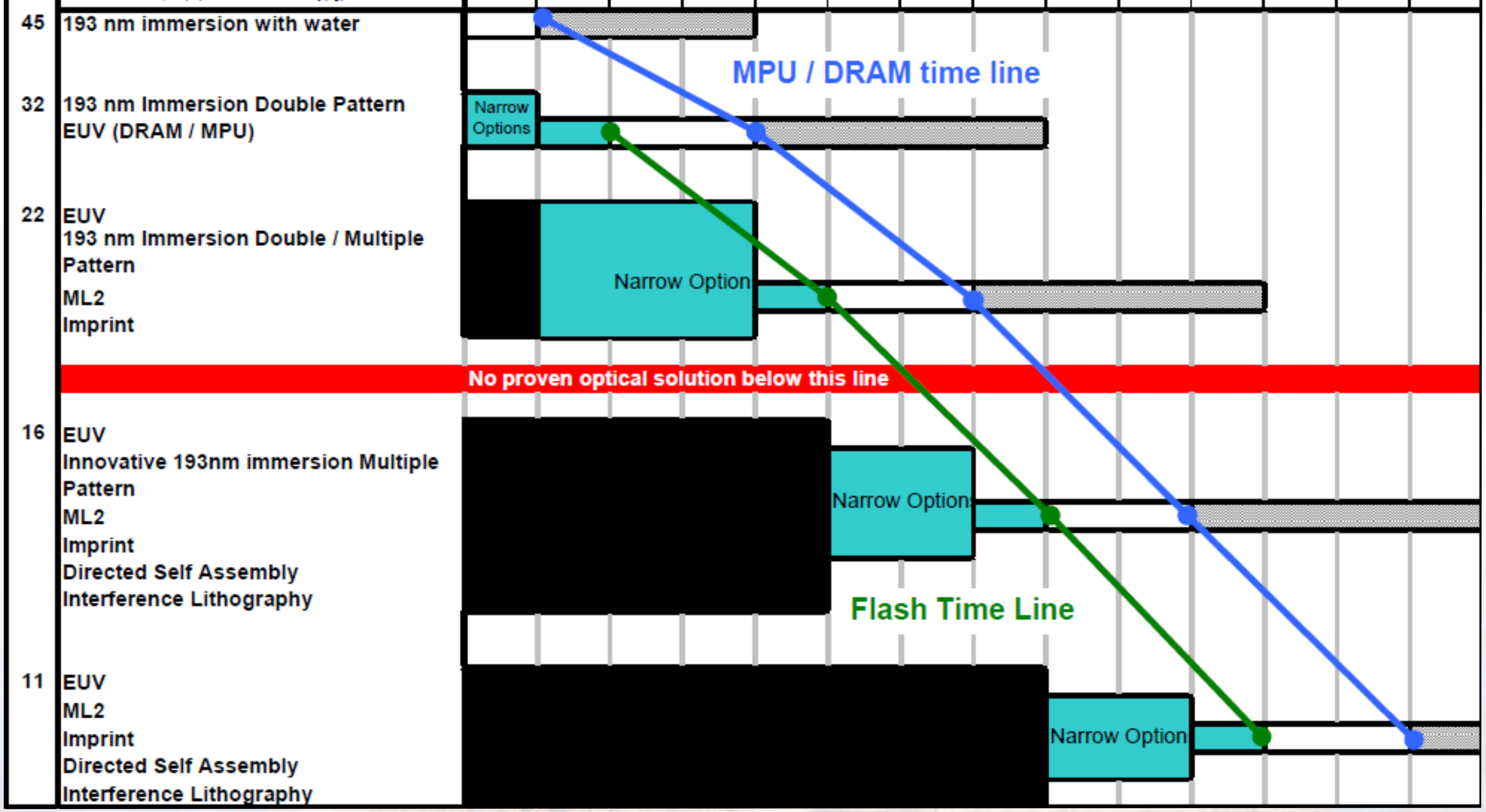
Doing Moore with the Same?

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



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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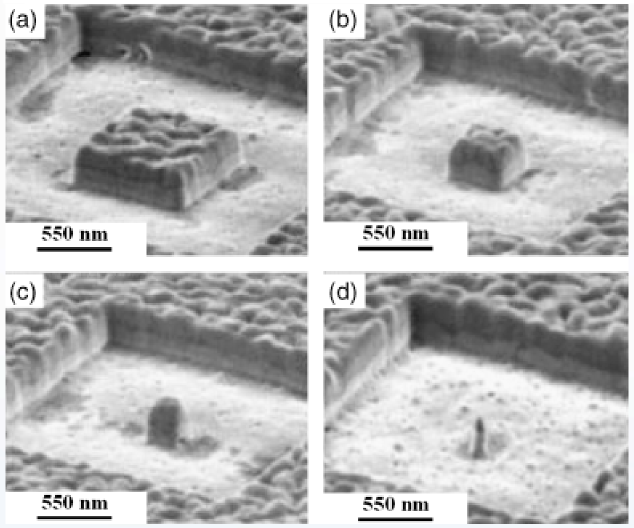
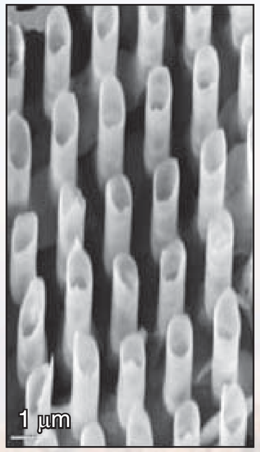
Micro-, Nano-Patterning of Arbitrary Materials

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

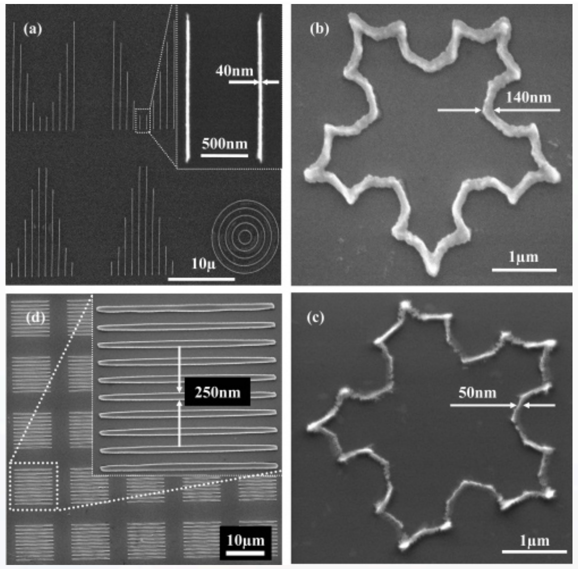
Fabrication | Patterning | Integration | Performance



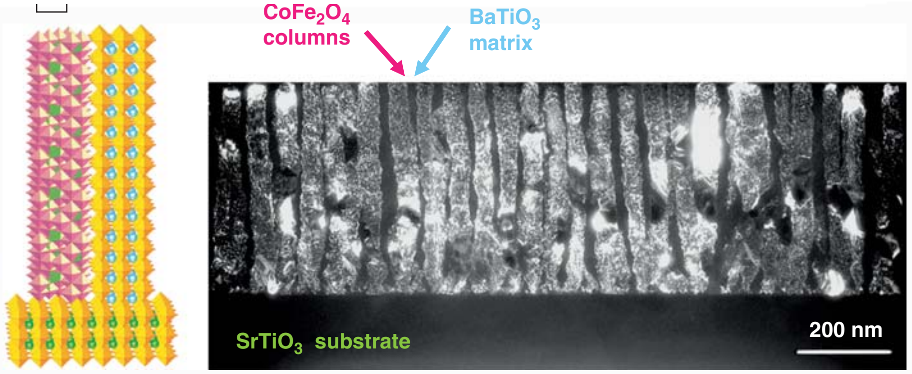
Ganpule et al., MRS Proc. (2001)



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

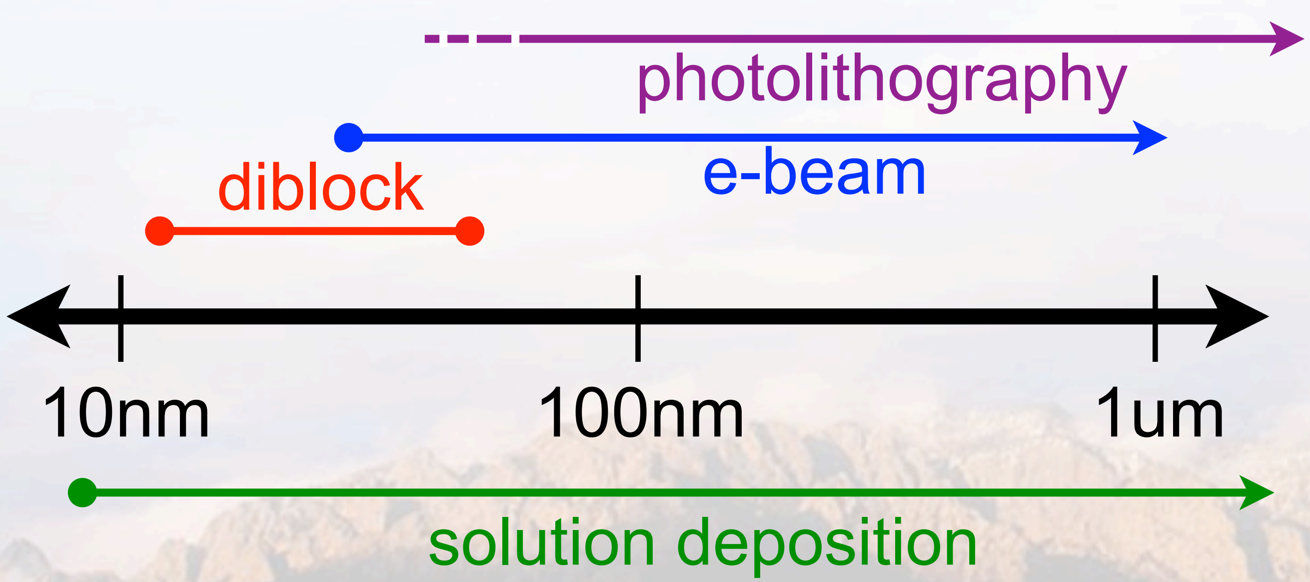
- Fabrication
- Patterning
- Integration
- Performance

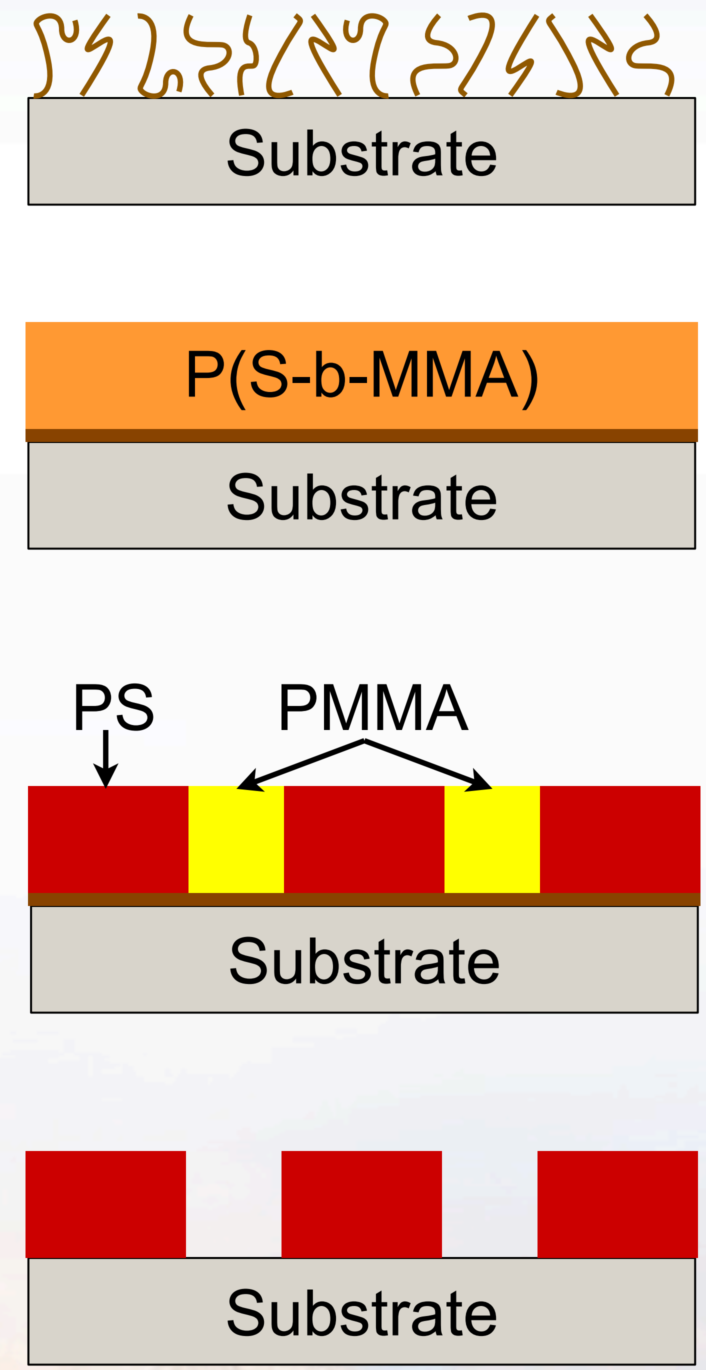
Challenges:

- 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

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)

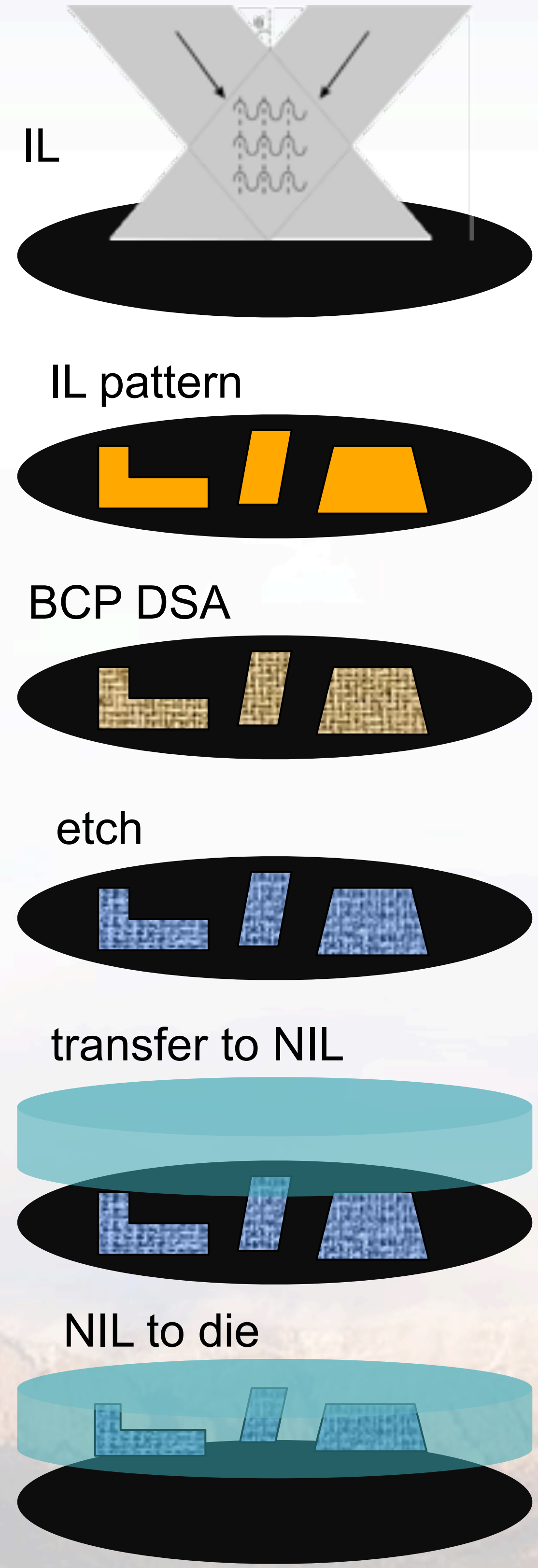
(+) rapid, large area, parallel process
(+) **low cost** (rapid, large area, maskless)
(+) tunable symmetry, period, motif
(-) layer alignment & spatial pattern variation difficult

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

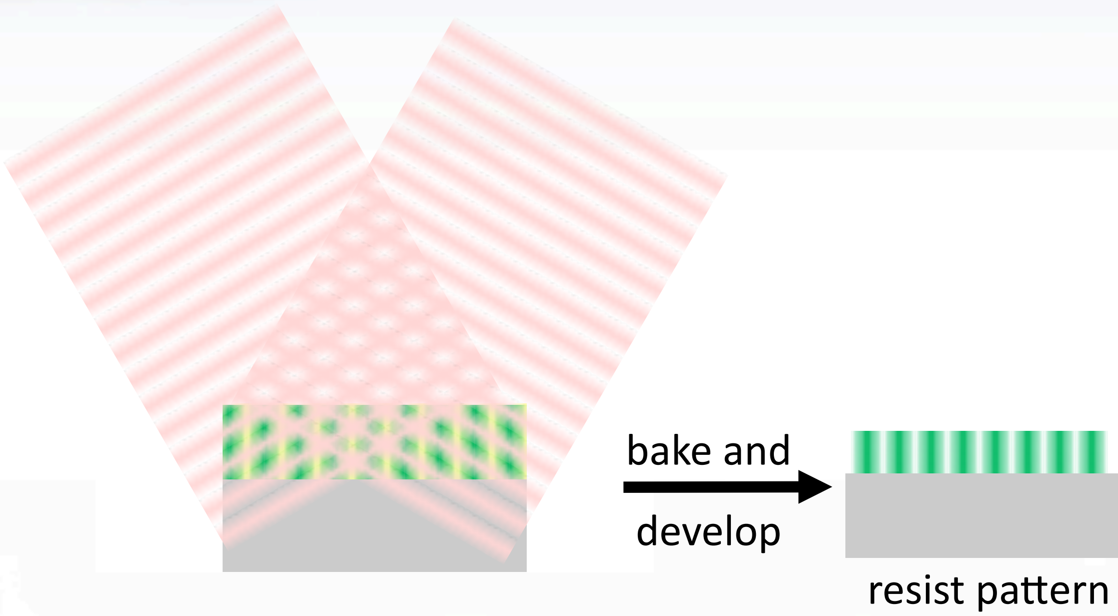
BCP Directed Self Assembly

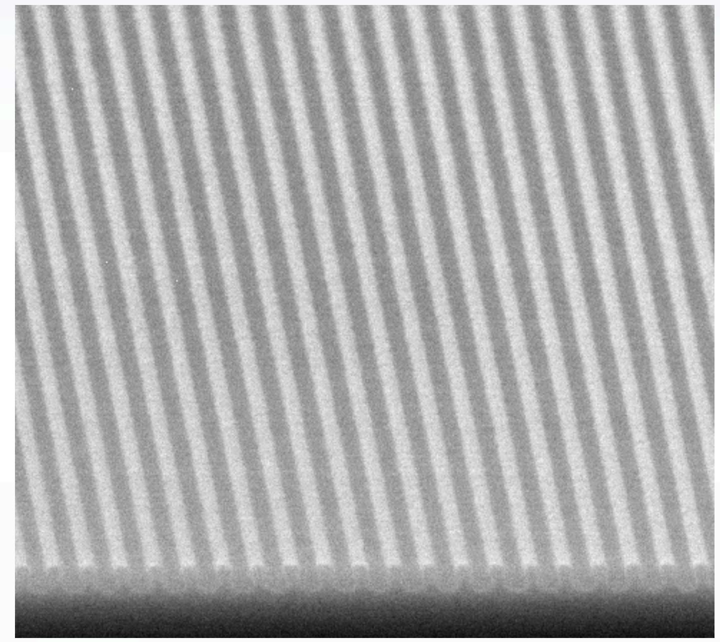
– 20-30 nm pitch device patterns
– 10-50 nm CDs
– Half-pitch to ~11 nm over ~4 cm^2 areas

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

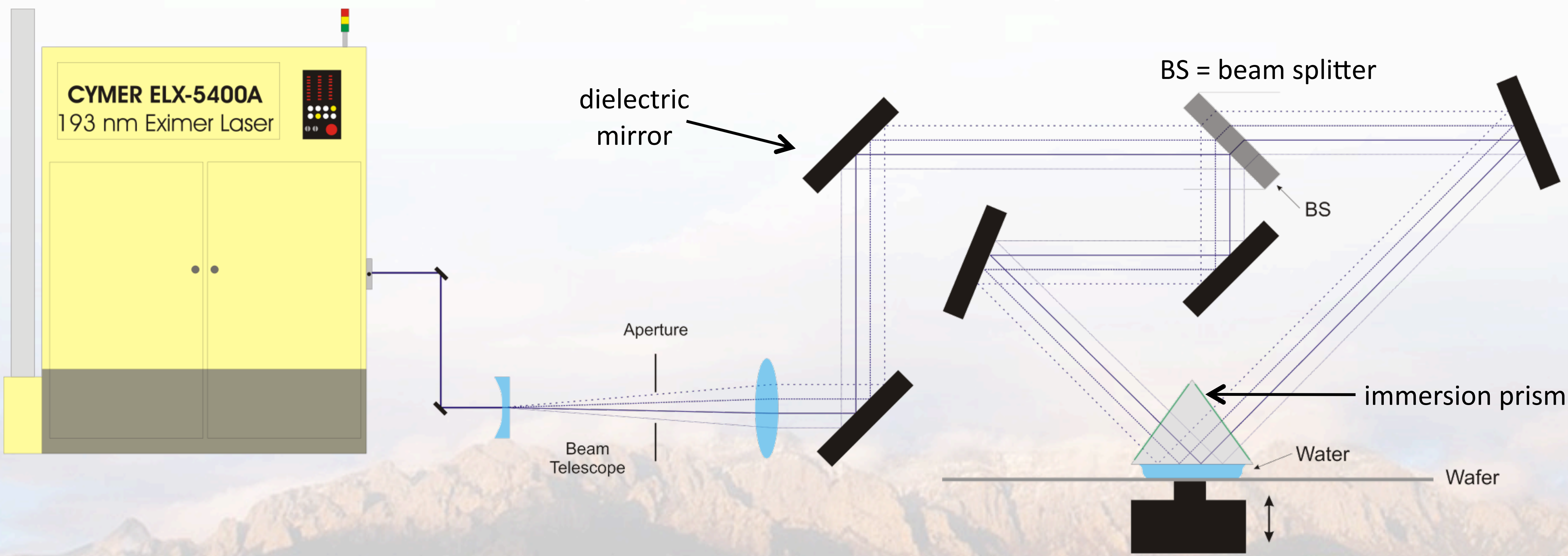
Optical Interference Lithography

with Prof. Steve Brueck





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



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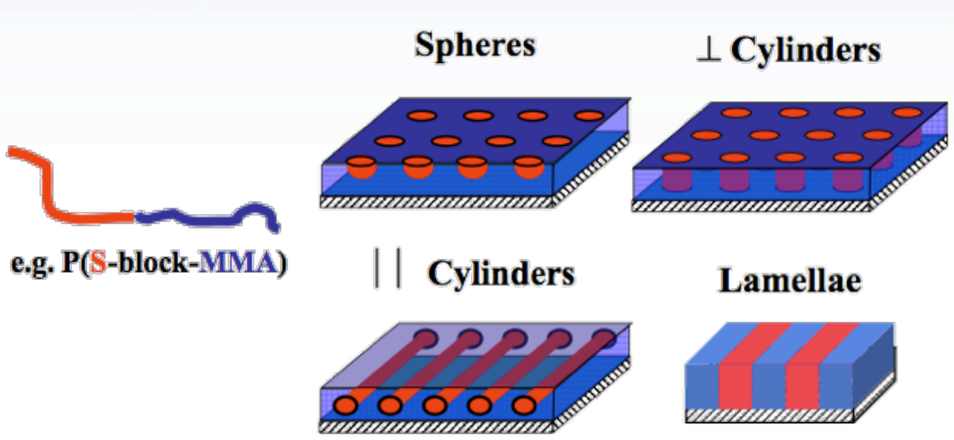
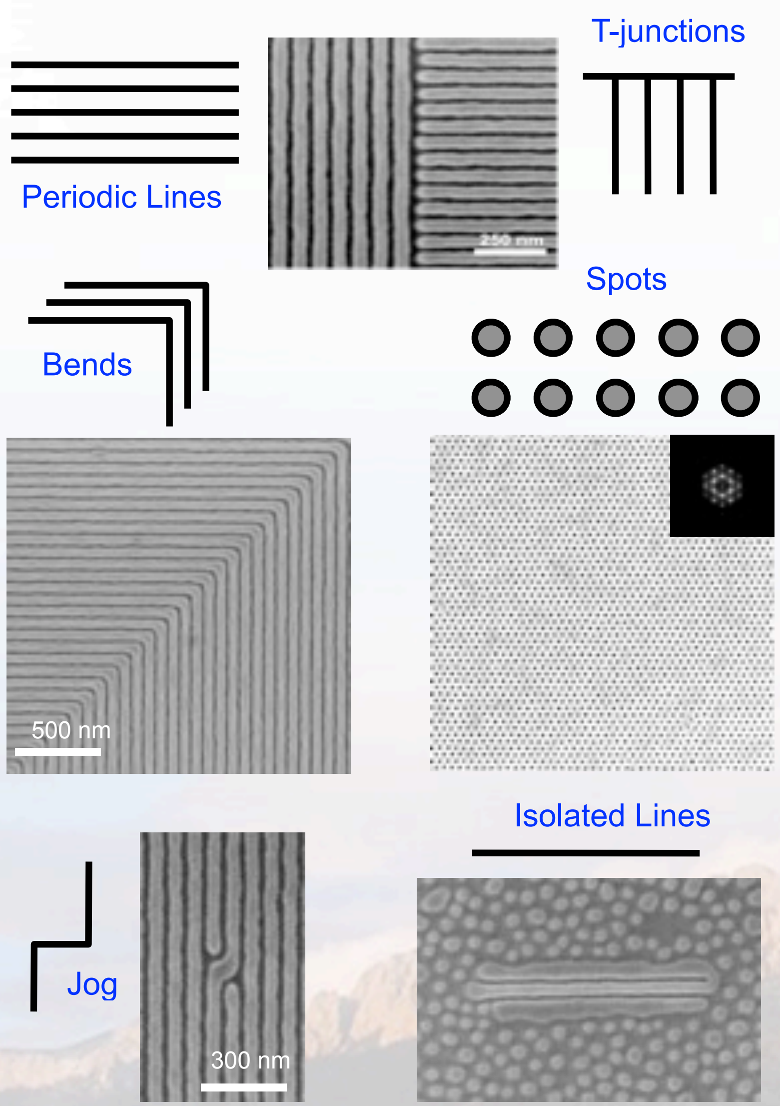
Block-Copolymer Directed Self Assembly

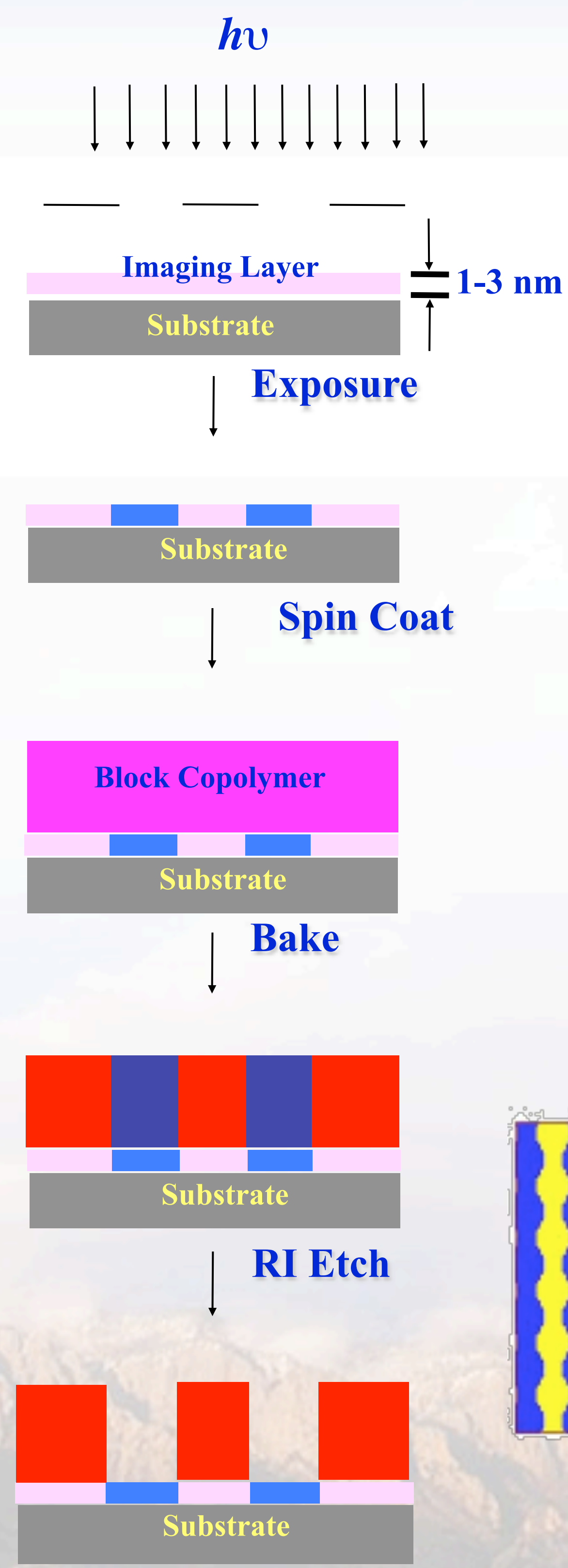
with Profs. Paul Nealey and Juan de Pablo

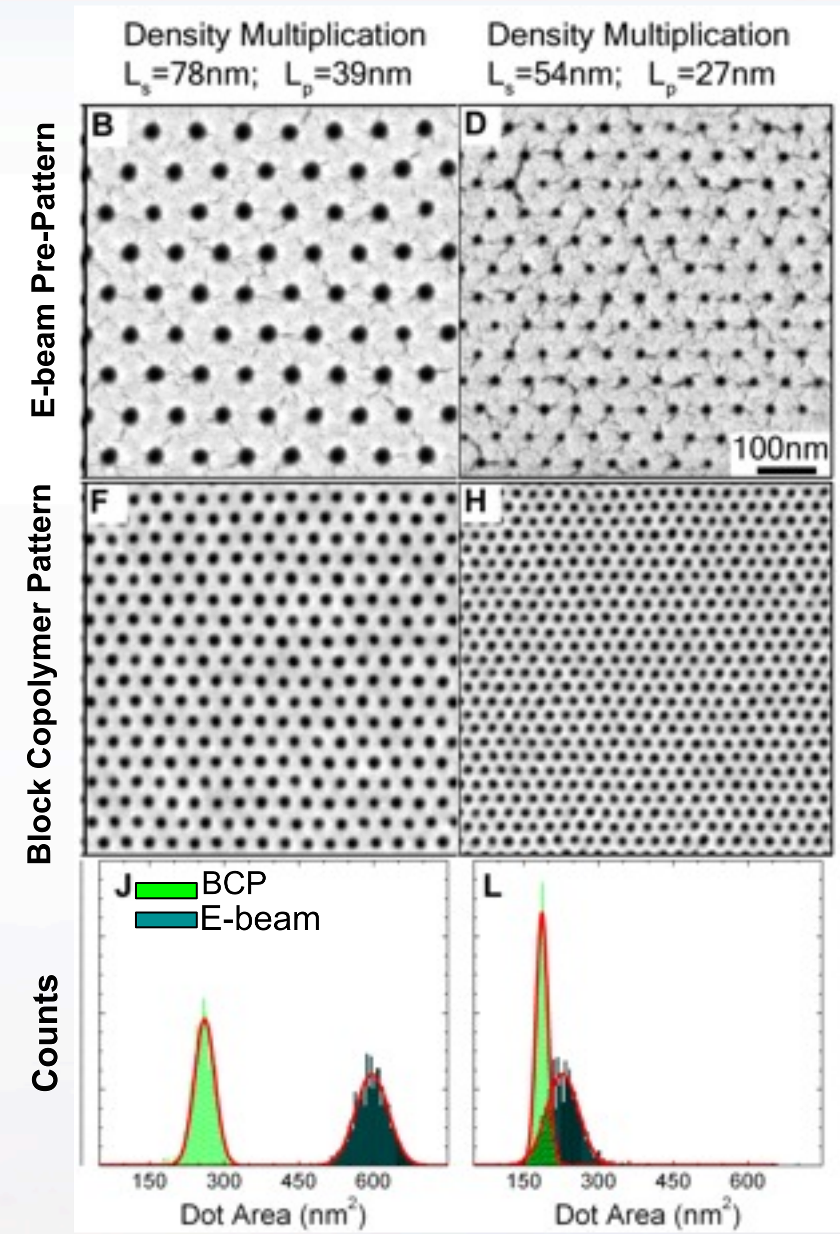
THE UNIVERSITY of WISCONSIN MADISON



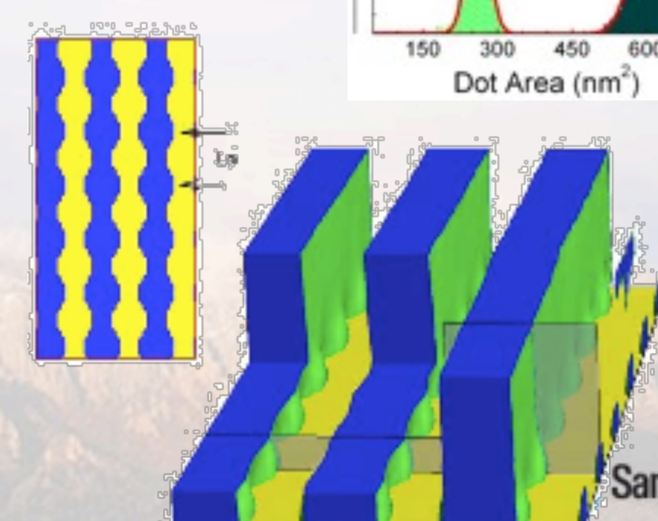


Stoykovich et al. *ACS Nano*, 2007, *Science* 2005





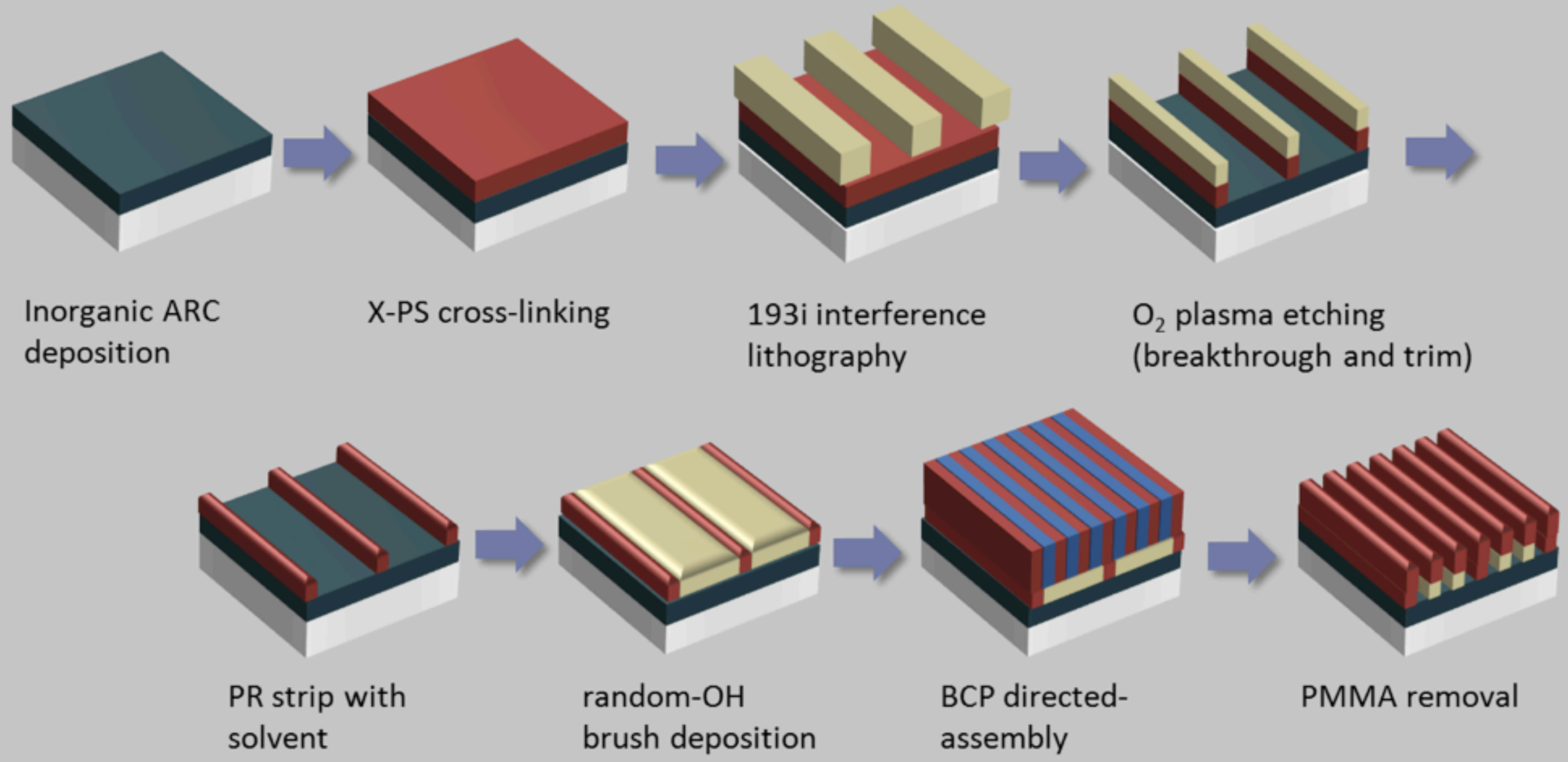
Ruiz, Nealey, de Pablo et al. *Science*, 2008



Daoulas et al., Langmuir, 2008

Density Multiplication

Process flow with ARC and 193i



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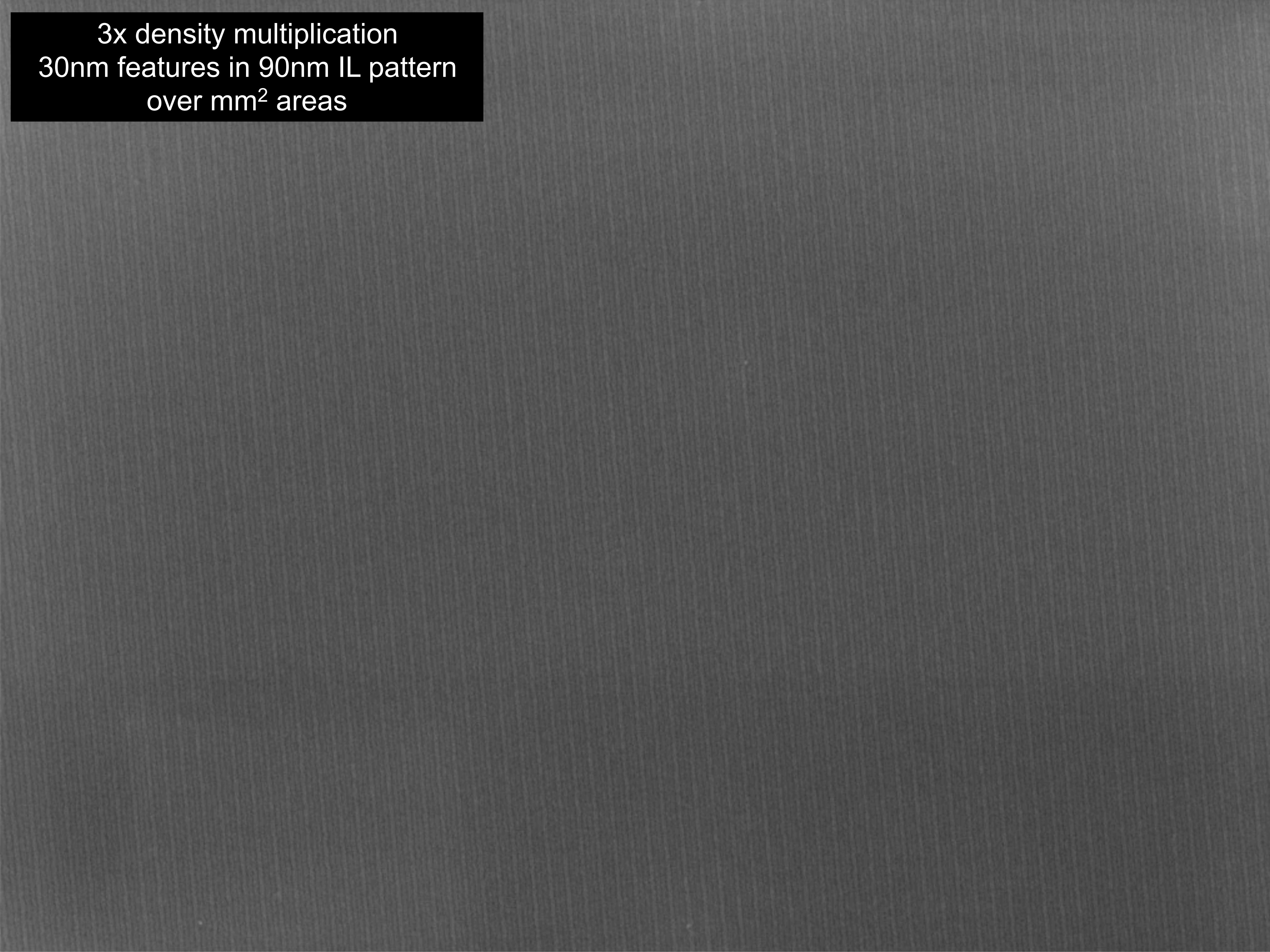
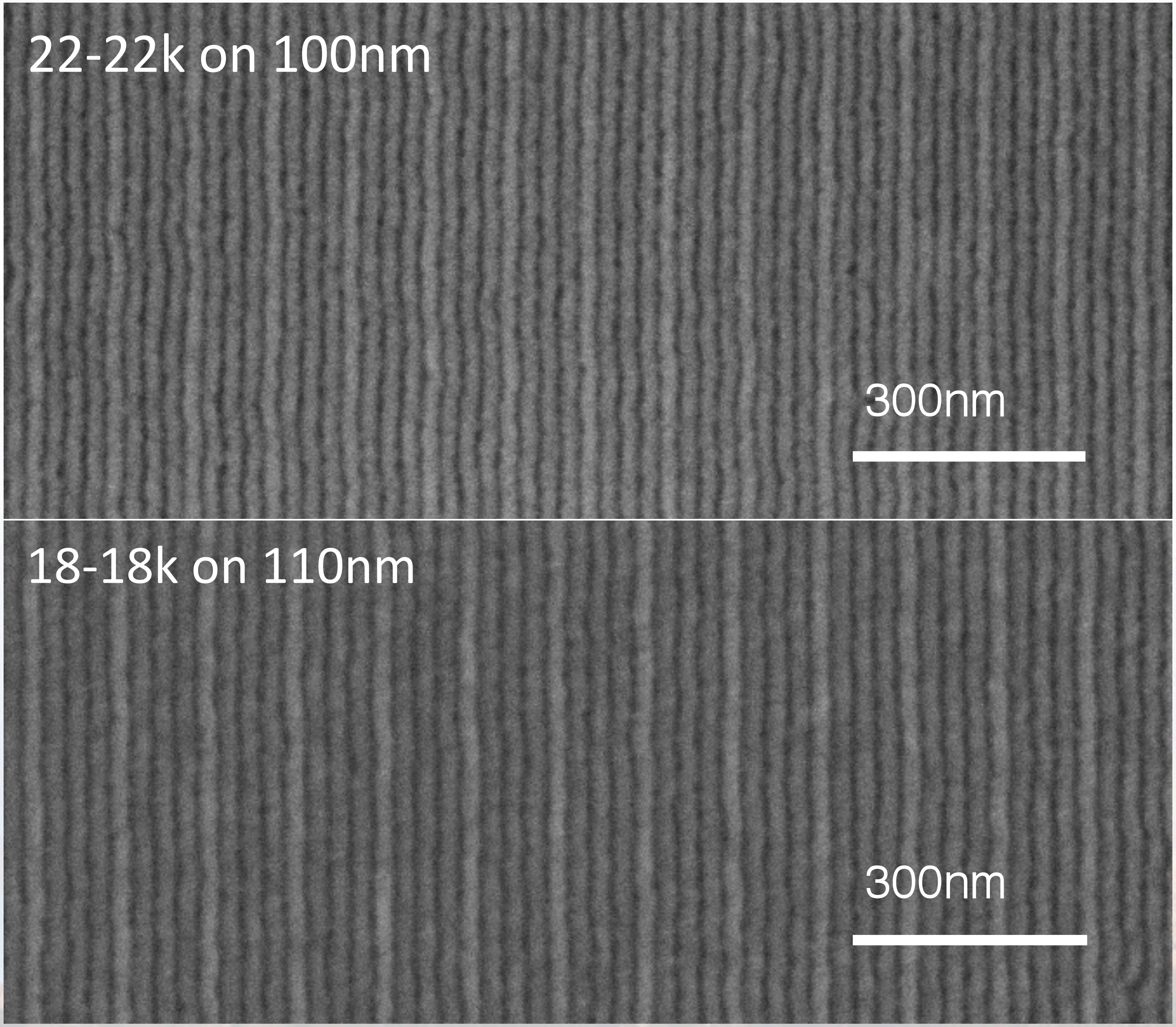

3x density multiplication
30nm features in 90nm IL pattern
over mm2 areas

Density Multiplication



4X Multiplication

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

Surface interactions are crucial

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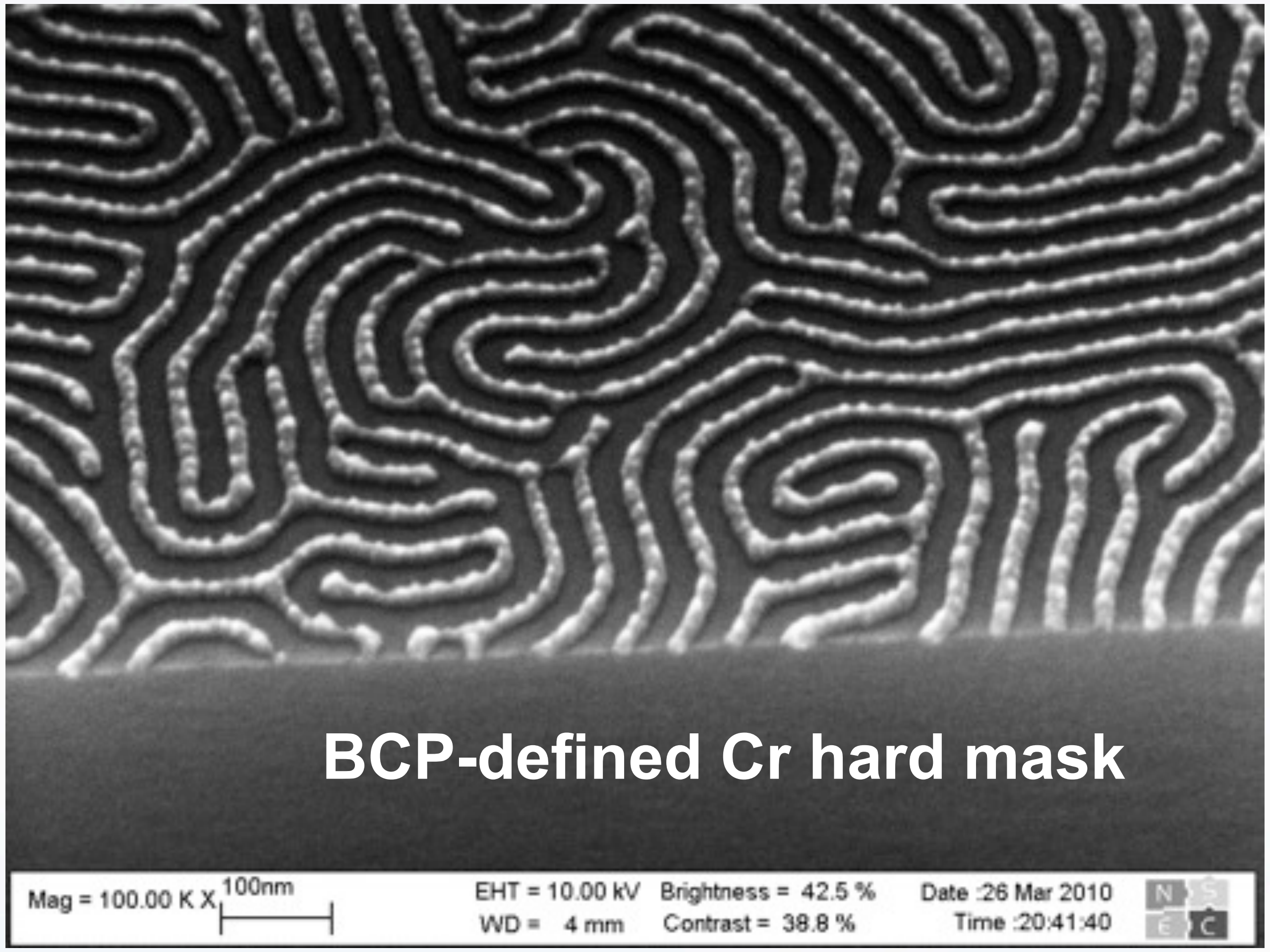
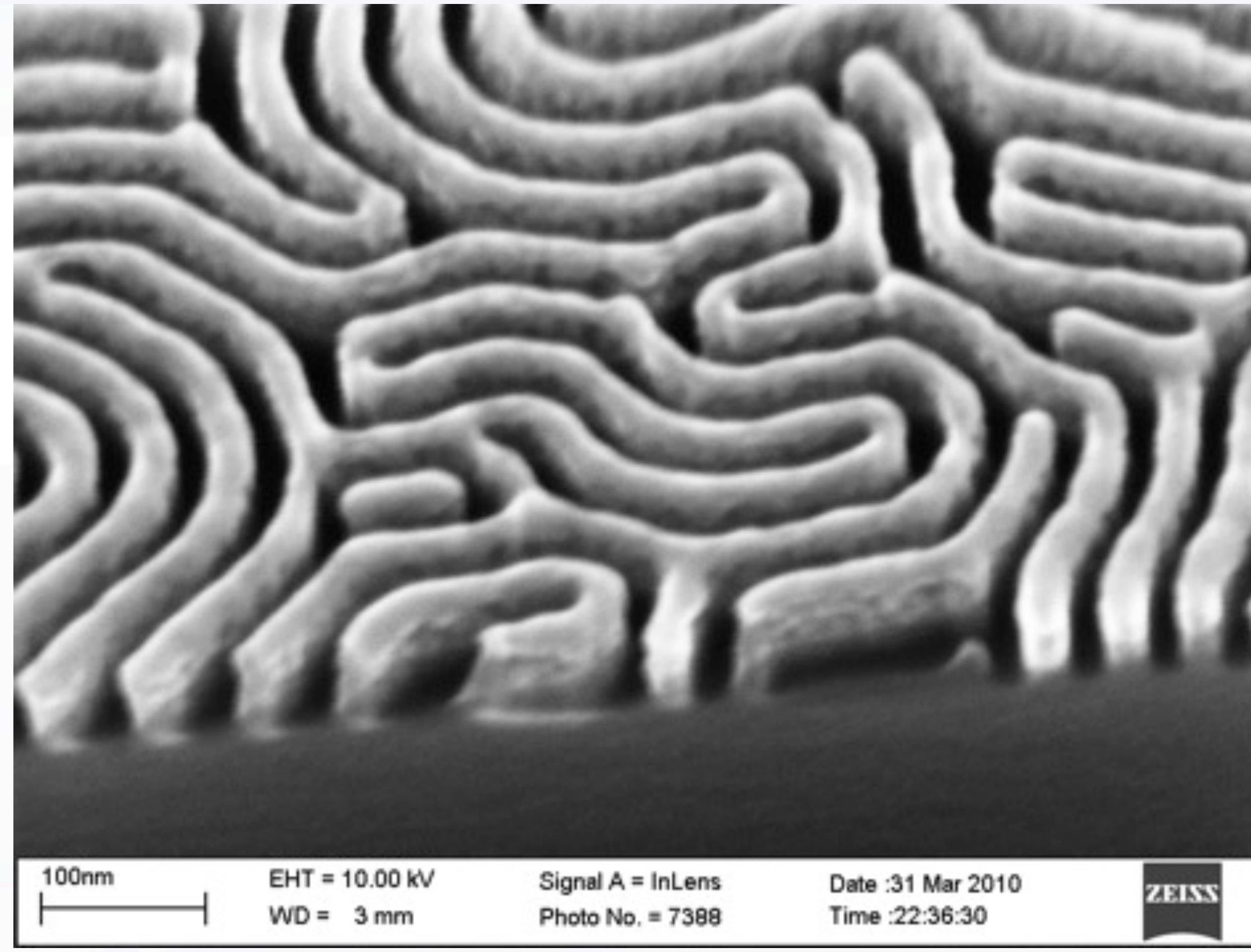
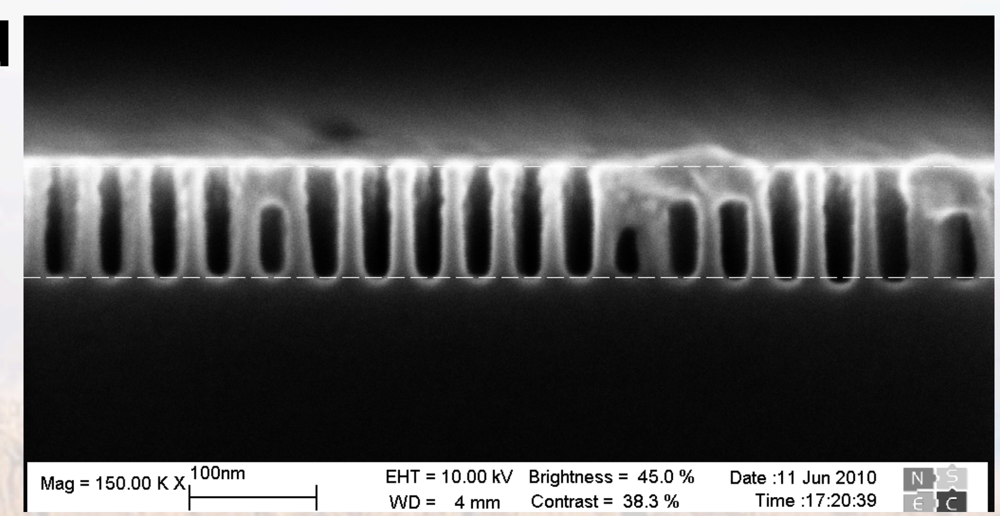
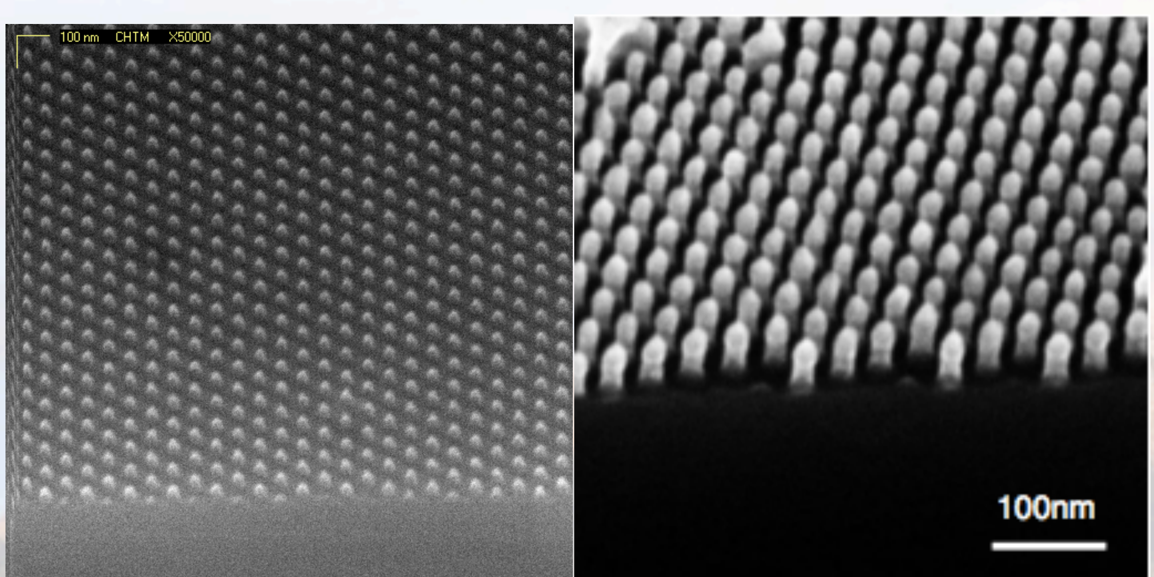
Pattern Transfer





Si etched through Cr mask





Si pillars defined by BCP for NIL master

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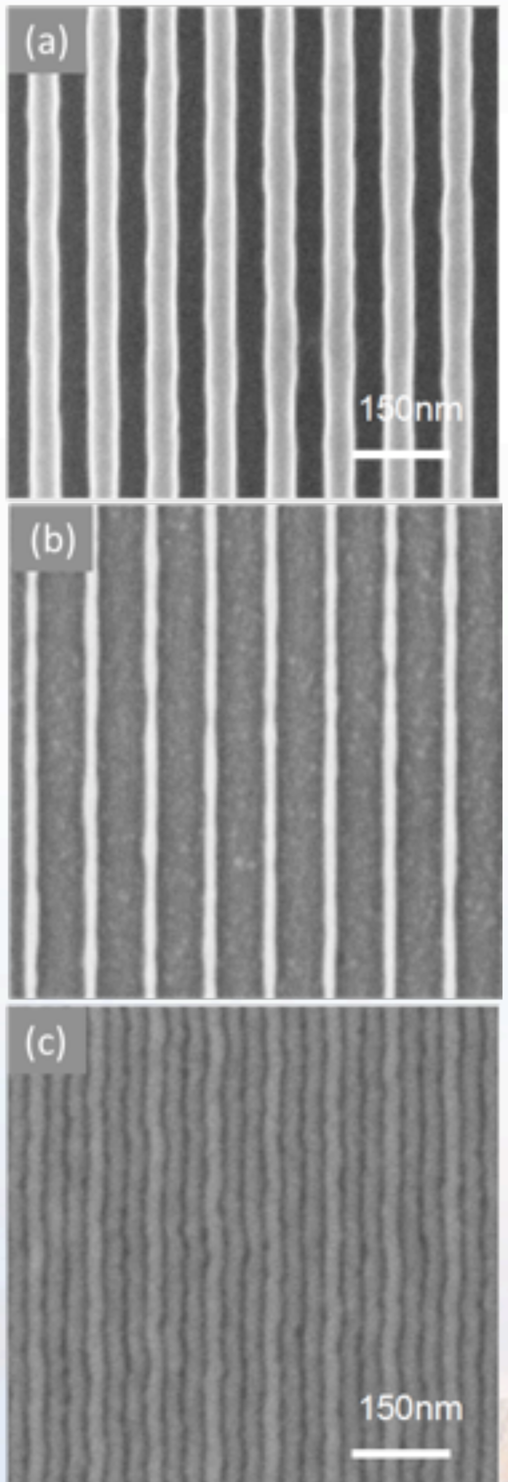
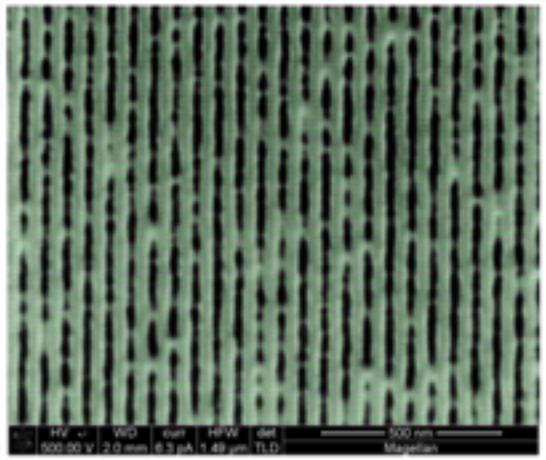
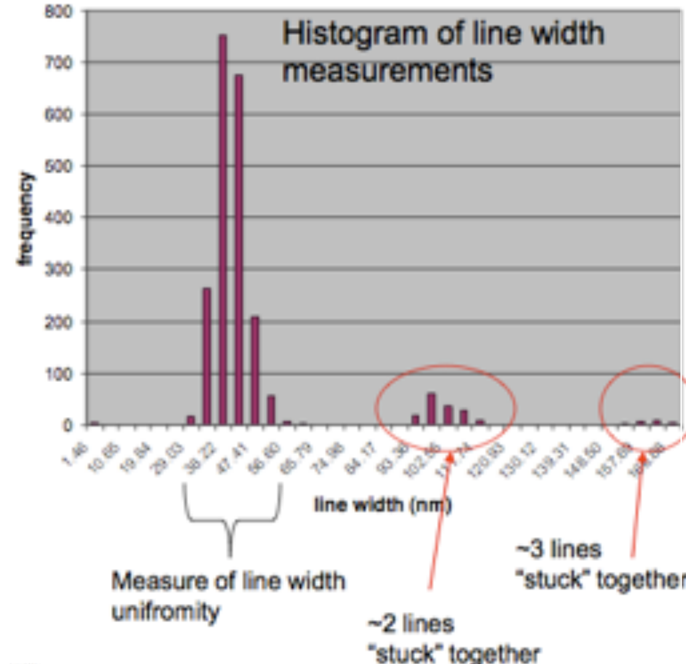
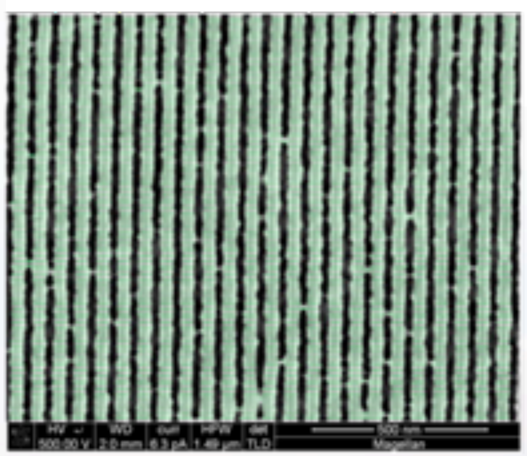
Metrology



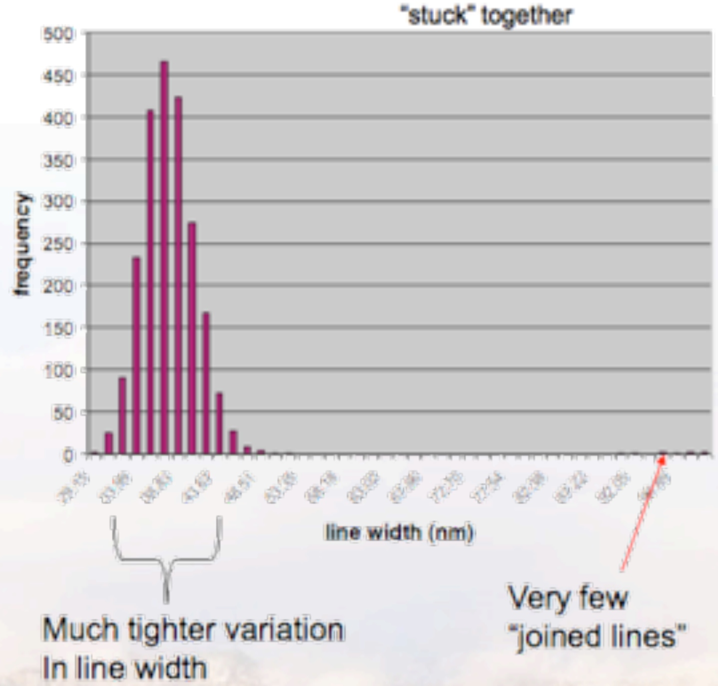


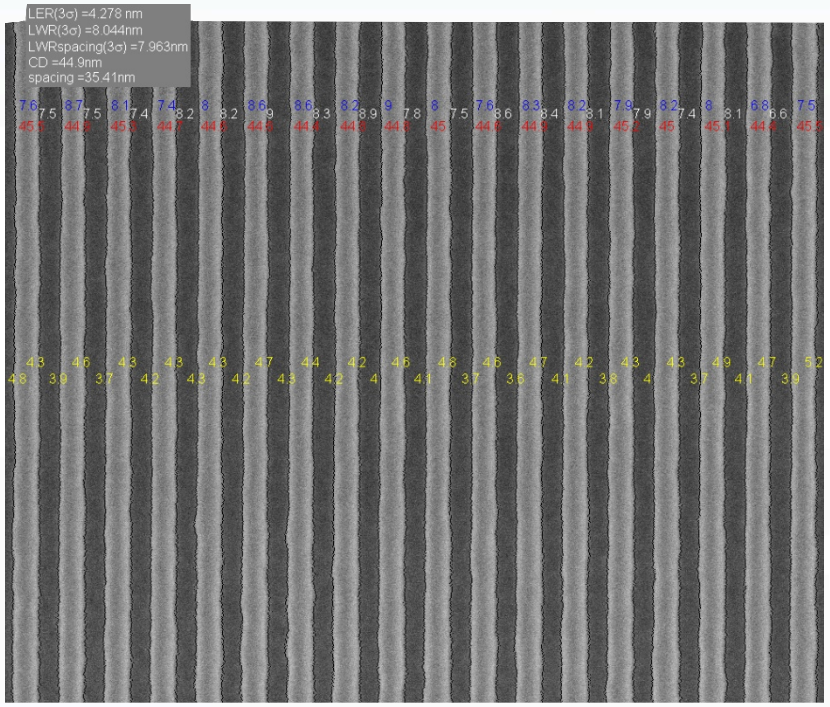
After insertion of 100 grid lines and BOOLEAN combination





Wafer090121-002_30nm_middle bo





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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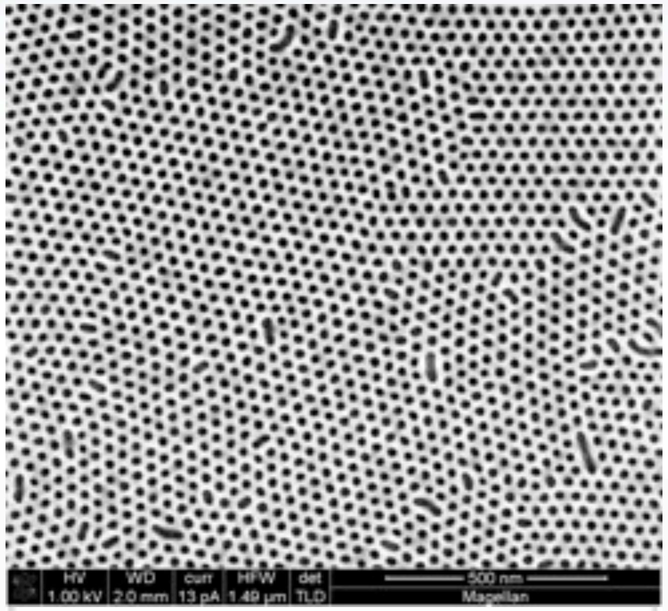
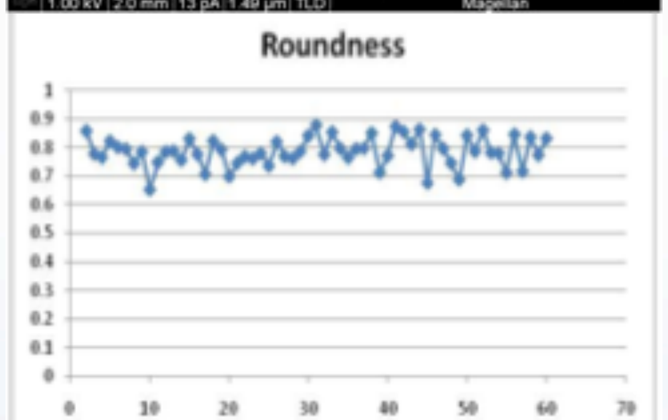
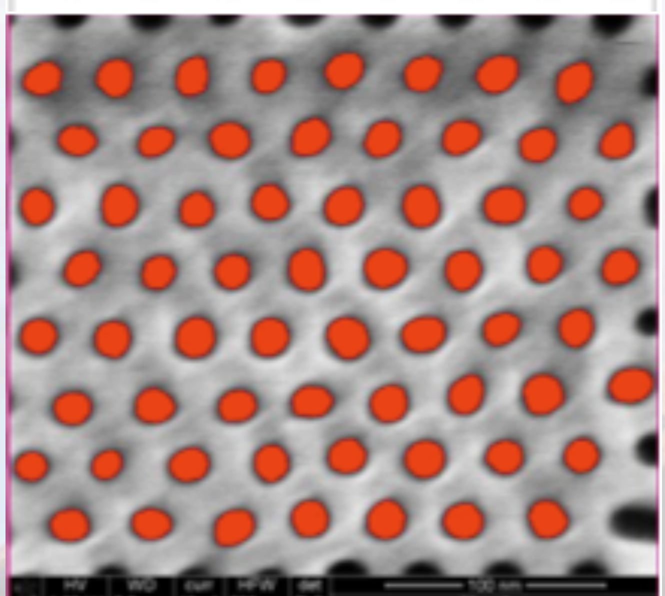
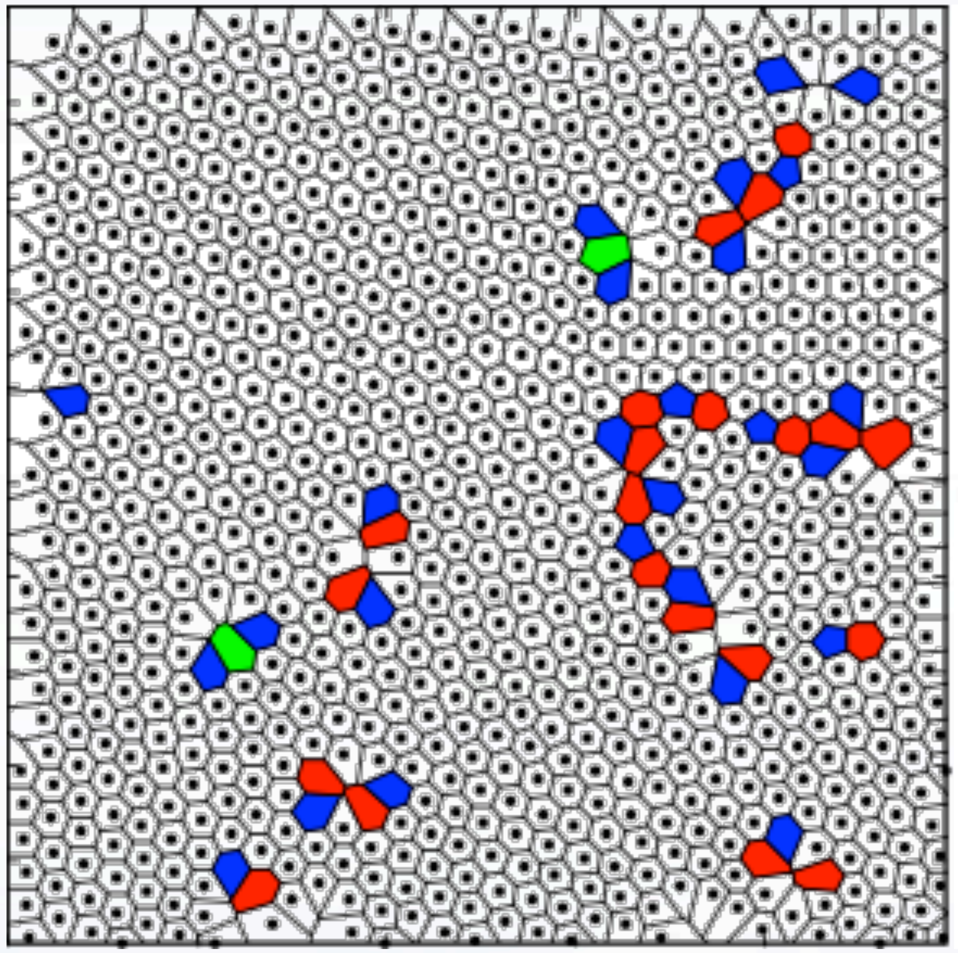
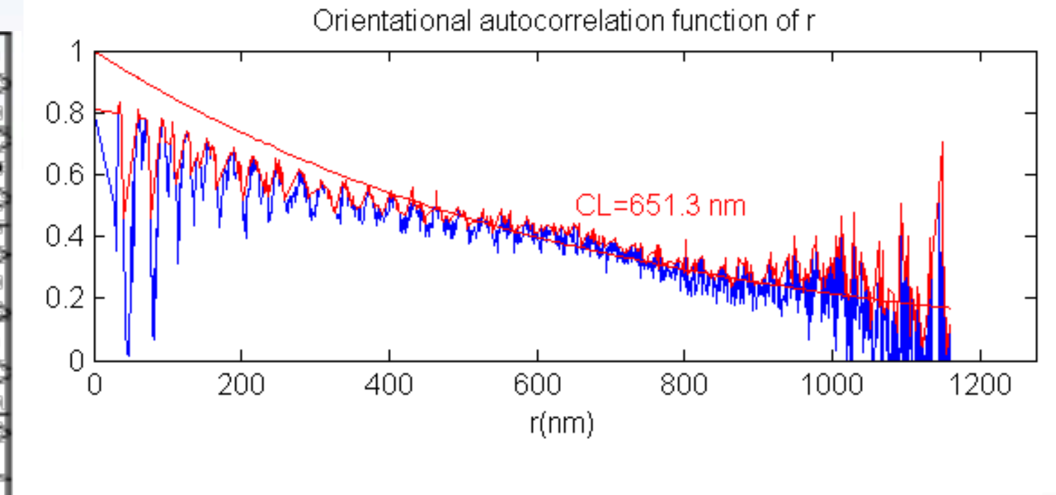
Metrology

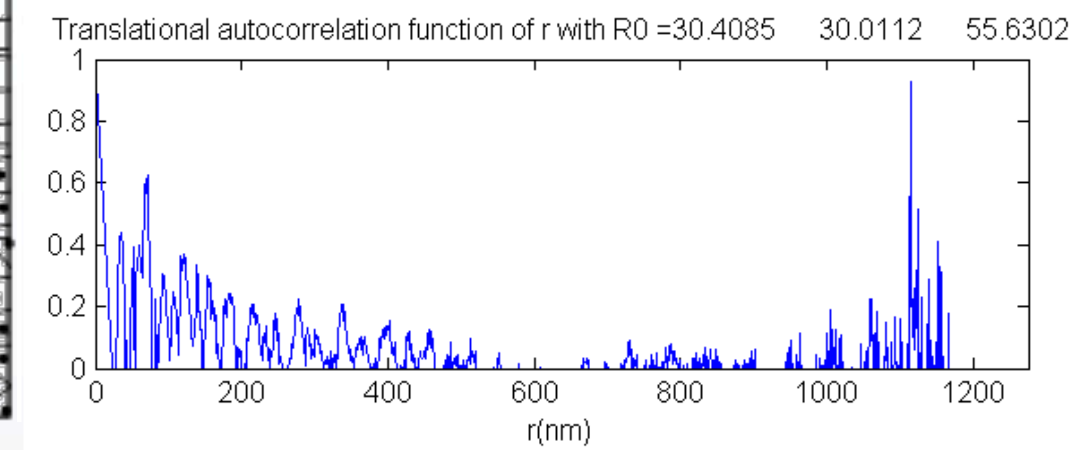












All made possible by FEI Magellan SEM: quantitative sub-nm measurements from ***uncoated*** samples

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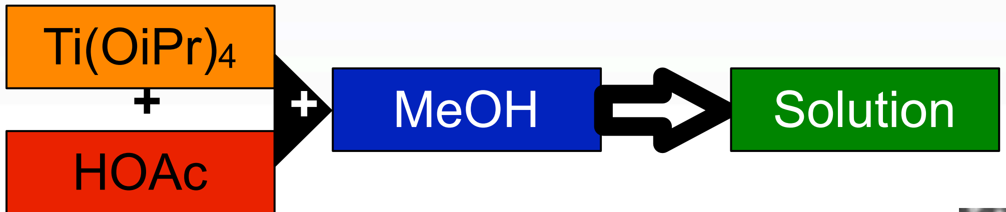
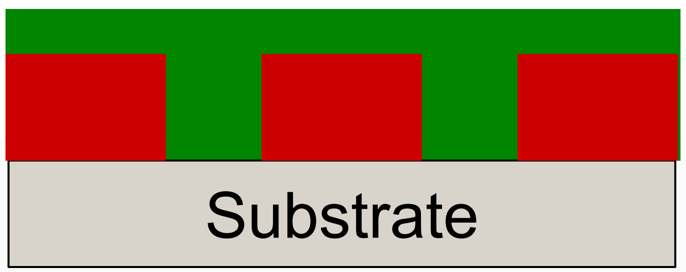
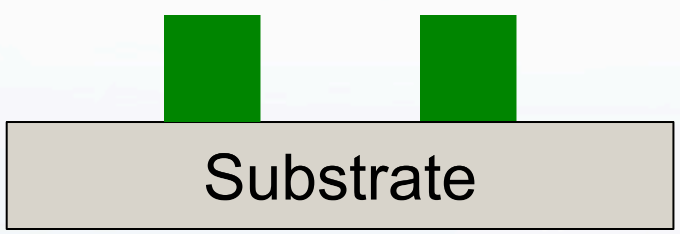
Additive Fabrication of Patterned Electronic Oxides



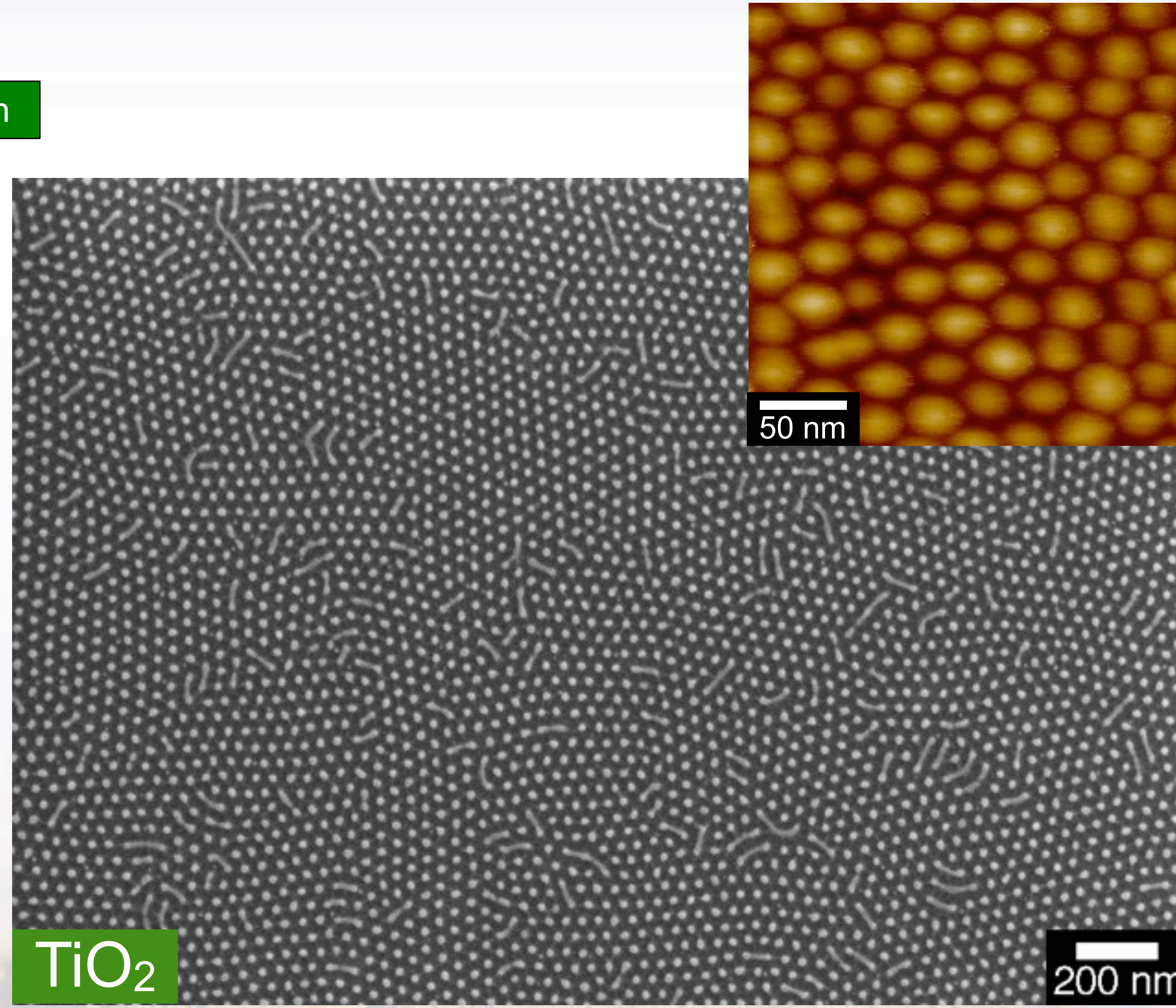


Fill, Gel



Remove Mask

$CHF_3 + O_2$



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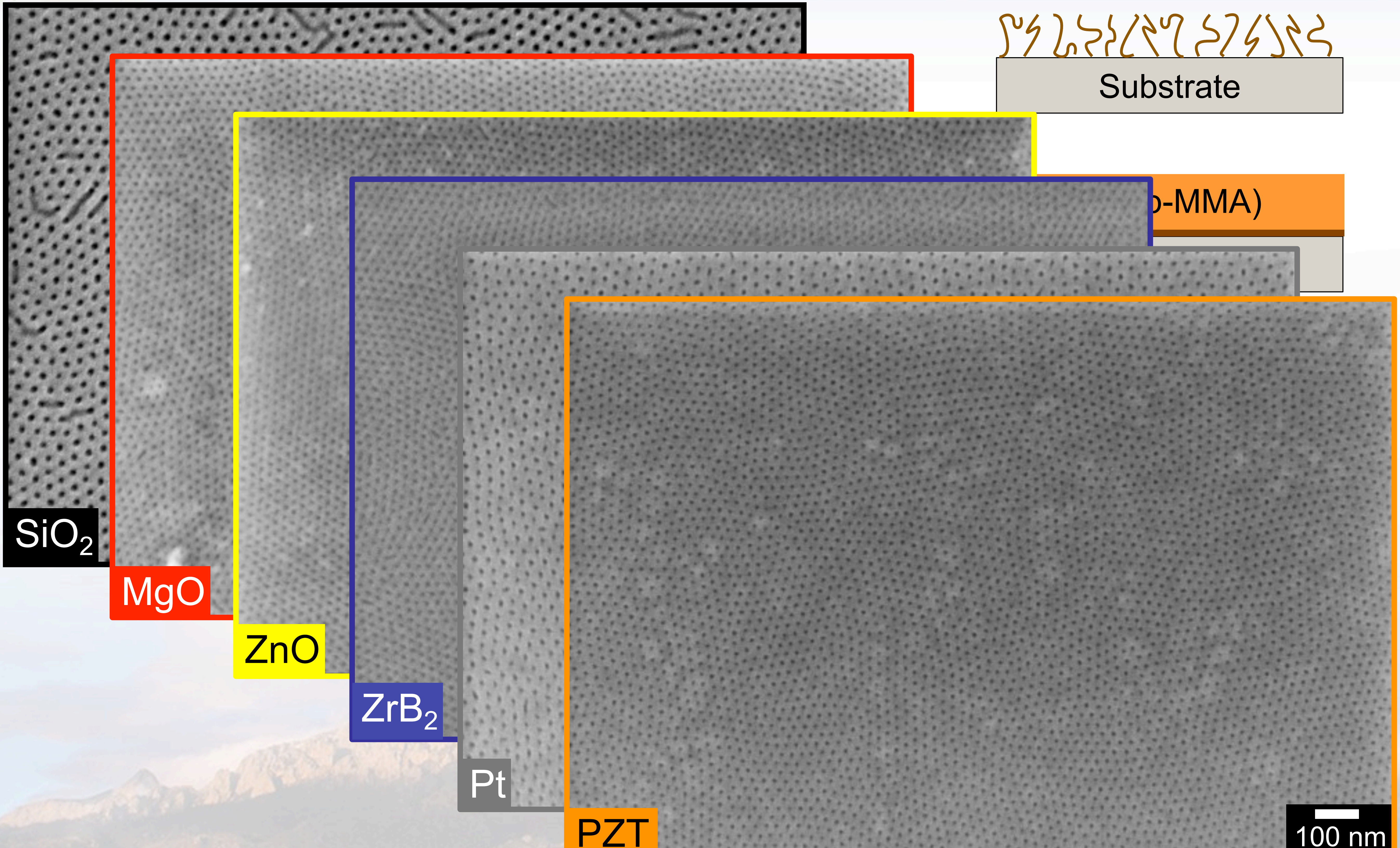
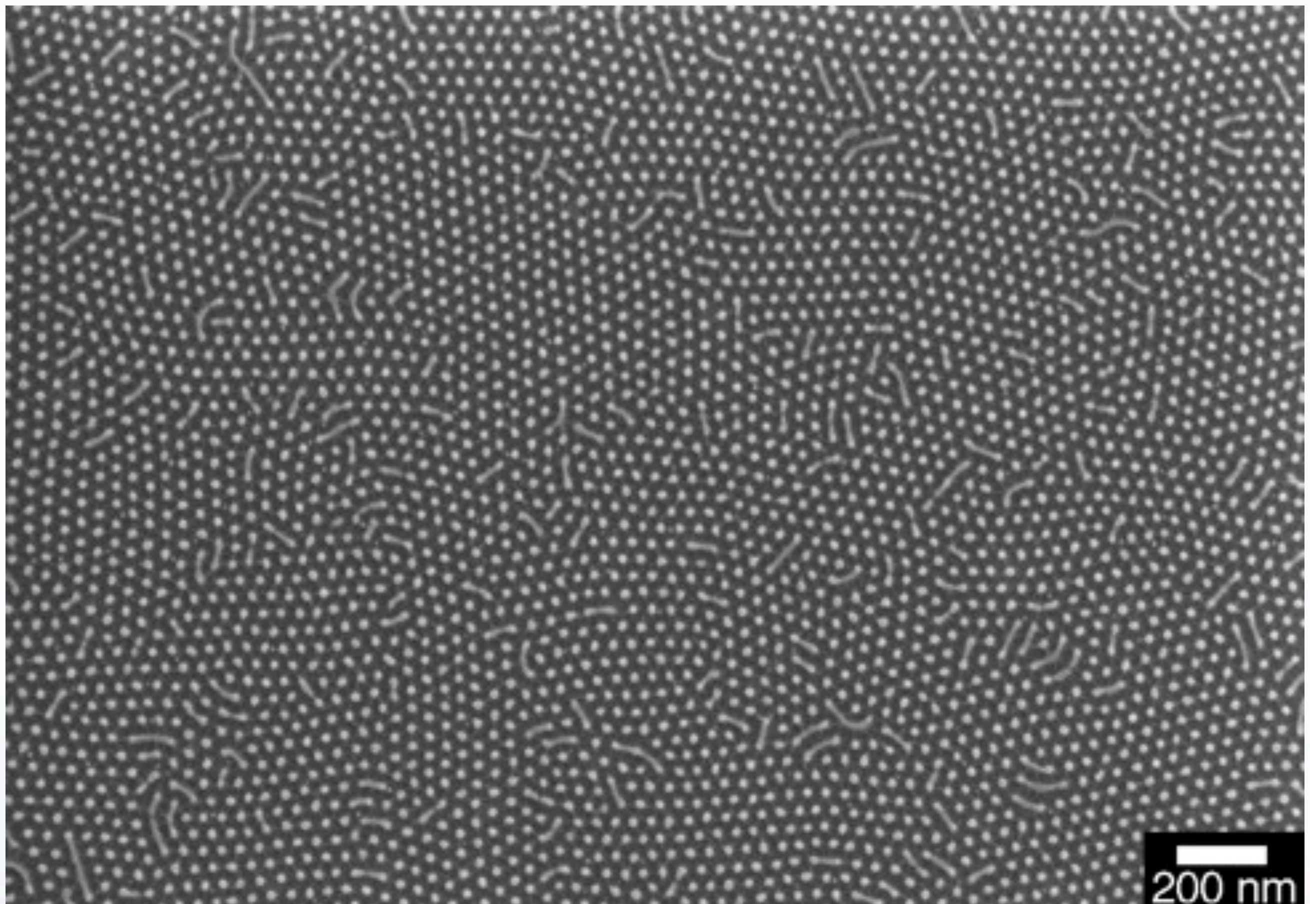
Diblock Assembly on Various Substrates

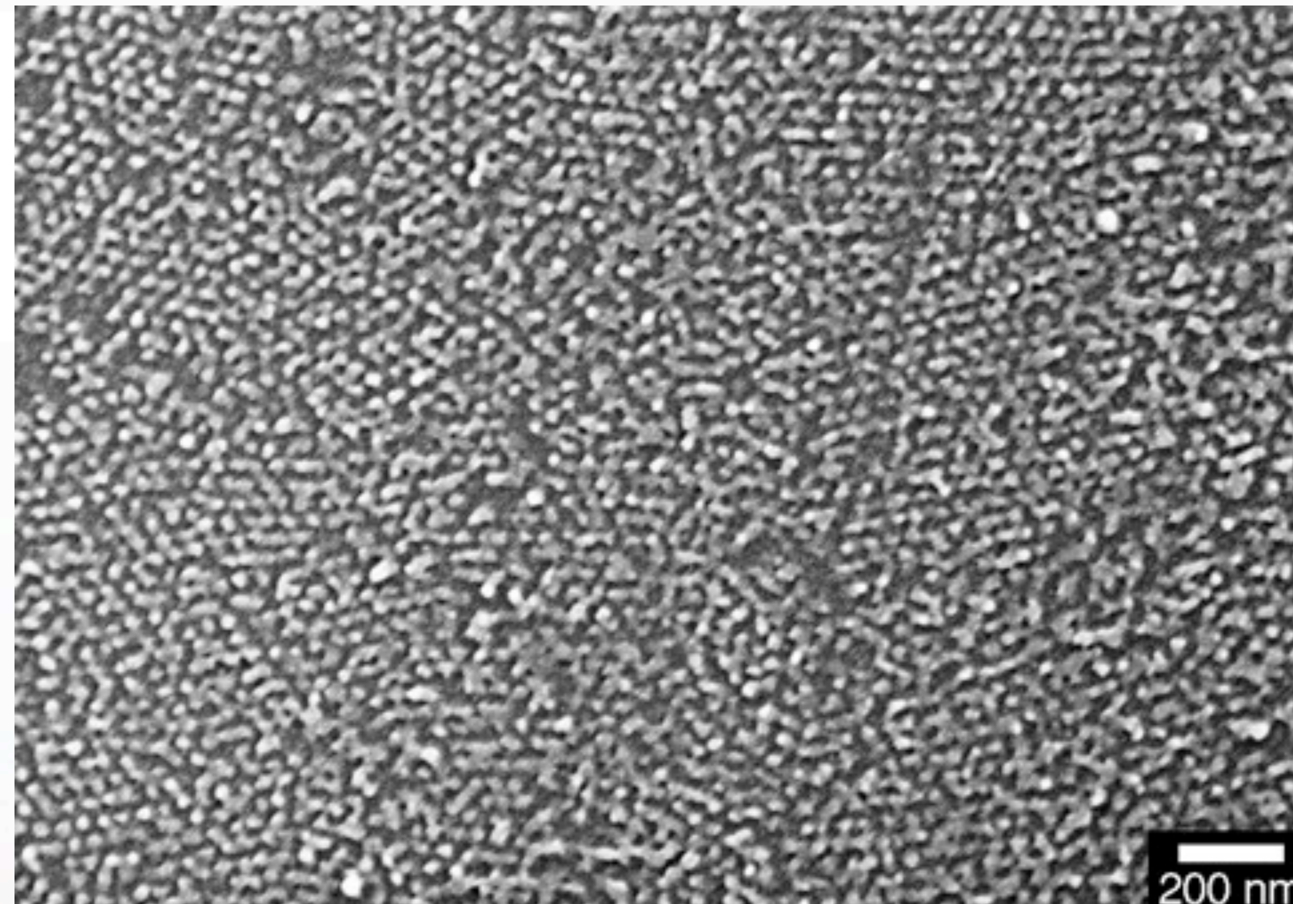


Crystallization Destroys Freestanding Nanofeatures

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



Amorphous TiO_2

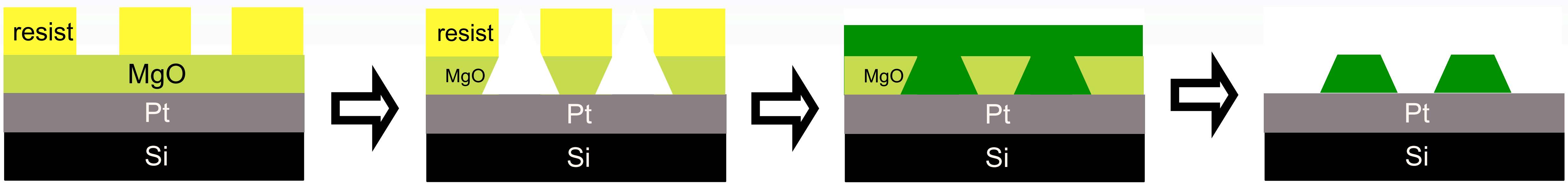


Crystalline TiO_2 (Anatase)

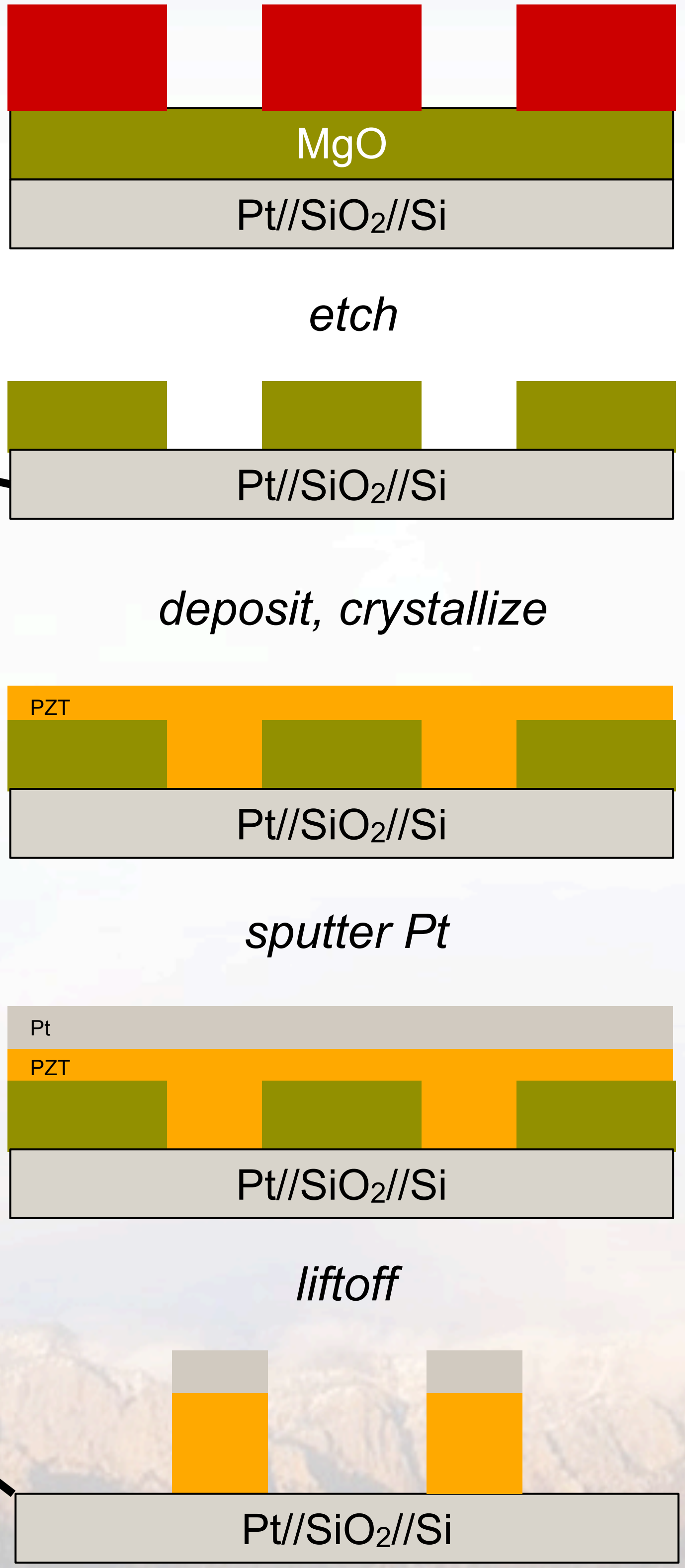
Still lacking:

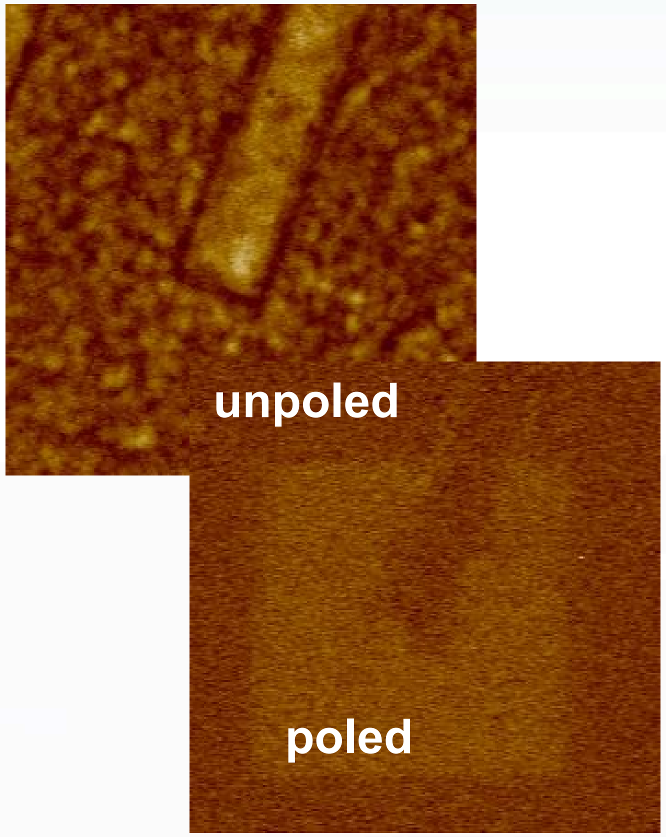
- Controlled long-range order for addressability
- Crystallization before patterning or within inert and removable mask

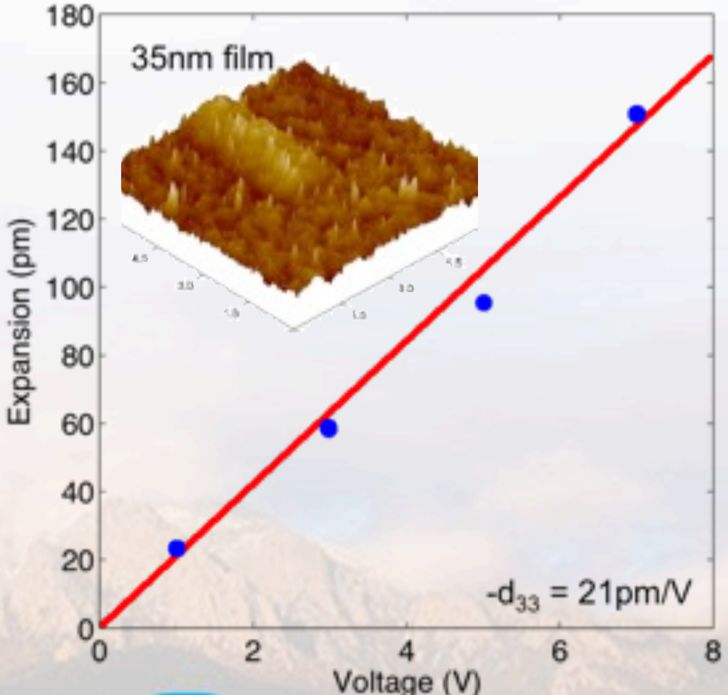
Maintaining Pattern Fidelity through Thermal Processing (>600°C)



Alternate Microscale Patterning



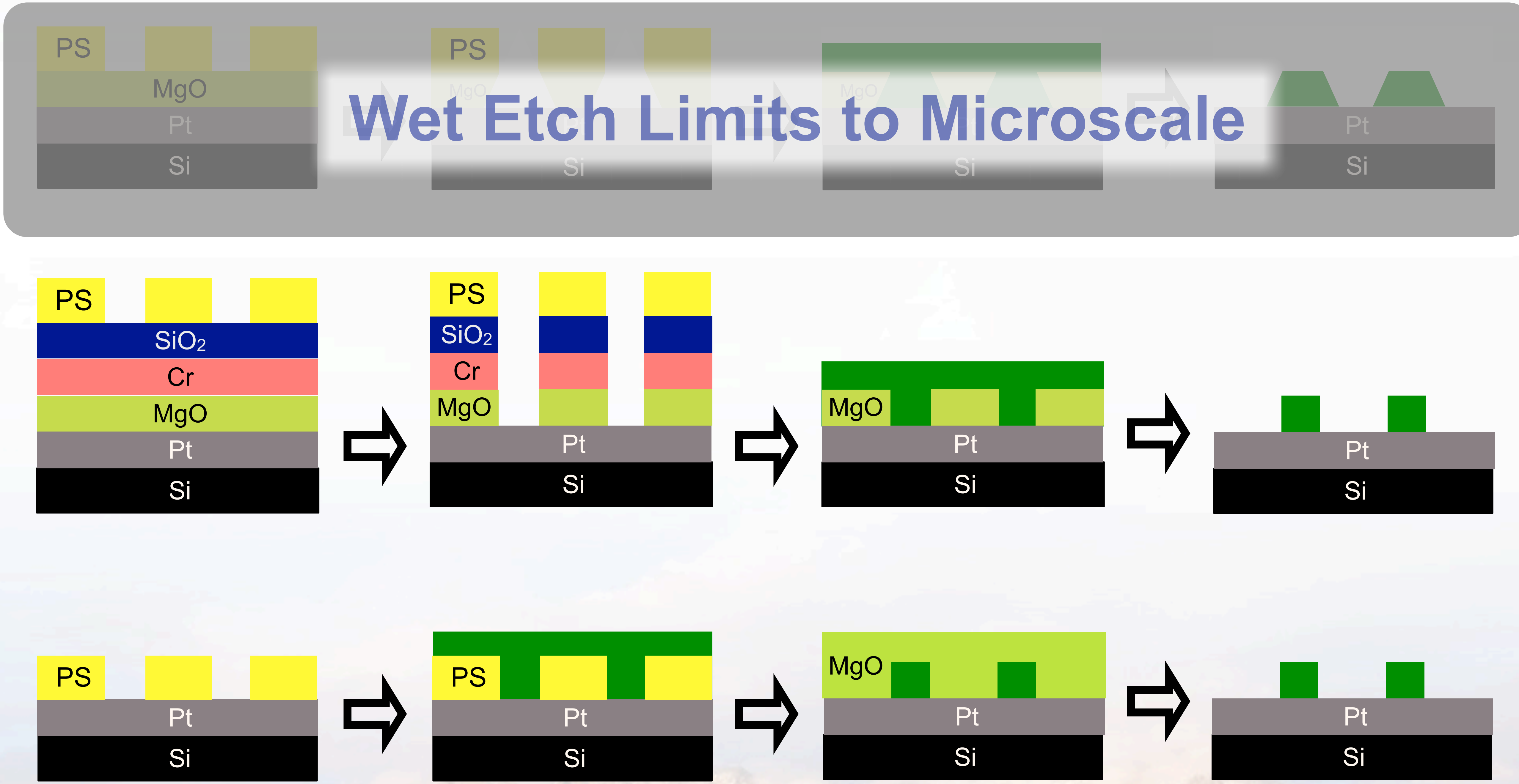




Maintaining Pattern Fidelity through Thermal Processing (>600°C)

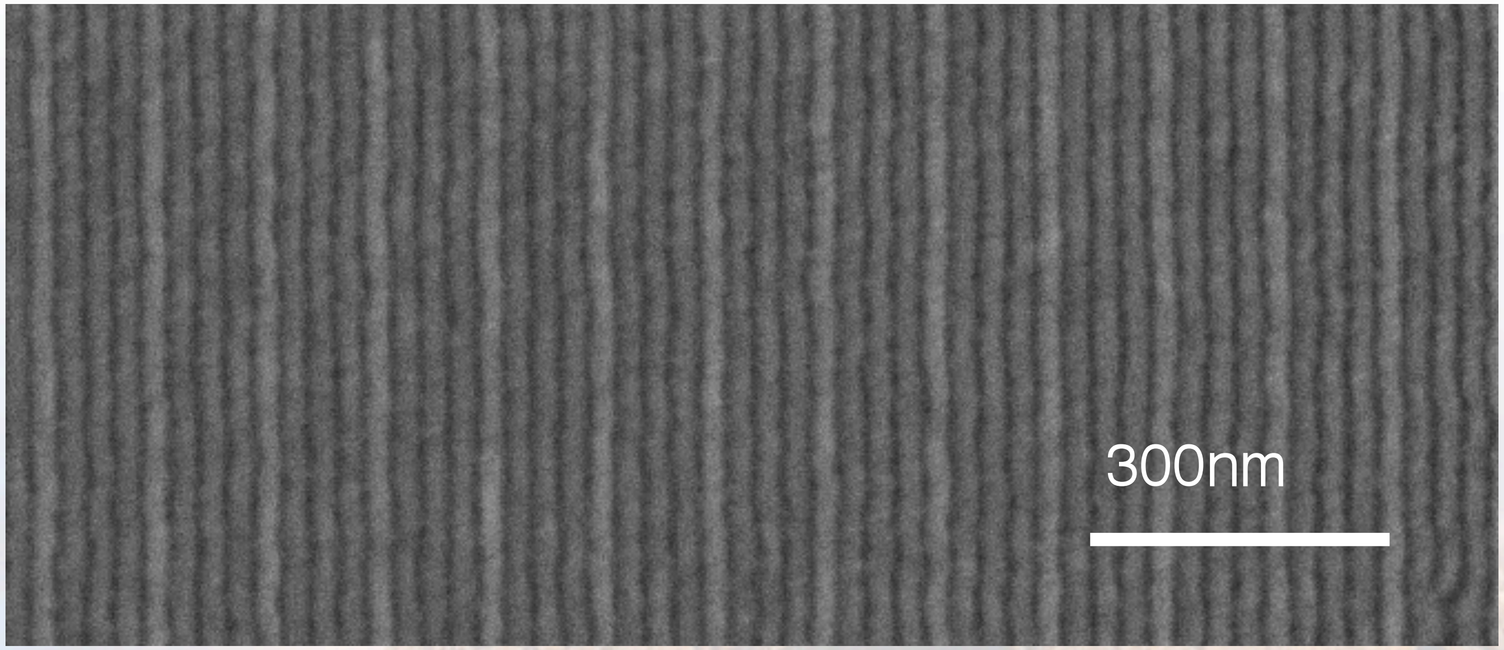
Wet Etch Limits to Microscale

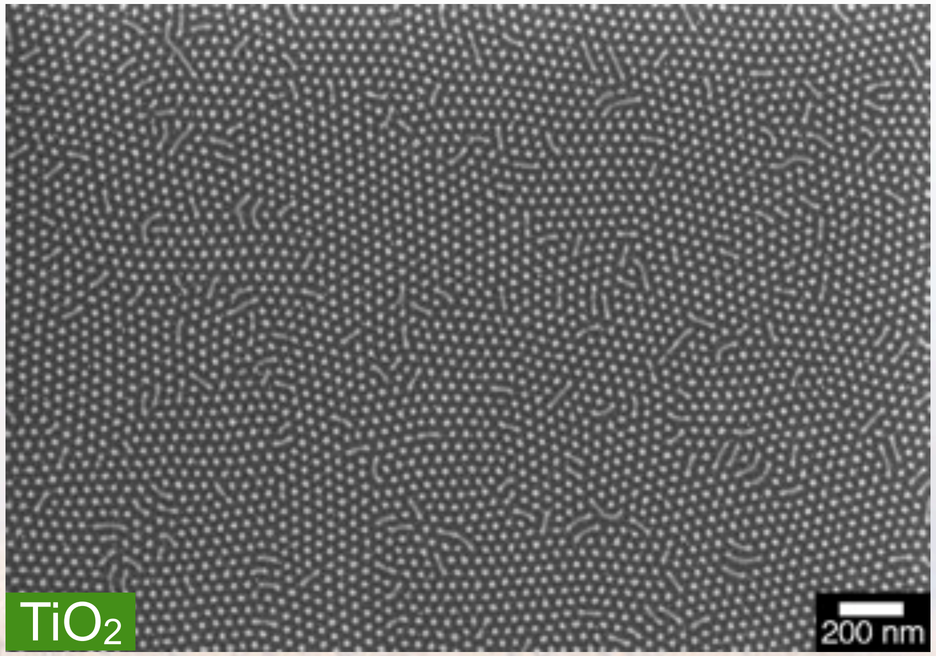
Maintaining Pattern Fidelity through Thermal Processing (>600°C)



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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- Dick Grant
- Michael Rye
- Jeff Stevens

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  - Charlie Liu
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  - 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