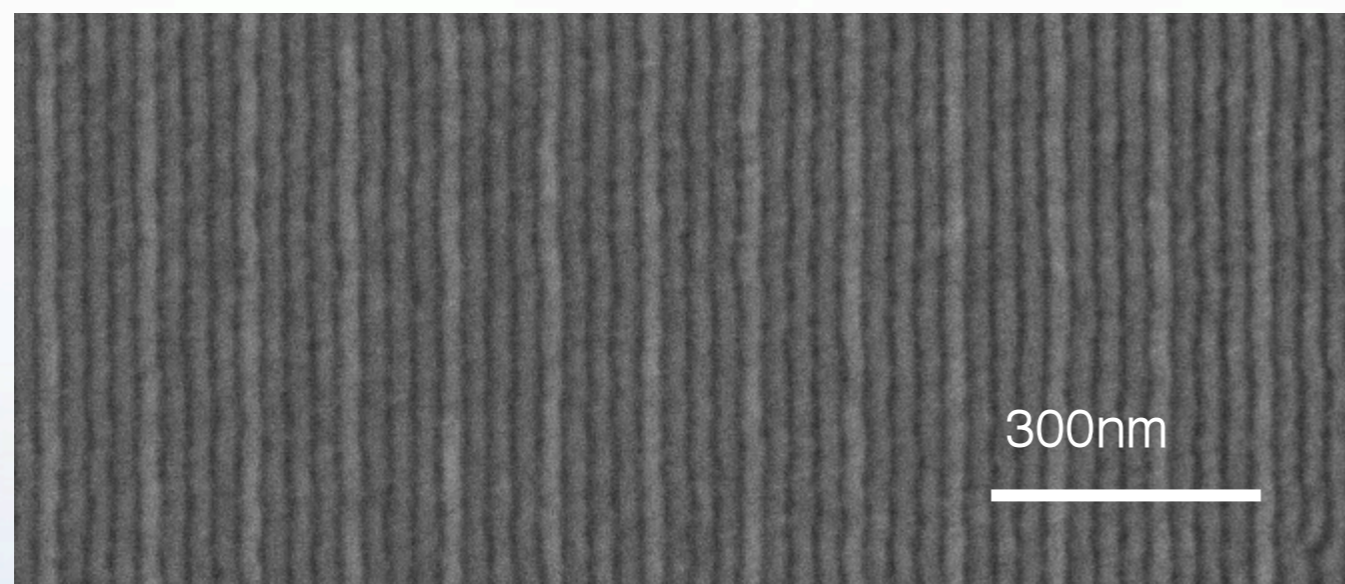
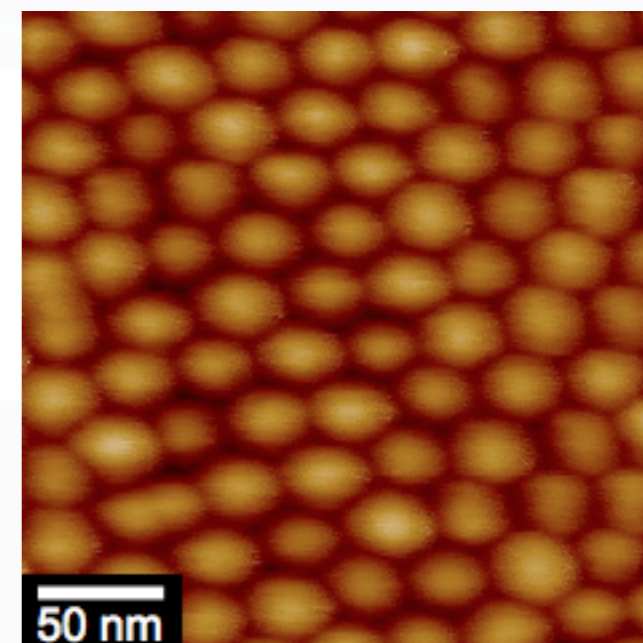
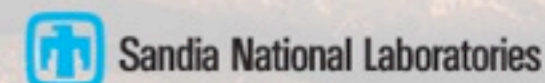


# Combined Lithography for Versatile Nanoscale Patterning and Integration



**Geoff Brennecka**  
Sandia National Laboratories



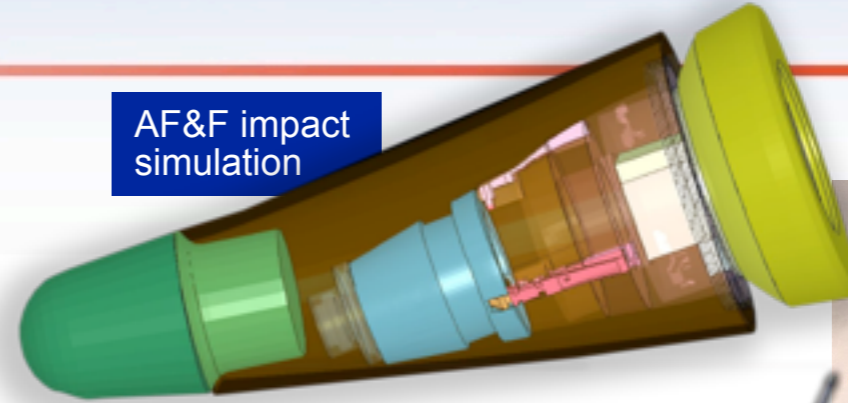
# Sandia's Work



Shuttle Orbital Inspection System



AF&F impact simulation



96% of total NW parts

## 4 Mission Areas

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



Predator UAV with SAR



Small robotic vehicles



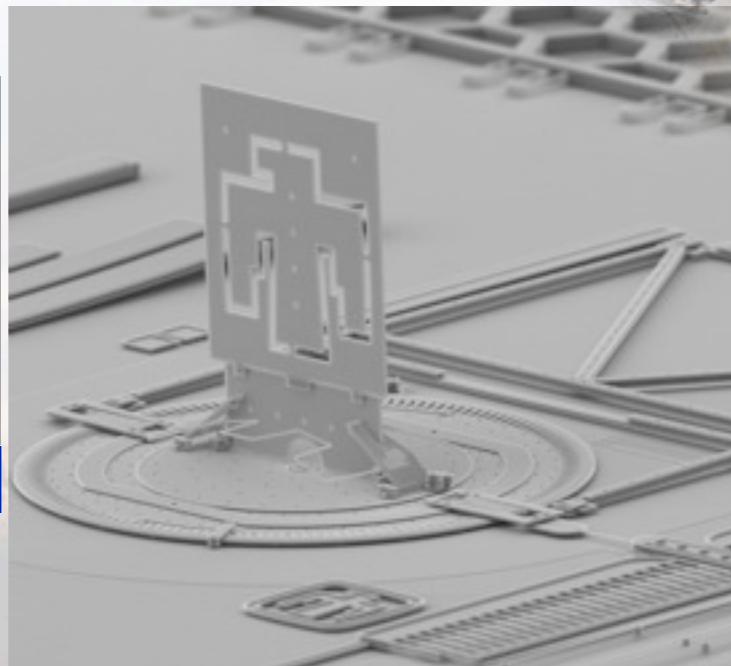
UGS



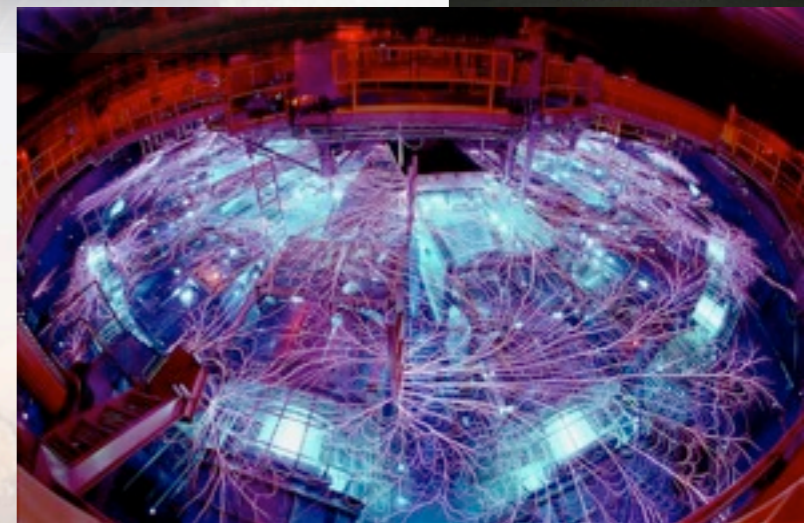
Renewable and alternative energy



µChemLab



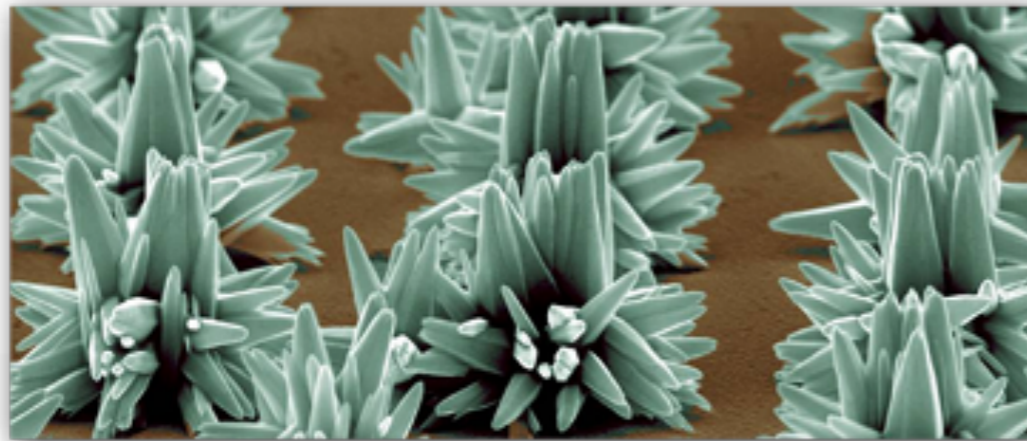
Clean room invented at SNL in 1963



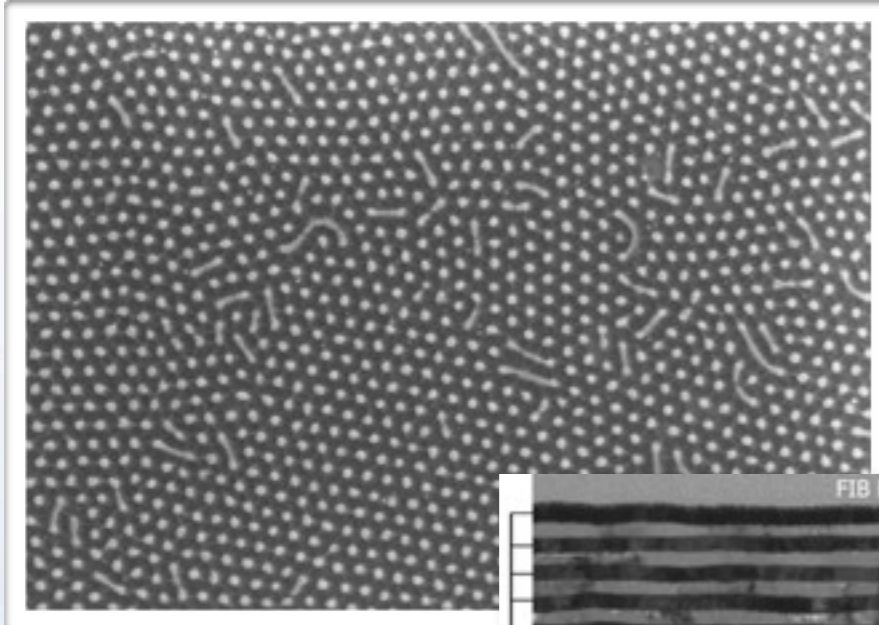
Z machine: the world's most powerful X-ray source



# Nanotechnology



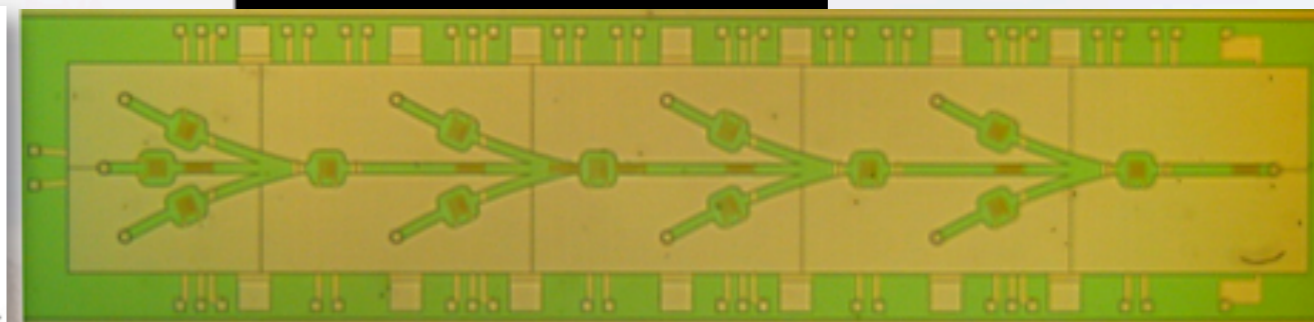
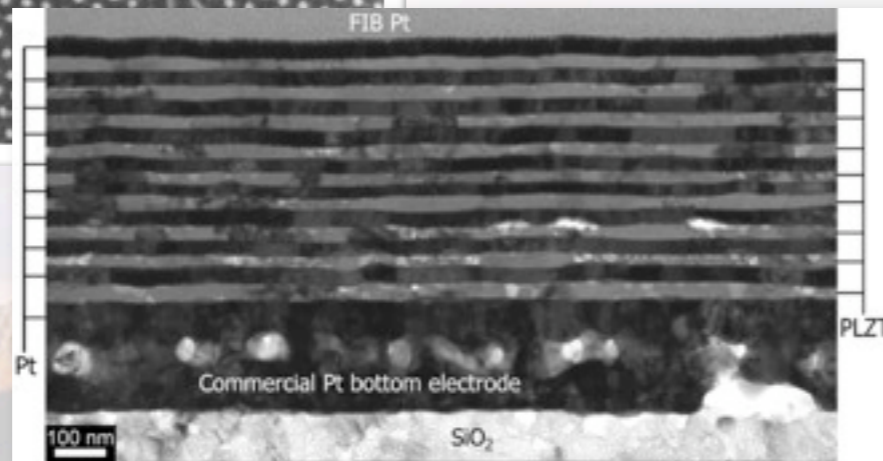
Complex functional nanomaterials



Nano-bio-micro interface



Microfluidic chip

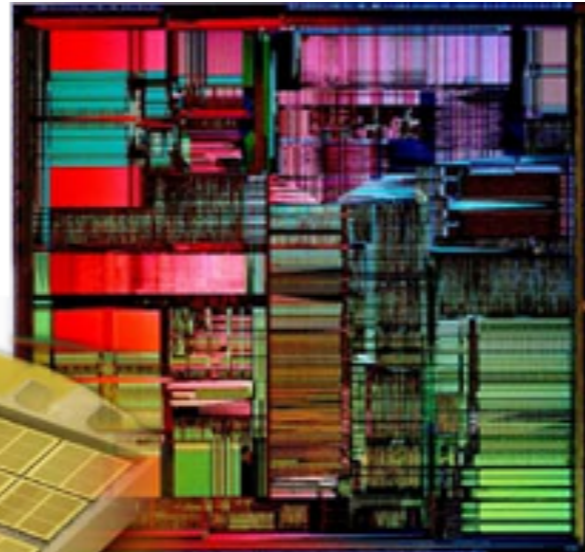


# Microsystems

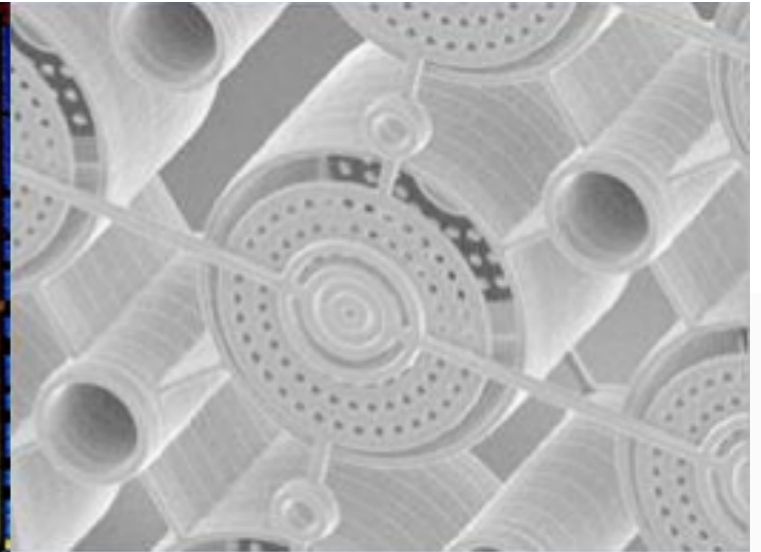
MEMS louvers  
manufactured at Sandia



Application-specific  
integrated circuit



Ion traps for quantum computing



Johns Hopkins/APL  
thermal regulator



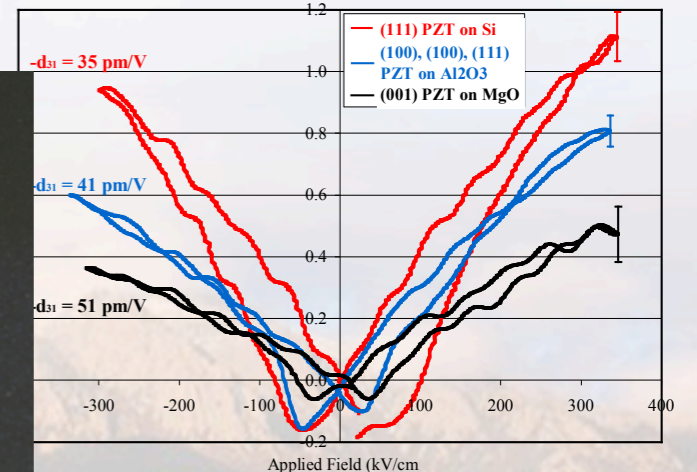
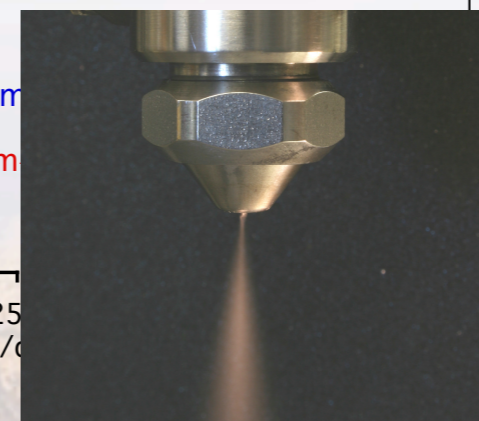
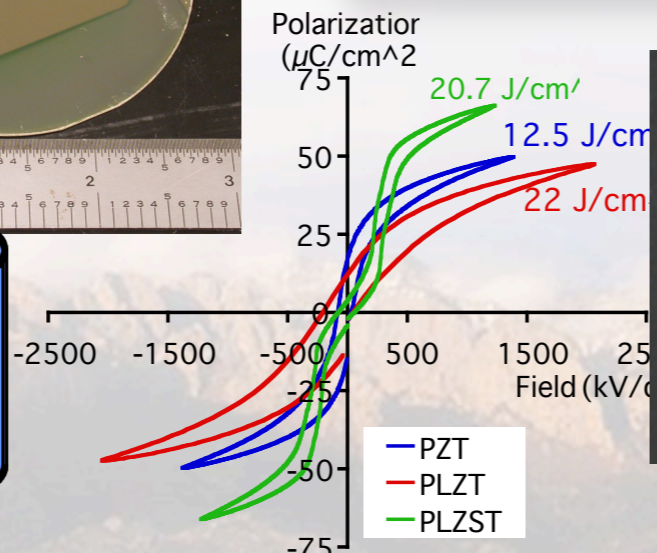
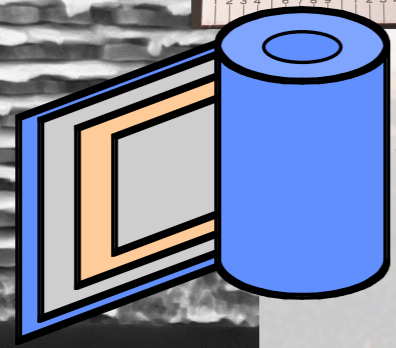
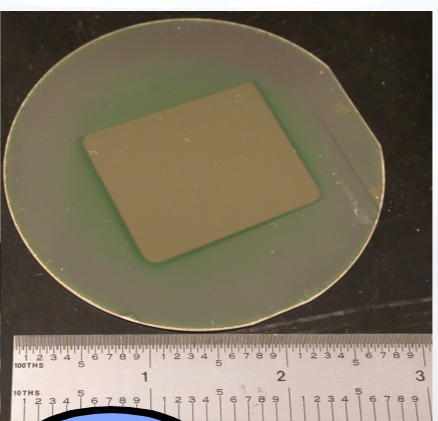
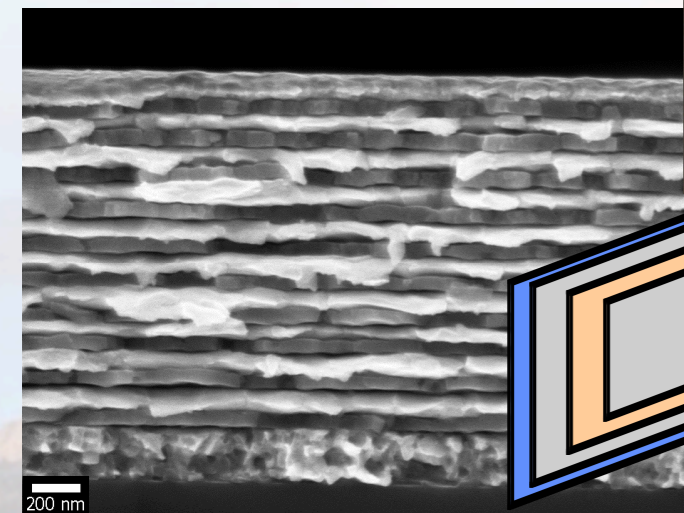
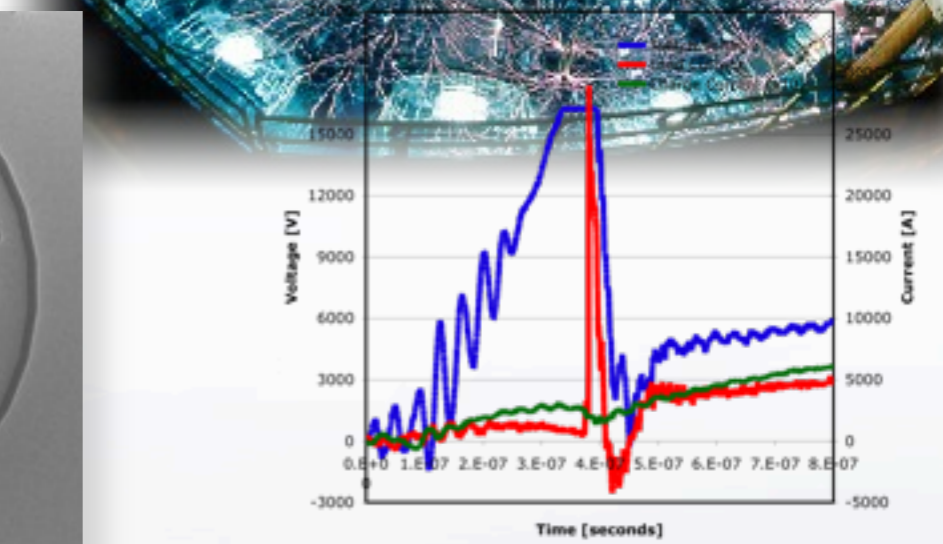
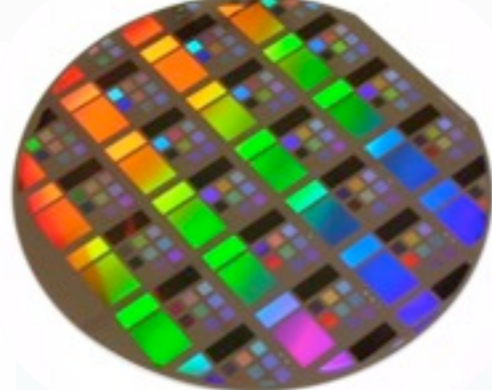
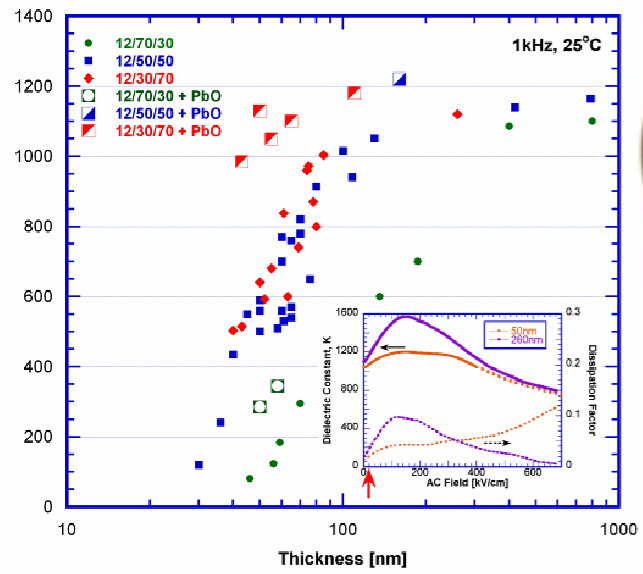
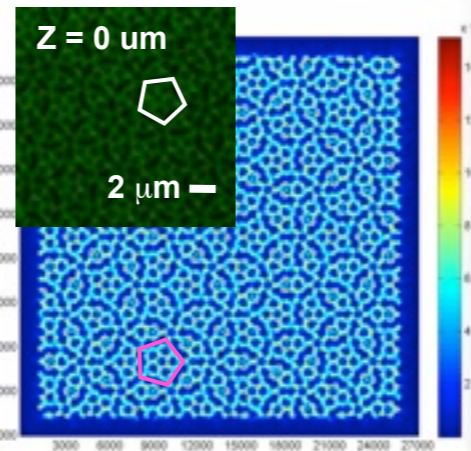
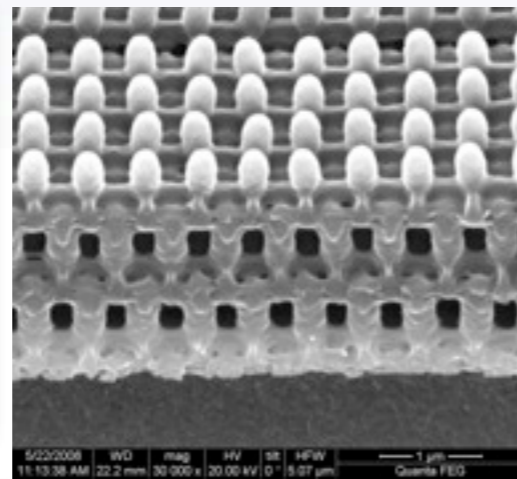
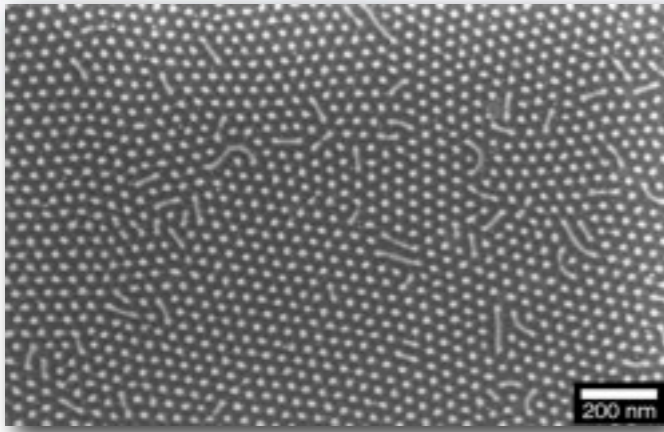
Microgears



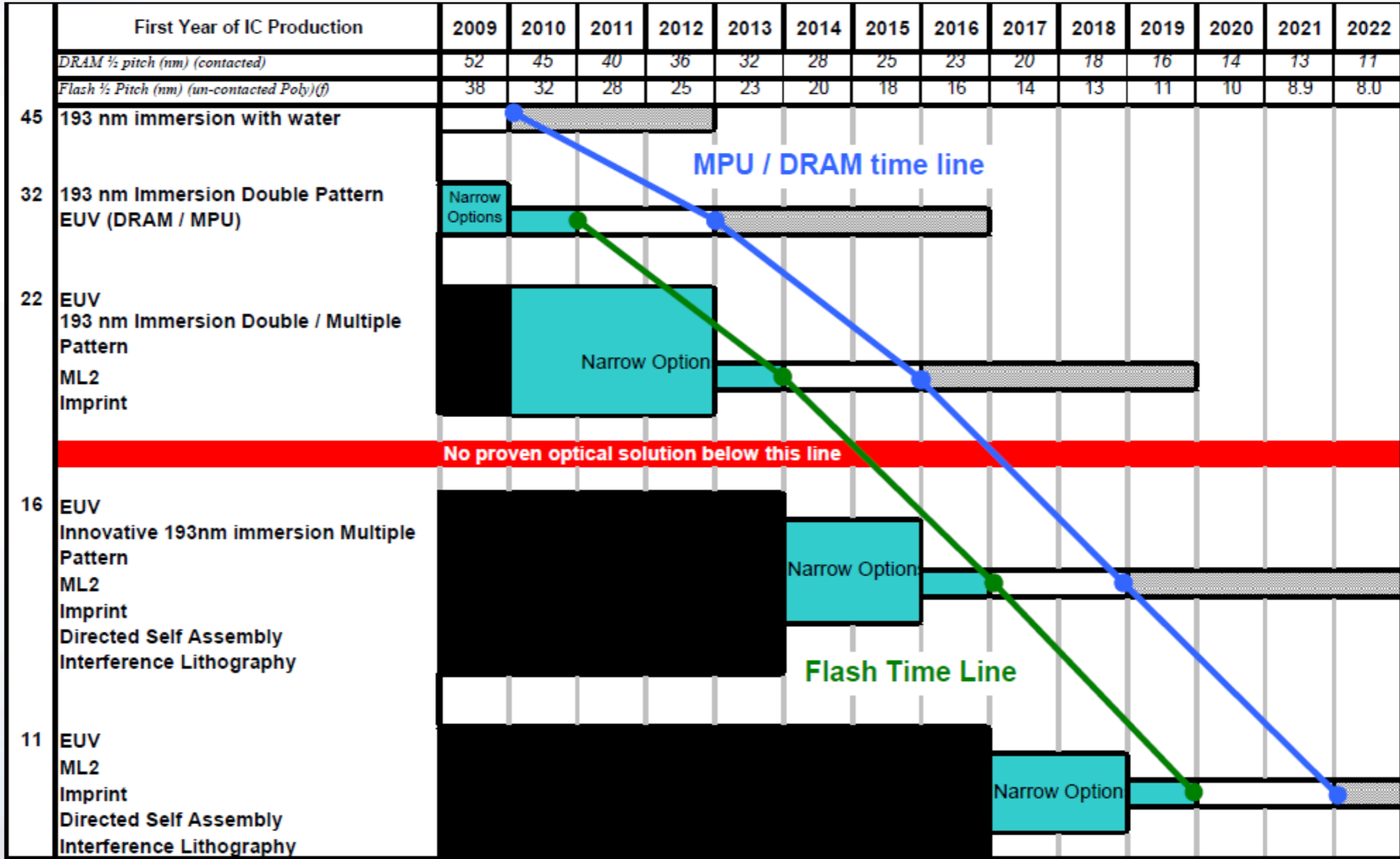
Outside view of the Microsystems Engineering for Strategic Applications (MESA)  
and clean room at MESA



# Project Sampler



# Doing Moore with the Same?



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



# Doing More with the Same?

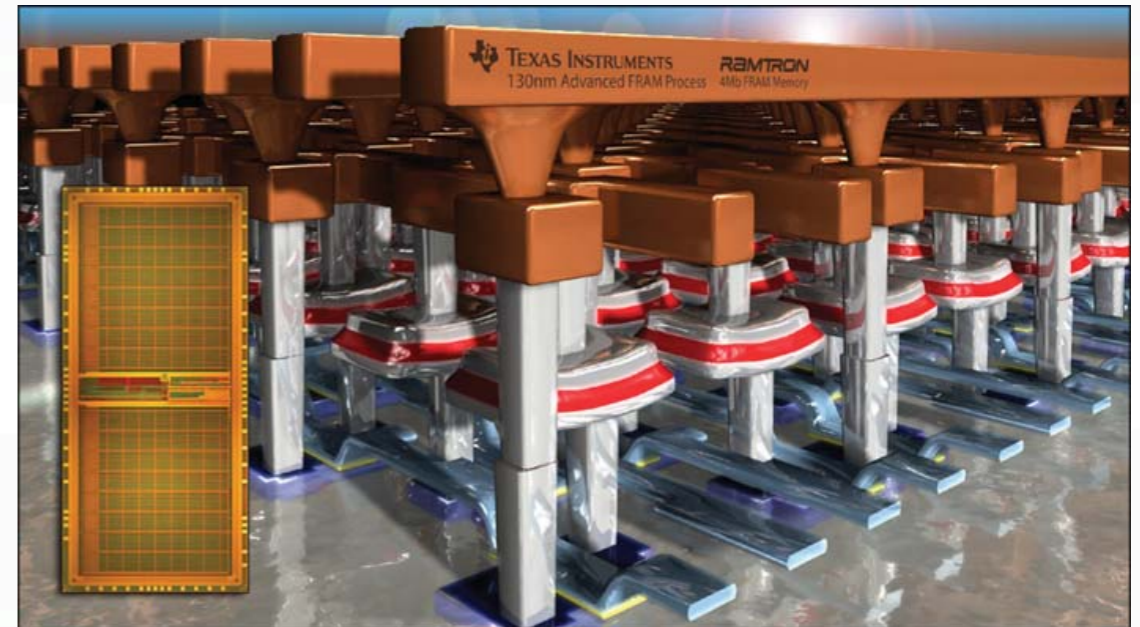
Integration of materials with new and/or increased functionality

## 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



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

## Target Demo Application Information Storage (NVRAM)

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

# 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)

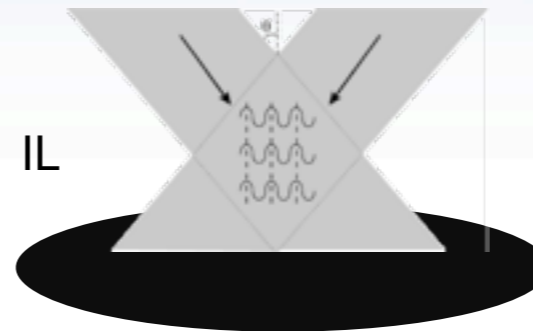
- (+) rapid, large area, parallel process
- (+) **low cost** (rapid, large area, maskless)
- (+) tunable symmetry, period, motif
- (-) layer alignment & spatial pattern variation difficult

## 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 pattern



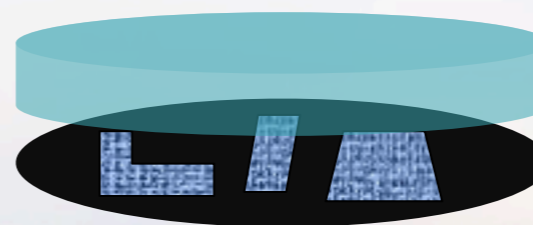
BCP DSA



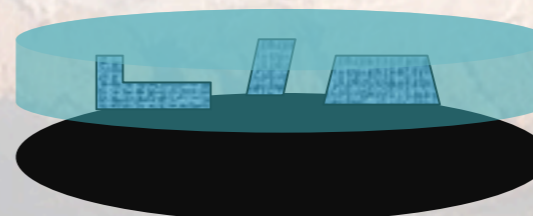
etch



transfer to NIL



NIL to die



### IL-defined chemical pre-patterns

- 60-90 nm pitch, ~4 cm<sup>2</sup> areas

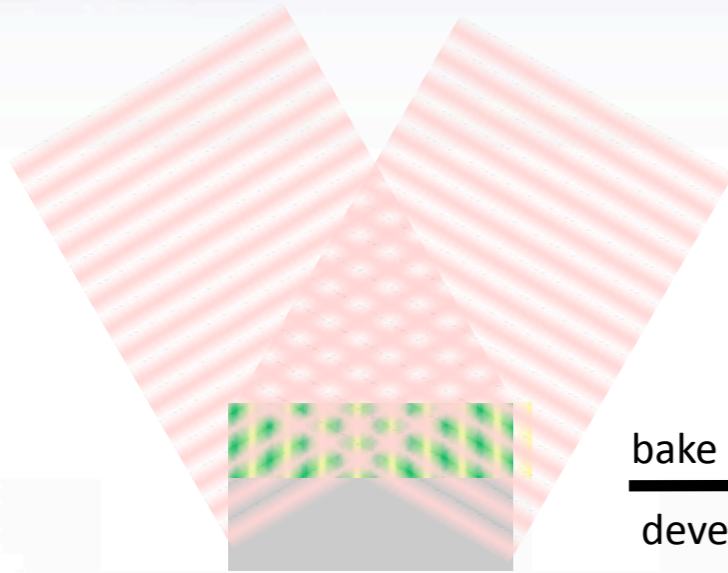
### BCP Directed Self Assembly

- 20-30 nm pitch device patterns
- 10-50 nm CDs
- Half-pitch to ~11 nm over ~4 cm<sup>2</sup> areas

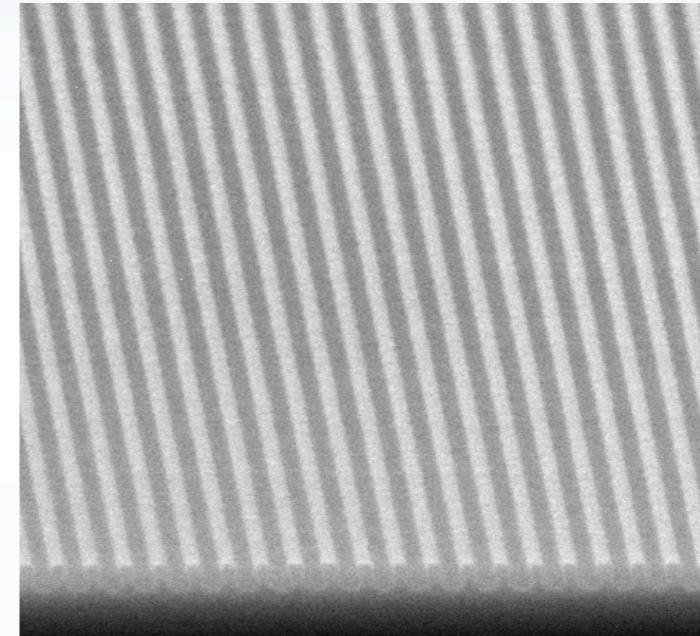
### Pattern transfer to create Nano-Imprint lithography (NIL) device masters

# Optical Interference Lithography

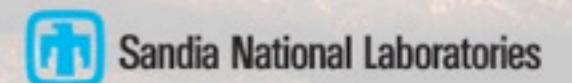
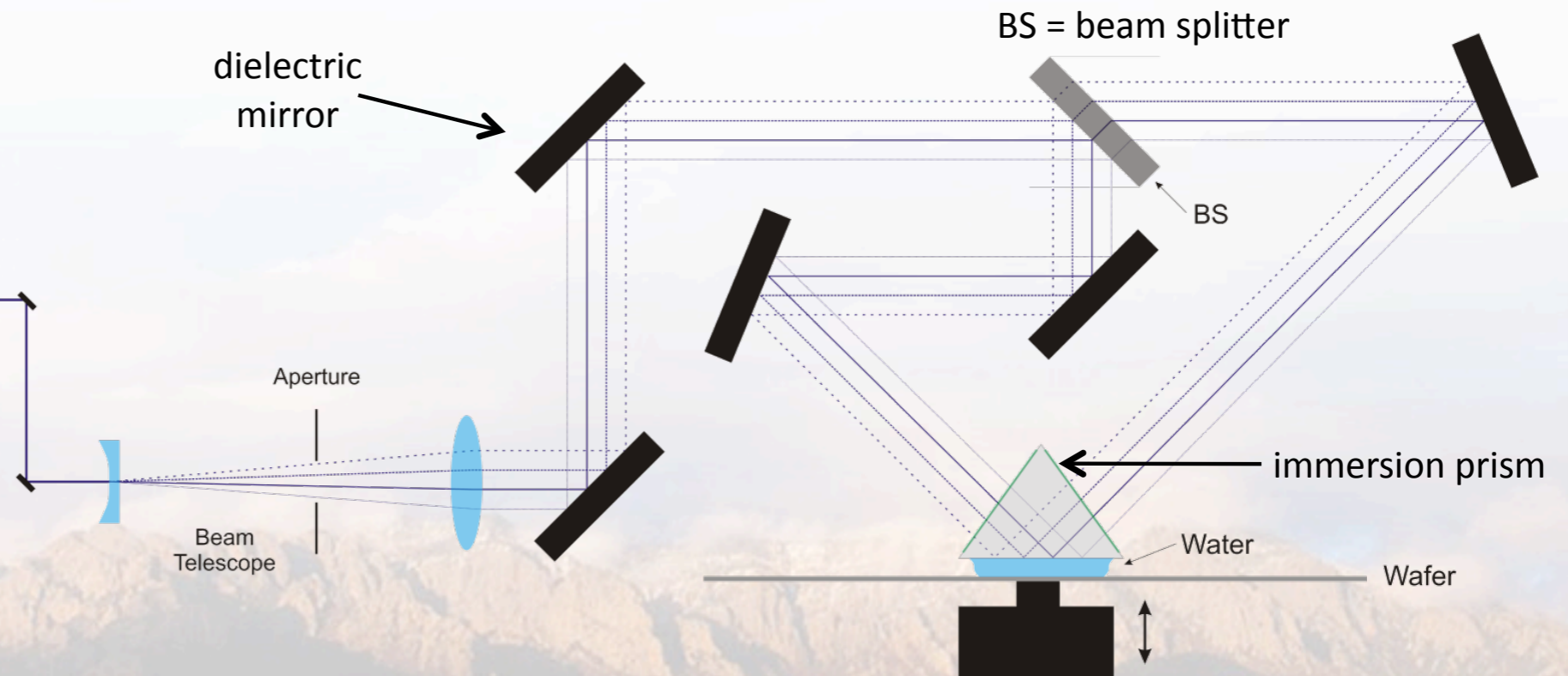
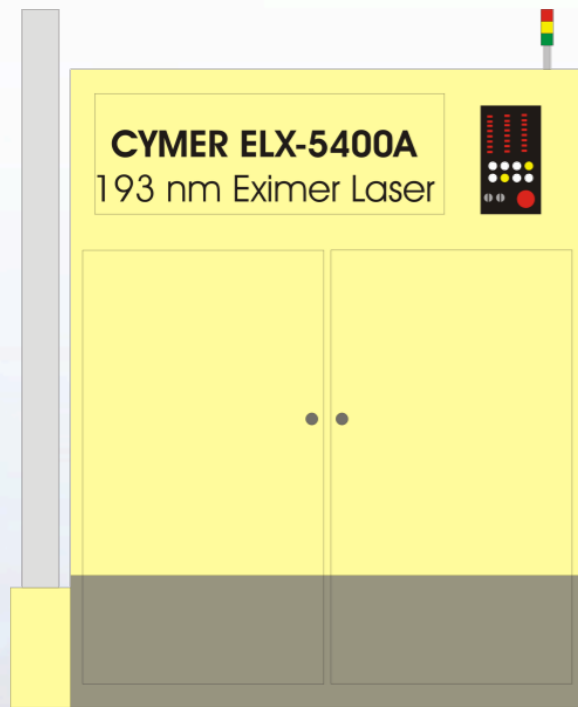
Prof. Steven J. Brueck, Alex Raub, Matt George



bake and develop

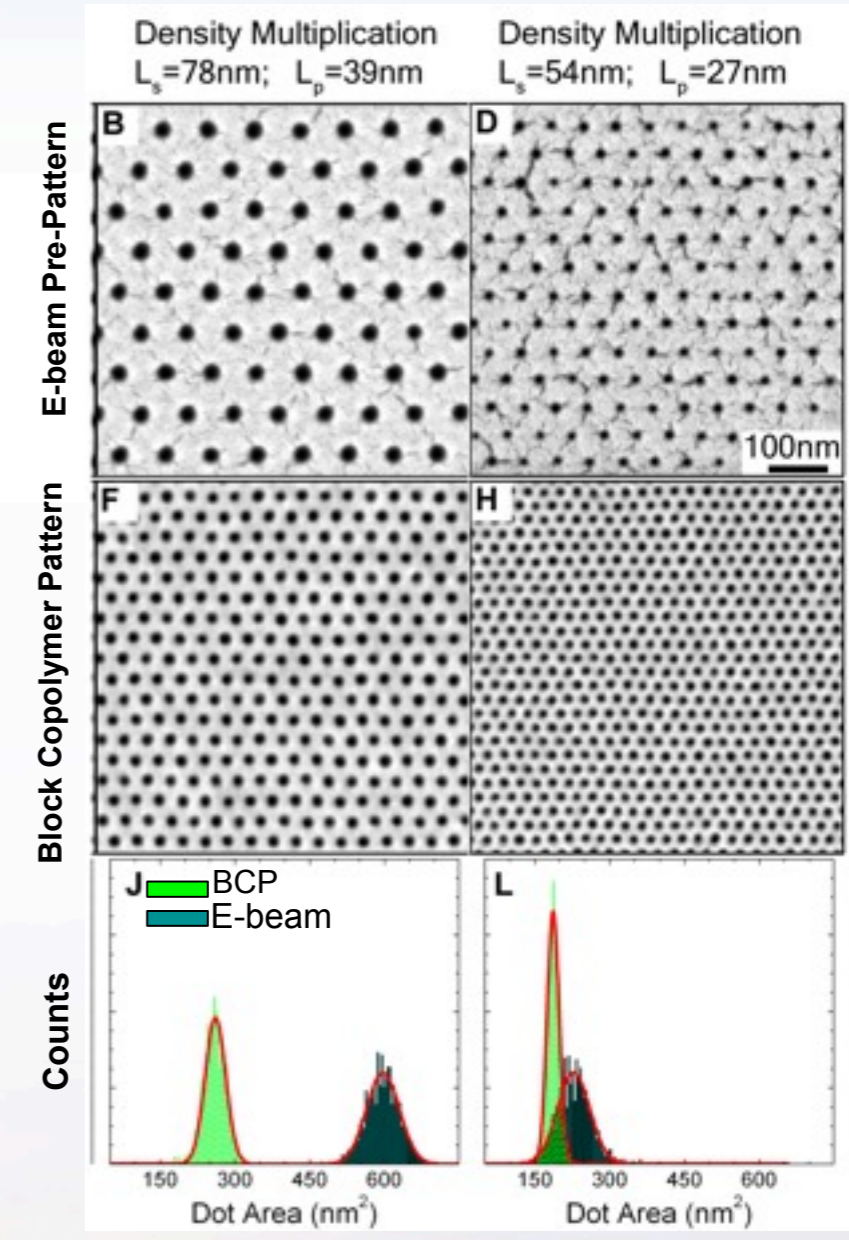
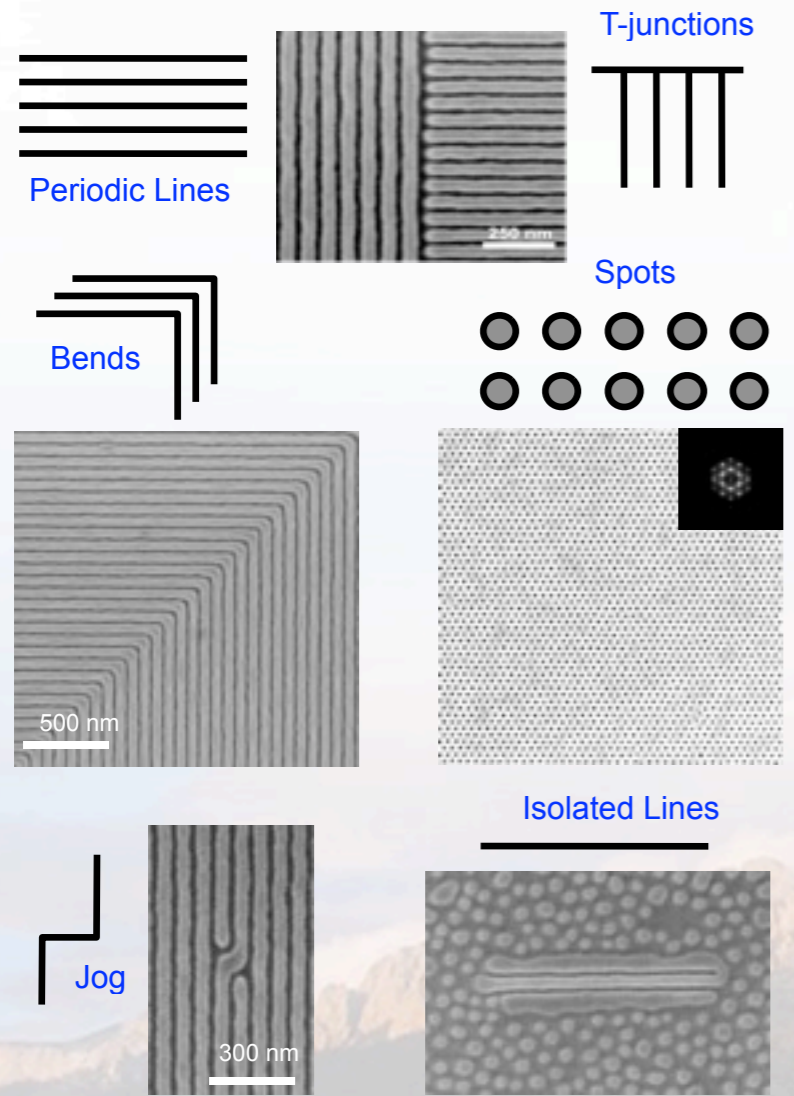
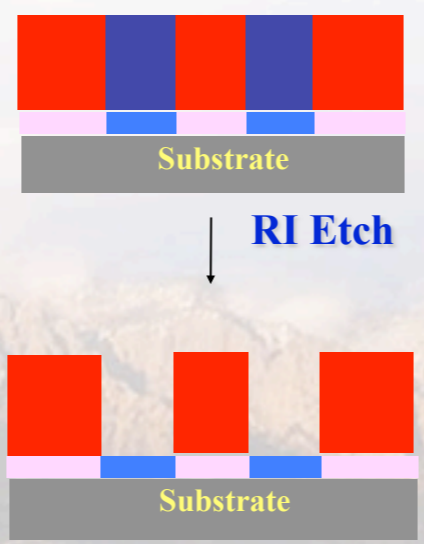
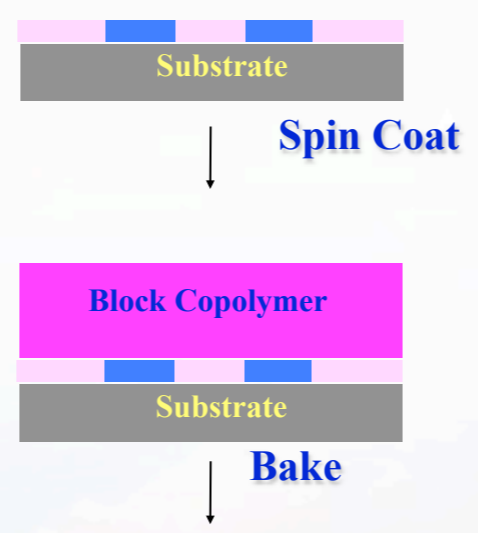
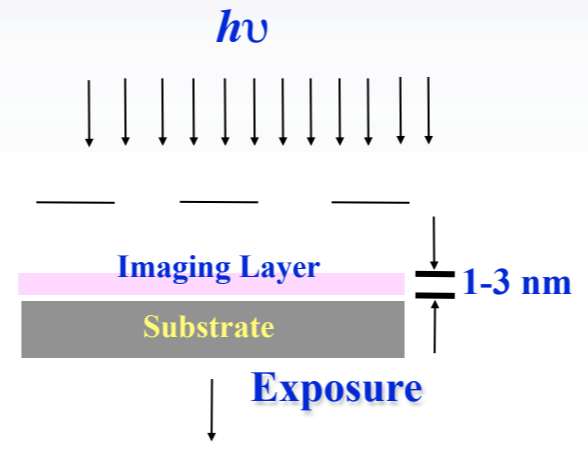
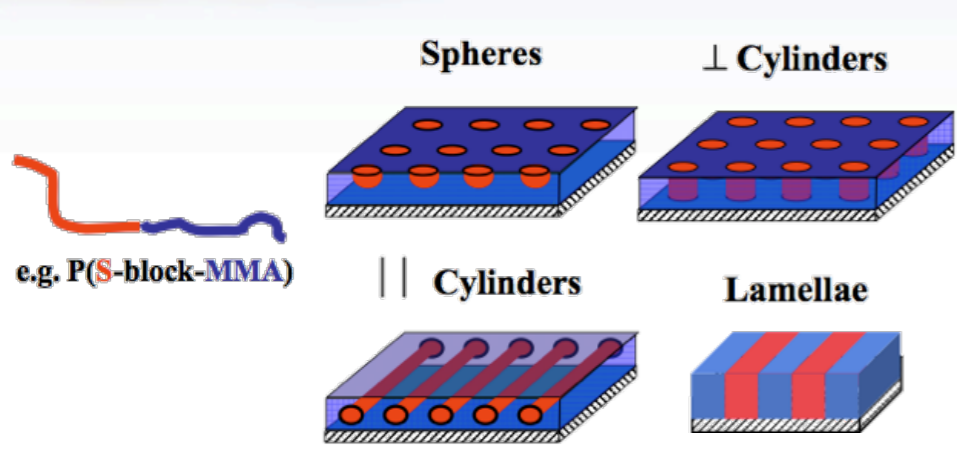


Critical dimensions approach 50 nm, patterned areas approach 4cm<sup>2</sup>



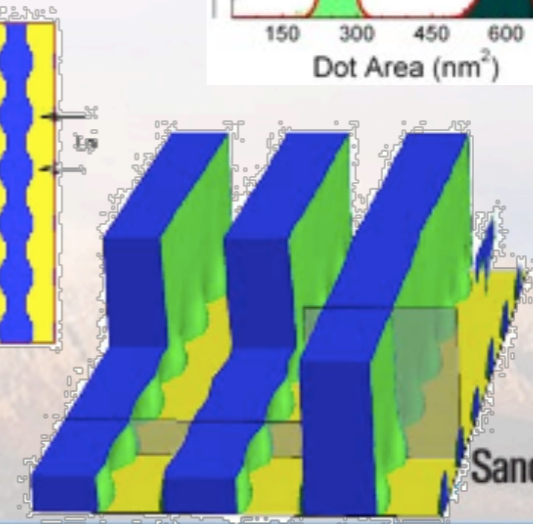
# Block-Copolymer Directed Self Assembly

Prof. Paul F. Nealey, Charlie Liu, Lance Williamson  
 Prof. Juan de Pablo, Darin Pike, Brandon Peters



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

Daoulas et al., *Langmuir*, 2008

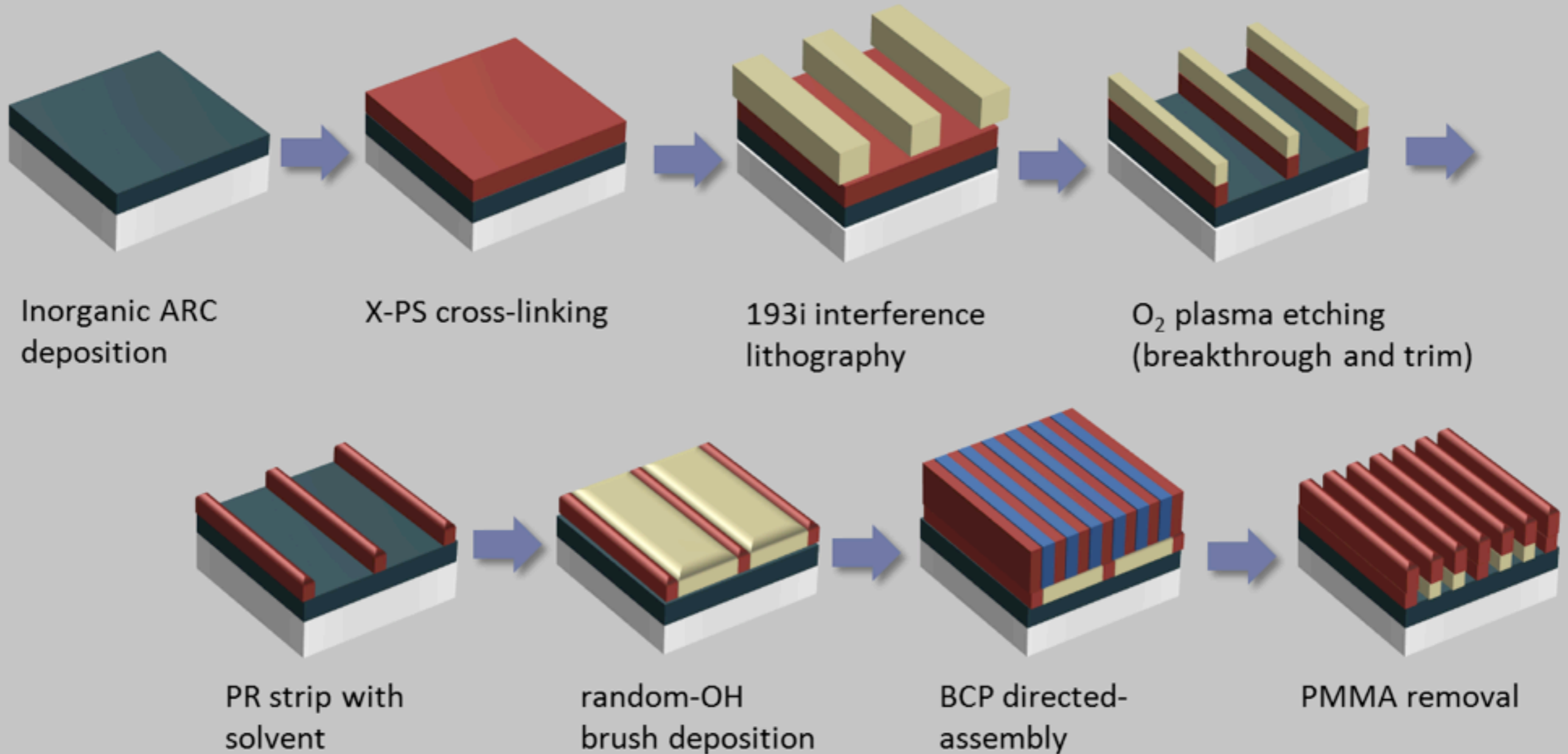


Sandia National Laboratories

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

# Density Multiplication

## Process flow with ARC and 193i



3x density multiplication  
30nm features in 90nm IL pattern  
over mm<sup>2</sup> areas

# Density Multiplication

22-22k on 100nm

300nm

18-18k on 110nm

300nm

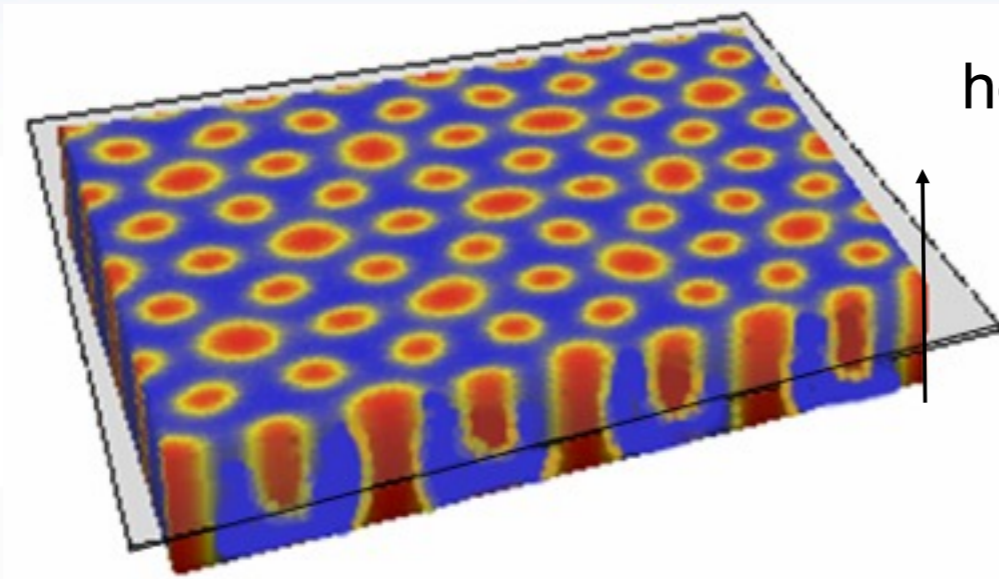
4X Multiplication

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

Surface interactions are crucial

# Interfaces Lead to non-Bulk Morphologies

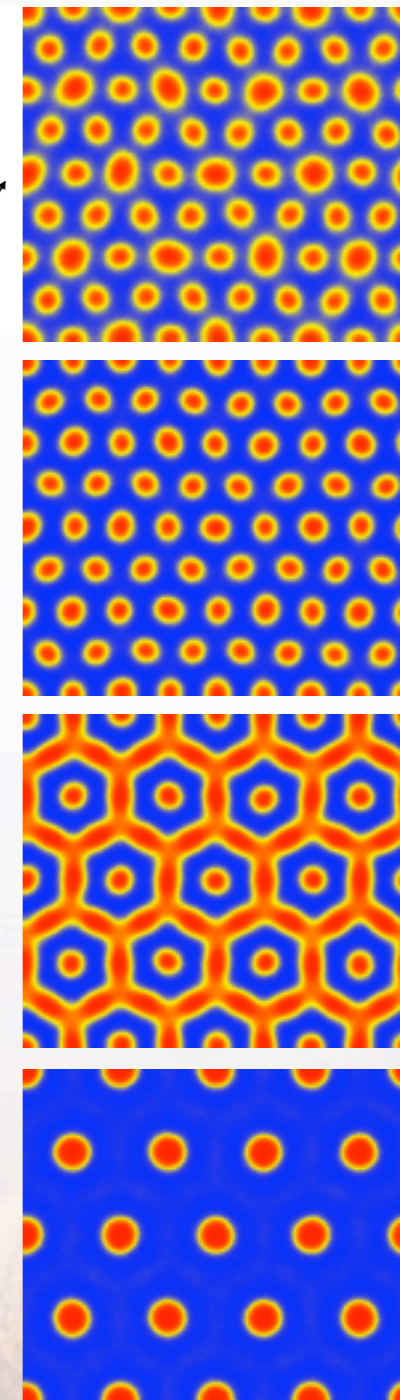
Monte Carlo simulations, consistent with SCFT and mean-field, but faster and more flexible



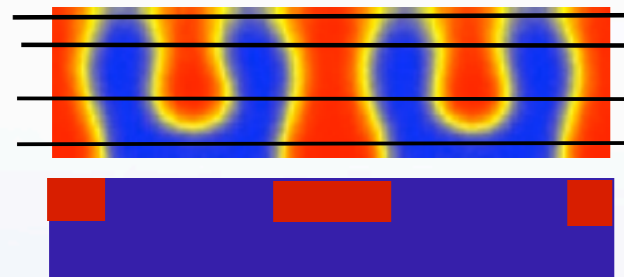
horizontal cross-sections

z

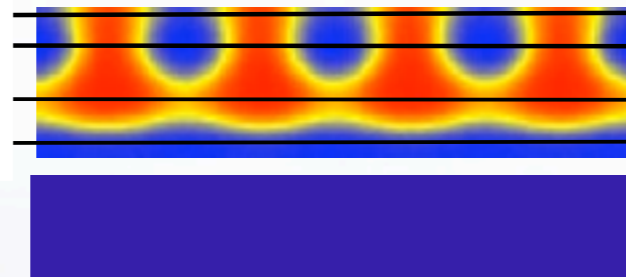
top surface



vertical cross-sections



patterned line



non-patterned line

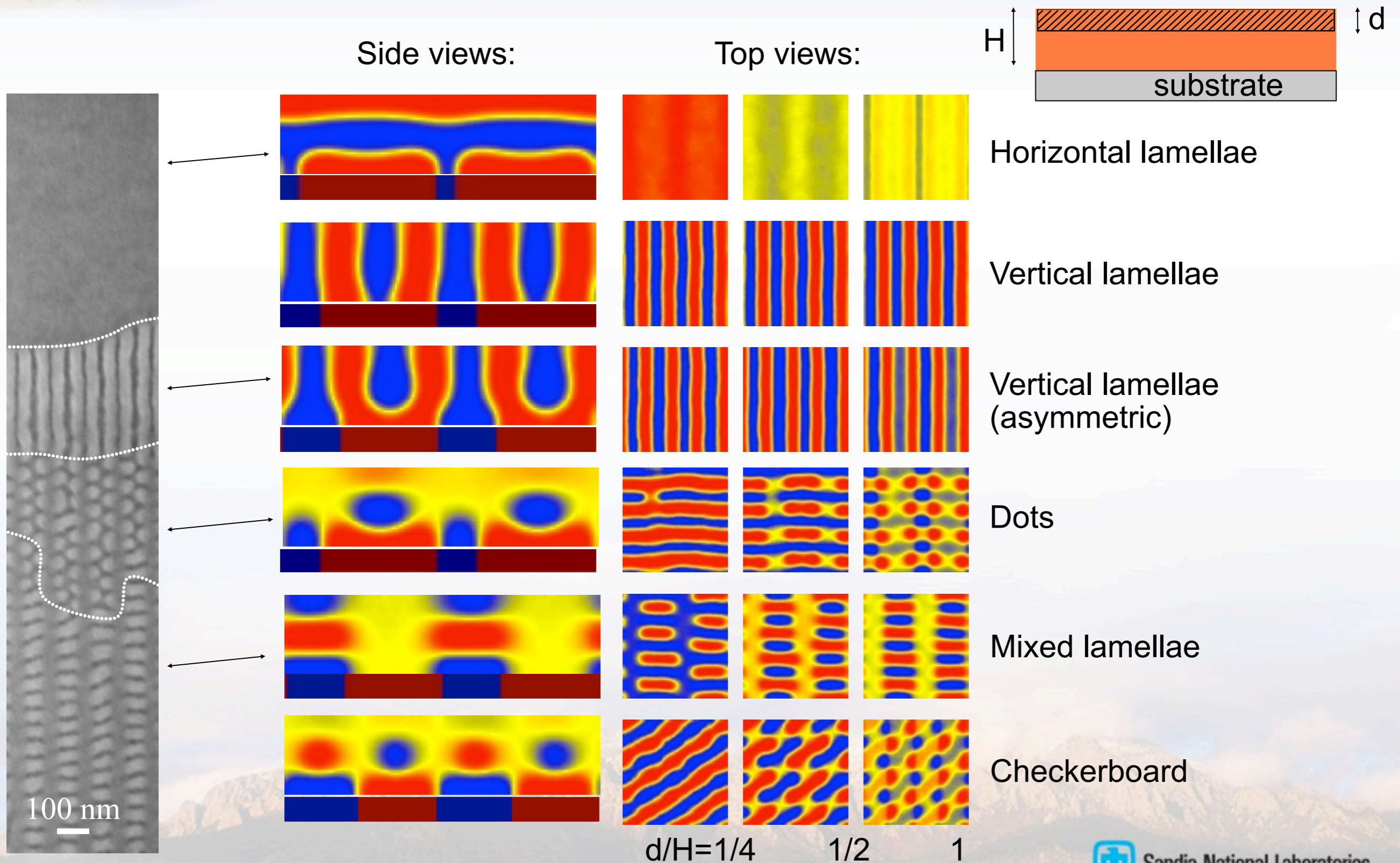
**strong attraction favors defect-free assembly but leads to hour-glass shaped domains.**

substrate

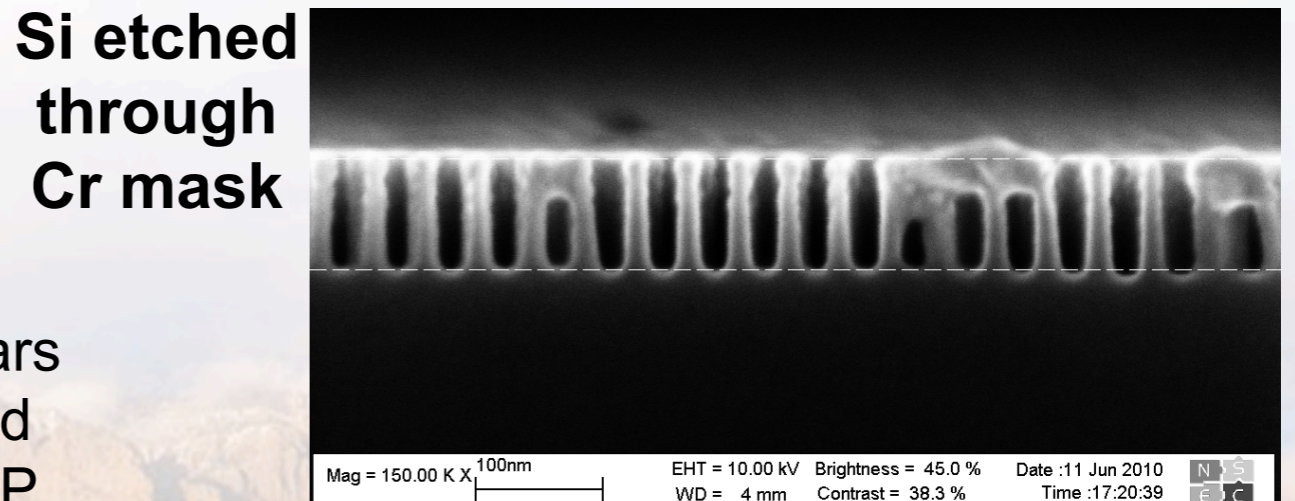
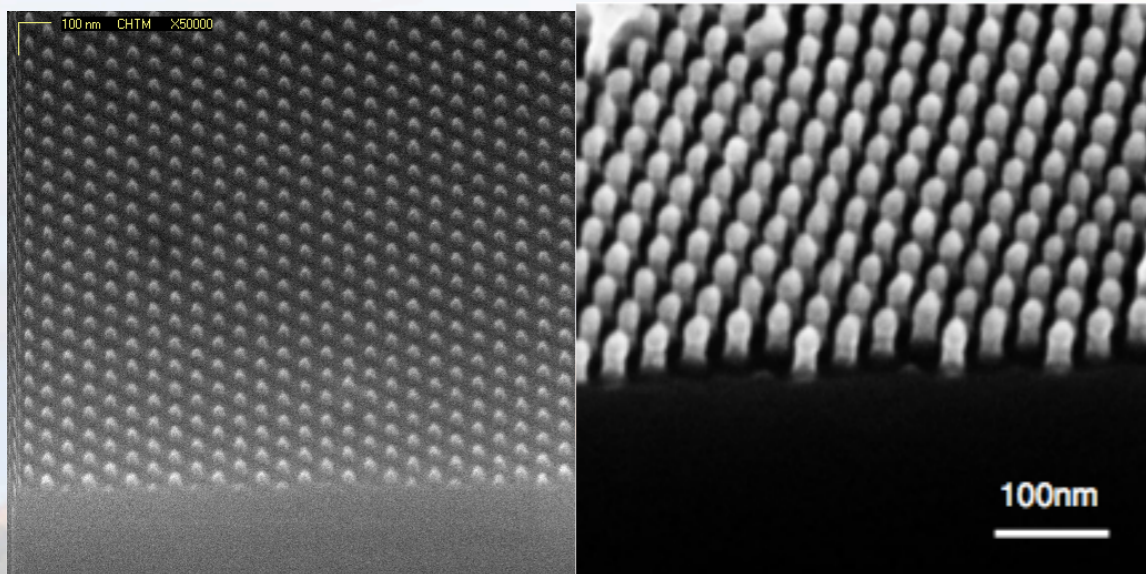
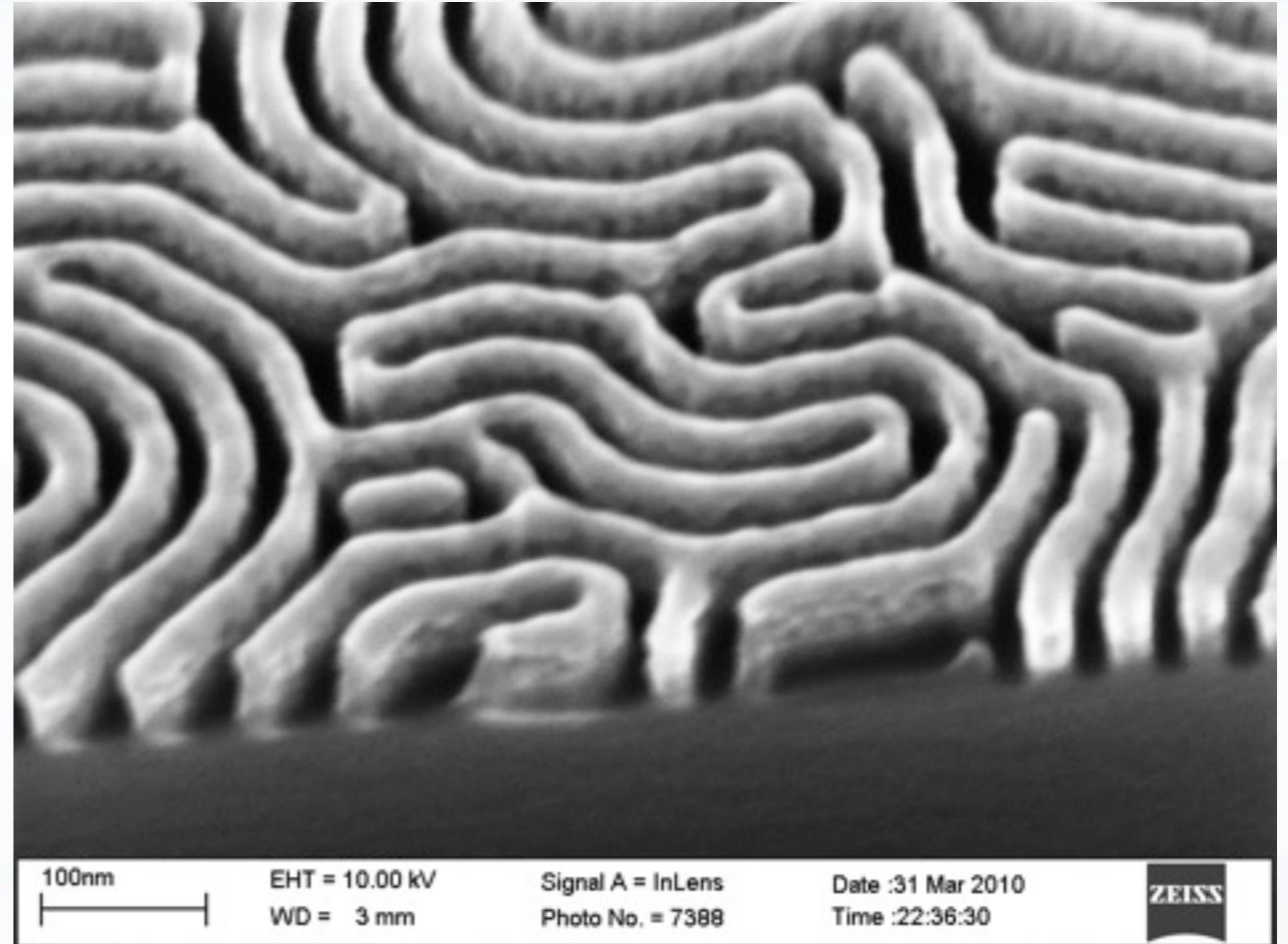
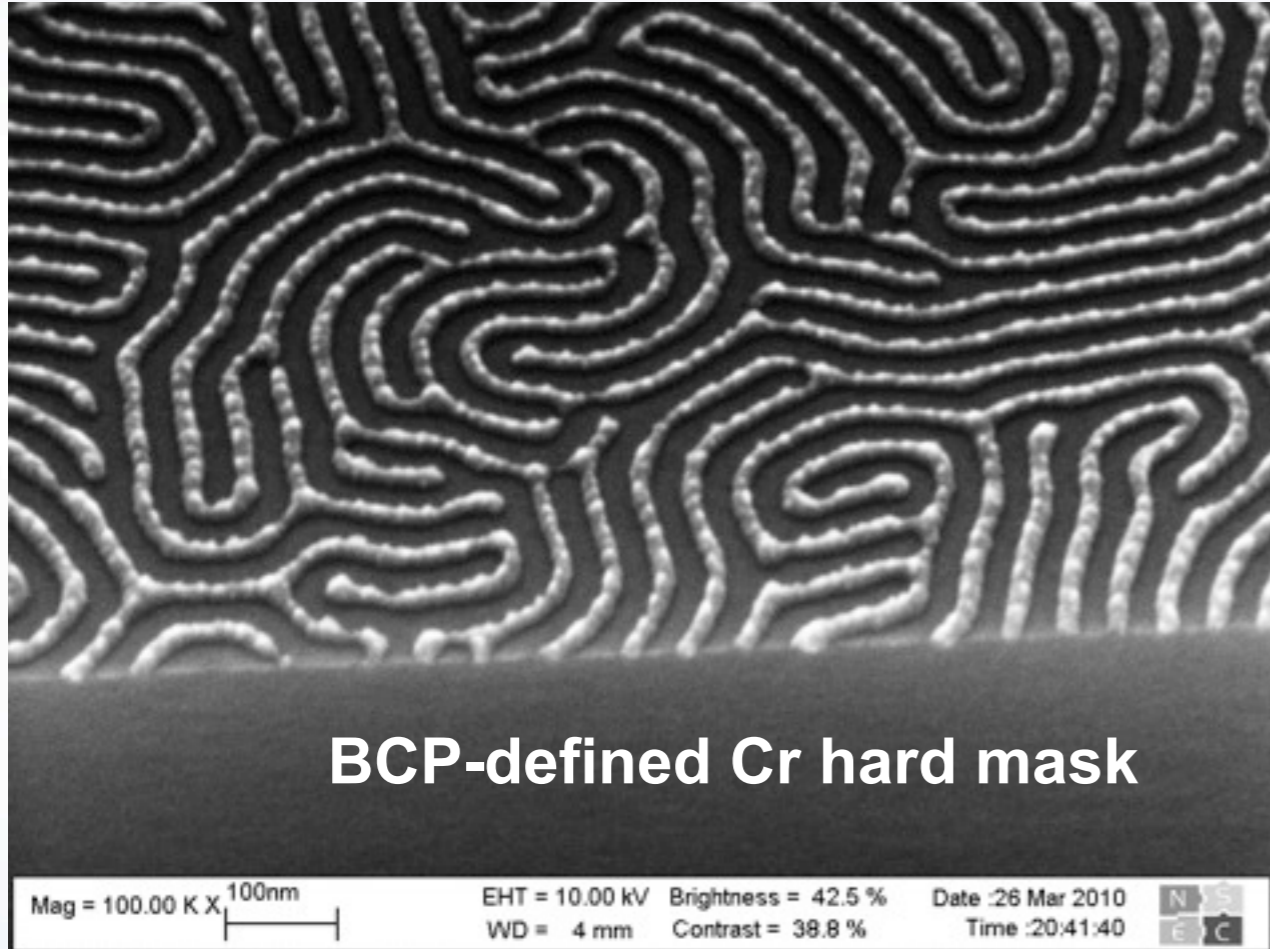


Sandia National Laboratories

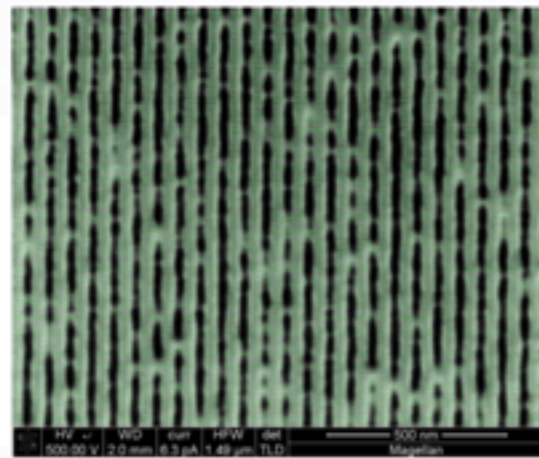
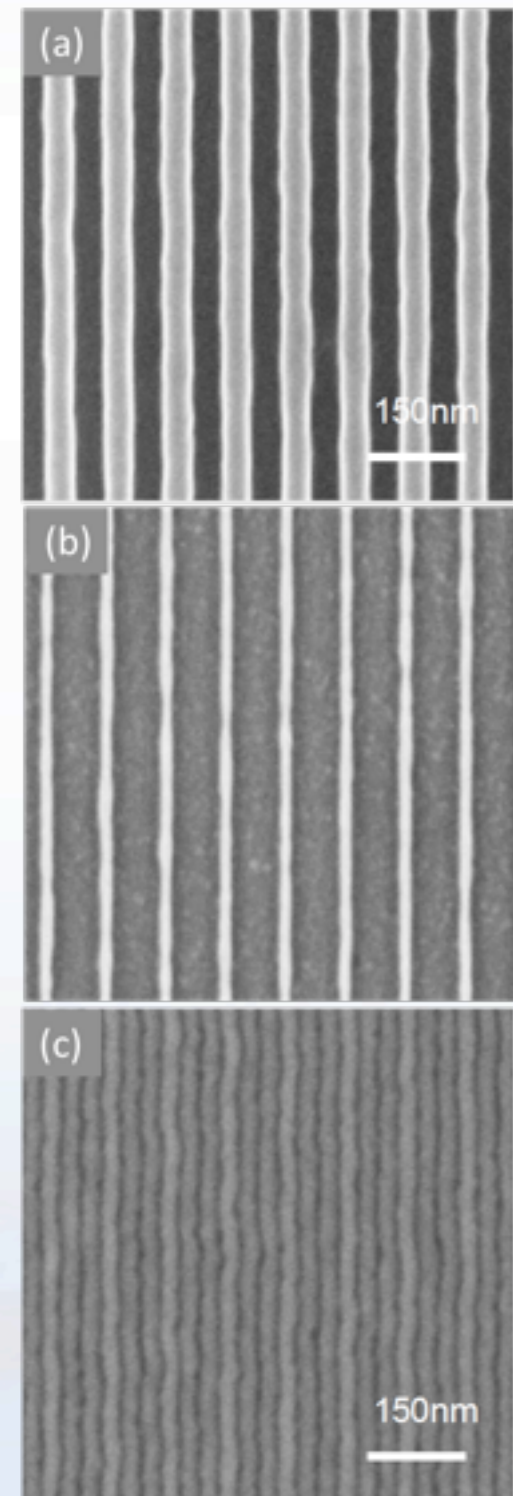
# Simulation Can Explain Variety of Experimental Morphologies



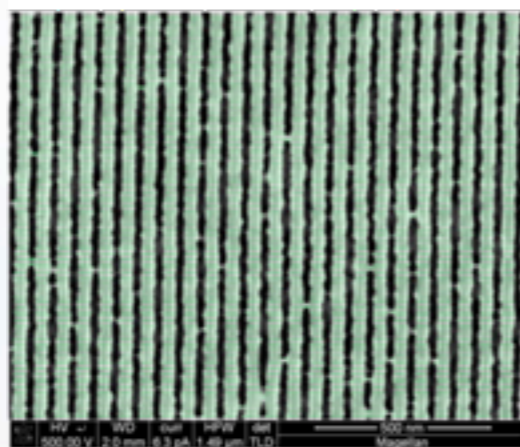
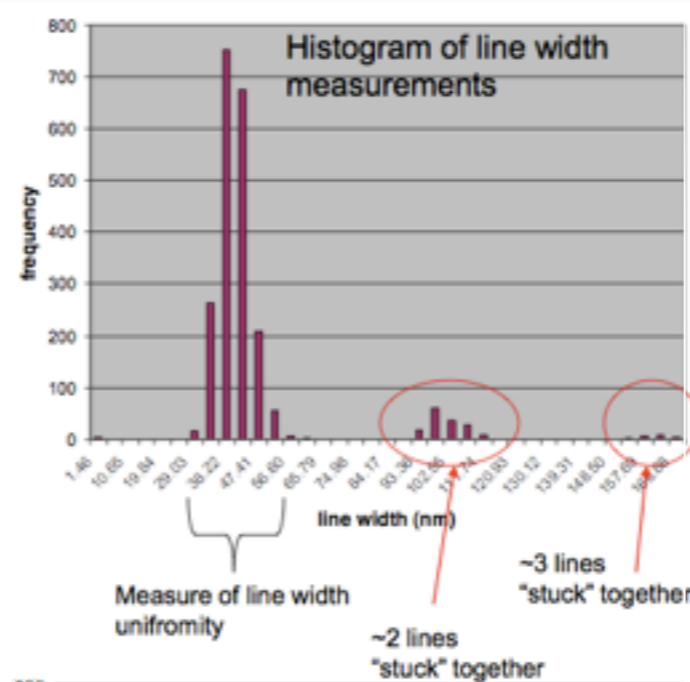
# Pattern Transfer



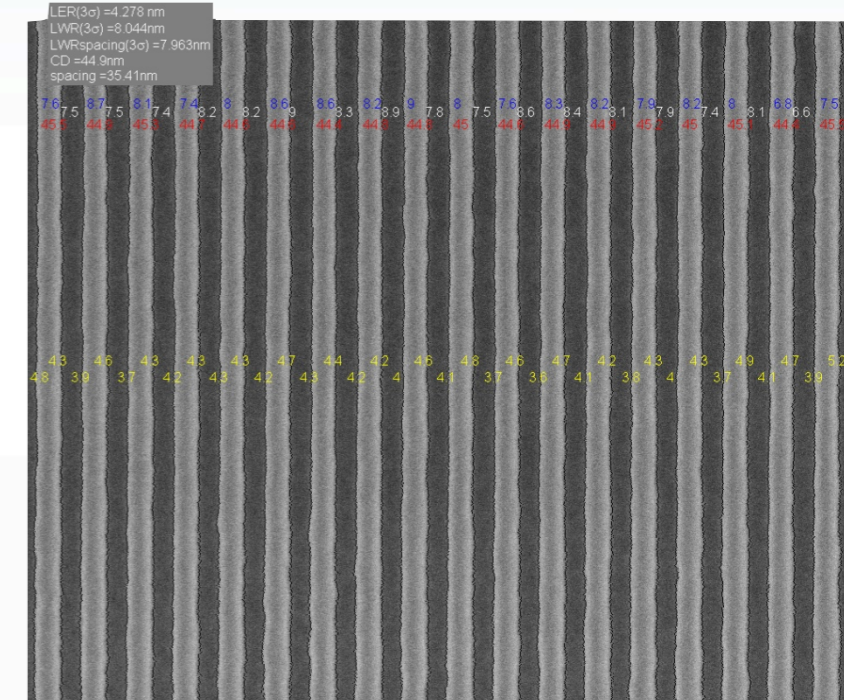
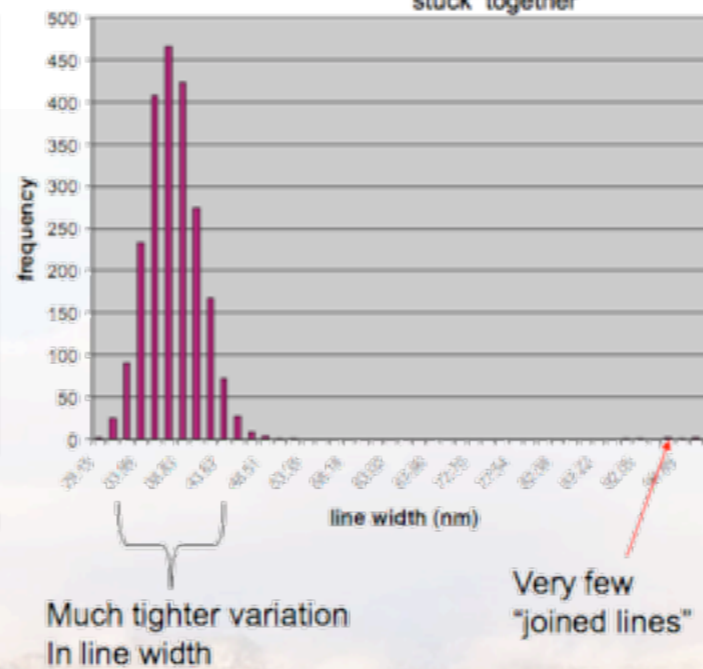
# Metrology



After insertion of 100 grid lines and BOOLEAN combination



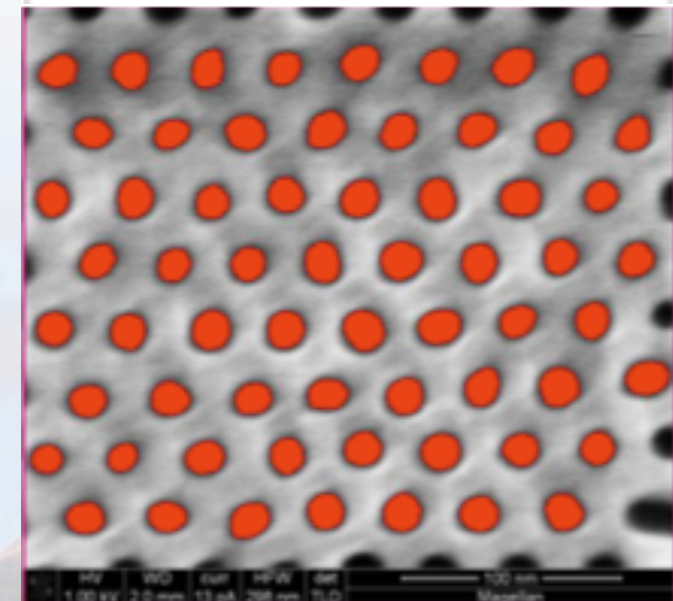
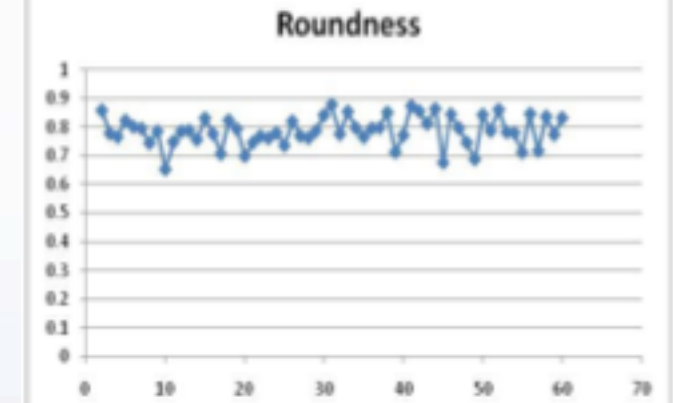
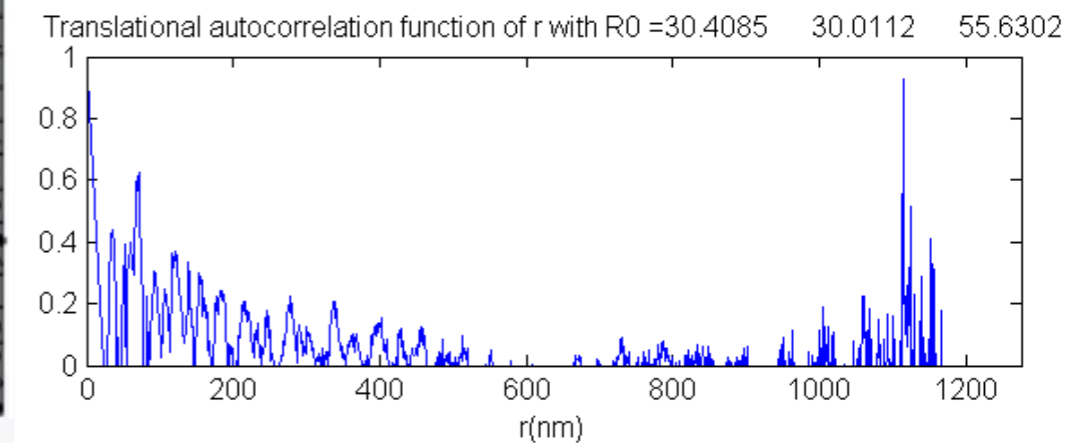
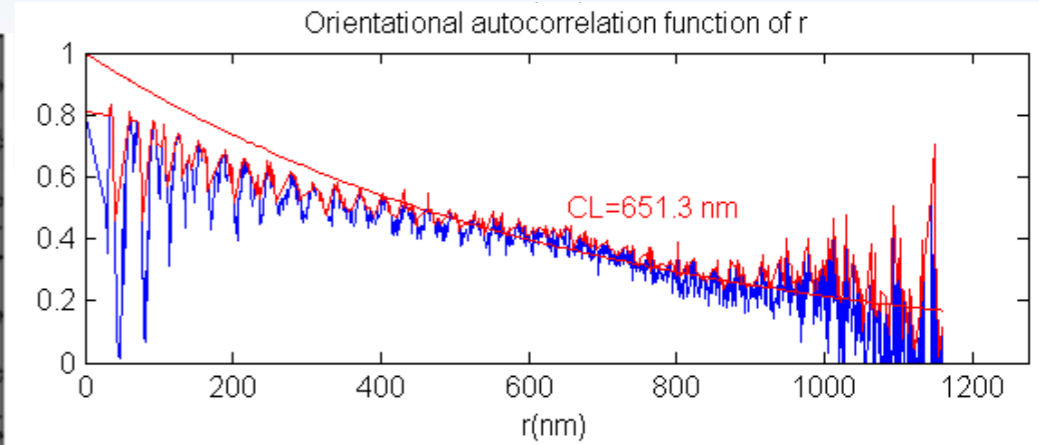
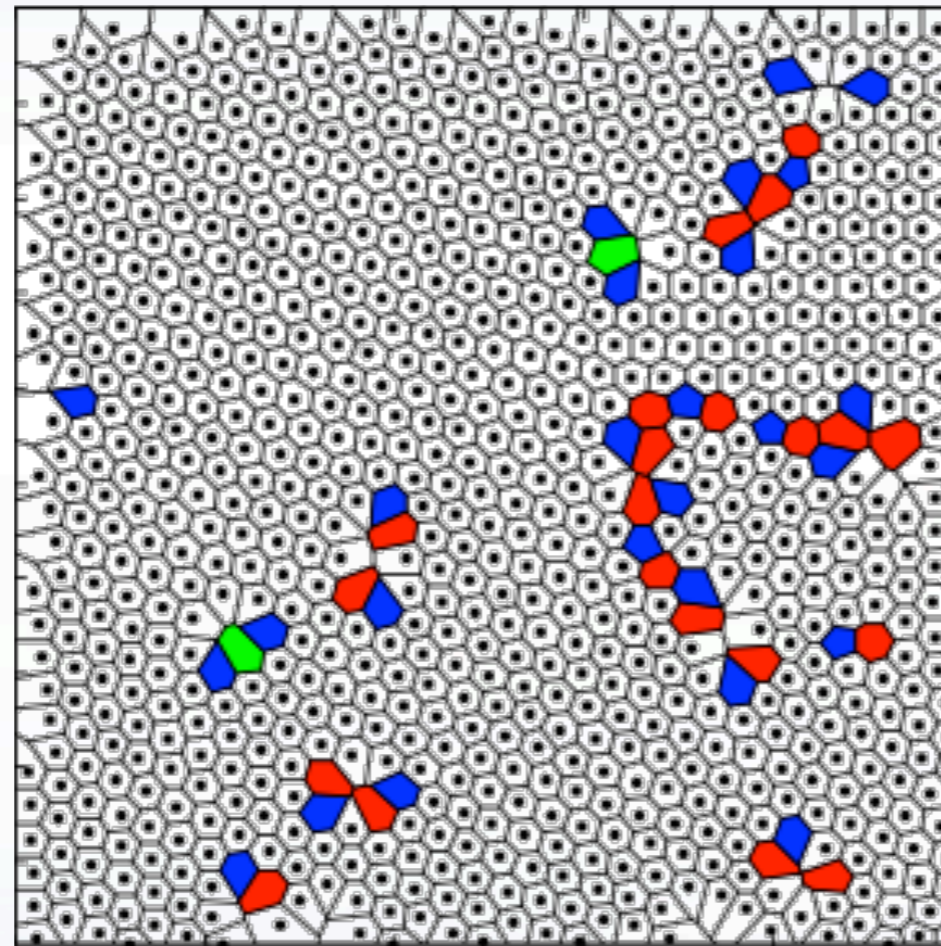
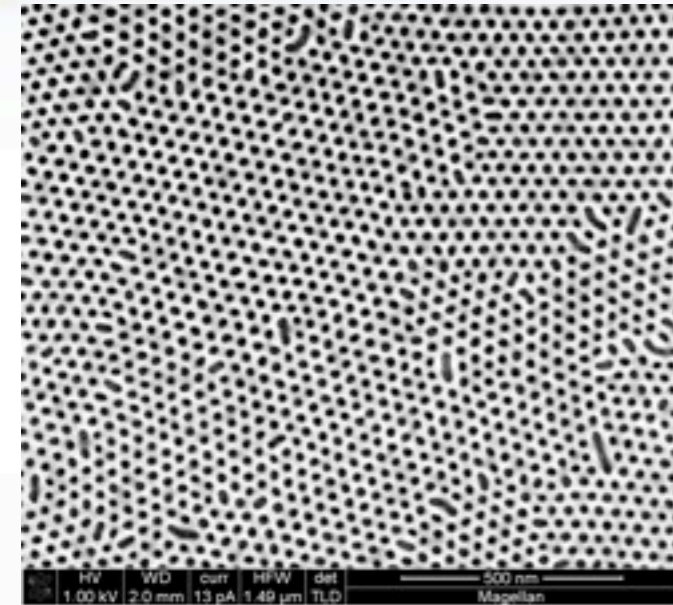
Wafer090121-002\_30nm\_middle bc



**Line Edge Roughness (LER)**  
 $3\sigma$  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

# Metrology



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

# Nano-Imprint Lithography

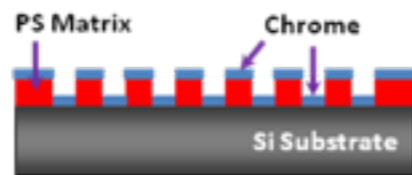
Jack L. Skinner, Peter Yang, Elaine Yang

## NIL mold via BCP

① PS-PMMA DBCP Formation



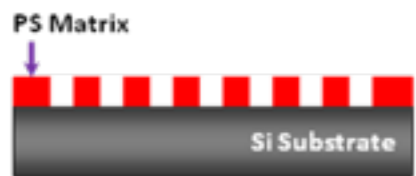
③ Cr Hard Mask Deposition



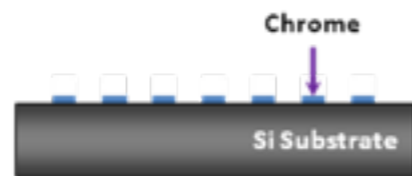
⑤ Si Etch to Produce Posts



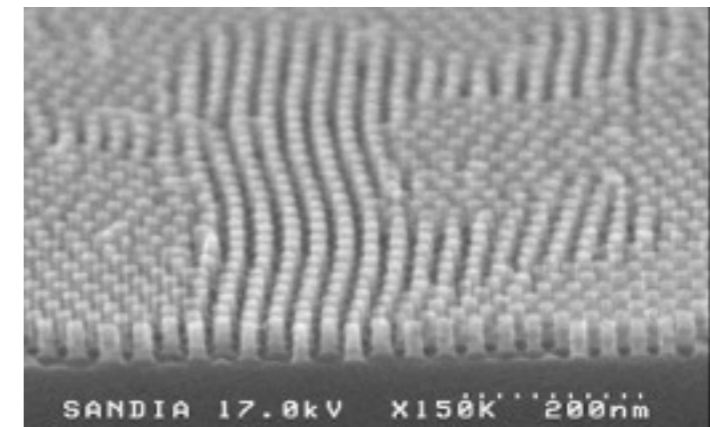
② PMMA Cylinders Removal



④ PS Matrix Removal

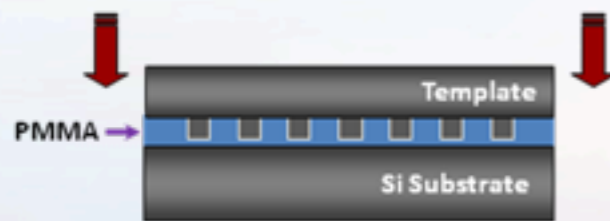


⑥ Final Template for NIL

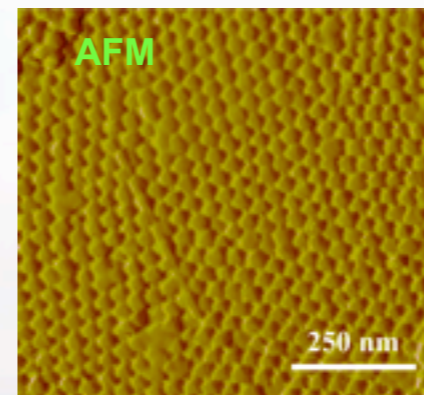
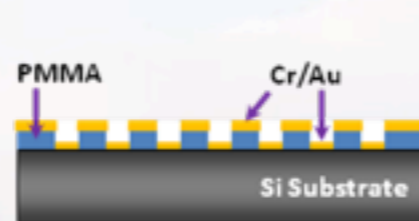


## SERS device via NIL

① Imprint of Template into PMMA



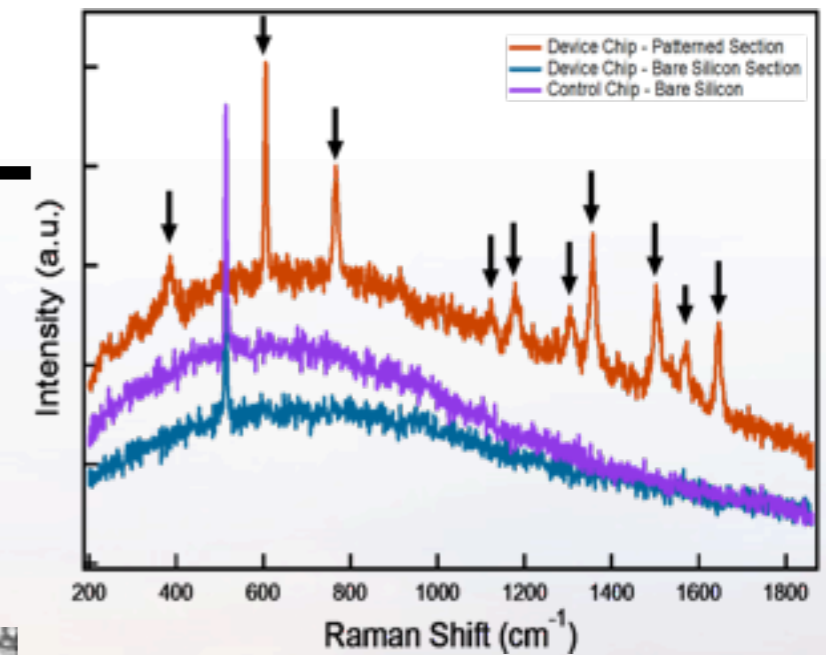
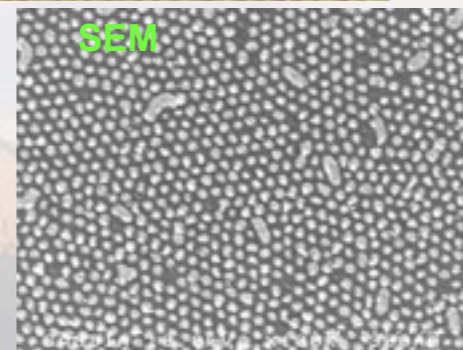
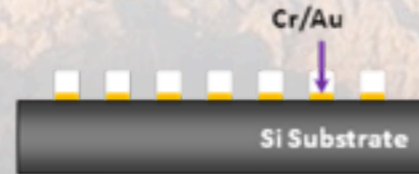
③ Metal Deposition



② PMMA Breakthrough Etch



④ Metal Lift-Off



SERS nature of the resulting nanodots was investigated using Rhodamine 6G (R6G) as the interrogation molecule.

# Doing More with the Same?

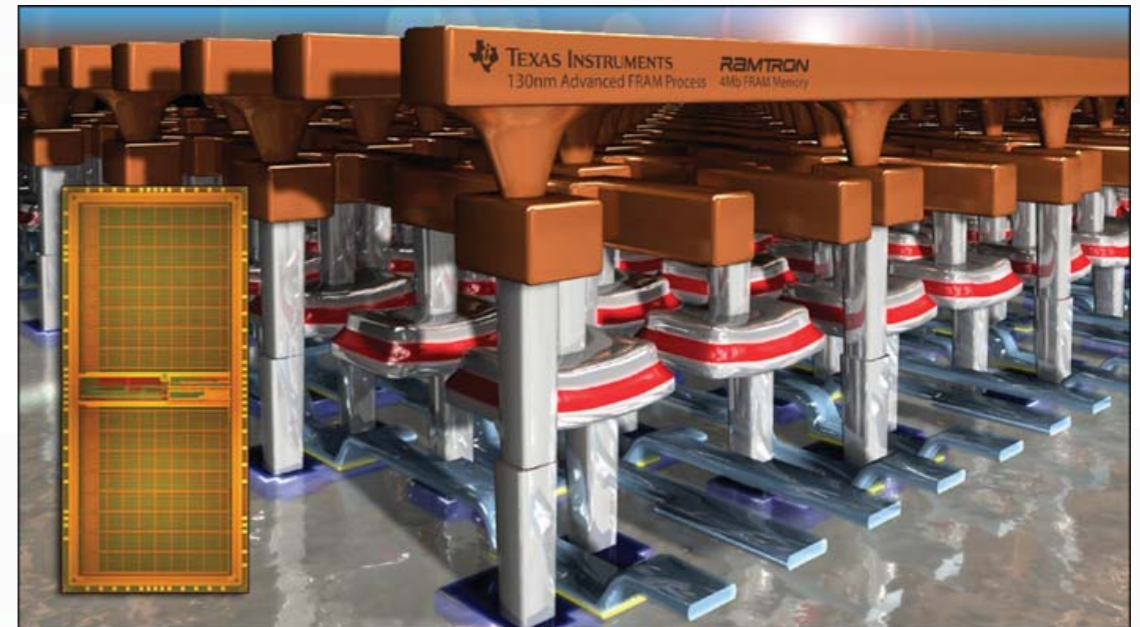
Integration of materials with new and/or increased functionality

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

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# Micro-, Nano-Patterning of Arbitrary Materials

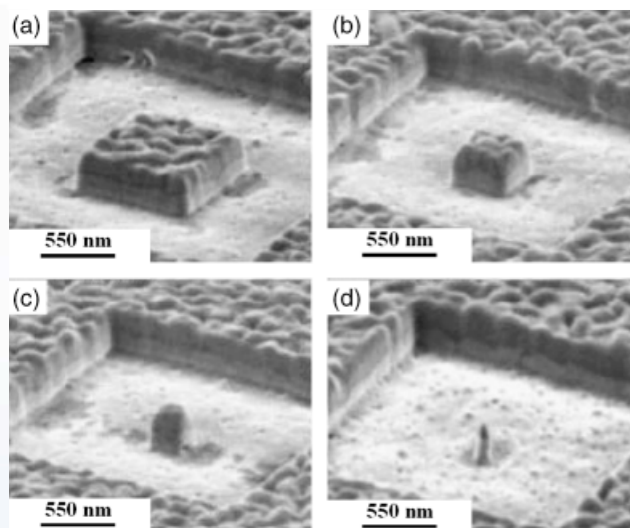
## Challenges of expanding beyond 'standard' materials

Fabrication

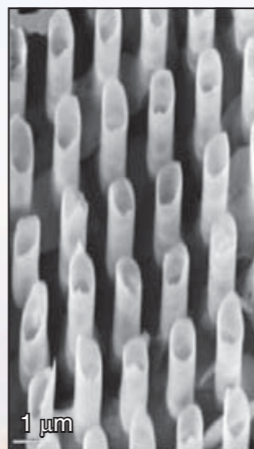
Patterning

Integration

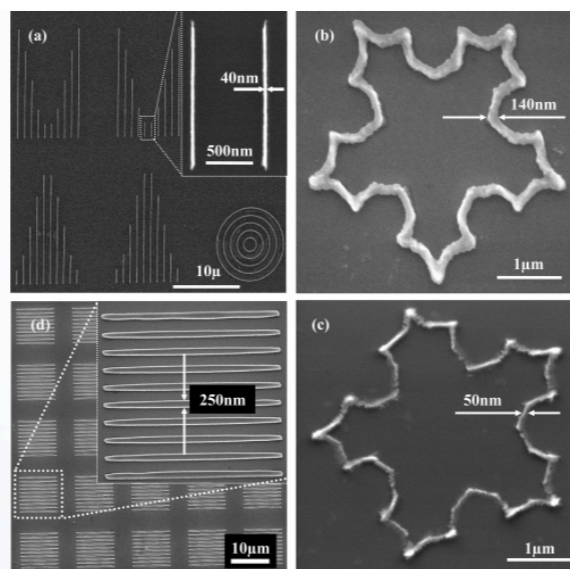
Performance



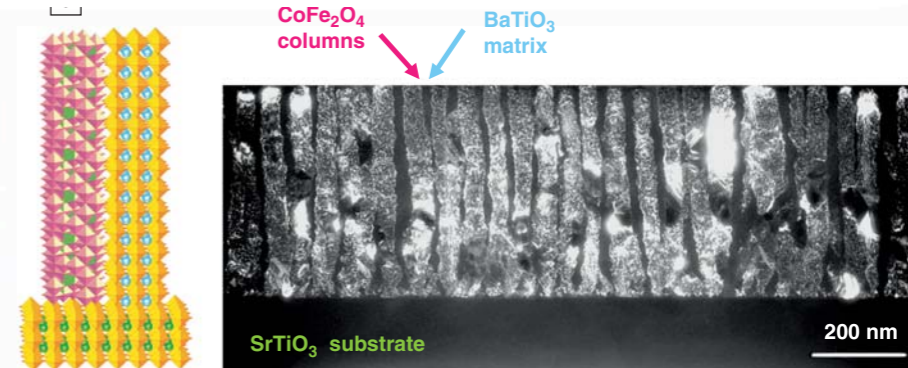
Ganpule et al., MRS Proc. (2001)



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**

# 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

## e-beam, BCP

Fabrication

Patterning

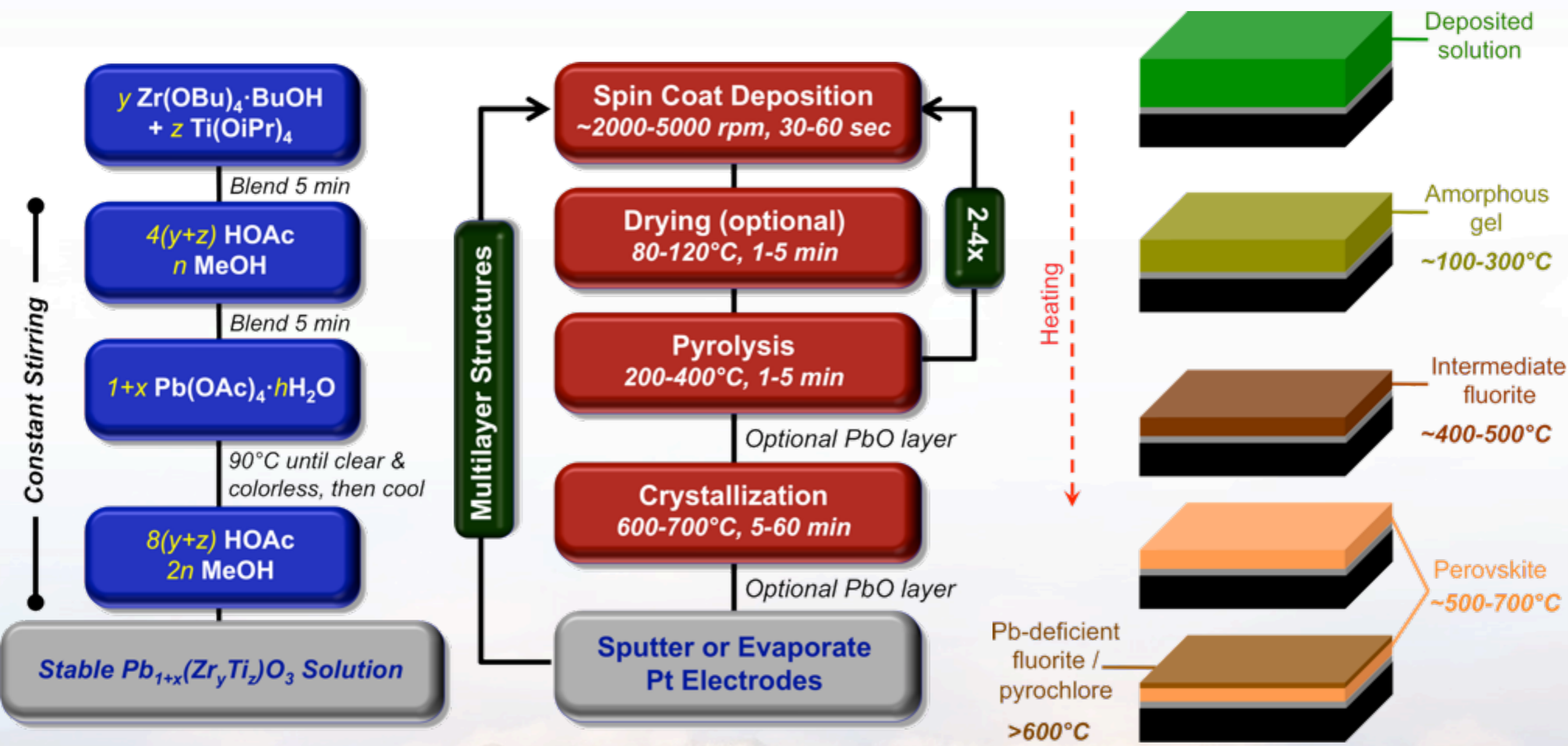
Integration

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

# SNL IMO-based Solution Route



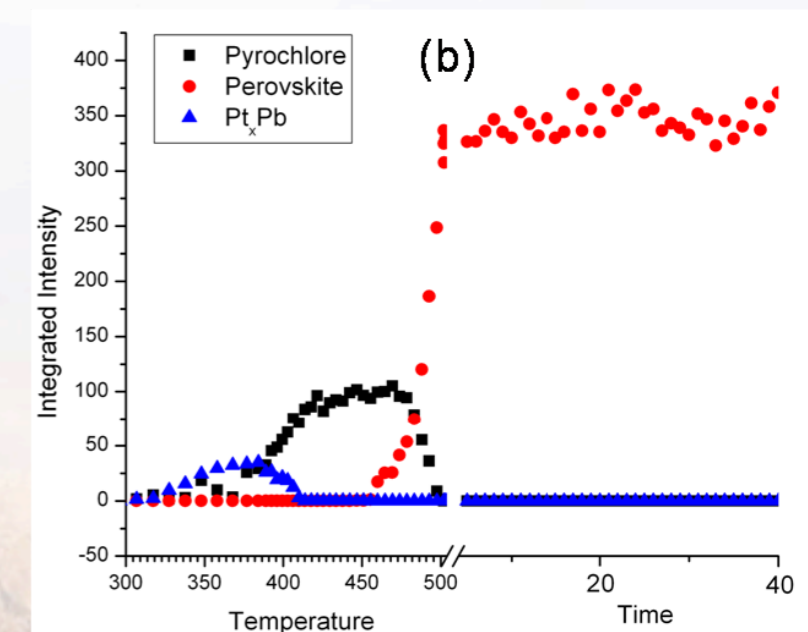
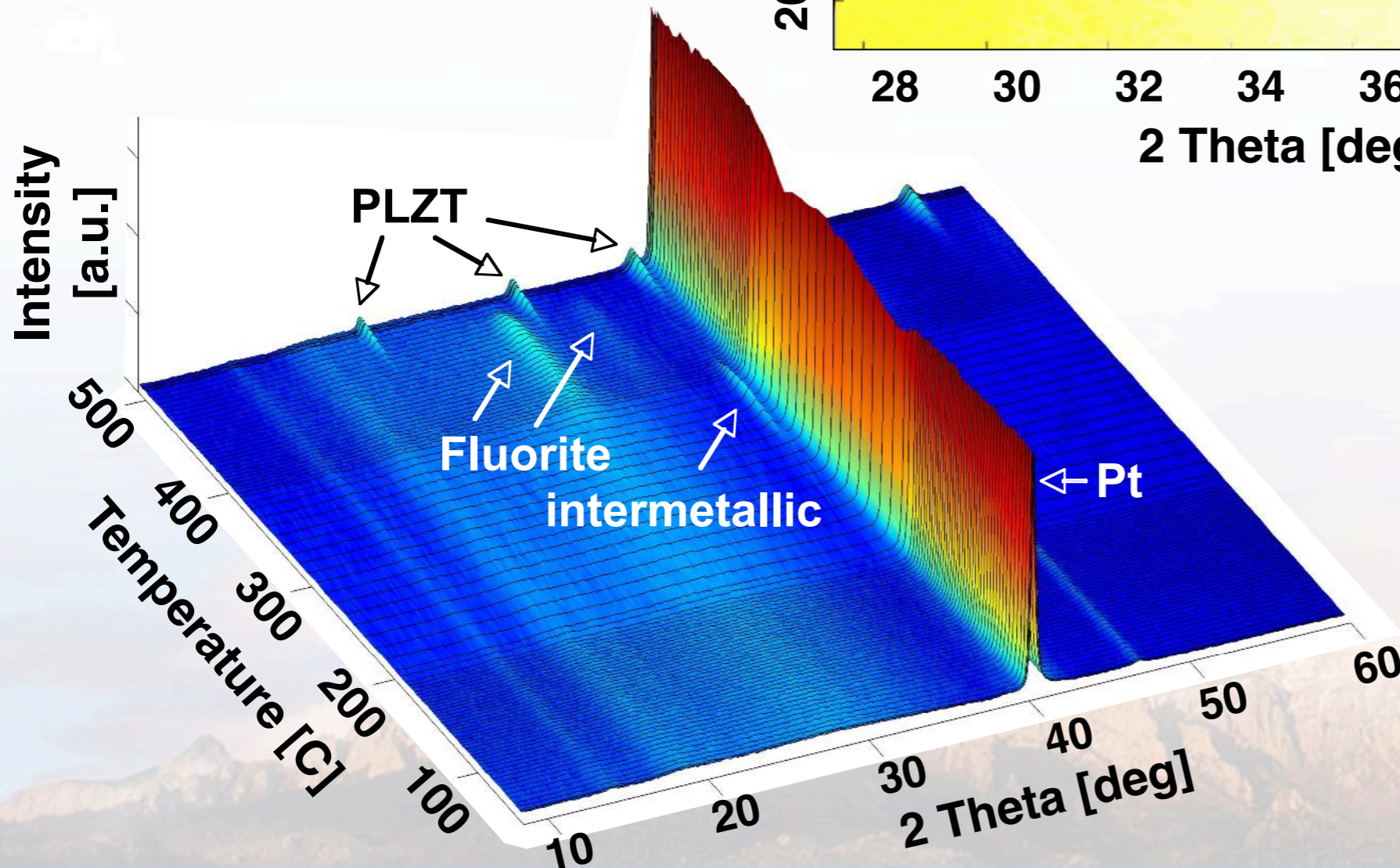
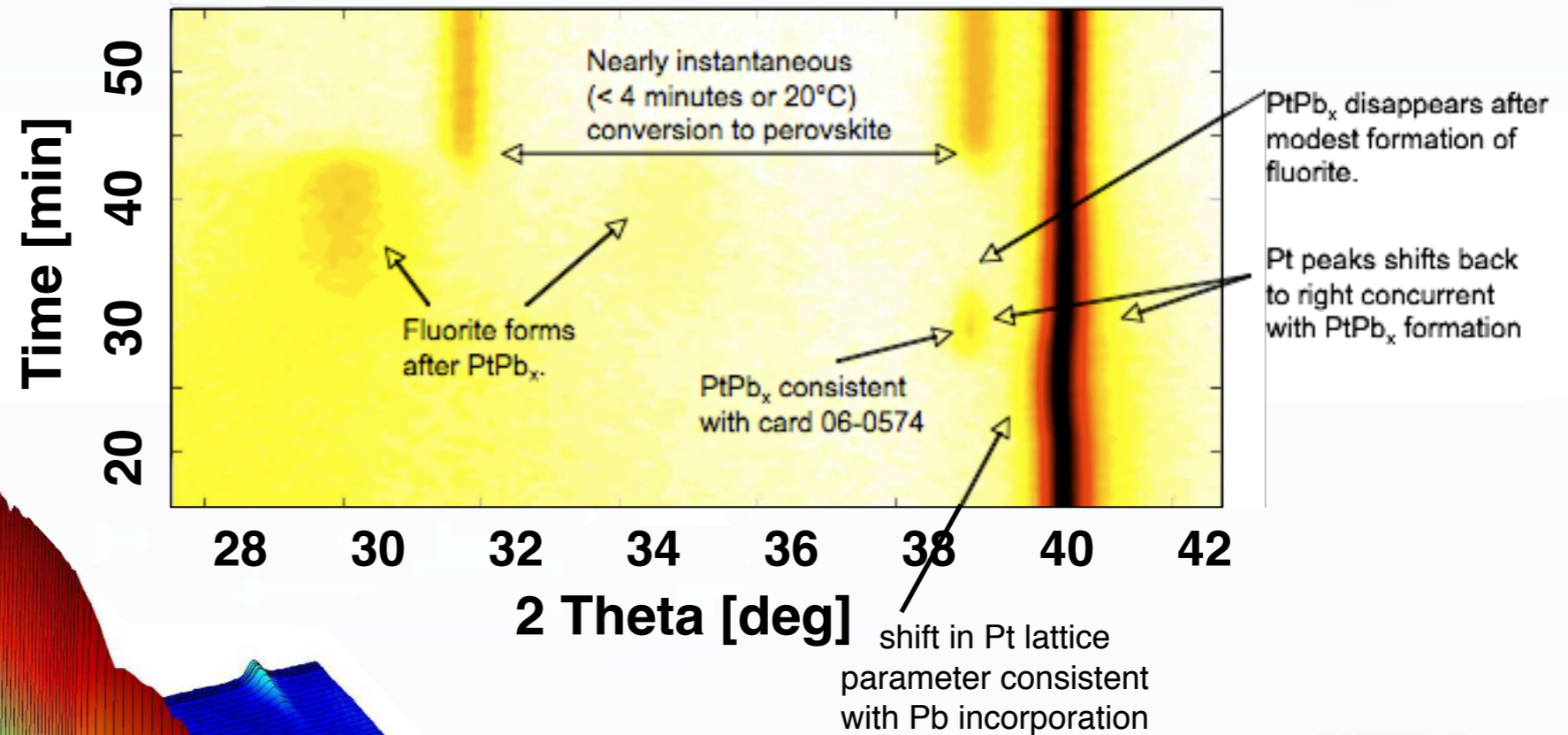
R.A. Assink and R.W. Schwartz; *Chem. Mater.* (1993)

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

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

# in-situ X-Ray Diffraction

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



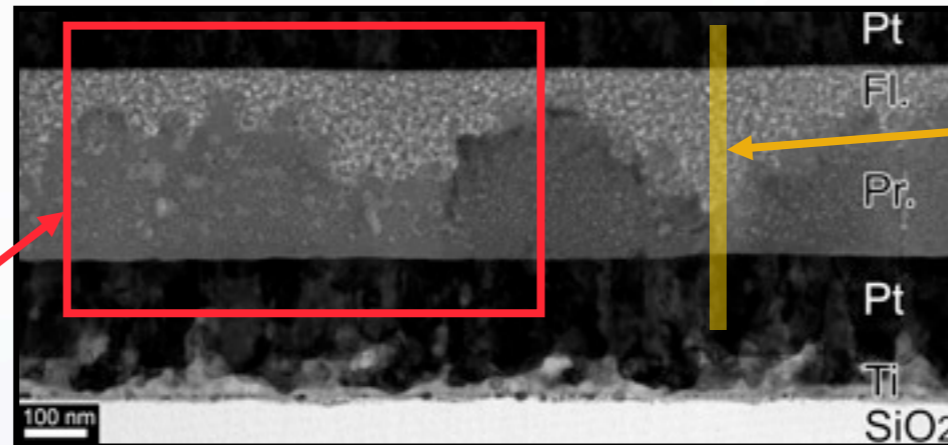
# Quantitative Cation Mapping in PLZT Films

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



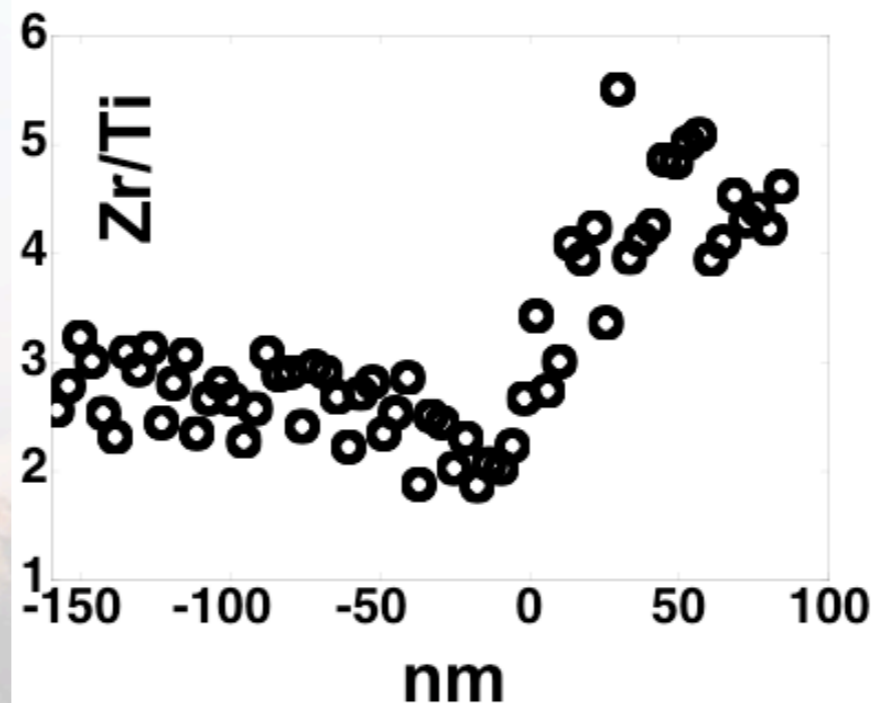
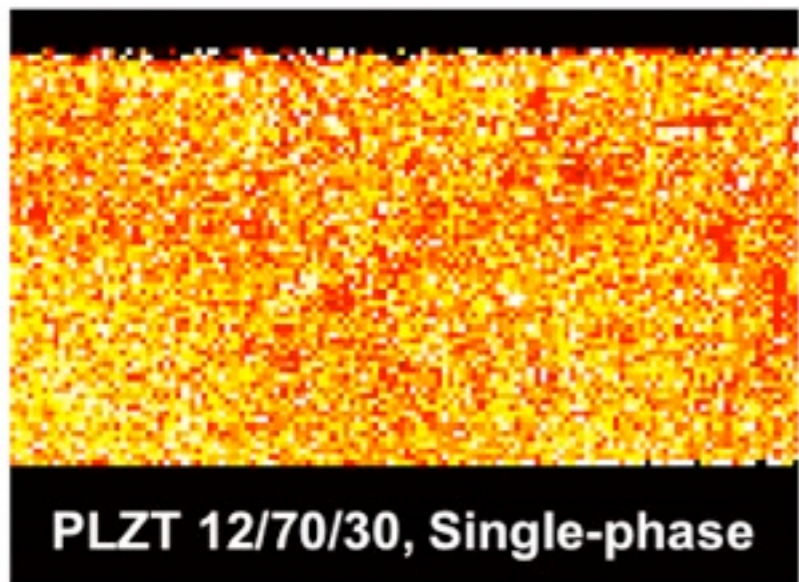
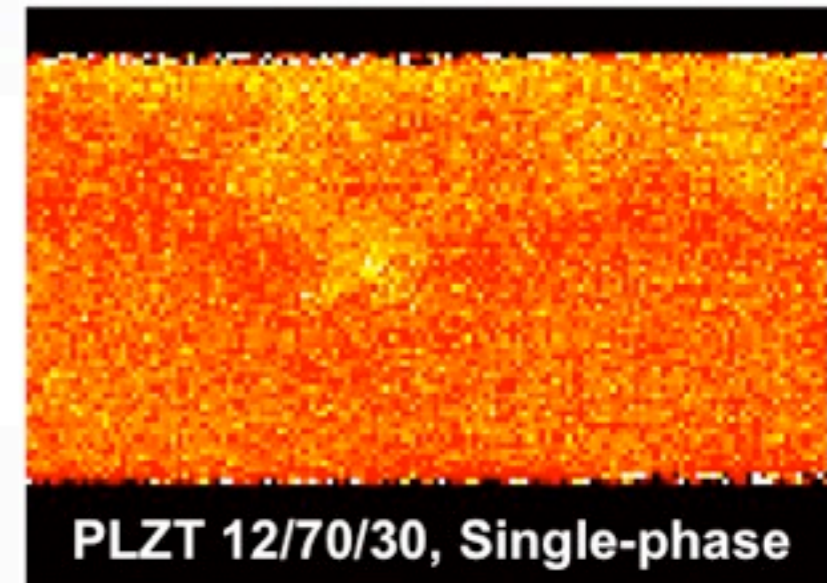
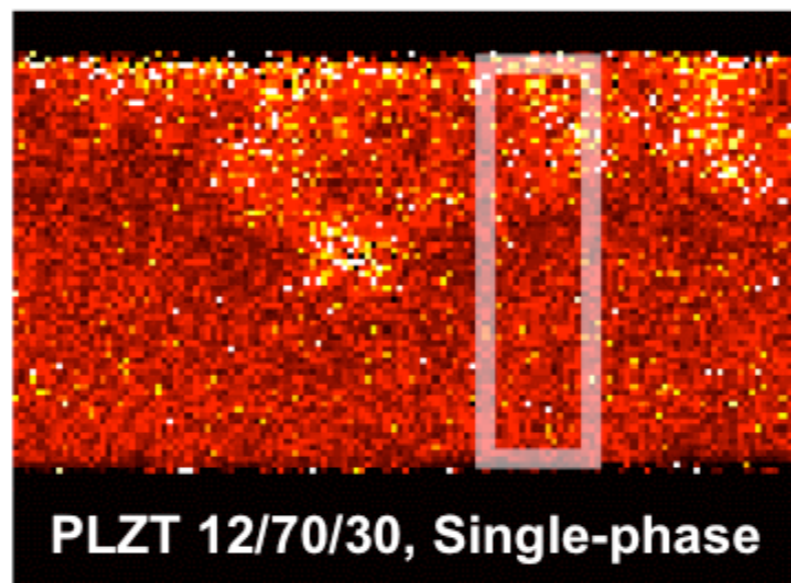
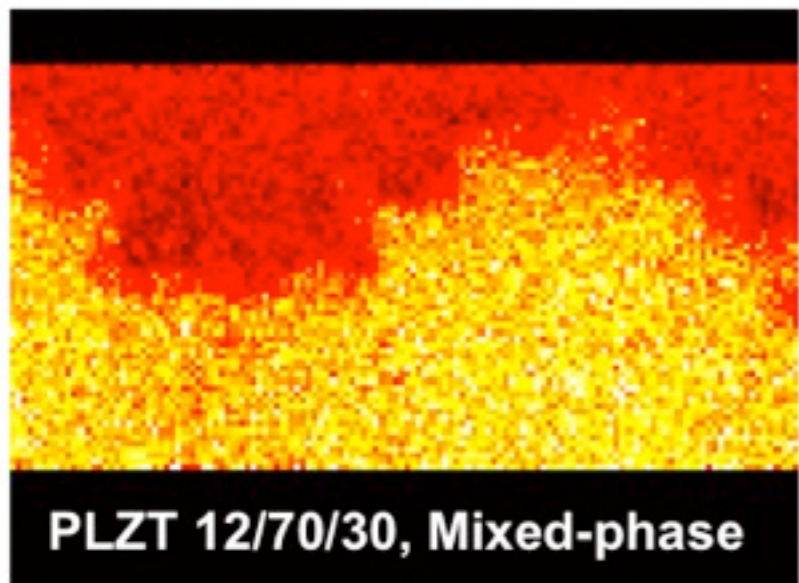
Feature size  
~hundreds of nms

Used STEM-EDS SIs to  
sample this scale



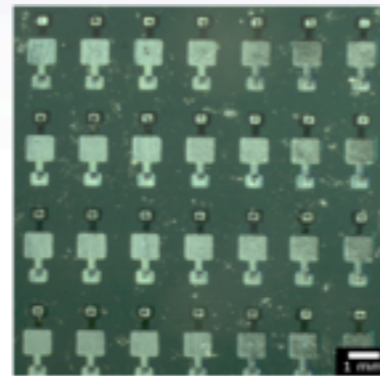
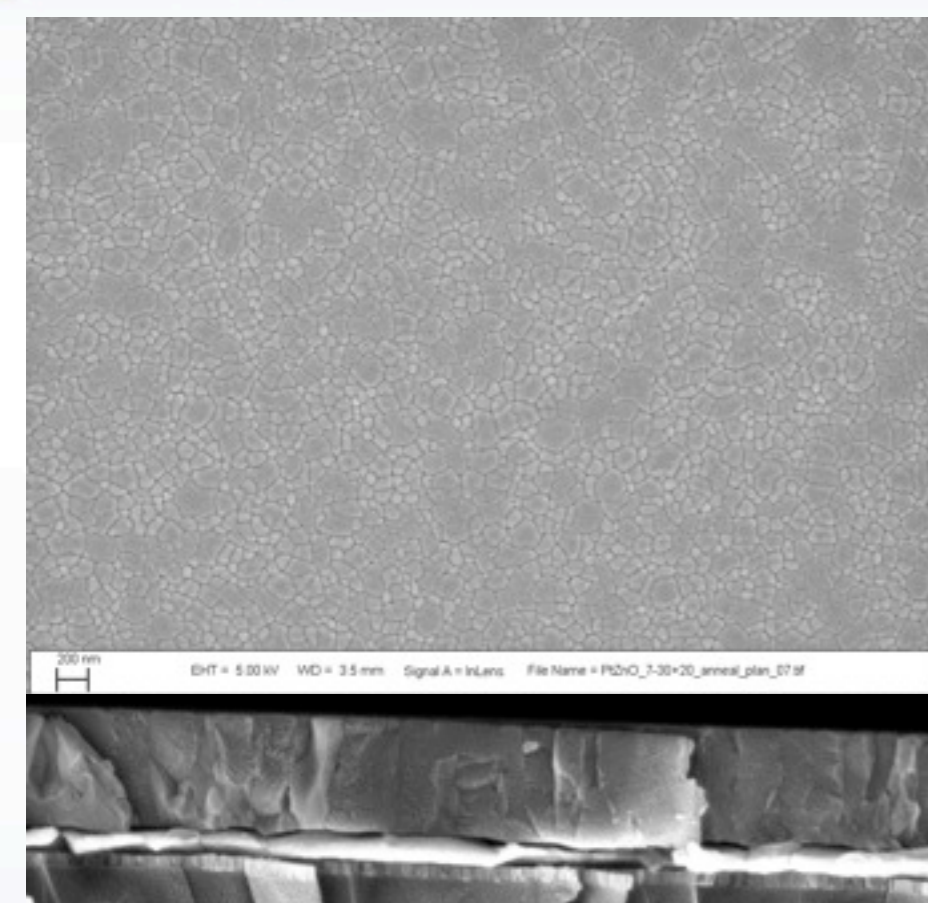
EDS linescan sampling  
~several nanometers  
≠ feature size

# Quantitative Cation Mapping in PLZT Films

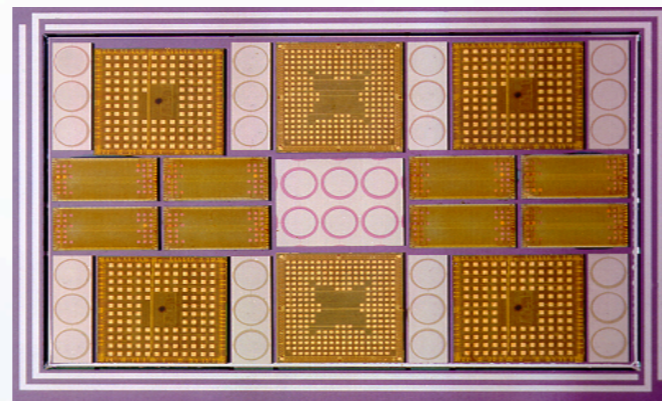
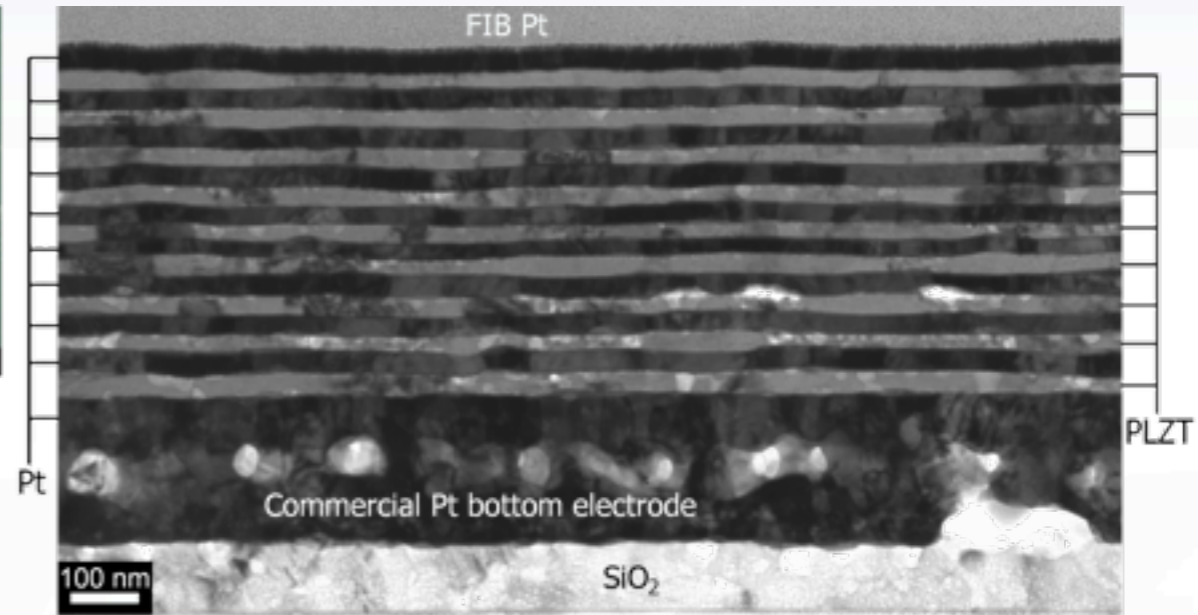


- Pb stoichiometry and homogeneity can be restored through Pb-rich annealing step
- B-site heterogeneities remain
- Evidence for co-segregation of La and Zr
- No Zr/Ti segregation observed for rapidly-crystallized PZT

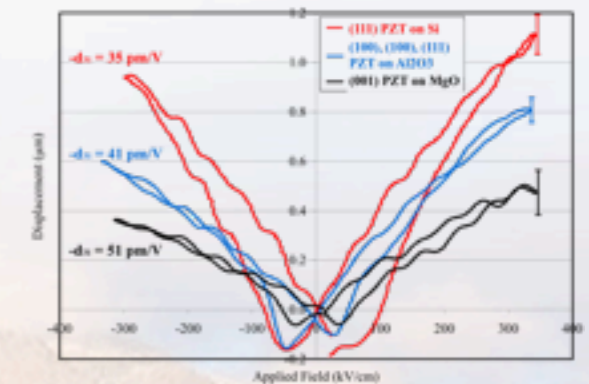
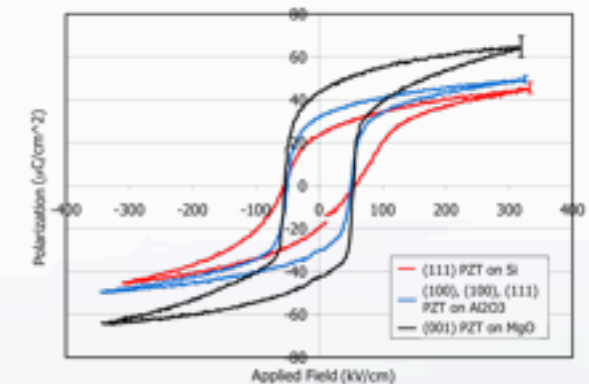
# Functional Solution-Derived Ferroelectric Thin Films



Functional PZT-based multilayer capacitor structures

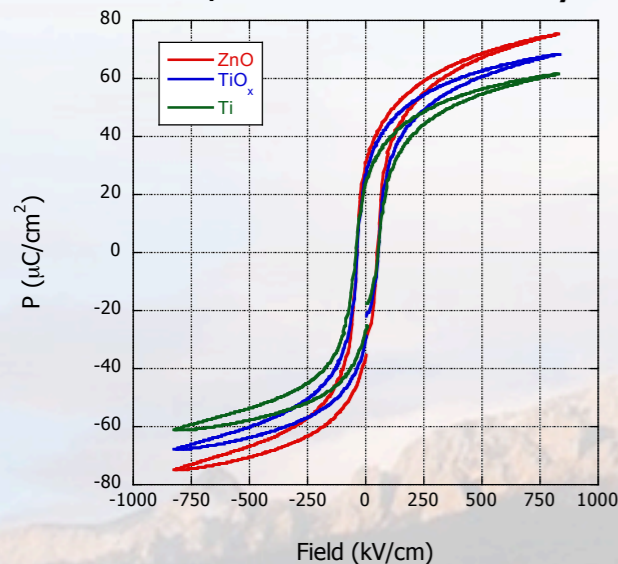


Multichip module with PZT thin-film capacitor arrays

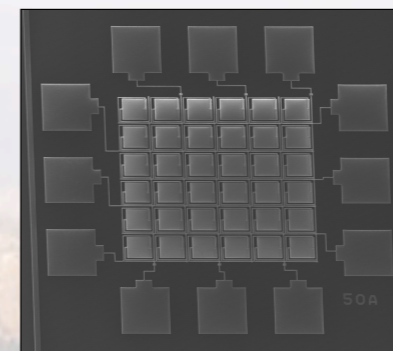


Ferro/Piezoelectric response tuned through thermal strain

PZT 52/48 on various adhesion layers

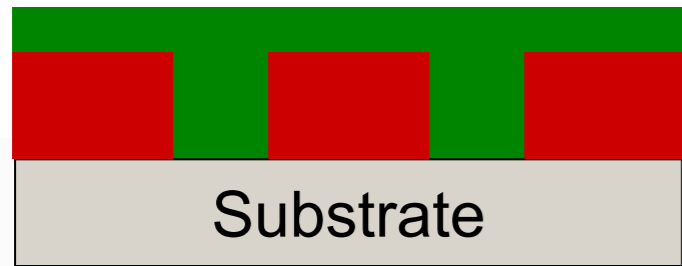


PZT-MEMs piezo cantilever beam for energy harvesting

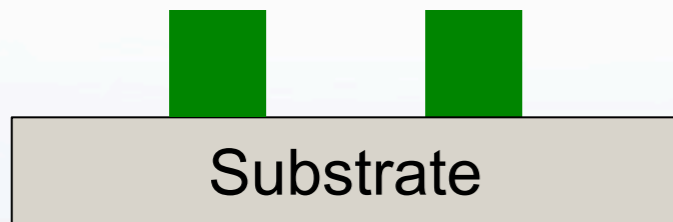


Pyroelectric pixels w/aerogel insulation

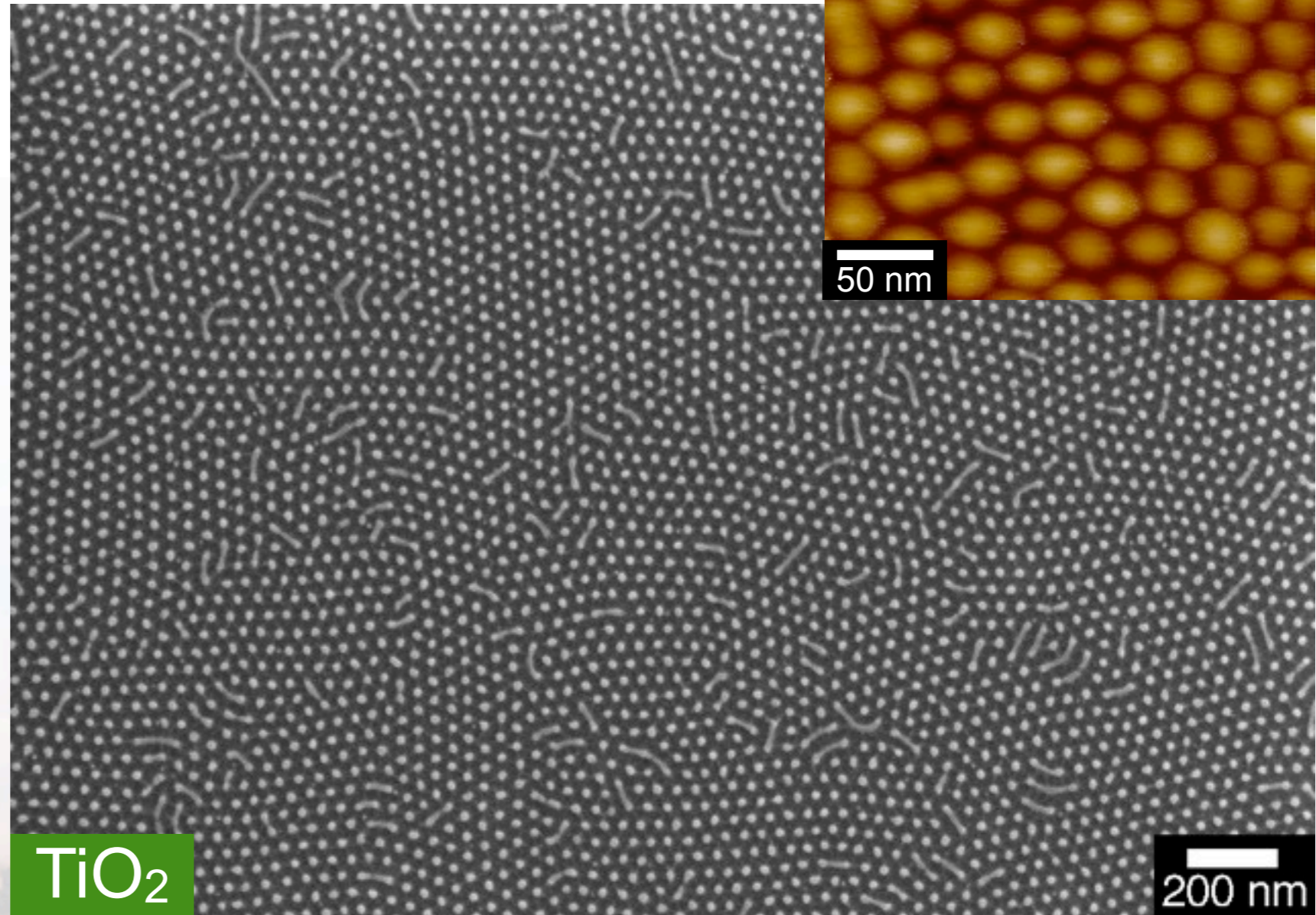
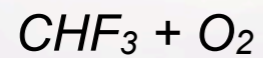
# Additive Fabrication of Patterned Electronic Oxides



Fill, Gel

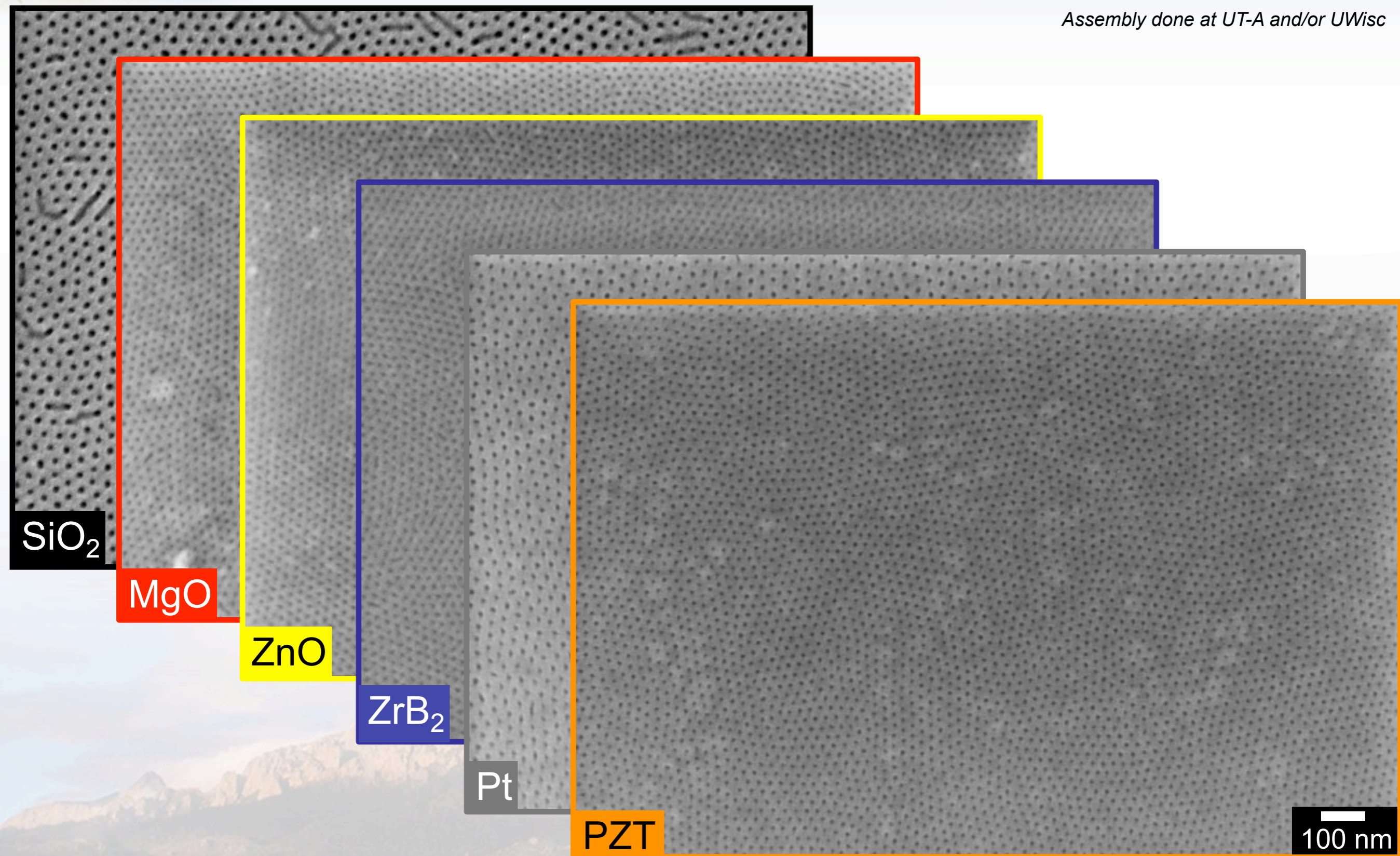


Remove Mask



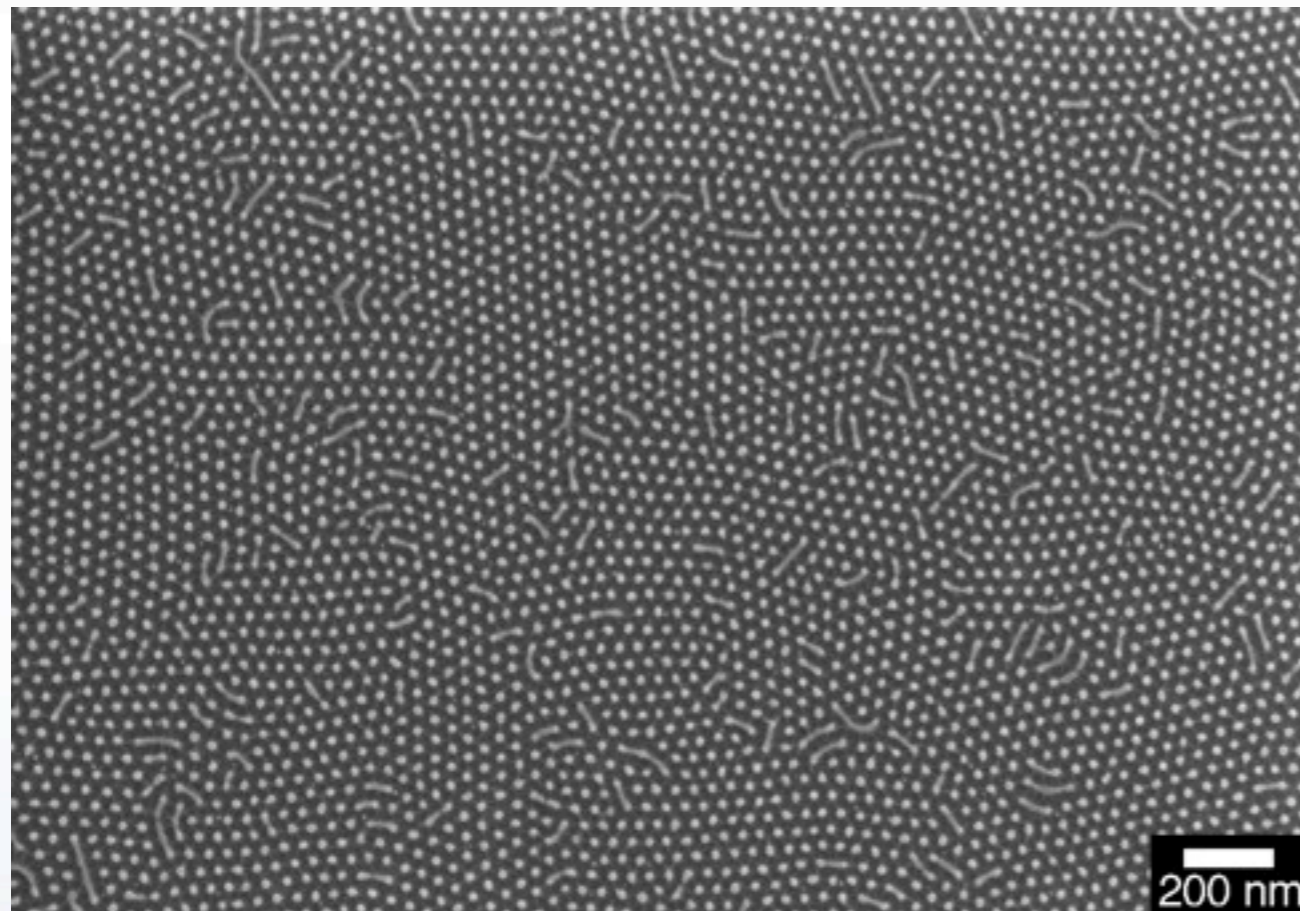
# Diblock Assembly on Various Substrates

*Assembly done at UT-A and/or UWisc*

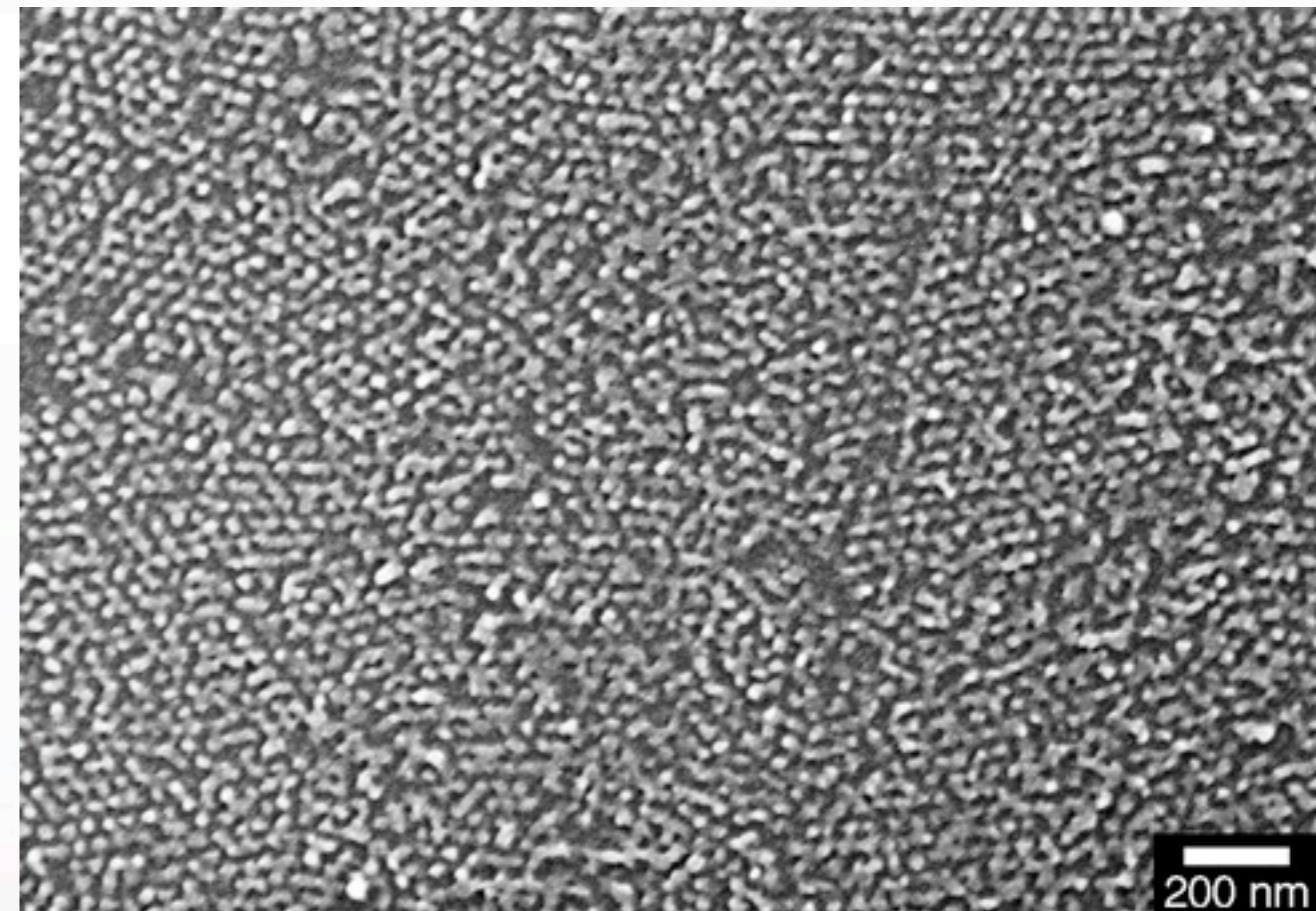


# Crystallization Destroys Freestanding Nanofeatures

After removal of PS mask, TiO<sub>2</sub> nanopillars were heated to 550°C for 30min to crystallize



Amorphous TiO<sub>2</sub>

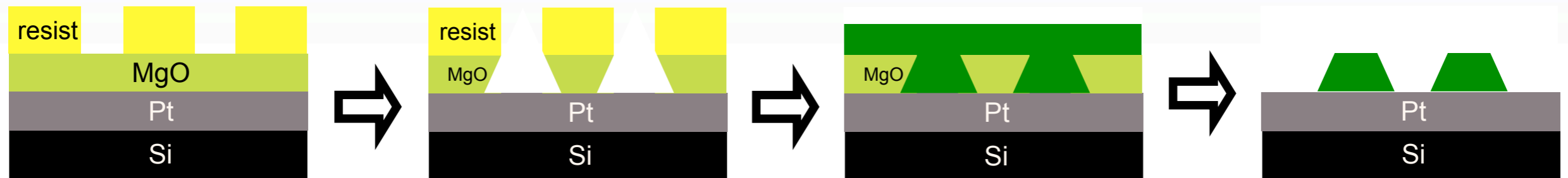


Crystalline TiO<sub>2</sub> (Anatase)

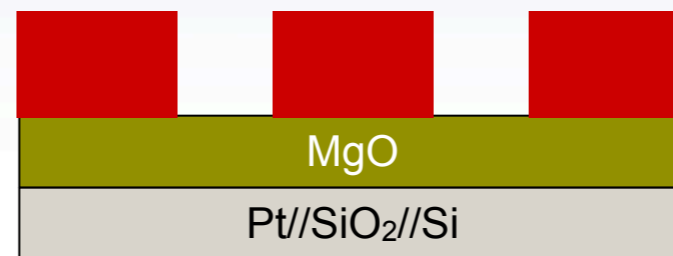
Still lacking:

- 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



*etch*



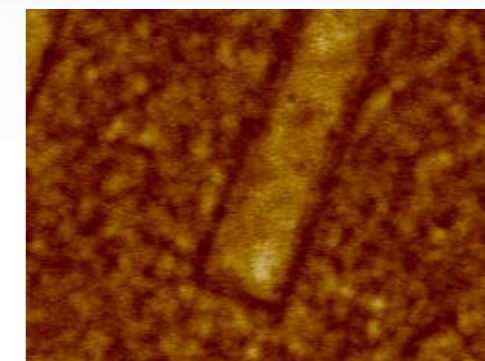
*deposit, crystallize*



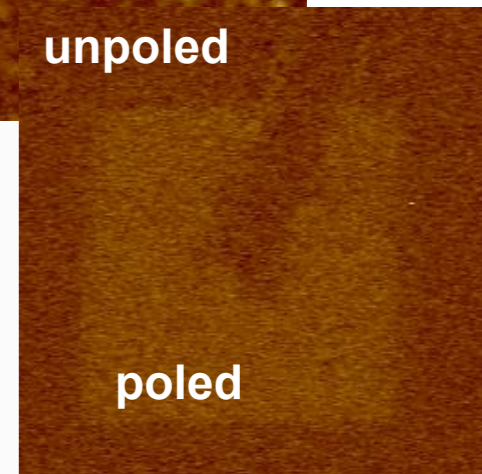
*sputter Pt*



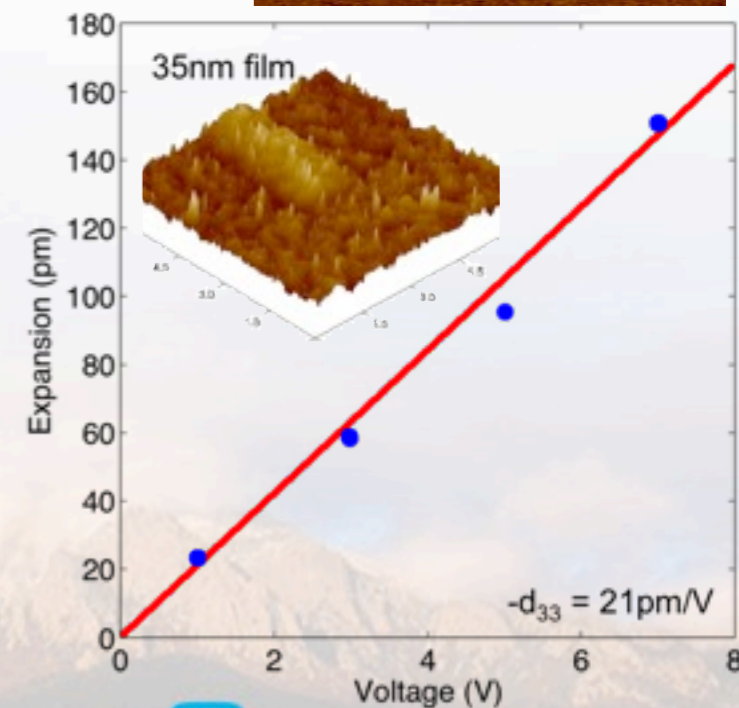
*liftoff*



unpoled



poled

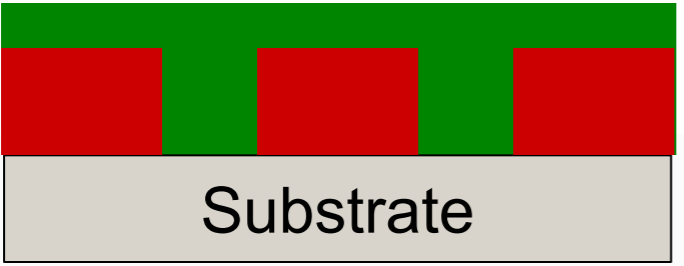
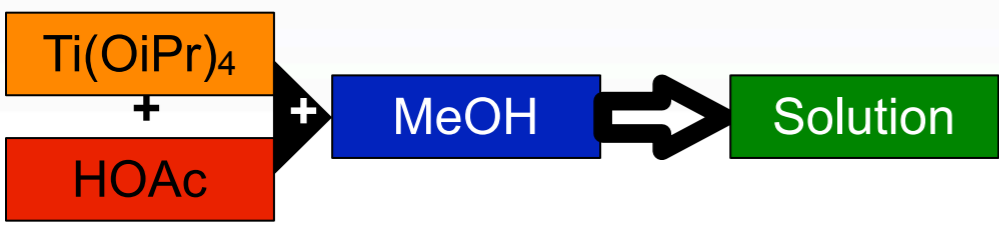


# Maintaining Pattern Fidelity through Thermal Processing (>600°C)

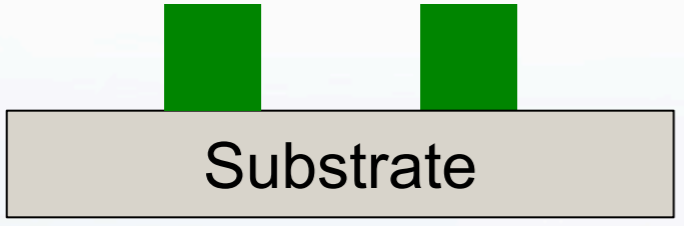
Wet Etch Limits to Microscale



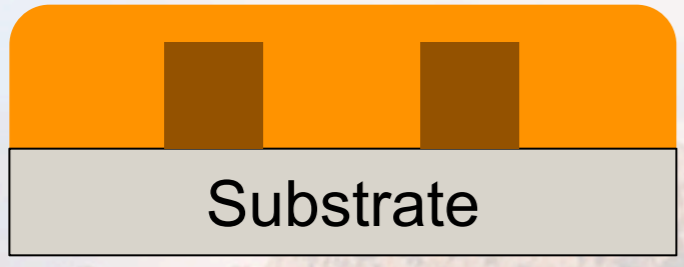
# 'Capped' Crystallization



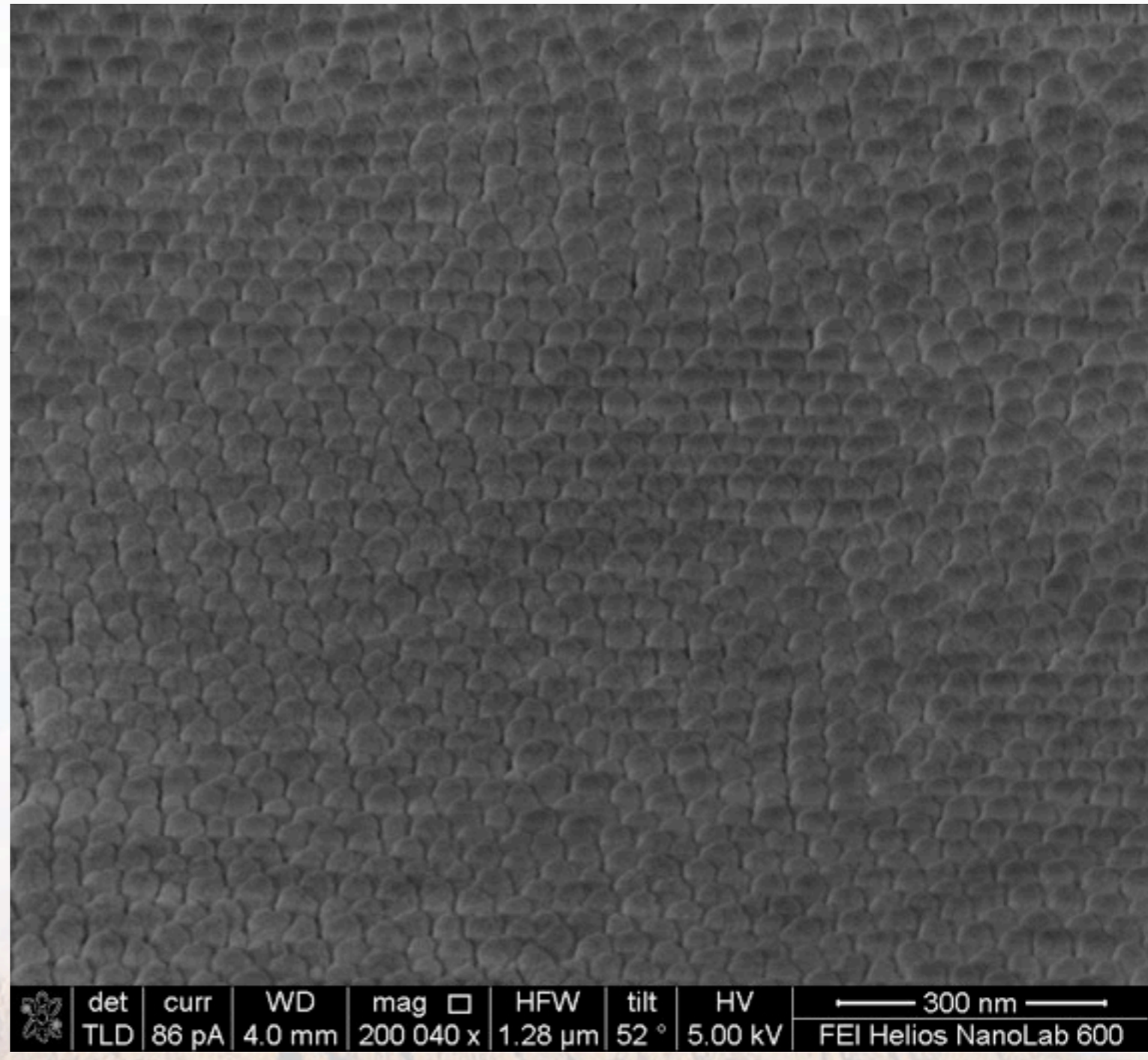
Fill, Gel



Remove Mask

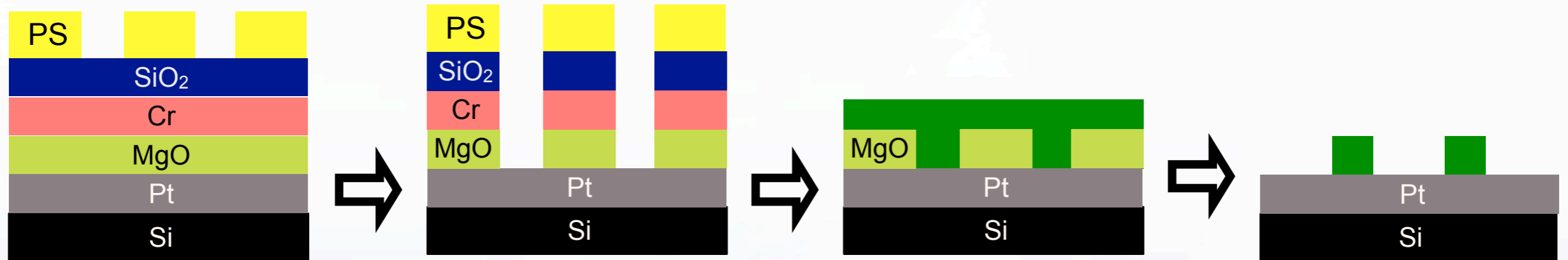


Crystallize



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

Wet Etch Limits to Microscale

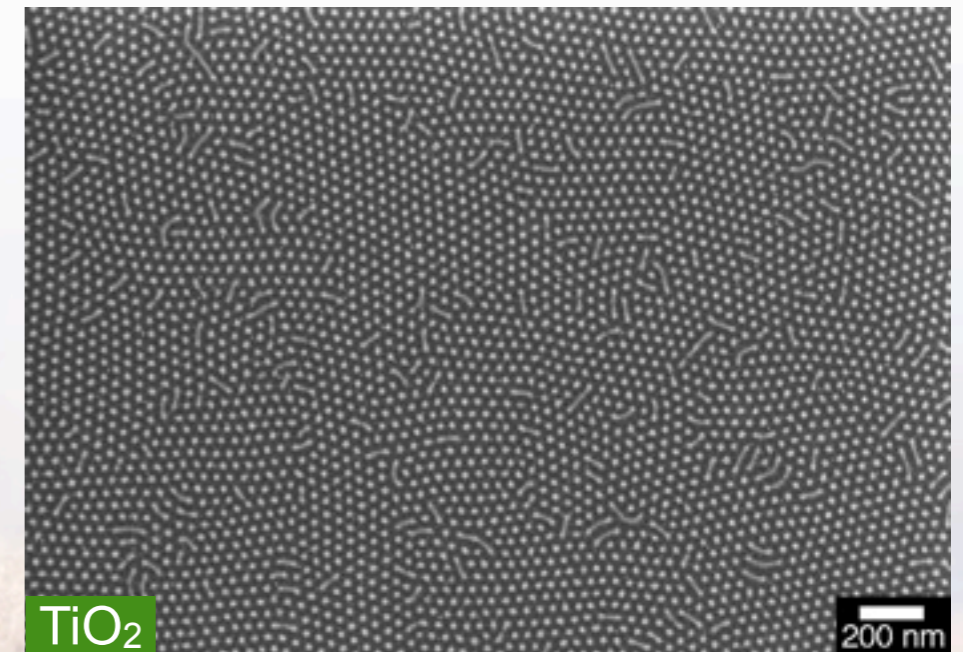
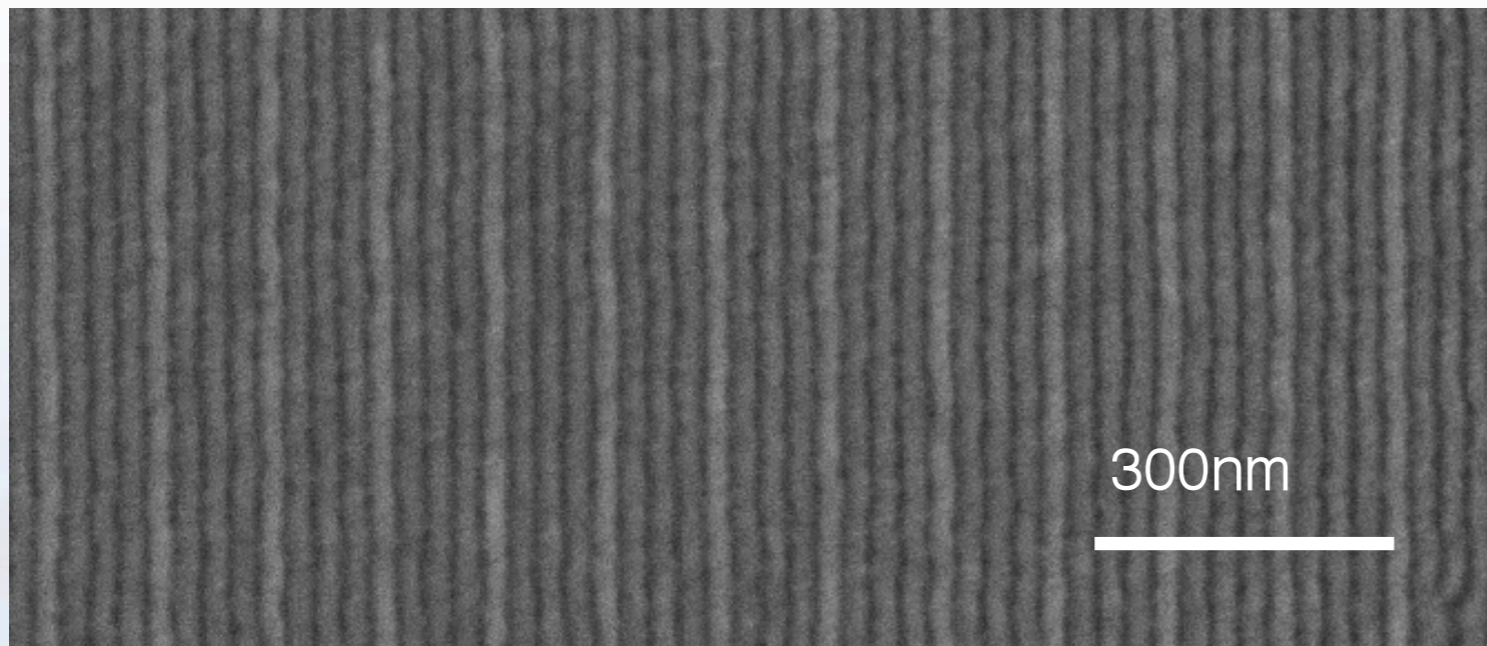


Contamination/Reaction?



# Summary

- Demonstrated combined IL + DSA-BCP + NIL
- Up to 4x density multiplication with DSA-BCP over mm<sup>2</sup> 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



# Acknowledgments

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  - David Shykind
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  - Amy Herhold

