Lecture 16:
Top Down Meets Bottom Up

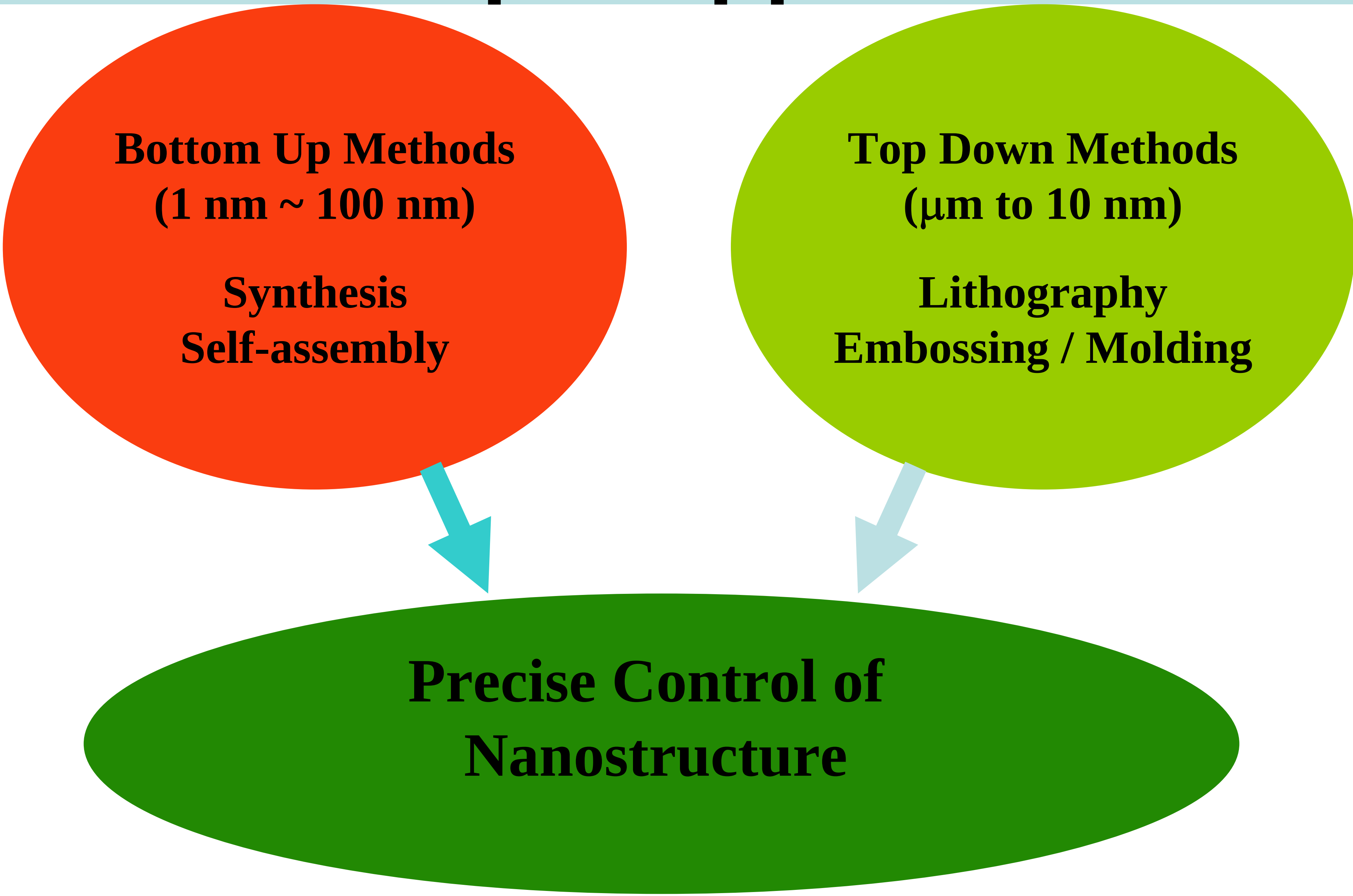
- TOP DOWN & BOTTOM UP -> CONTROL OF STRUCTURE

- ORIENTATION OF BCP MICRODOMAINS

  - Patterned Thin Films: Nanolithography

- CONTROLLING FORCES
  - Graphotaxy (Topographic Patterning)
  - Epitaxy (Crystal-Crystal Lattice Matching)
  - Directional Solidification
  - Combination of Graphotaxy and Directional Solidification
  - Combination of Epitaxy and Directional Solidification

2 Principal Approaches



Top-down vs. Bottom-up

E-beam Lithography

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Please see Fig. 2b in Goodberlet, James G., et al. “Performance of the Raith 150 Electron-beam Lithography System.” *Journal of Vacuum Science and Technology B* 19 (November/December 2001): 2499-2503.

- Arbitrary patterns.
- High precision and accuracy.
- Small area and low throughput.

Self-assembled Structures

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Please see Fig. 1a in Cheng, Joy Y., et al. “Templated Self-Assembly of Block Copolymers: Effect of Substrate Topography.” *Advanced Materials* 15 (October 2, 2003): 1599-1602.

- Periodic nanoscale patterns.
- Short-range ordering.
- Simple and high throughput.

Combining the advantages of two nanofabrication methods: Templated Self-assembly

Potential Applications

Plasmon Waveguide

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Please see Fig. 5a in Naito, Katsuyuki, et al. “2.5-Inch Disk Patterned Media Prepared by an Artificially Assisted Self-Assembling Model.” *IEEE Transactions on Magnetics* 38 (September 2002): 1949-1951.

Image removed due to copyright restrictions.

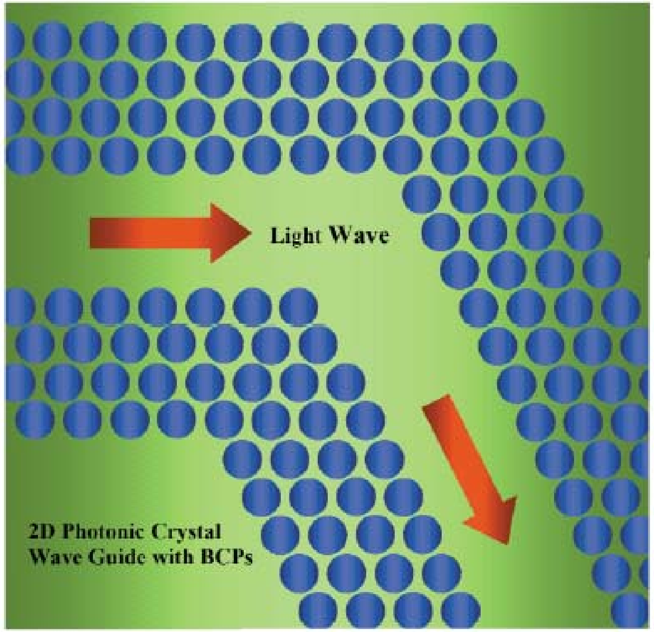
Please see Fig. 5a in Maier, Stefan A., et al. “Plasmonics – A Route to Nanoscale Optical Devices.” *Advanced Materials* 13 (October 2, 2001): 1501-1505.

Patterned Magnetic Media

DNA separation and detection

Image removed due to copyright restrictions.

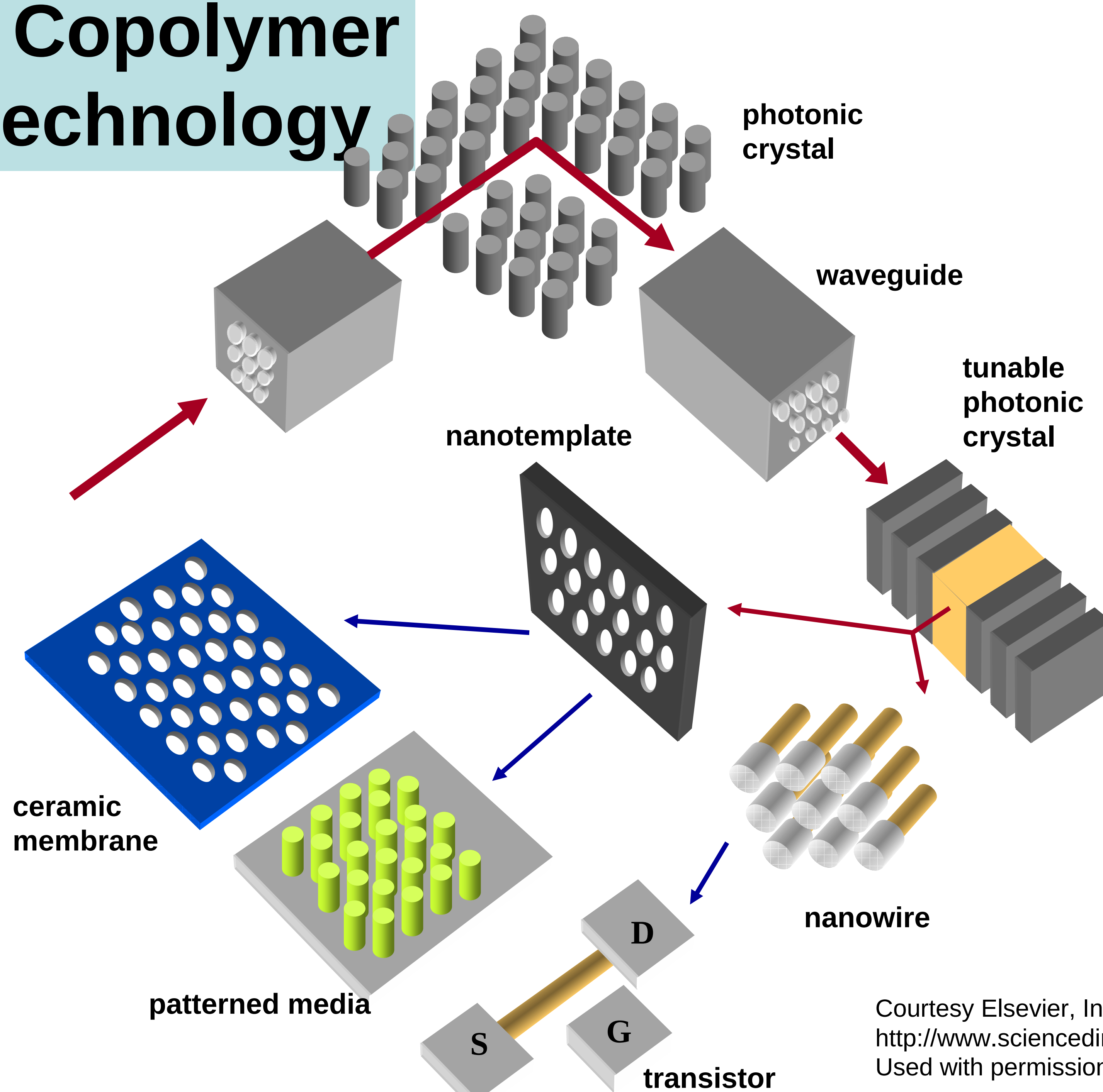
Please see Fig. 2 in Austin, Robert H., et al. “Scanning the Controls: Genomics and Nanotechnology.” *IEEE Transactions on Nanotechnology* 1 (March 2002): 12-18.



2D Photonic Crystal waveguide

C. Park, J. Yoon., E. L. Thomas, *Polymer* ***44*** *6725 (2003)*

Block Copolymer Nanotechnology



Templated Self Assembly

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Please see Fig. 1 in Cheng, Joy Y., et al. "Templated Self-Assembly of Block Copolymers: Top-Down Helps Bottom-Up." *Advanced Materials* 18 (2006): 2505-2521.

Self Assembly in a Thin Film Geometry

- Components
  - Block Copolymers/Homopolymers/Nanoparticles/LC mesogens
  - Solvent (including crystallizable solvents)
  - Substrate/Superstrate
- Issues
  - One step vs multistep processing
  - Surface treatments/anchoring conditions
  - Topographical features on substrate
- ***Control*** (need multi-axis control to eliminate degeneracies)
  - Bias self assembly for spatial registration, domain orientation and defect elimination
  - Mechanical flow fields, temperature gradients, E and M fields, Substrate topography (use 2 or more biasing factors)
  - Need anisotropies: molecular, domain, nanoparticle to strongly couple to applied fields

Top Down & Bottom Up: Rack and Roll:

Self Assembly on Topographically Patterned Substrates For UltraDense Magnetic Storage

Magnetic Recording System

IBM hard disk drive

Old: Hard Disk Media

New: Patterned Media

Image removed due to copyright restrictions.

Please see Fig. 1 in Ross, C. A., et al. "Fabrication of patterned media for high density magnetic storage." *Journal of Vacuum Science and Technology B* 17 (November/December 1999): 3168-3176.

- Bit size defined by the read-write head
- A bit is read by averaging 250 to 500 grains

↓

High transition noise and low density

- Bit size defined by lithography
- A bit is stored in a single domain magnetic particle

↓

Low transition noise and high density

Patterned Magnetic Media

Patterning Requirements:

- ✓ Areal density > 200 Gbit / in^2

  Ex: A 50 nm-period square dot array gives 250 Gbit / in^2

- ✓ Large area arrays of magnetic elements with high spatial precision.

Fabrication Methods

- **Top Down Methods:**

  Focused ion beam, E-beam lithography, Optical-X-ray lithography & Nanoimprint lithography.

- **Bottom Up Methods:**

  Self-organizing magnetic nanoparticles & block copolymers

New Method : Bottom Up + Top Down

Self-assembled block copolymers + Optical lithography

Block Copolymers as Lithographic Masks

Image removed due to copyright restrictions.

Please see Fig. 2 in Harrison, Christopher, et al. “Lithography With a Mask of Block Copolymer Microstructures.” *Journal of Vacuum Science Technology B* 16 (March/April 1998): 544-552.

❖ 2D Structures of Block Copolymers

- Periodic structures : perpendicular cylinders or spheres: p6mm packing
- Feature size ∝ (MW of minority block copolymer)$^{2/3}$

  Feature spacing ∝ (MW of majority block copolymer)$^{2/3}$

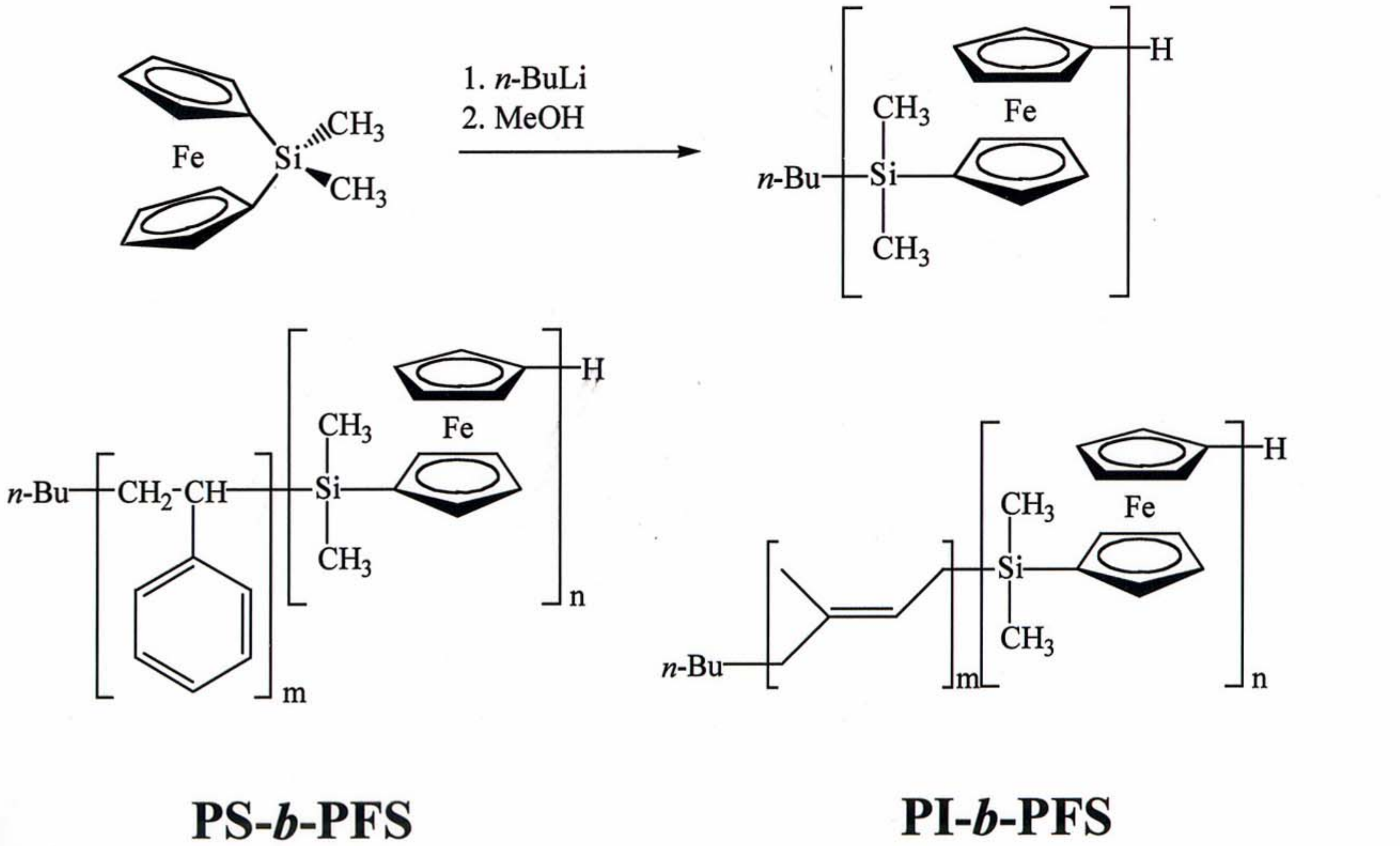
❖ Surface Compatibility

- High glass transition temperature to ensure structure stability.
- Low interfacial energy between polymer and substrate to avoid dewetting.

❖ Etch Selectivity between Two Blocks

- ***Organometallic-organic polymers*** give much higher selectivity than organic-organic polymers.

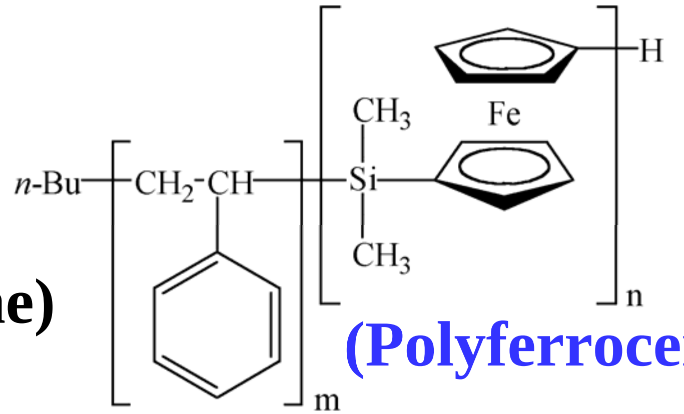
Organic-*block*-Organometallic Copolymers



I. Manners, Bristol Univ.

Organometallic BCPs

PS
(Polystyrene)



PFS
(Polyferrocenyldimethylsilane)

30 ~ 60 nm

15 ~35 nm

Block Copolymer Thin Film

Monolayer of Spherical Domains

Pitch, P

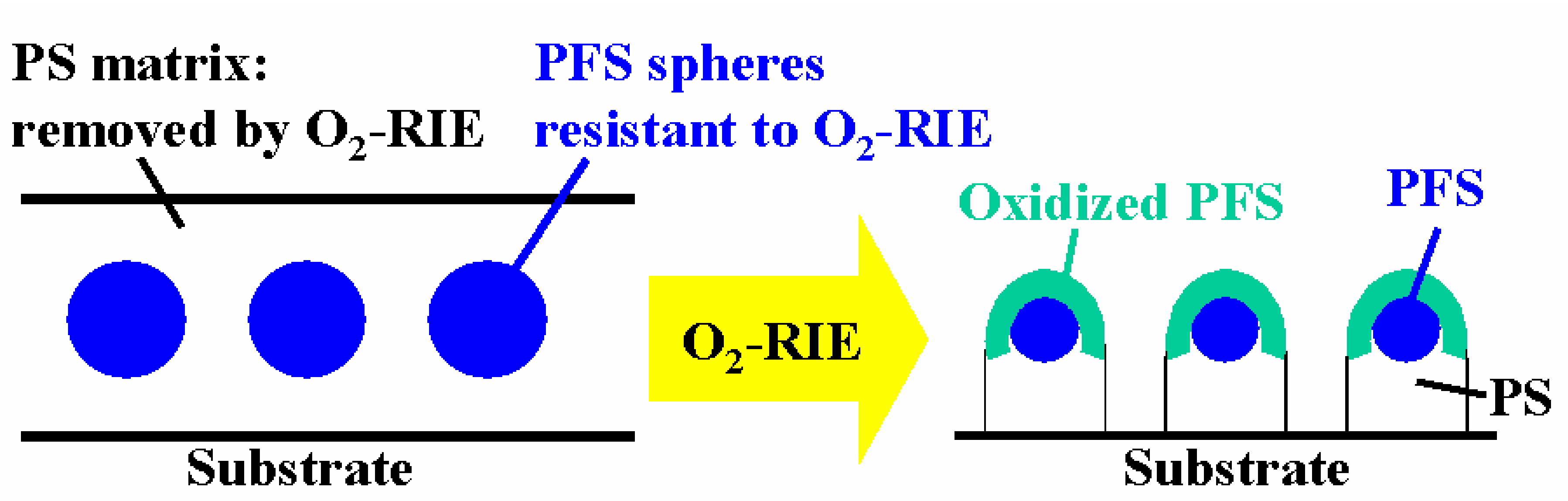
P~ 60 nm ~ 250 G particles/ in^2

P~ 30 nm ~ 1,000 G particles/ in^2

Image removed due to copyright restrictions.

Please see Fig. 1b in Cheng, Joy Y., et al. “Templated Self-Assembly of Block Copolymers: Effect of Substrate Topography.” *Advanced Materials* 15 (October 2, 2003): 1599-1602

PS-PFS Etch Selectivity in O_2-Plasma



Block Copolymer Thin Film — Lithographic Mask from Copolymer

Surface chemistry analysis of PFS polymer

Element	PFS Homopolymer Before O_2-RIE	PFS Homopolymer After O_2-RIE
C 1S	85.7	37.7
O 1S	0.6	41.2
Si 2P	6.0	7.6
Fe 2P	7.7	13.5

PFS forms iron-silicon-oxide in the O_2 plasma

High etching selectivity between PS and PFS (10:1).

Fabrication of 2D Gratings in SiO_2 on Silicon

Please see: Fig. 2 in Ross, C. A. "Patterned Magnetic Recording Media." *Annual Review of Materials Research* 31 (2001): 203-235.

Block Copolymer Lithography - Formation of Co Magnetic Nanodots

Please see Fig. 2 in Cheng, Joy Y., et al. “Formation of a Cobalt Magnetic Dot Array via Block Copolymer Lithography.” *Advanced Materials* 13 (August 3, 2001): 1174-1178.

Final magnetic NPs

Block Copolymer Lithography - SEM Study of Co Magnetic Nanodots

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Please see Fig. 3 in Cheng, Joy Y., et al. "Formation of a Cobalt Magnetic Dot Array via Block Copolymer Lithography." *Advanced Materials* 13 (August 3, 2001): 1174-1178.

Magnetic Dot Arrays Made by Block Copolymer Lithography

Please see Fig. 8a in Cheng, Joy Y., et al. "Magnetic Nanostructures from Block Copolymer Lithography: Hysteresis, Thermal Stability, and Magnetoresistance." *Physical Review* B 70 (2004): 064417.

- **Co, NiFe, CoFe/Cu/NiFe** dots have all been made.
- Center-to-center spacing ~ 60 nm.
- Averaged dot diameter ~ 25 nm.
- Magnetic dot arrays are locally close-packed BUT are not globally ordered.

Status Report: Magnetic Dot Arrays from Block Copolymer Lithography

❖ **Block copolymer lithography** is a simple, large-area, low-cost process to make high-density nanostructures of a variety of materials.

❖ Feature size and spacing can be adjusted through molar mass of polymers (2/3rds power of MW scaling law).

❖ **Co, NiFe, CoFe/Cu/NiFe dot arrays made and characterized.**

❖ Strong magnetostatic interactions are observed due to limited short-range ordering - undesirable for magnetic data storage application.

The Path Forward:

1. Make dots from materials of high out-of-plane crystalline anisotropy to reduce interactions and provide controlled orientation of magnetization.
2. Improve ordering of dots via **templated self-assembly (TSA)**.

Templated Self Assembly

A method to induce the orientation and ordering of self-assembled materials by a topographical or chemical pattern or both.

Example:

Controlling order of colloidal particles:
Topographical Boundaries and period commensuration.

Width =
4 rows

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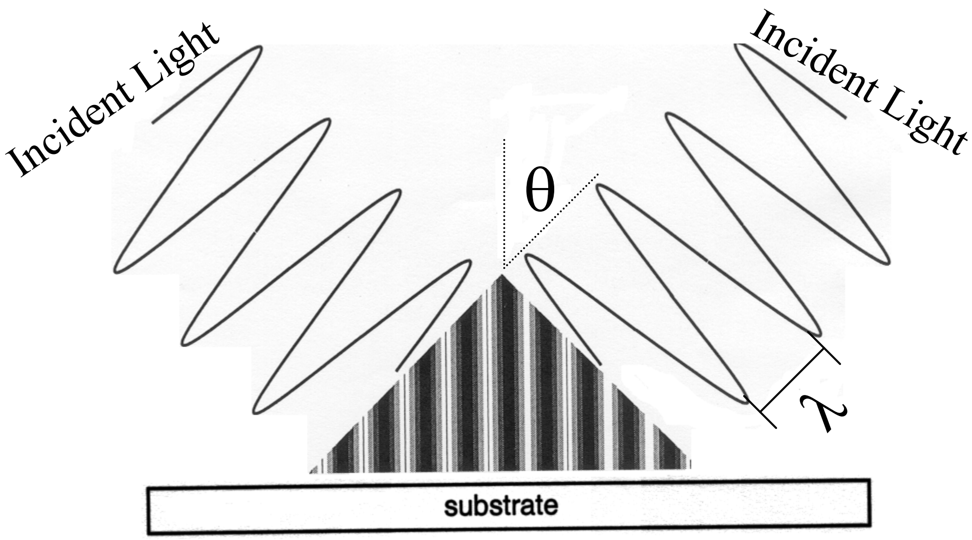
Please see Fig. 3 in Kumacheva, Eugenia, et al. “Colloid Crystal Growth on Mesoscopically Patterned Surfaces: Effect of Confinement.” *Advanced Materials* 14 (February 5, 2002): 221-224.

Width =
5 rows

Incommensurate

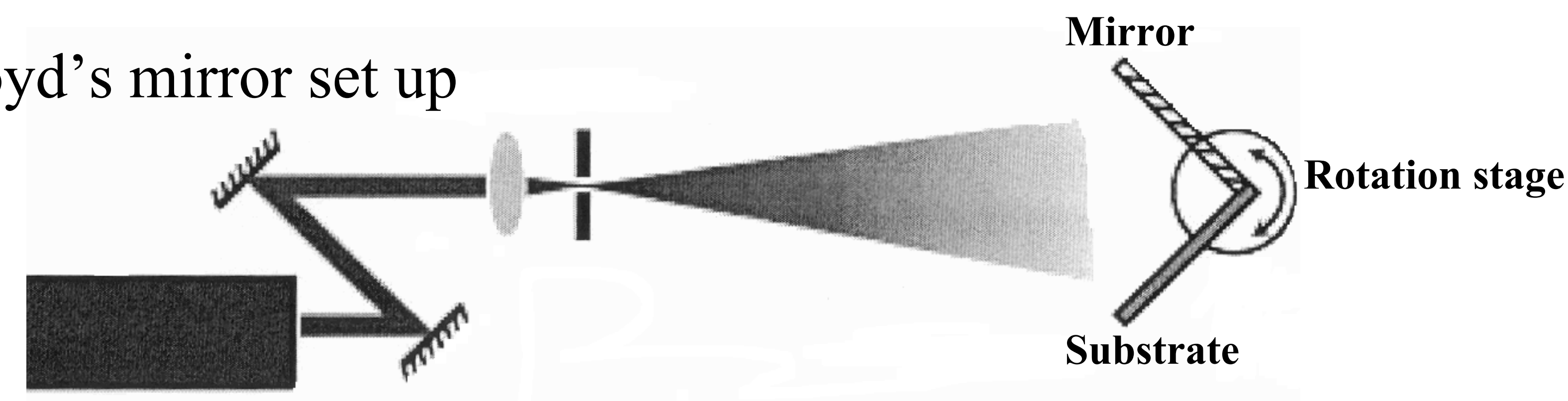
Substrate Topography via Interference Lithography



The period of the fringe pattern

$p = \lambda/2\sin\theta$

Lloyd's mirror set up



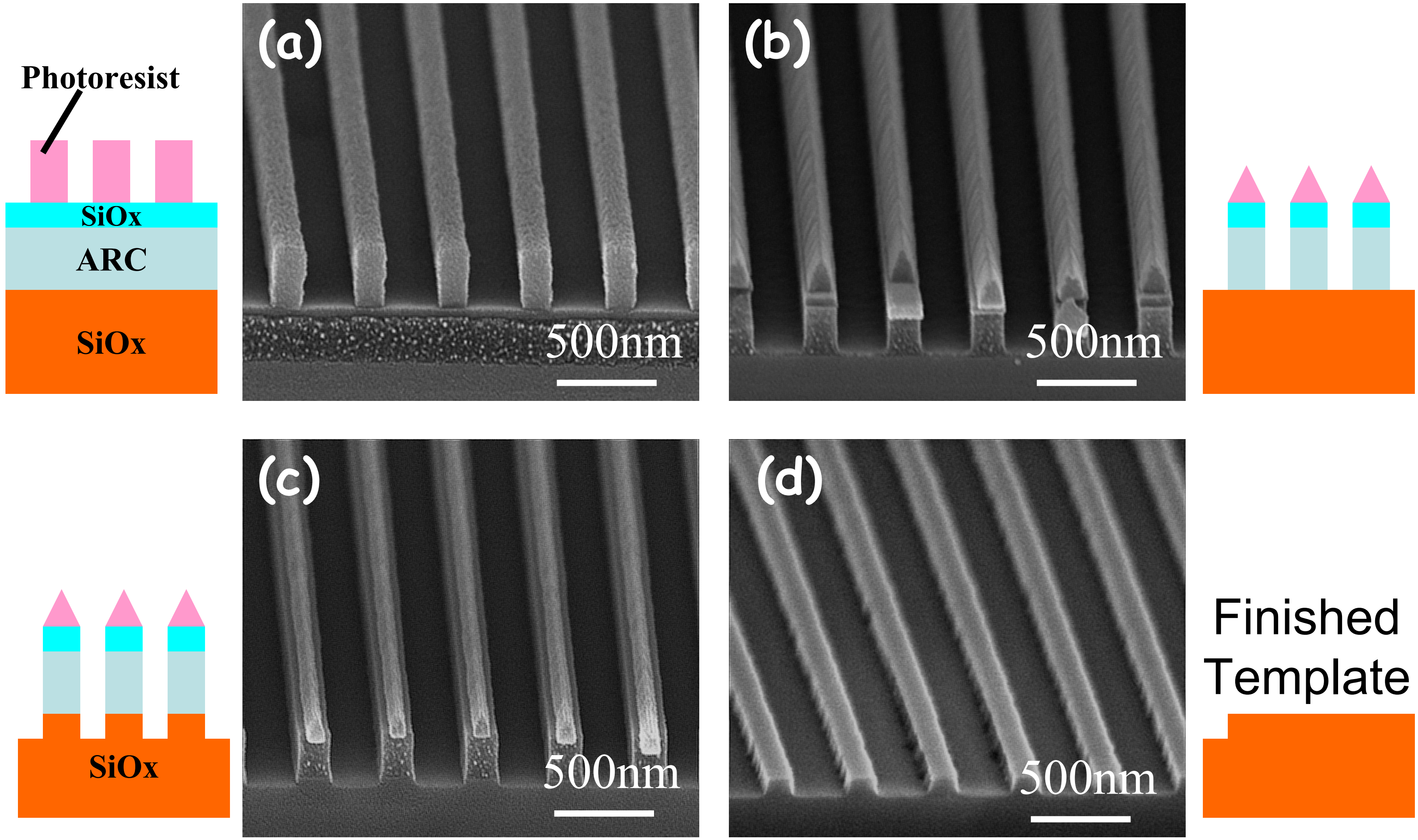
HeCd Laser operated at 325 nm

Can fabricate gratings with the p from 180 nm to 1500 nm

H. Smith, Nanostructures Lab, MIT

From Walsh, Michael E. "Nanostructuring Magnetic Thin Films Using Interference Lithography." Master's Thesis, MIT, 2000. http://dspace.mit.edu/handle/1721.1/8812

Fabrication of Topographical Substrates



From Cheng, Joy. "Fabrication and Characterization of Nanostructures from Self-Assembled Block Copolymers." PhD Thesis, MIT, 2003.
http://dspace.mit.edu/handle/1721.1/29963

Assembly of a Monolayer of Spherical Domains on Flat Substrate

Image removed due to copyright restrictions.

Please see Fig. 1a, c, and 2c in Cheng, Joy Y., et al. “Templated Self-Assembly of Block Copolymers: Effect of Substrate Topography.” *Advanced Materials* 15 (October 2, 2003): 1599-1602.

Block copolymers- Rack 'em up!

Image removed due to copyright restrictions.

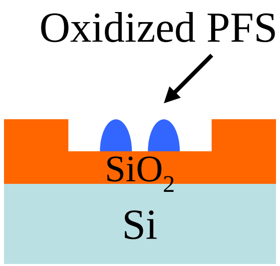
Please see Fig. 1a and c in Cheng, Joy Y., et al. "Fabrication of Nanostructures with Long-range Order Using Block Copolymer Lithography." *Applied Physics Letters* 81 (November 4, 2002): 3657-3659.

Commensuration: Period vs Width

Image removed due to copyright restrictions.

Please see Fig. 2 in Cheng, Joy Y., et al. “Fabrication of Nanostructures with Long-range Order Using Block Copolymer Lithography.” *Applied Physics Letters* 81 (November 4, 2002): 3657-3659.

- Long-range ordered block copolymers inside the groove.
- No grain boundaries observed.
- Polymer domains align with the groove edge.
- 9 rows of polymer domains in a 230 nm wide groove.



Registration and Tracking

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Please see Fig. 4a in Cheng, Joy Y., et al. "Templated Self-Assembly of Block Copolymers: Effect of Substrate Topography." *Advanced Materials* 15 (October 2, 2003): 1599-1602.

And

Fig. 25b in Park, Cheolmin, et al. "Enabling Nanotechnology with Self Assembled Block Copolymer Patterns." *Polymer* 44 (October 2003): 6725-6760.

Data

Track

- Sharp edge feature on the template leads to a missing polymer domain and pins the lateral position of the array in the groove.

Commercial Application

Image removed due to copyright restrictions.

Please see Fig. 5 in Naito, Katsuyuki, et al. "2.5-Inch Disk Patterned Media Prepared by an Artificially Assisted Self-Assembling Model." *IEEE Transactions on Magnetics* 38 (September 2002): 1949-1951

2.5 inch circumferential patterned media

via Templated Self Assembly of BCP

(Toshiba, Japan)

Naito et al. *IEEE Trans Magn* **2002**, 38, 1949.

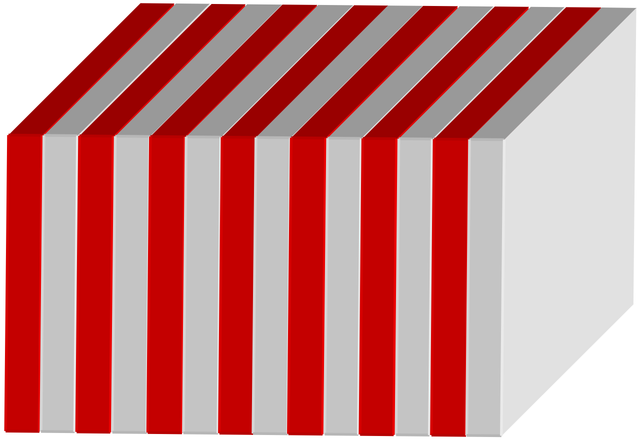
Chemical Patterning

By providing a chemical pattern on a flat substrate that has an affinity and width appropriate for each block, the resultant BCP structure is directed to template over the specific locations. In the case below, the 4 χ parameters between the 2 types of blocks and the two types of chemical patterns, favors the location of PMMA over the polar SiO_2 and the PS over the Au stripes and thus a vertically oriented lamellar microdomain structure.

Image removed due to copyright restrictions.

Please see Fig. 6a in Cheng, Joy Y., et al. "Templated Self-Assembly of Block Copolymers: Top-Down Helps Bottom-Up." *Advanced Materials* 18 (2006): 2505-2521.

Vertically patterned Lamellae

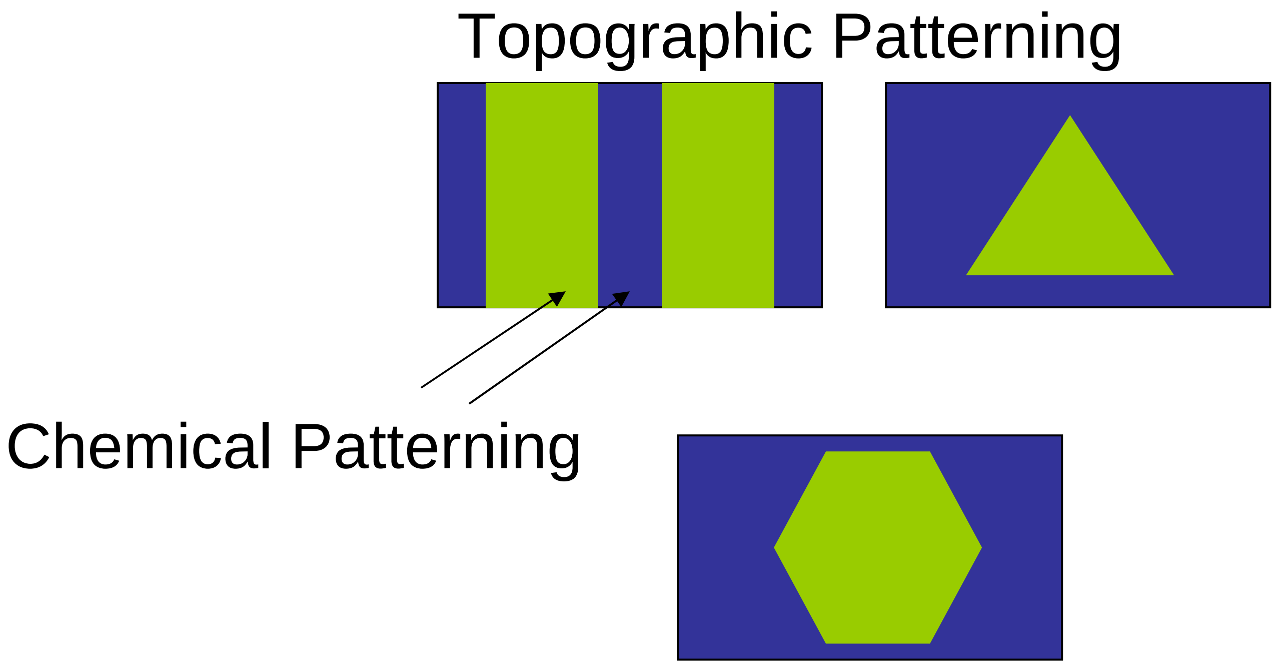


What's Next?

Chemical Pattern + Topographic Pattern

– Biased Surface and Wall Confinement

Pay attention to symmetry and commensuration!



Vertical Alignment of BCP Microdomains: Electric Field

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Please see Fig. 1 in Thurn-Albrecht, T., et al. "Ultrahigh-Density Nanowire Arrays Grown in Self-Assembled Diblock Copolymer Templates." *Science* 290 (December 15 2000): 2126-2129.

❖ BCPs comprised of blocks with different dielectric constants orient under an applied electric field

- E-field: 10^6-10^8 V/m
- Induce uniaxial orientation of BCP microdomain along the field

- Note resulting orientation of a grain in a lamellar and cylindrical BCPs is still azimuthally degenerate!
  → many defects and grain boundaries since no in plane guidance

BCP Templated Self Assembly

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Please see Fig. 4 in Cheng, Joy Y., et al. “Templated Self-Assembly of Block Copolymers: Top-Down Helps Bottom-Up.” *Advanced Materials* 18 (2006): 2505-2521.

PS-PFS diblock copolymer forming PFS spheres

The PS is removed via a O_2 plasma etch

The number of rows of spheres increases as a step function

Block Copolymer Epitaxy

Image removed due to copyright restrictions.

Please see Fig. 8 in Cheng, Joy Y., et al. “Templated Self-Assembly of Block Copolymers: Top-Down Helps Bottom-Up.” *Advanced Materials* 18 (2006): 2505-2521.

By creating specific patterns in the template precise control over the block copolymer can be achieved

Defect structures can be intentionally created and manipulated

These types of structures can be useful for nanopatterning, microfluidics, or photonic applications

BCPs as nanopatterning templates

Triblock copolymers used to create complex nano-patterned structures on a thin film

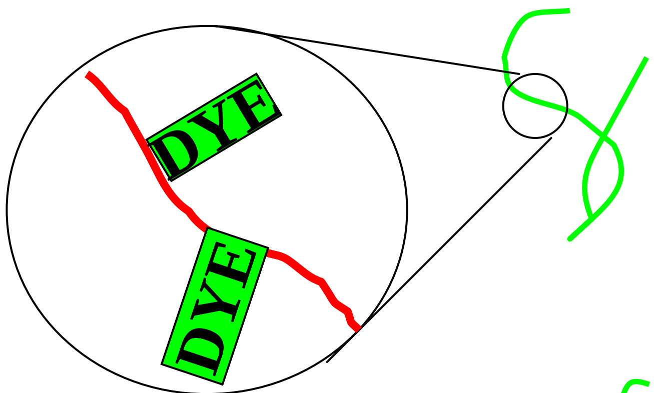
Image removed due to copyright restrictions.

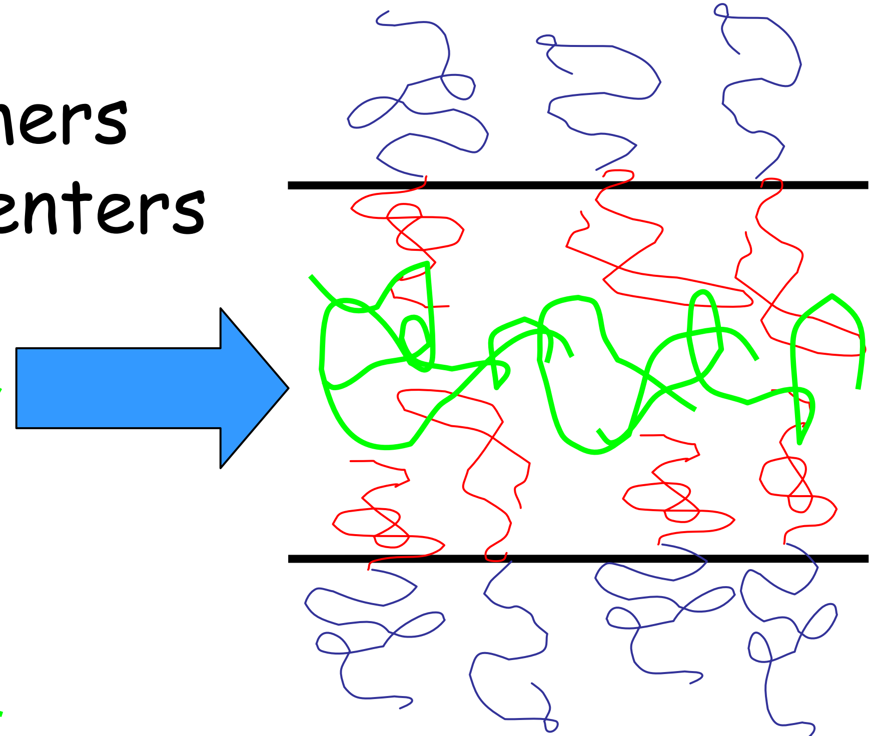
Please see Scheme 1, Fig. 1, and Fig. 2 in Guo, Shouwo, et al. "Nanopore and Nanobushing Arrays from ABC Triblock Thin Films Containing Two Etchable Blocks." *Chemistry of Materials* 18 (2006): 1719-1721.

Etching of one or more blocks can lead to isolated pillars, holes or tubes

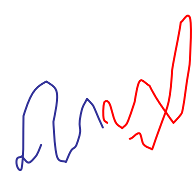
Templating Fluorescent Additives into BCPs

Labeled homopolymers locate at domain centers



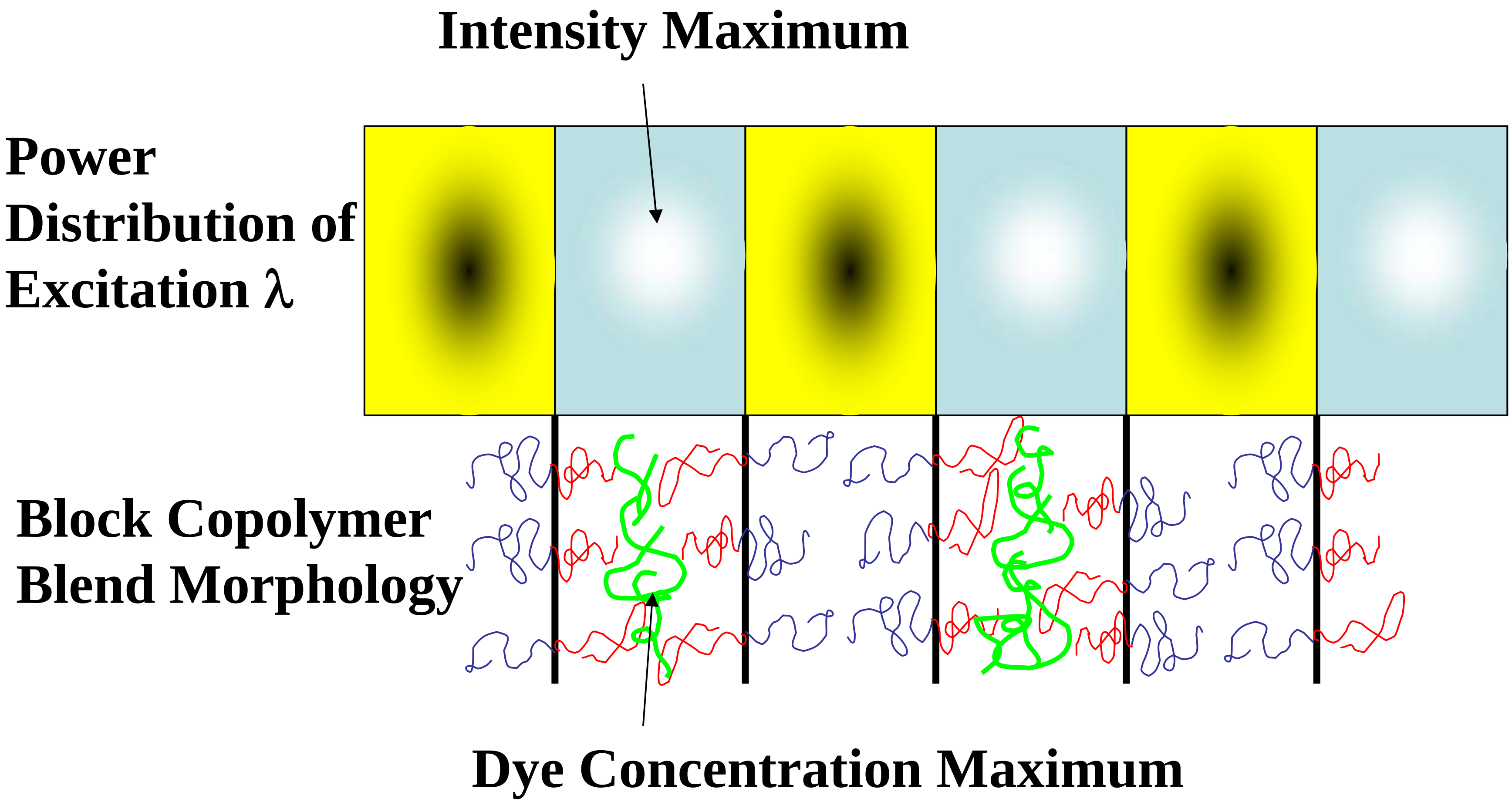


 **= Fluorescently labeled homopolymer**

 **= Block copolymer**

Can specifically access chromophores via near gap propagating modes

Increase Efficiency of Excitation



Doped BCPs systems maximize the overlap of the intensity distribution with the dye