Lateral confinement of cylindrical domain thin polymer films

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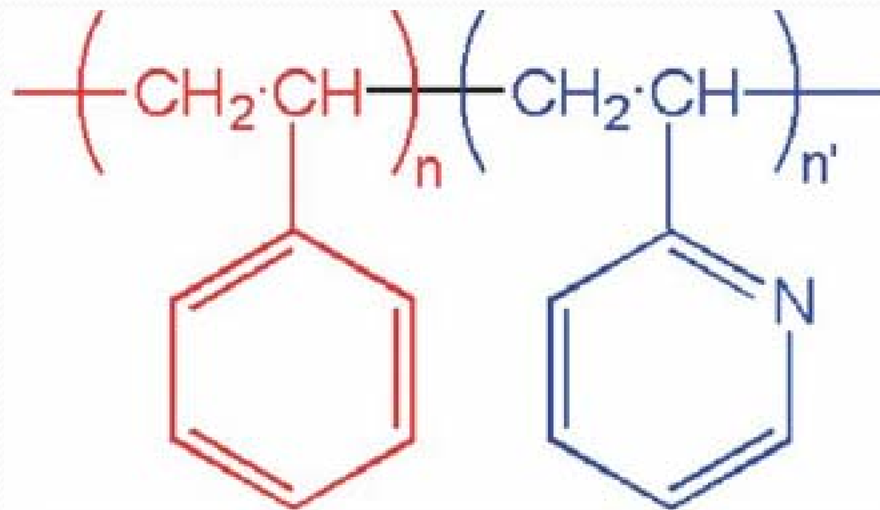
What is a polymer?

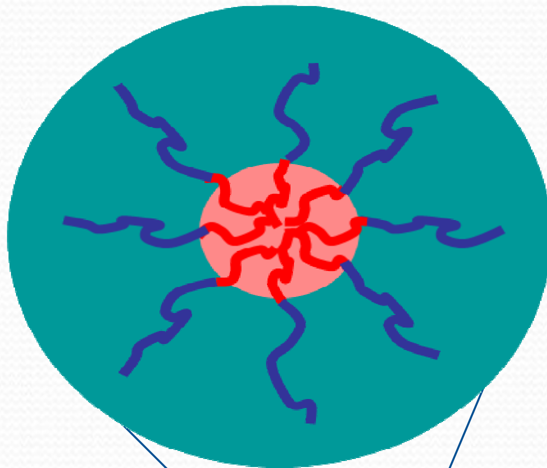
- Repeated structural units linked by covalent bonds
- Block copolymers
  - Two polymer chains linked by a covalent bond

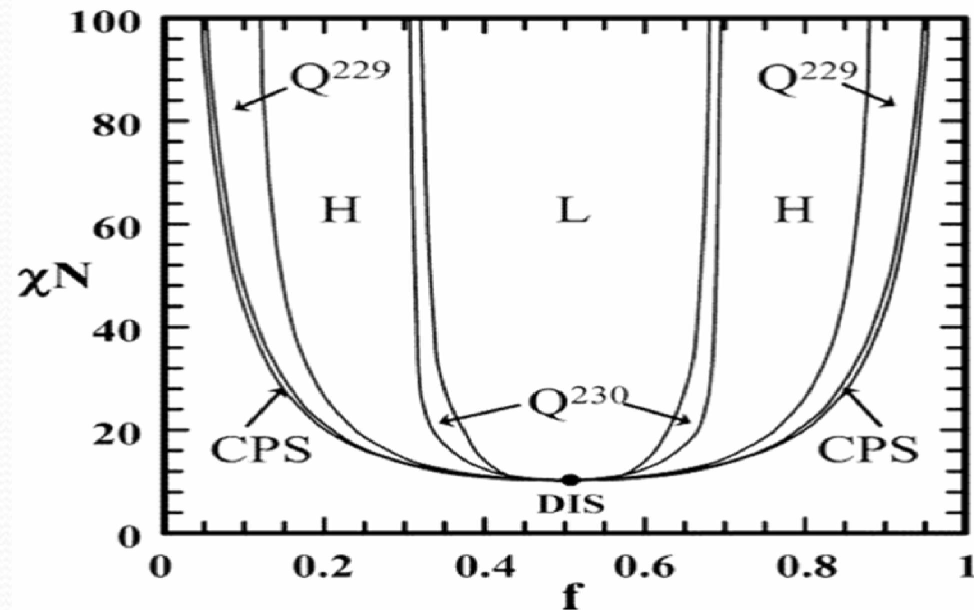


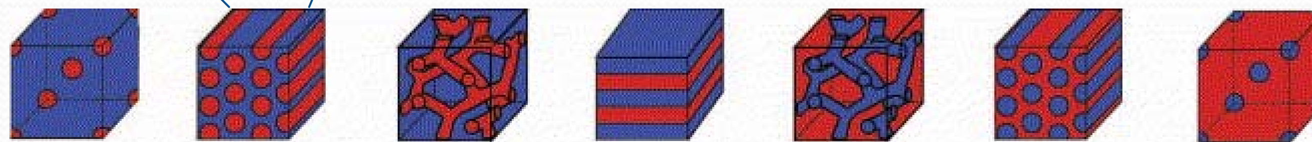
Poly (styrene-b-vinyl pyridine)

Block copolymer phase behavior

Cross-sectional view





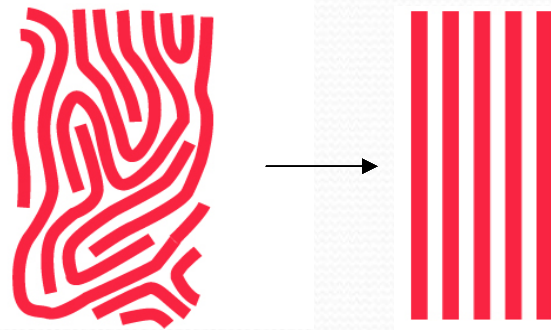


Why study this system?

- Nanolithography: alternate method for creating masks with nanofeatures
- Current methods: photolithography, e-beam lithography
    - Can't create structures smaller than wavelength (λ) of light
    - Ultraviolet and X-rays possible, but still expensive
- Obtain even smaller features
- Nanowires
- Etch away the PVP to leave nanocylindrical holes behind
- Fill with metallic salt to make nanowires

What do we hope to accomplish?

- The block copolymer Poly (styrene-b-2-vinyl pyridine), or PS-PVP, self-assembles into a cylindrical array
  - 25% PVP : volume ratio
- Pattern is disordered
- We aim to improve translational and orientational order by graphoepitaxy
  - Using substrate to direct growth of overlying material



Disordered system   Ordered system

Experimental Method

- Film casting
- Annealing
- Imaging
  - Secondary Ion Mass Spectrometry (SIMS)
  - Atomic Force Microscopy (AFM)

Preparation of ordered films

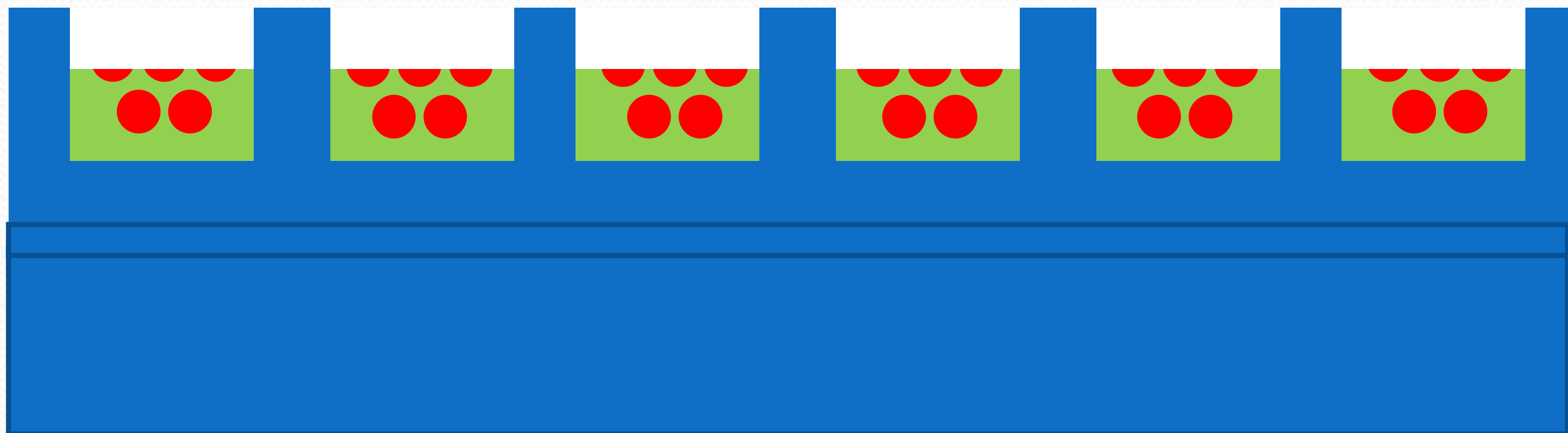
- Dissolve polymer in toluene
  - 2% mass solution
- Spin coat on a silicon (Si) wafer at a specific rpm for 45 seconds
  - Thickness is inversely proportional to spin speed
  - We are targeting films of a specific thickness

Annealing

- Heat beyond the Order-Disorder Temperature (ODT)
  - ODT for PS-PVP is ~ 220°C
- Cool down to the annealing temperature
  - Range of annealing temp. (AT) is ~150-200° C
  - We hold it at the AT for 2 days

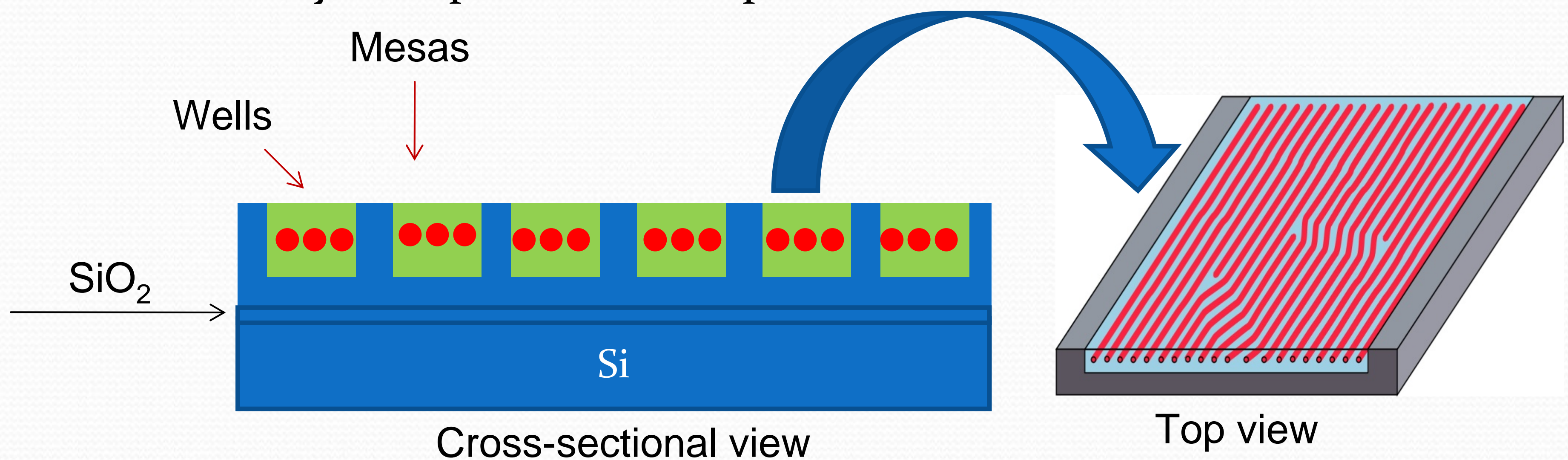
Accessing the 'buried structure'

- Secondary Ion Mass Spectrometry (SIMS) to etch through PS film
  - Process exposes cylinders
- Analyze cylinder patterns using Atomic Force Microscopy (AFM)

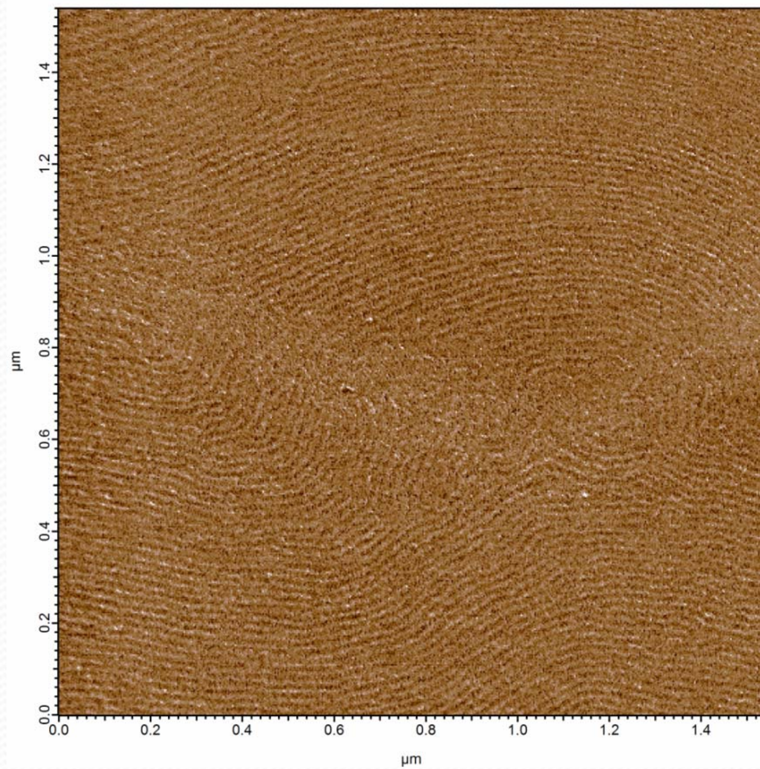


Data collection

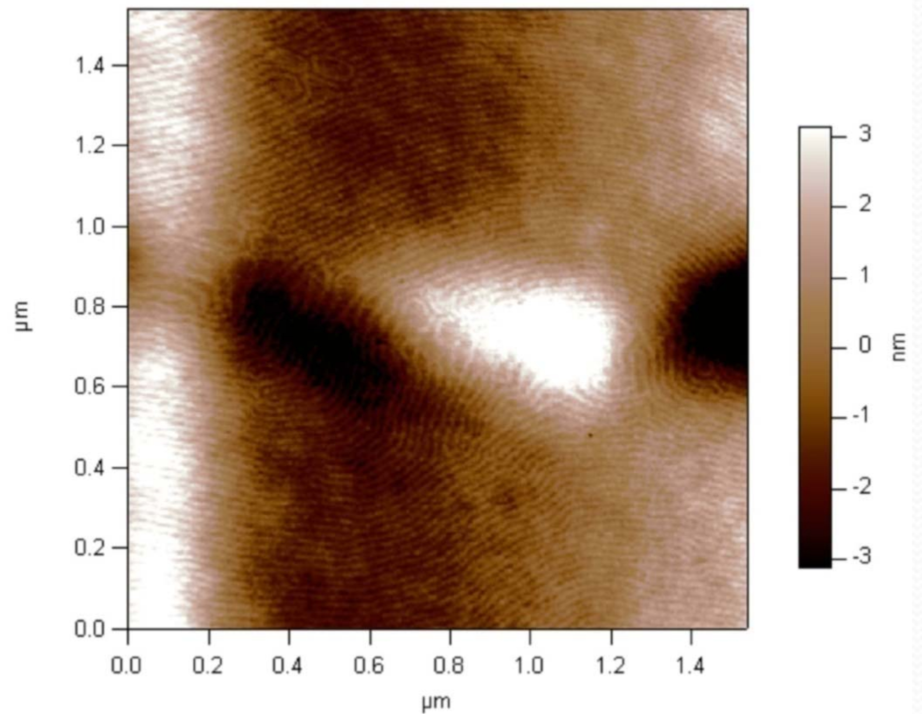
- We looked at two different kinds of films
  - Unconfined films
    - Polymer spun coat on a plain Si wafer
  - Confined films
    - Polymer spun coat on a patterned wafer



Disordered System (Plain Si wafer)

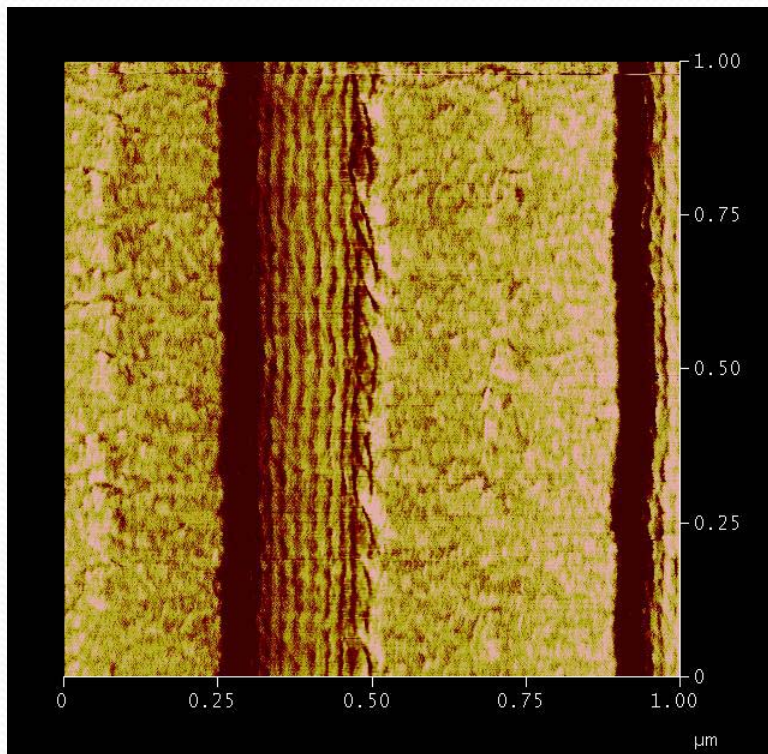


AFM Phase Scan



AFM Height Scan

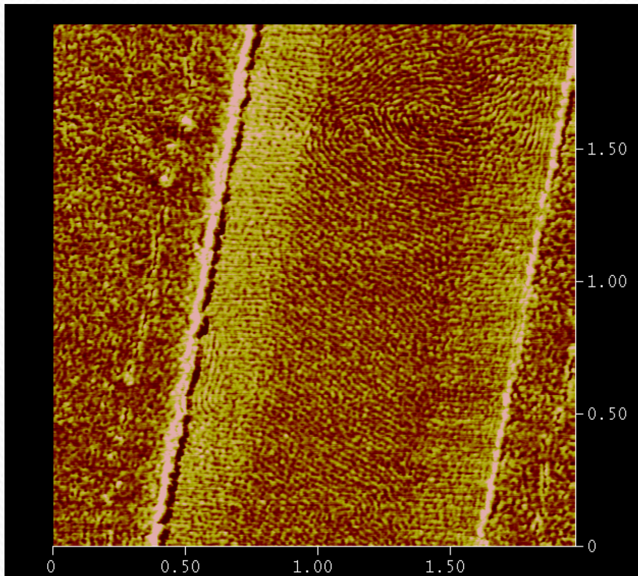
Confined system (patterned wafer)



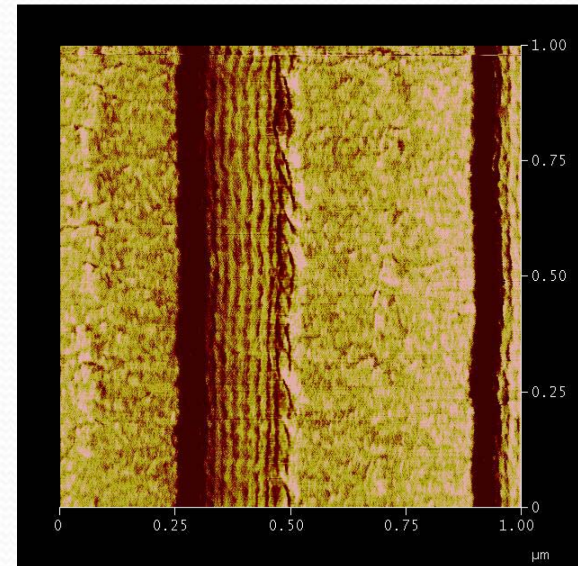
AFM Height Scan

AFM Phase Scan

Comparison of width



Width of channel ~ 1.36 μm

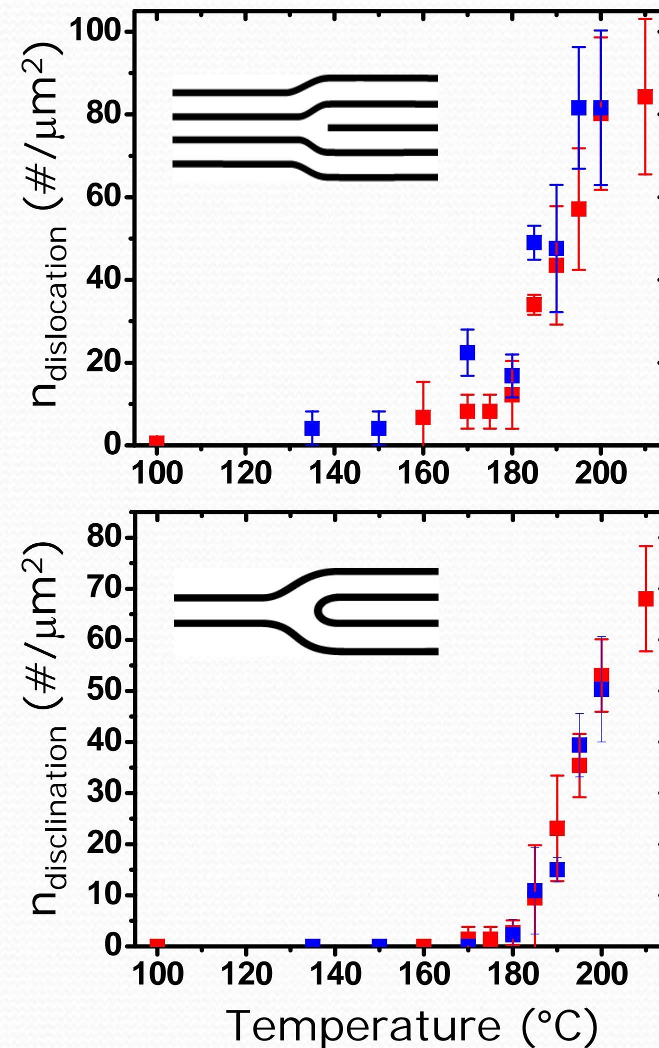


Width of channel ~ 0.23 μm

Defects

- For monolayer, dislocation density is low but nonzero
- Disclination density is zero

Monolayer Defect Densities



Graphs courtesy of M. R. Hammond: *In-Plane Microdomain Order in Cylindrical Block Copolymer Thin Films,* 2005, Macromolecules

Summary

- Accomplishments
  - Learned about block copolymers
  - Improved translational and orientational order of cylinders
  - Learned how to operate AFM
  - Use existing methods to create smaller structures
  - Save $$$$$$

Future plans

- Quantification of defect density
- Compare the effects of channel walls to an unconstrained system
- Determine the effects of channel width and temperature
- Find the cause of defects

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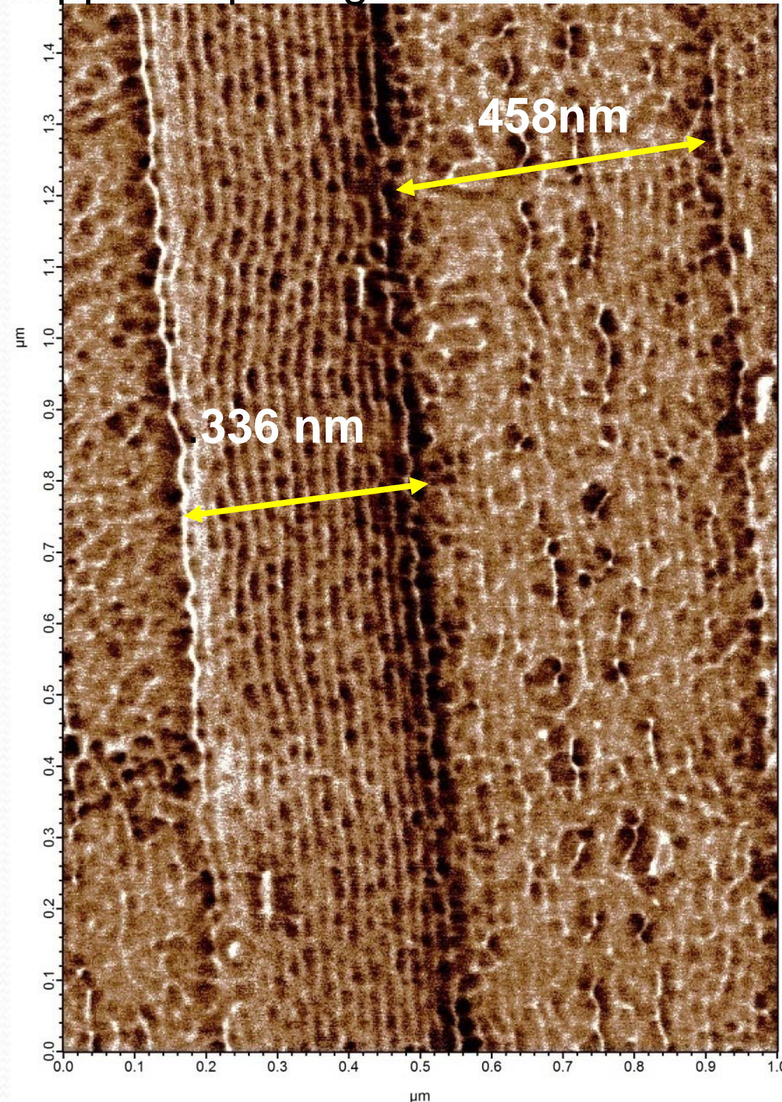
Block Copolymers

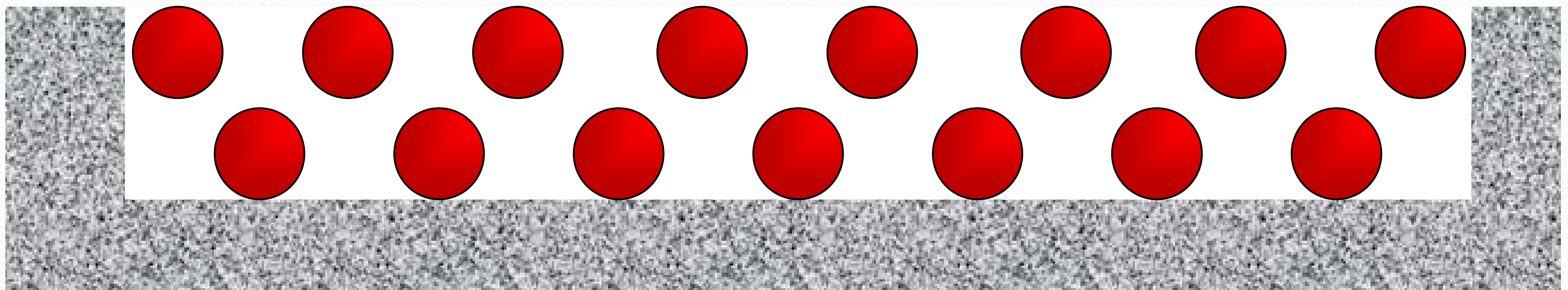
AFM Phase Image

Approx. width of cylinder = 9.08 nm
Approx. spacing = 11.3 nm

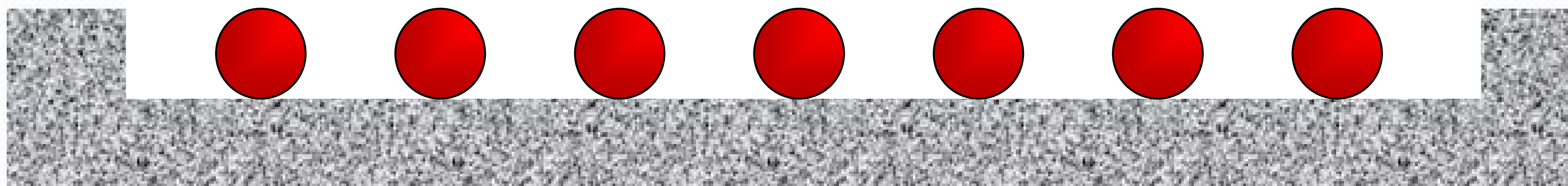


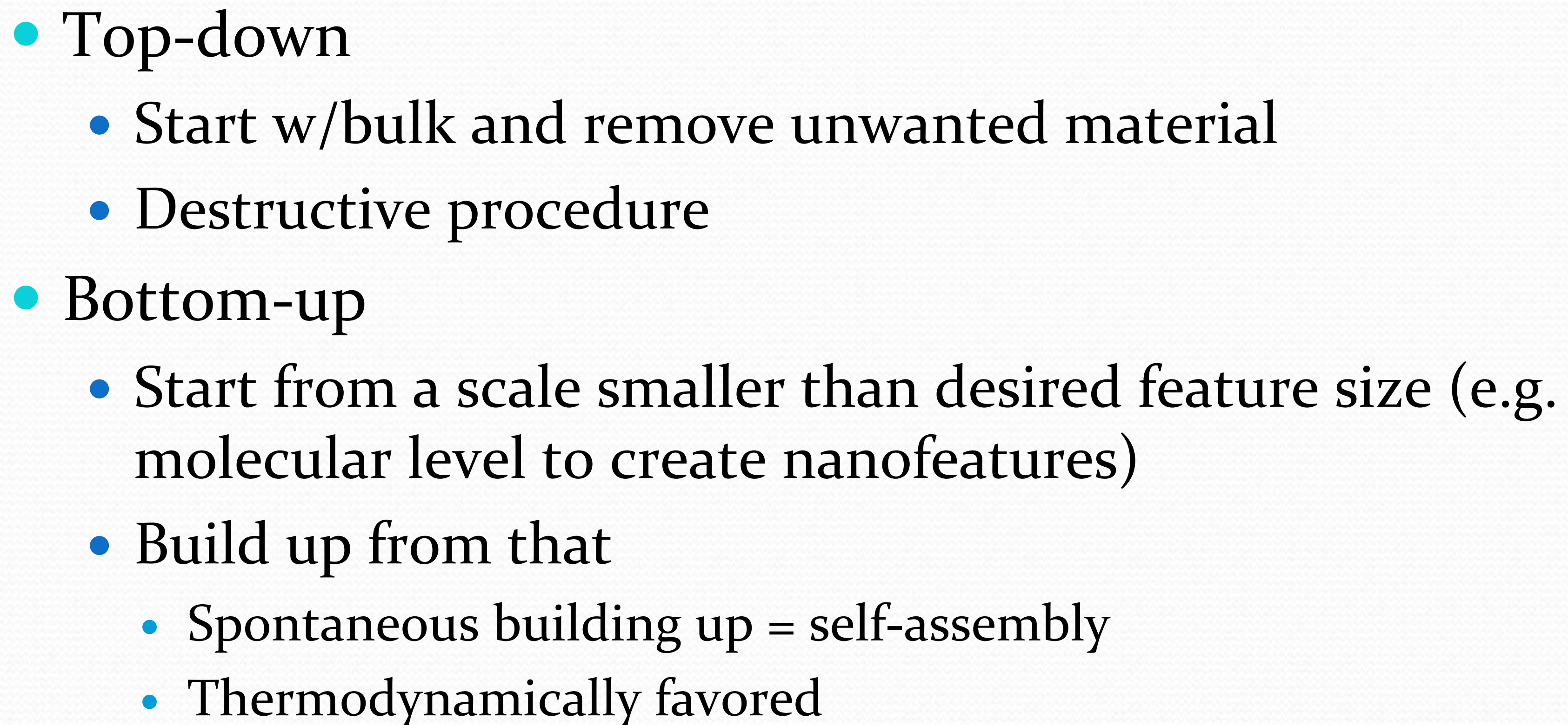
Patterned Si wafer

Bilayers



Monolayer




Top-down
Start w/bulk and remove unwanted material
Destructive procedure
Bottom-up
Start from a scale smaller than desired feature size (e.g. molecular level to create nanofeatures)
Build up from that
Spontaneous building up = self-assembly
Thermodynamically favored