

Lecture 19

Chemical Engineering for Micro/Nano Fabrication



5 MB hard disk drive





IBM's 5 MB Drive

1957



Toshiba's 4 GB Drive

TODAY

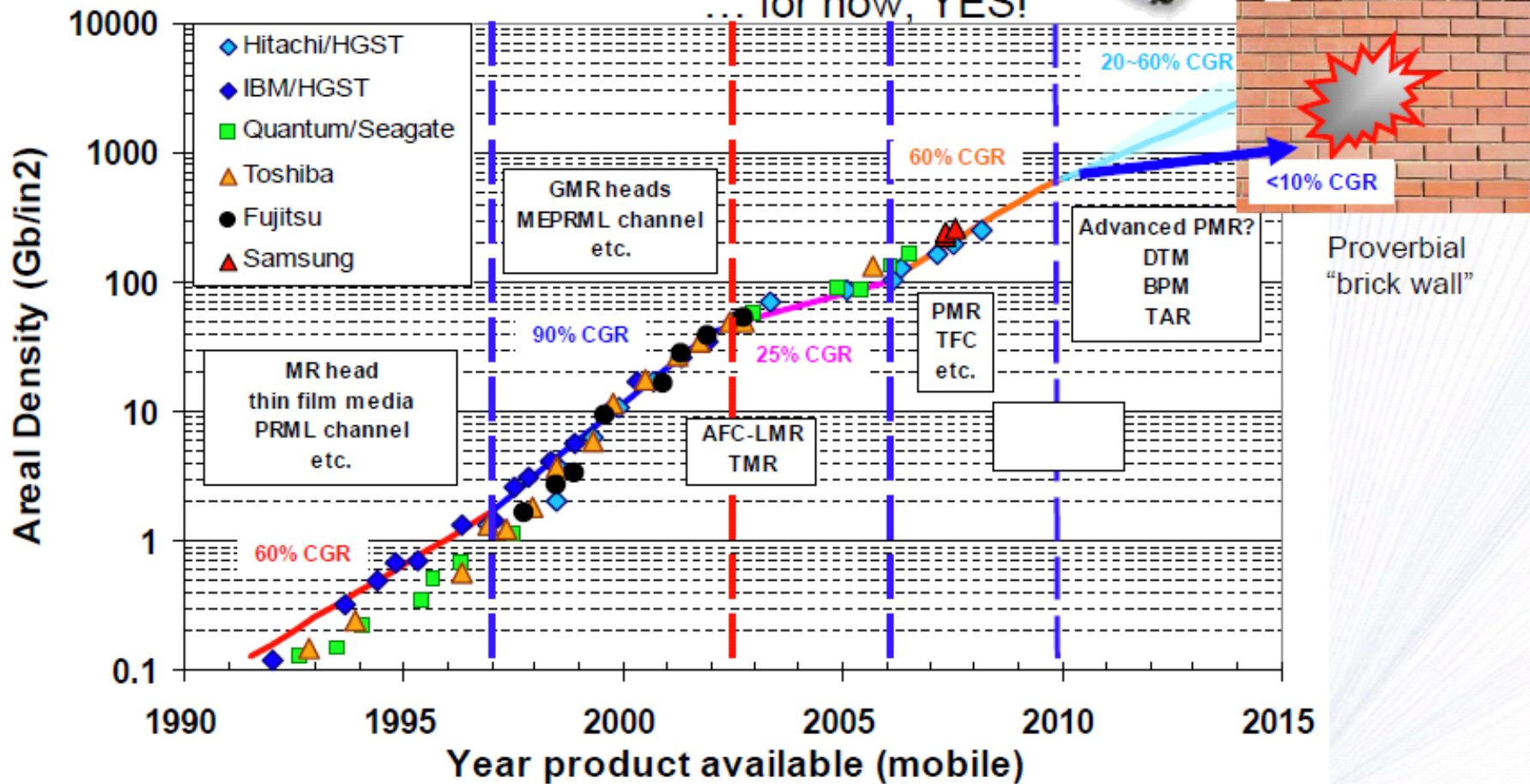
Areal Density Trend



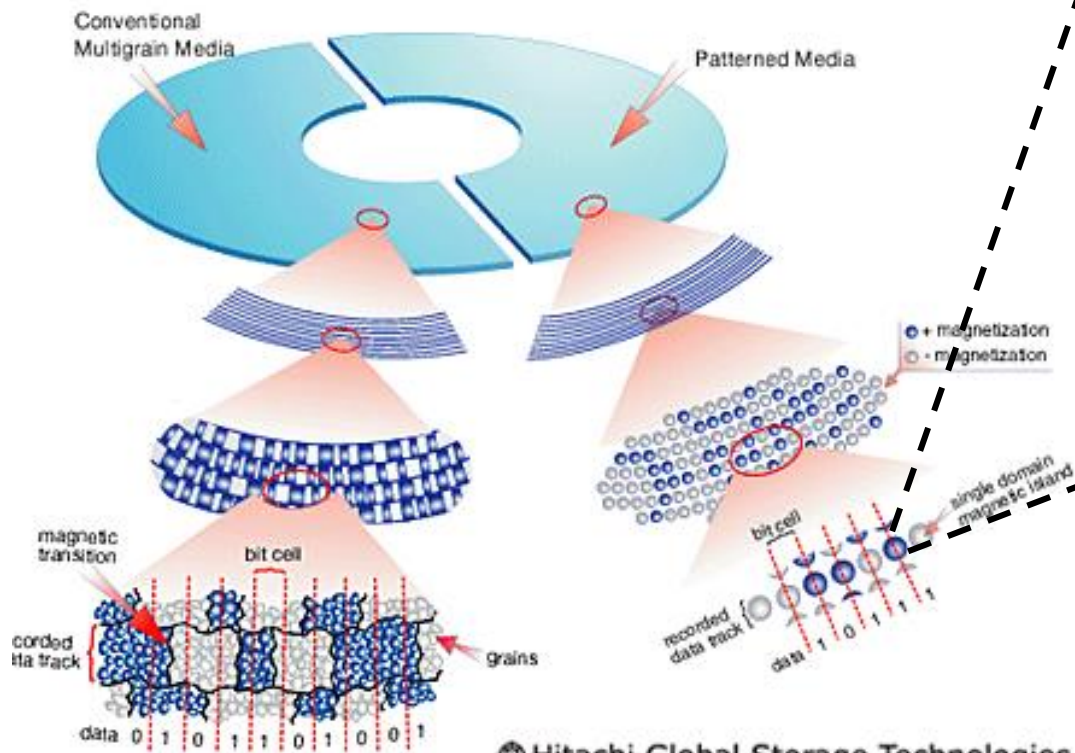
After 50 years of continuous progress...

...will we hit the brick wall?

... for now, YES!

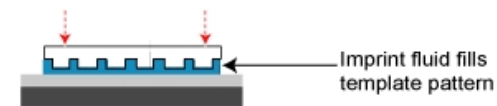


Very Small Features required for New Hard Disk Drives



Hitachi Global Storage Technologies

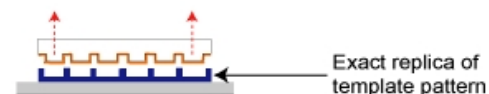
Nanoimprint Lithography



Lower template and fill pattern



Polymerize imprint fluid with UV exposure



Separate template from substrate

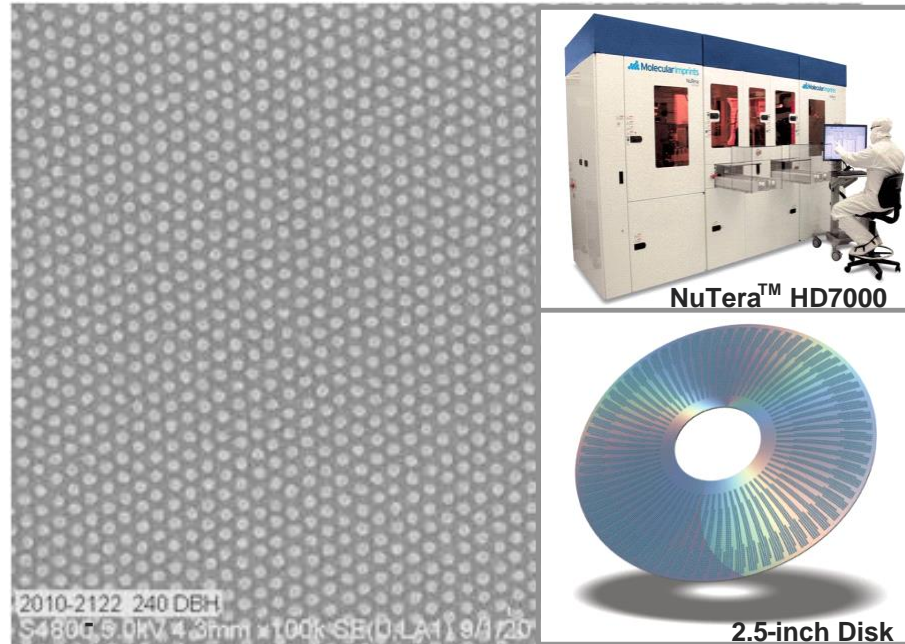
http://www.patrickcarlberg.dk/Lic/Intro%20mm/lith_image2.htm
<http://nextbigfuture.com/2009/06/electron-beam-lithography.html>
<http://www.itmweb.com/bimages/mitechnique.jpg>

Lodder, J.C., Journal of Magnetism and Magnetic Materials, 2004. p. 1692-1697.



Printing Bit Patterned Media

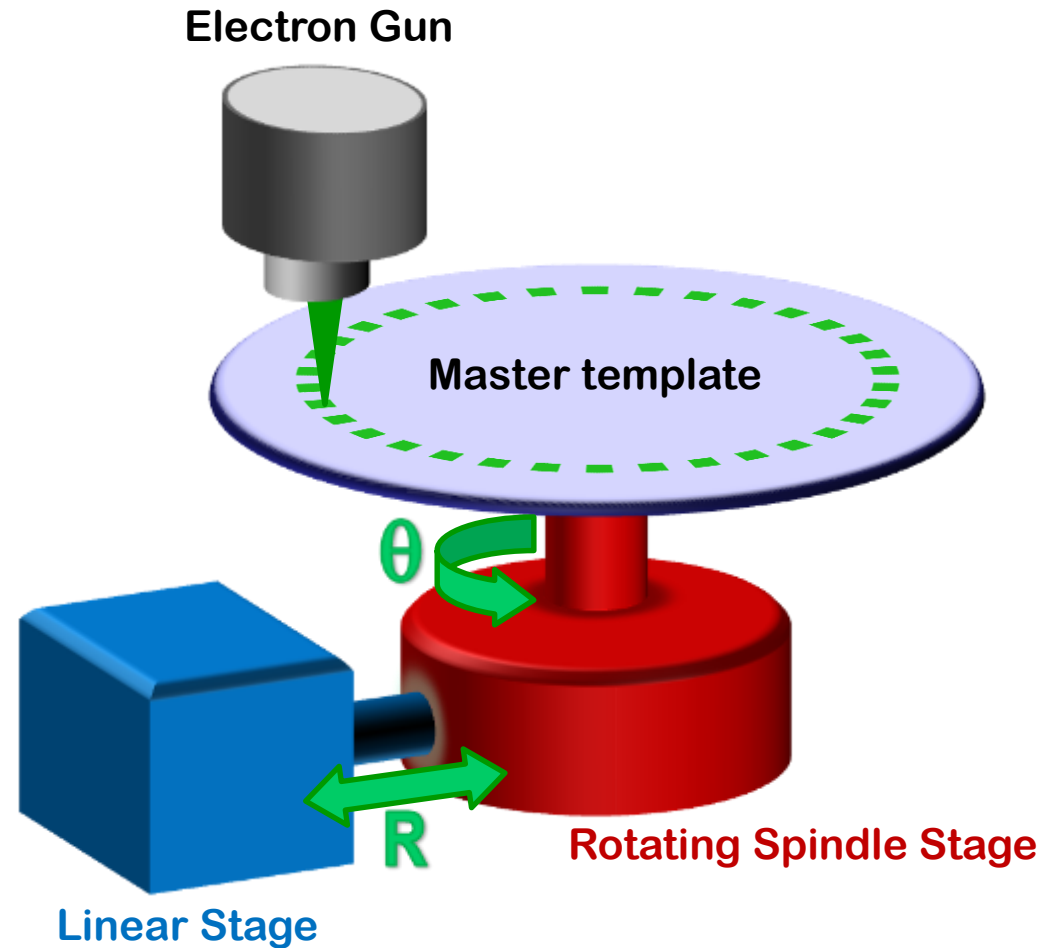
BPM Disk Imprint



12nm Half Pitch Resist Pillars on Disk
From a hole tone template

Template Mastering with Rotary E-beam

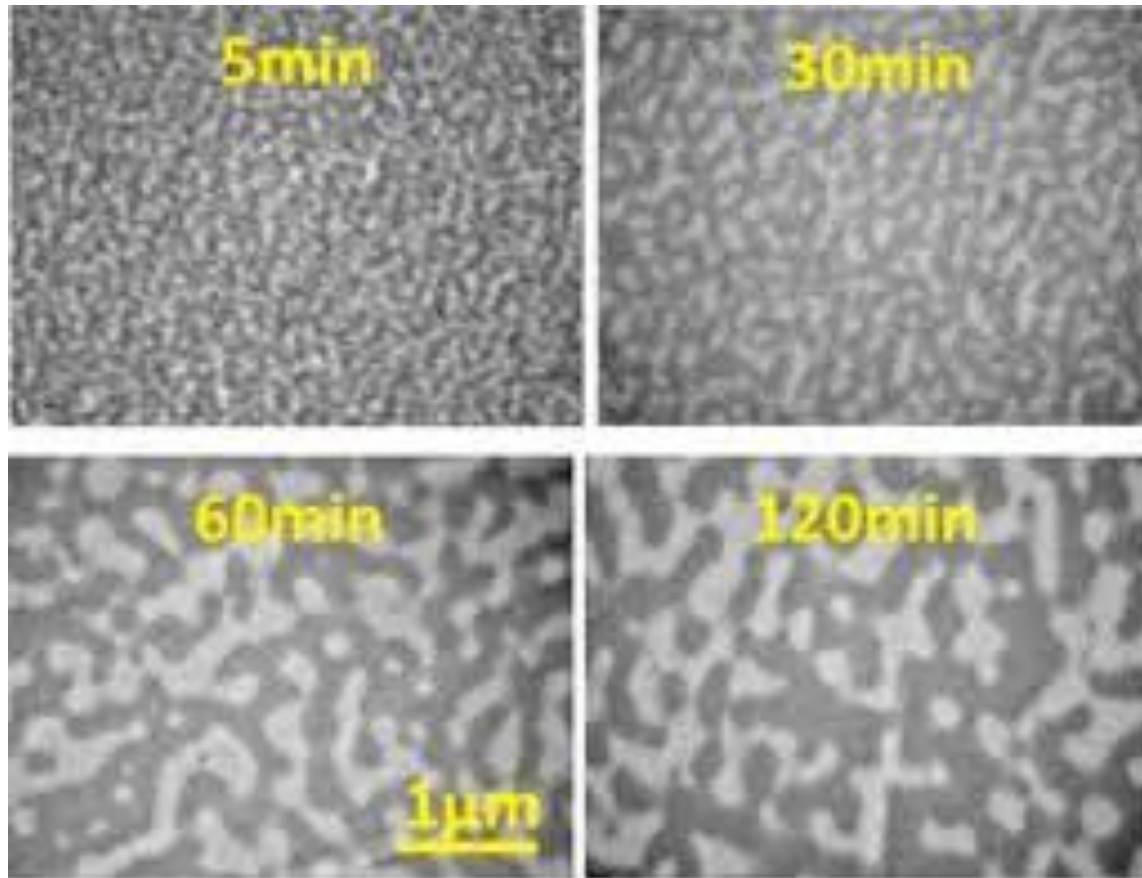
- ▶ Takes ~ 1 month to write one template !!!
- ▶ Cost ~ \$ 10^6 / template



This is just far too Slow!!!

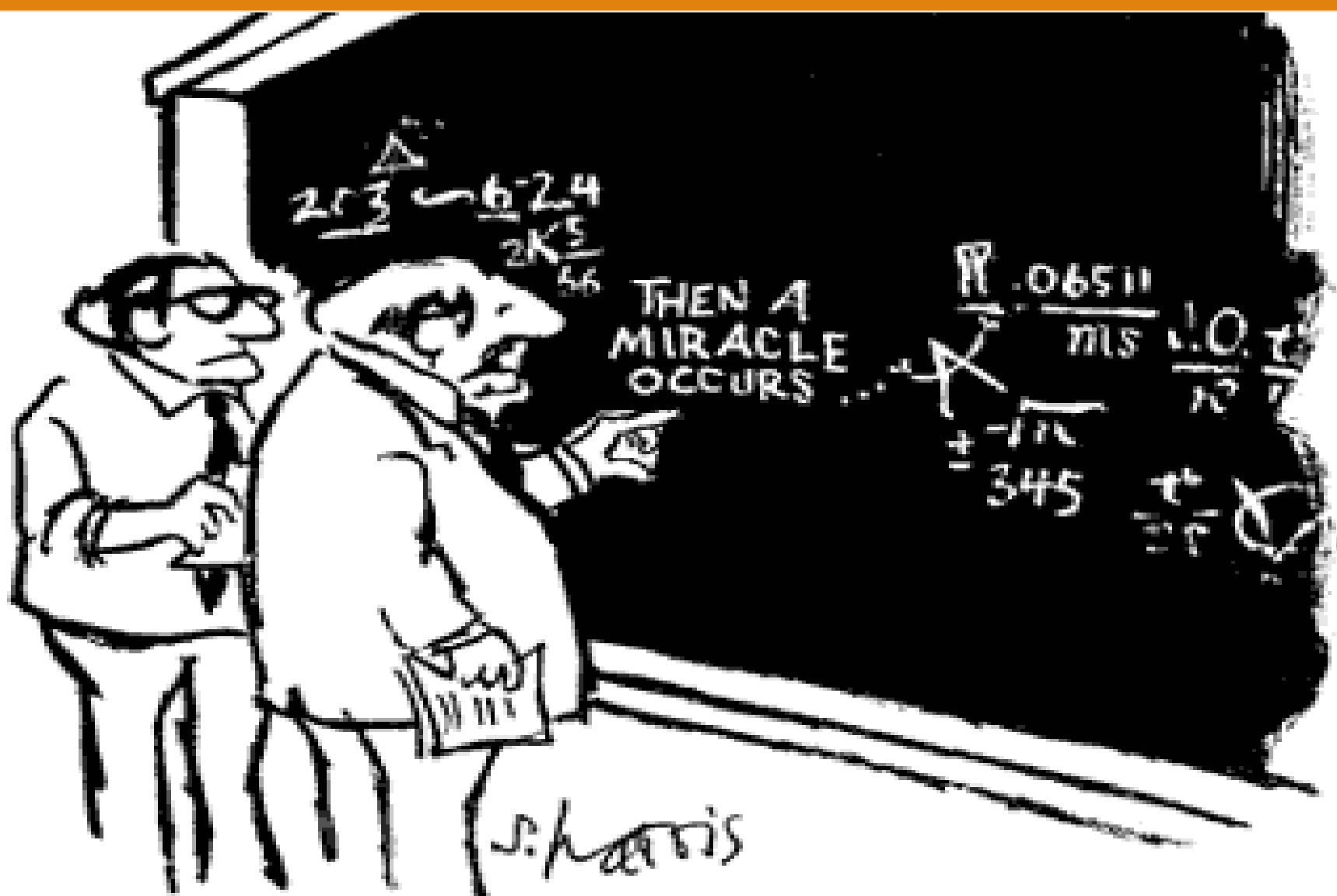


Polymer blends....



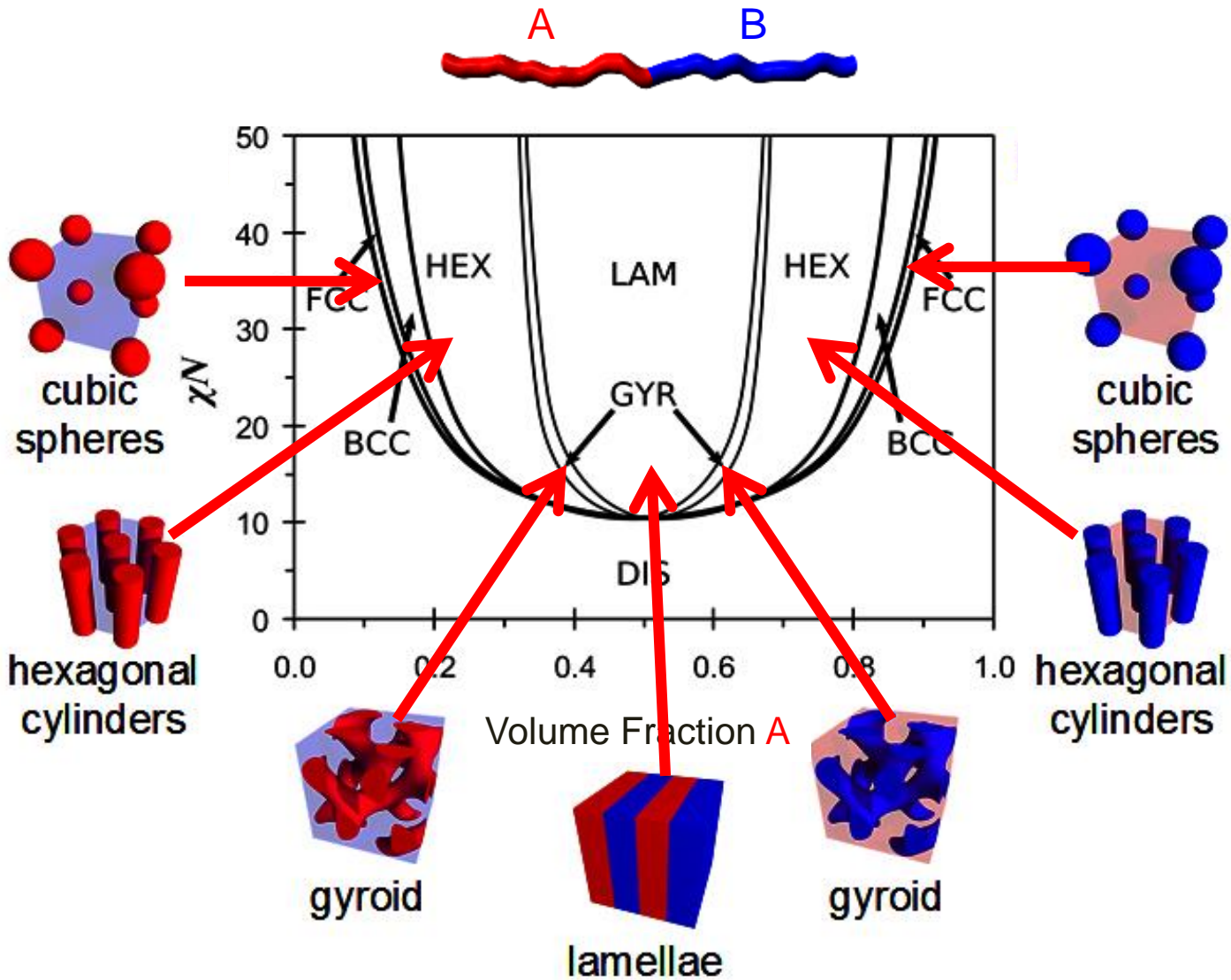
Effect of annealing on blend morphology





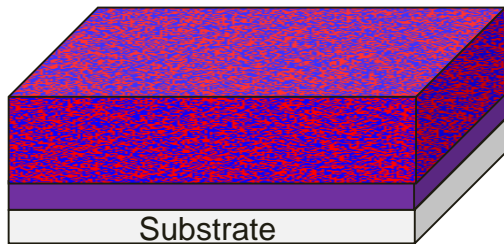
"I think you should be more explicit here in step two."

Miracle of Block Copolymers

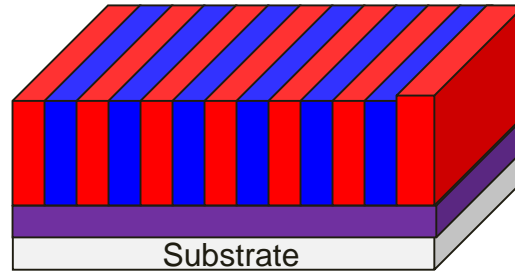


Miracle process flow.....

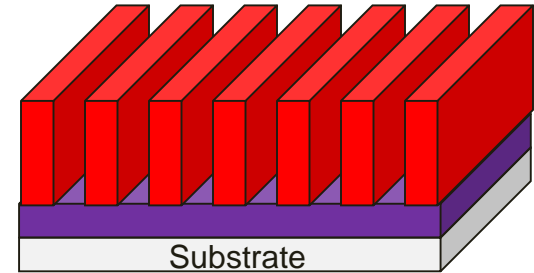
No optics



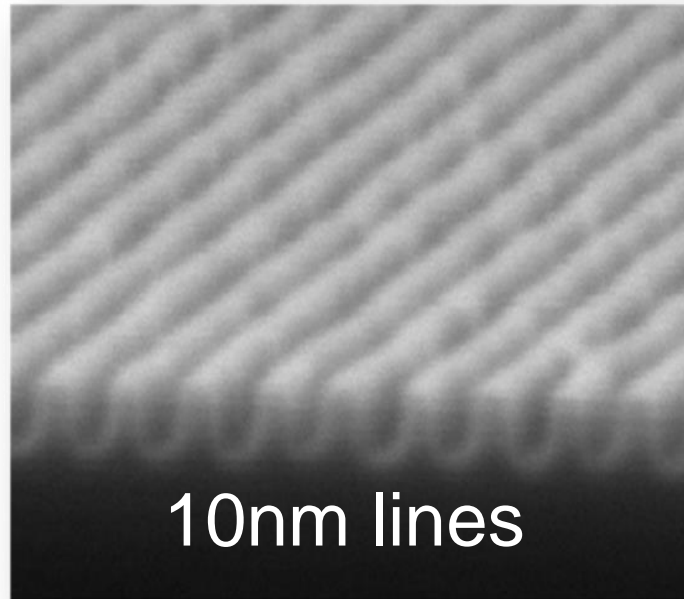
1. Spin coat BCP



2. anneal

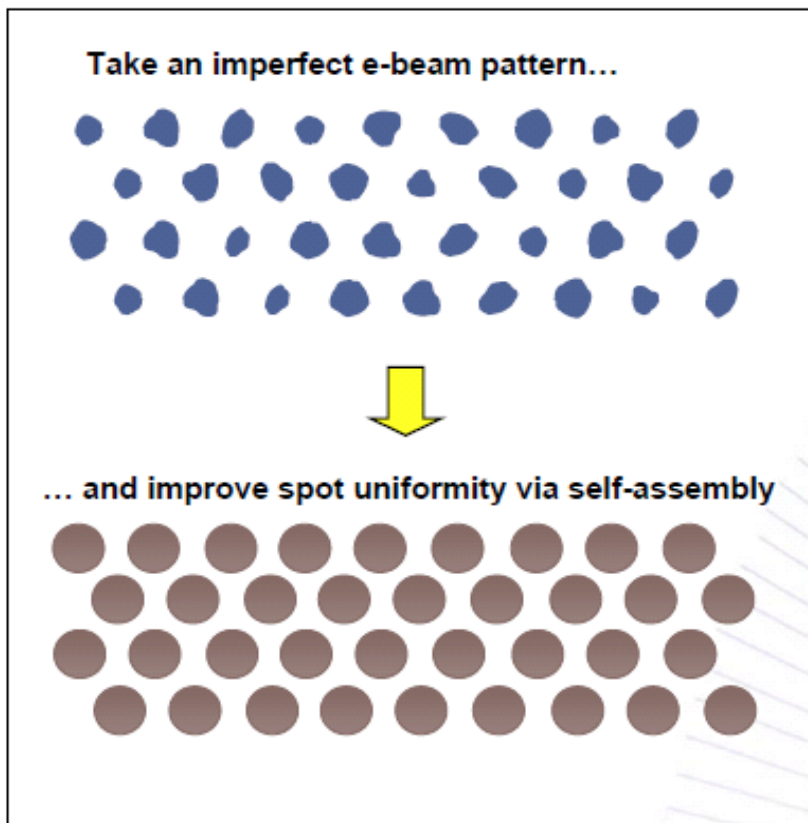


3. Selectively etch one block

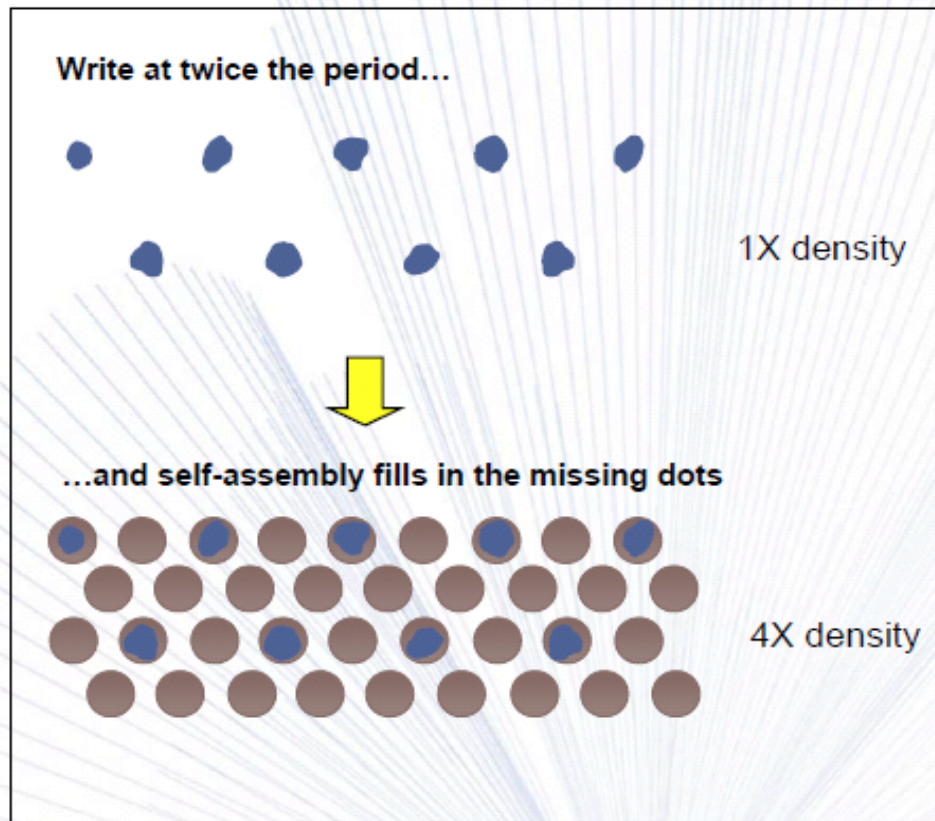


The *Miracle* of Block Copolymers

Pattern Rectification or "Clean Up" (1:1)



Interpolation for Density Multiplication (4:1)



100 nm

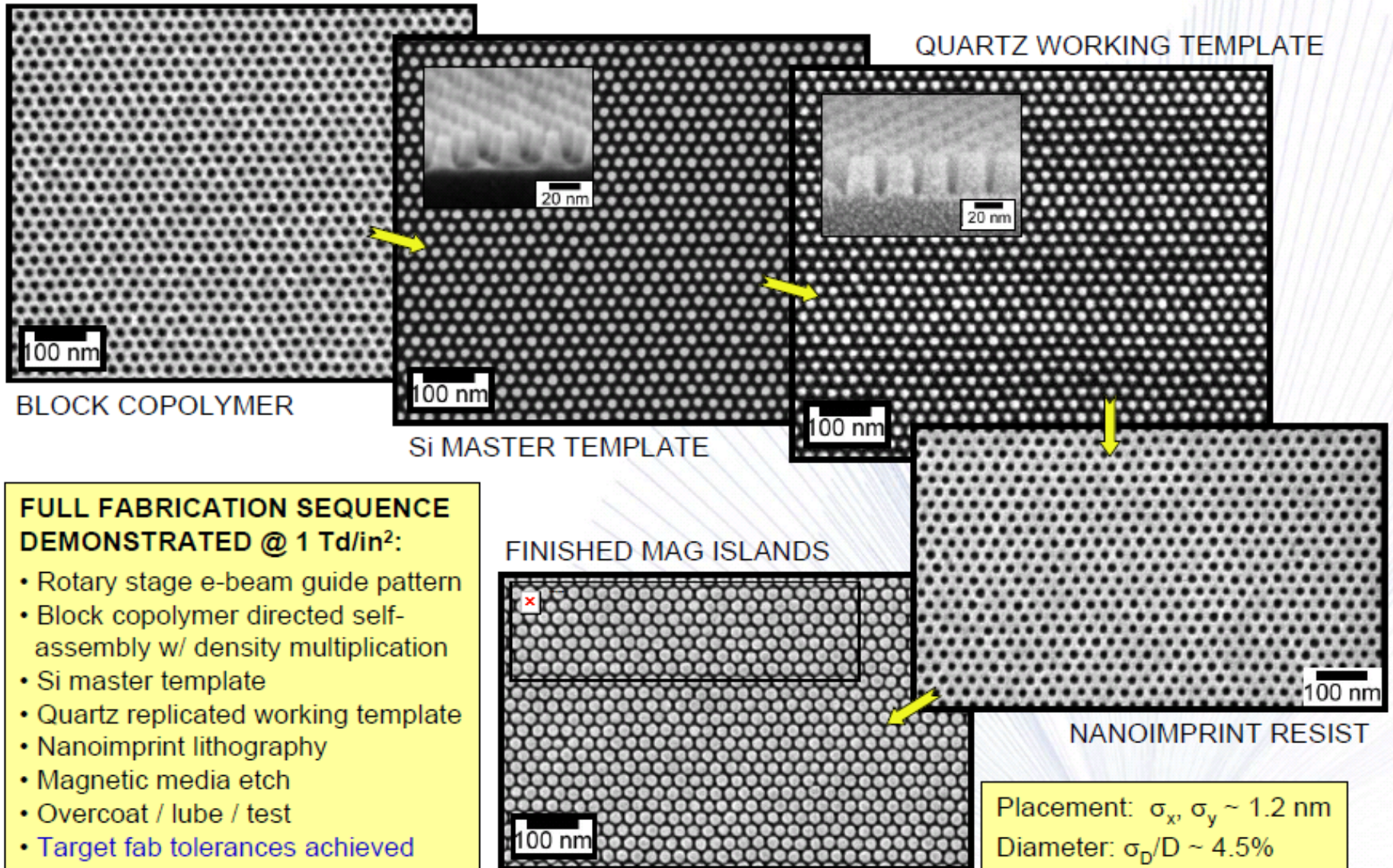
1X e-beam pattern

1/4X e-beam pattern

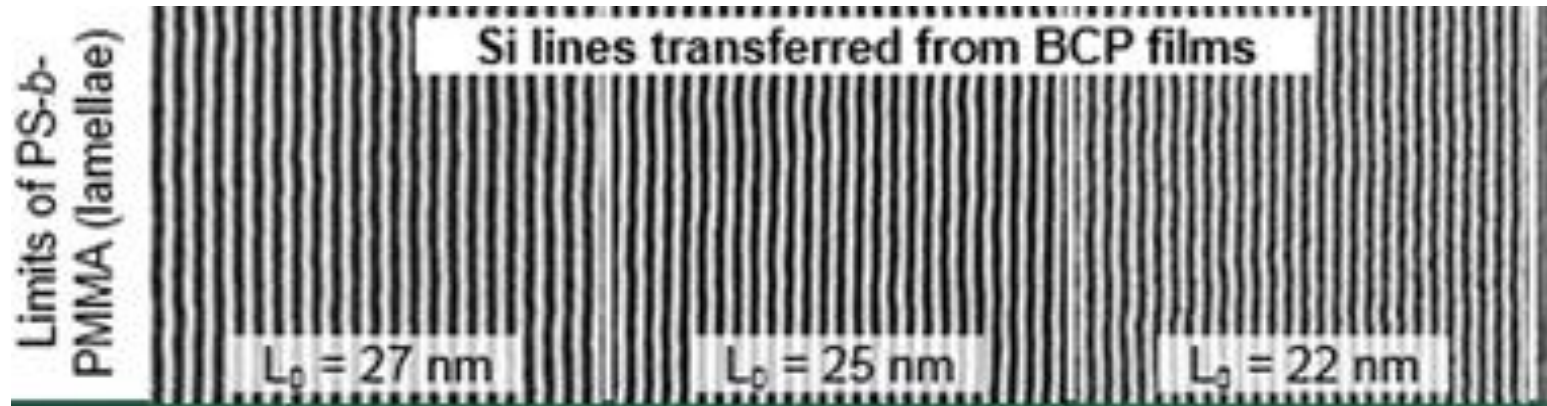
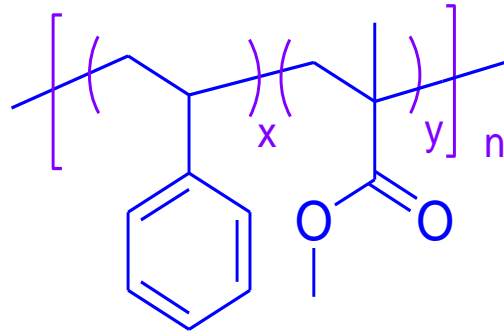
B
C
P

B
C
P





Resolution of PS-PMMA is limited to ca 22 nm by low χ



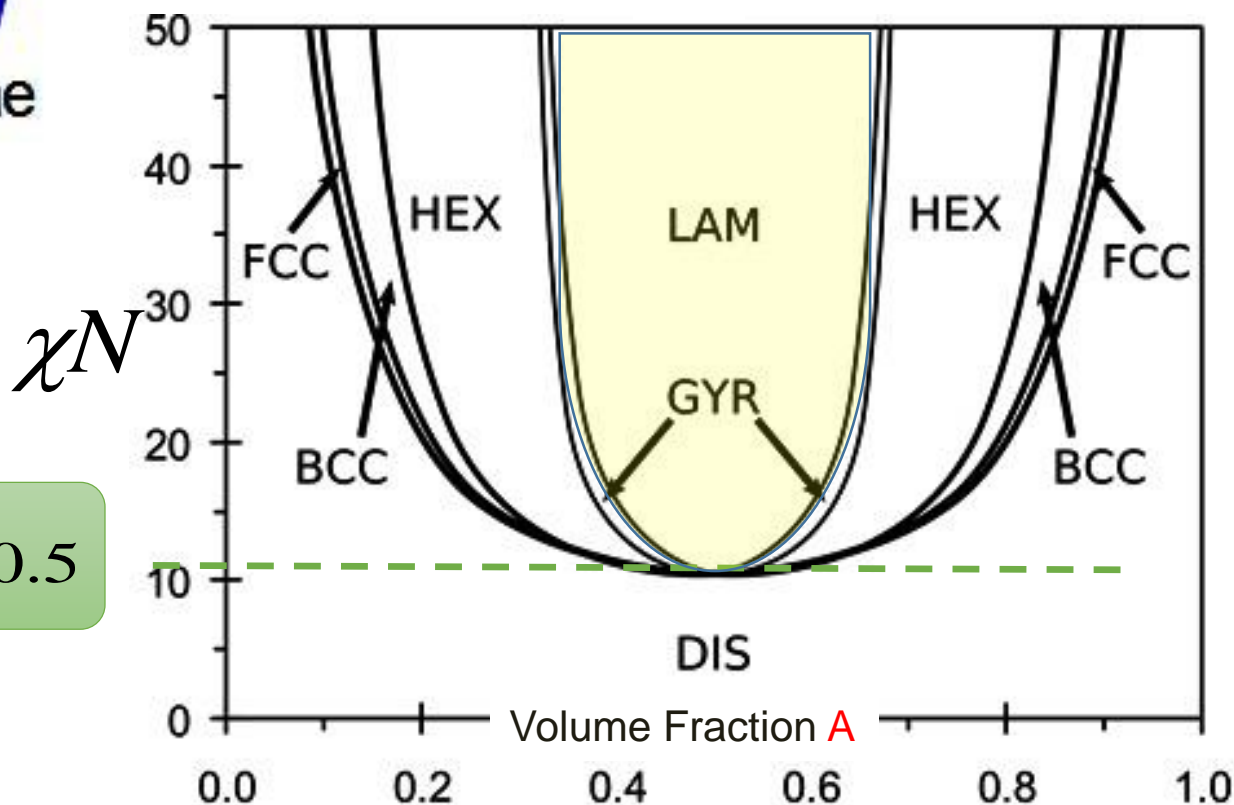
ACS Nano, 2015, 9 (7), pp 7506–7514



How to Shrink Block Copolymer Domains



lamellae



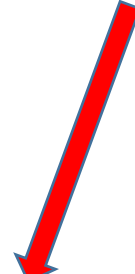
$\chi N > 10.5$

We need high χ and small N



So...what is this χ thing anyhow??

Flory Huggins Mixing Theory

$$\Delta G_m = RT [n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12}]$$


here χ , the “interaction parameter” describes the enthalpy change due to interspersing the two polymers. It is a function of variables including temperature.....

Polymer pairs with big χ hate each other!!

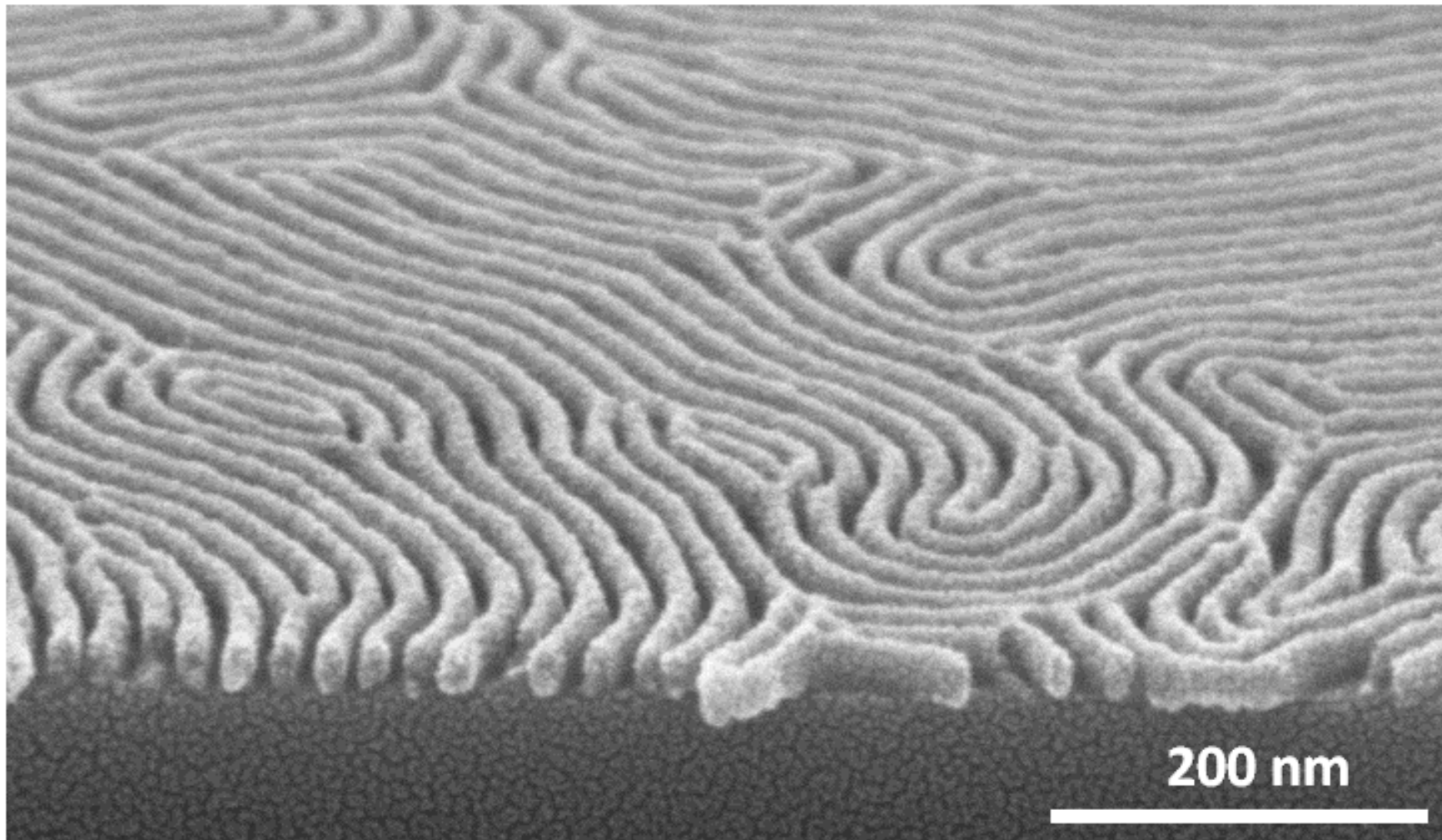


Design Criteria for New BCP

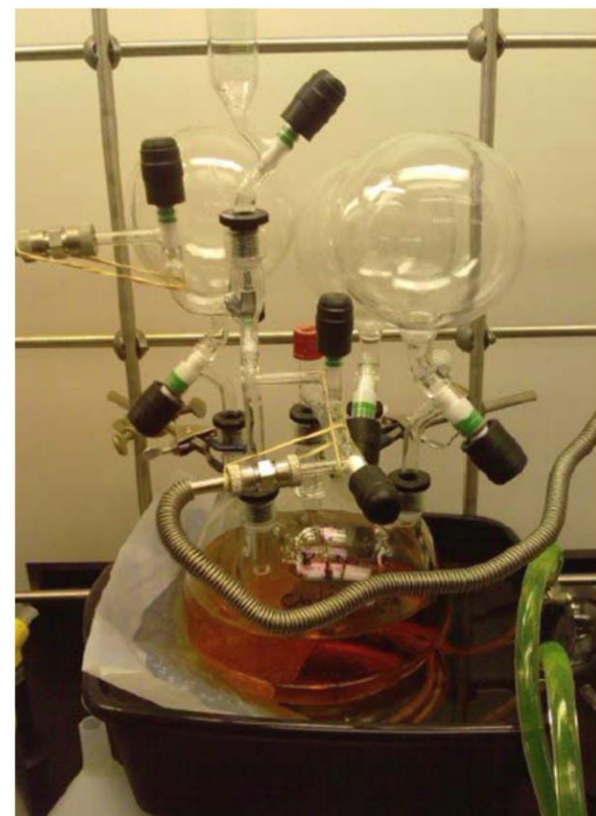
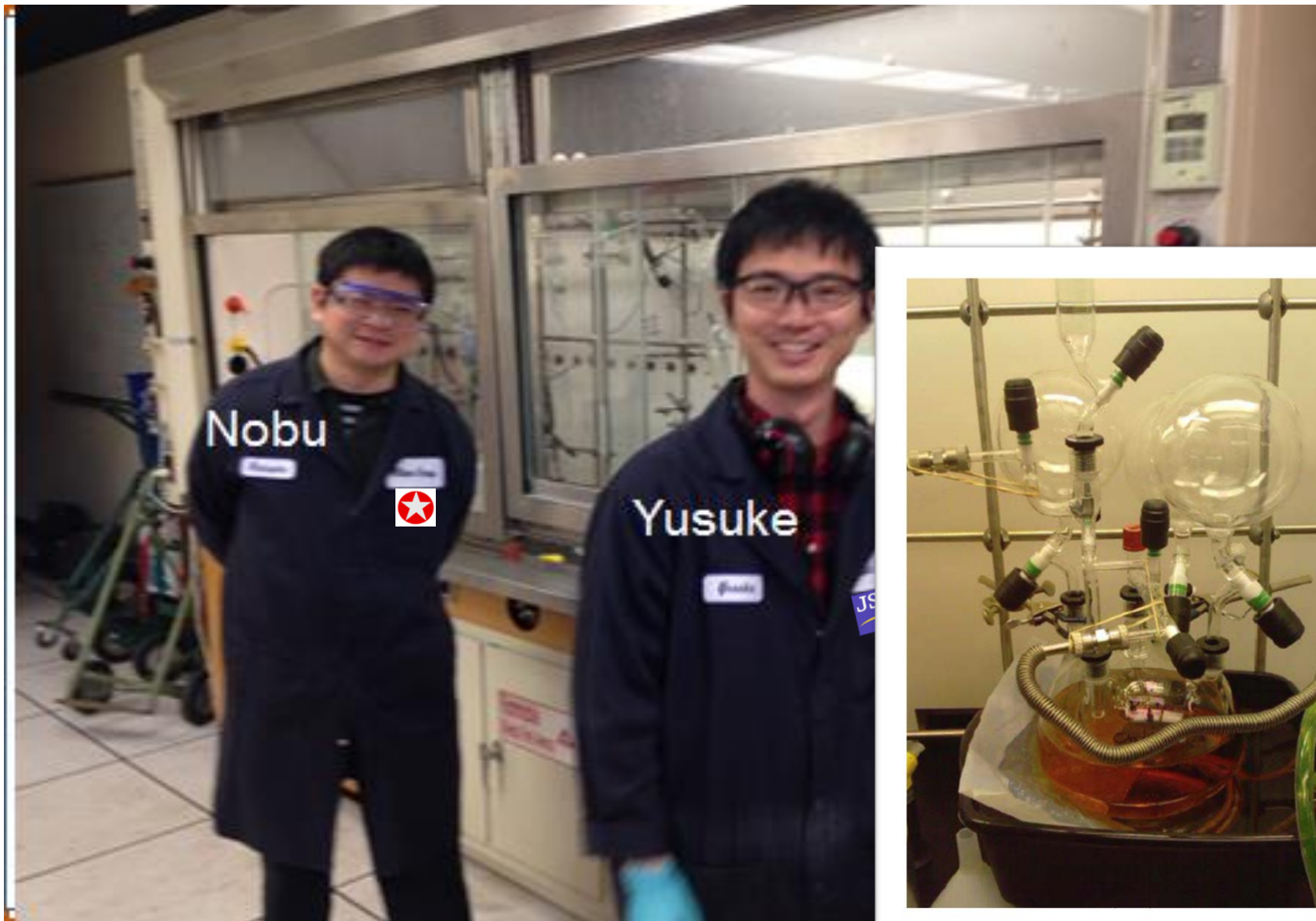
- High χ ... gives small structures
- Incorporate Si in one block..... etch contrast
- Amenable to *orientation* and *alignment*
- *No new Unit processes required for mfg*



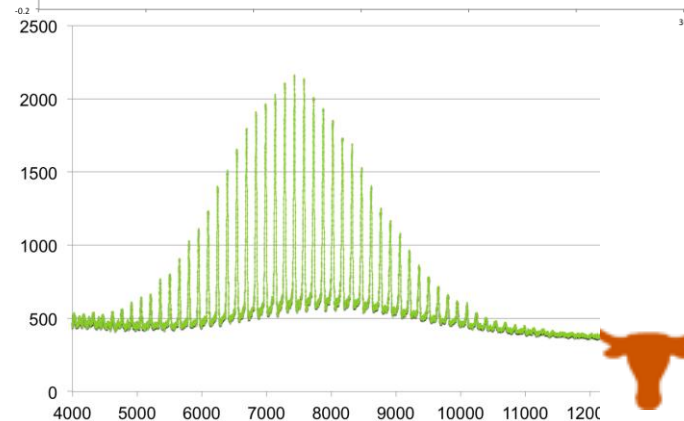
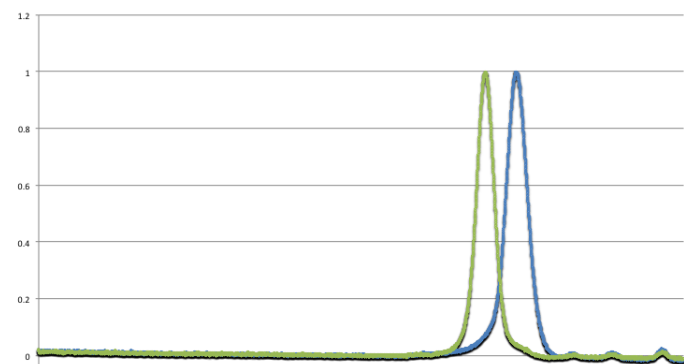
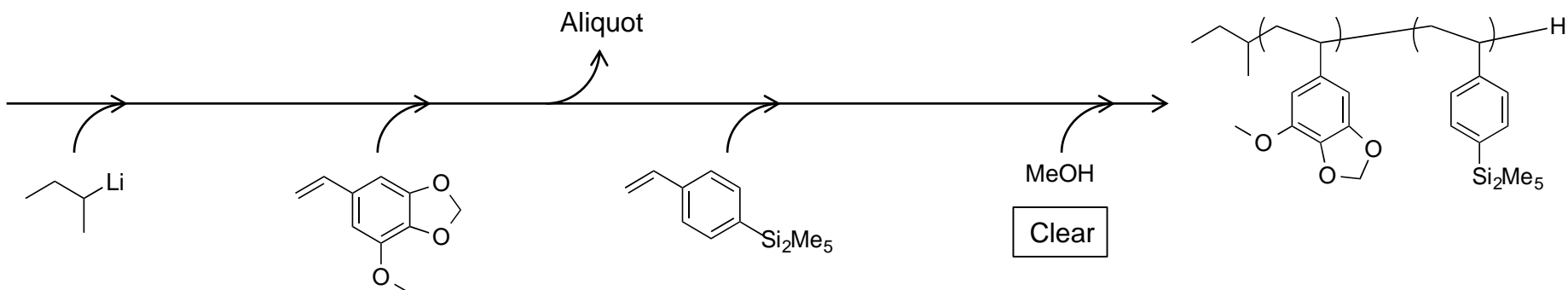
Reactive Ion Etch Development



Synthesis challenge → Anionic

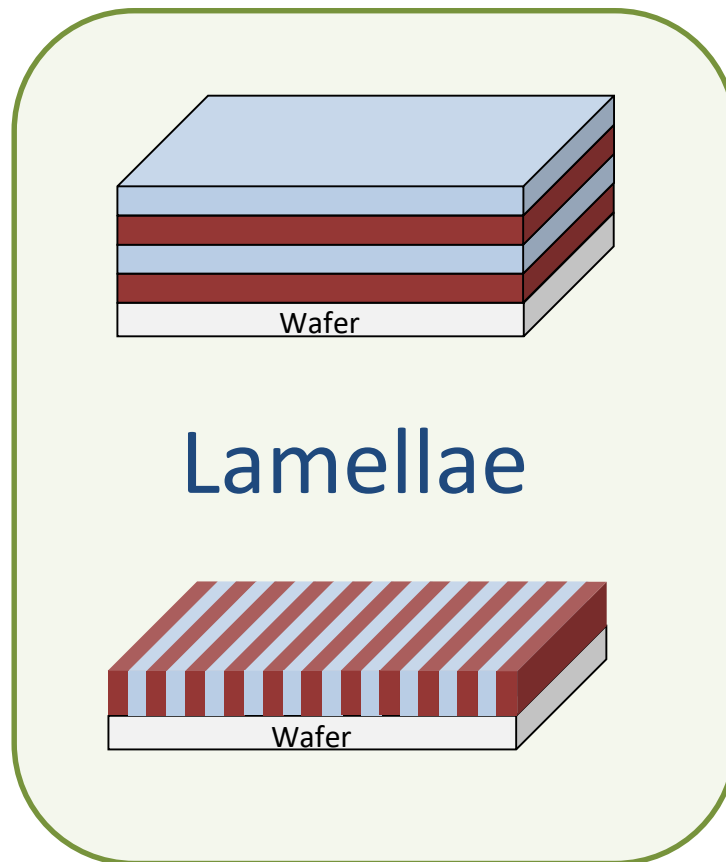


Anionic Polymerization



	Aliquot	BCP
Mn	3,997	7,677
Mw	4,261	7,924
PDI	1.07	1.03

Next...The Orientation Control Challenge

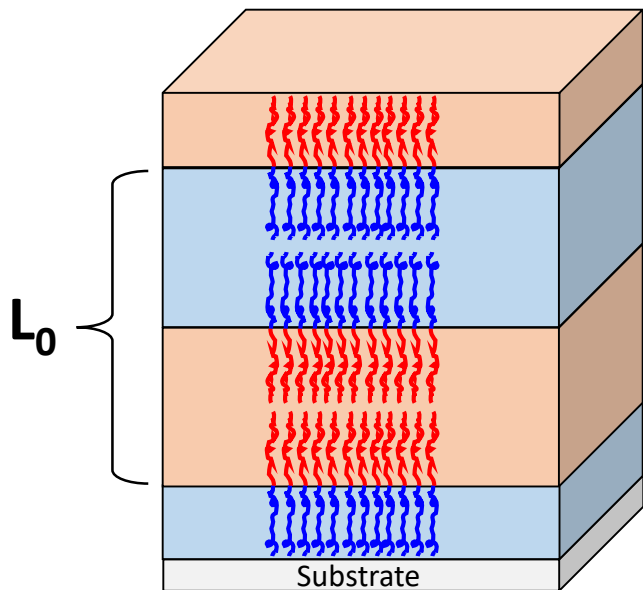
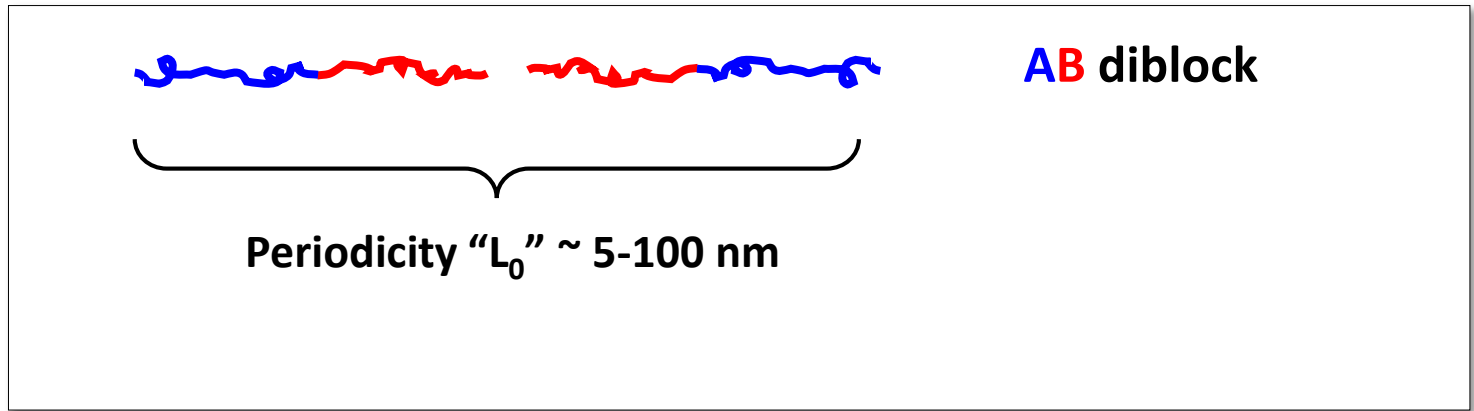


Bates et al. Science **338**, 775 (2012)

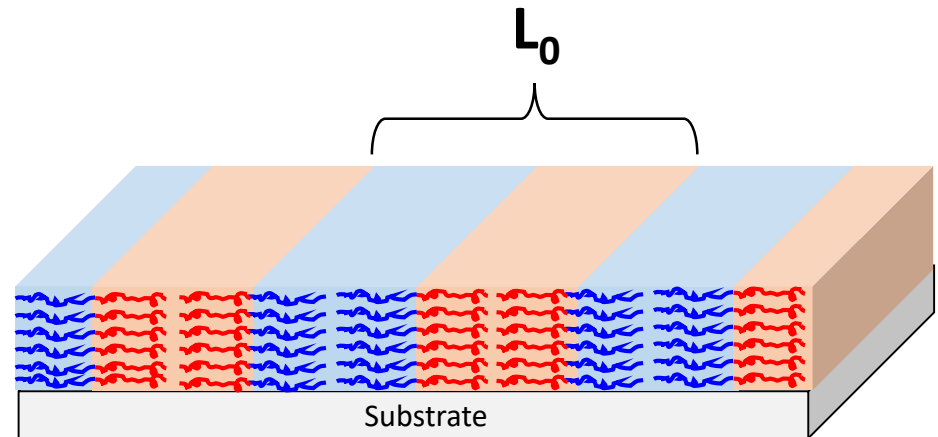
Maher et al. *Chem. Mater.* **2014**, 26, 1471



Block Copolymer Orientation



Parallel



Perpendicular



As cast film thickness $> L_0$?

As-cast film thickness $< L_0$?

$2 * L_0$

Islands

Holes

$1.2 * L_0$

$1 * L_0$

$1 * L_0$

$0.8 * L_0$

Surface Prefers Red Block

ChE 3

Wafer

