Nanometer Scale Patterning and Processing

Spring 2016

Lecture 43

Advanced Lithography, Part 3

Directed Self-Assembly (DSA)

1. Di-block copolymer self assembly overview.
2. Guided (directed, aligned) self assembly.
3. Block copolymer lithography.

Block Copolymers

—A—A—A—A—A—A—A—A—A—A— 1

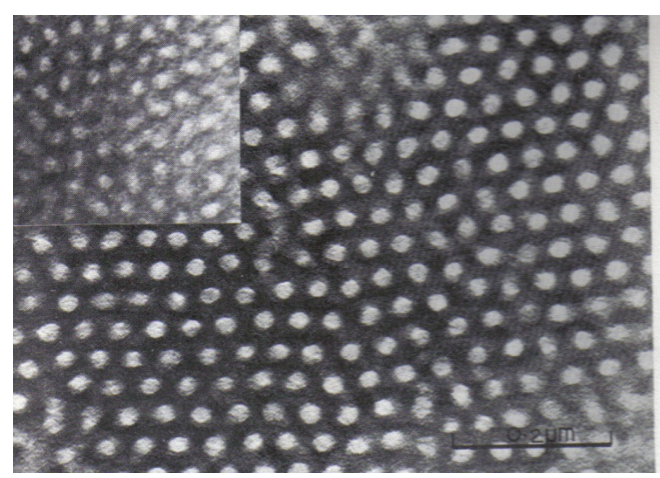
—A—B—A—B—A—B—A—B—A—B— 2

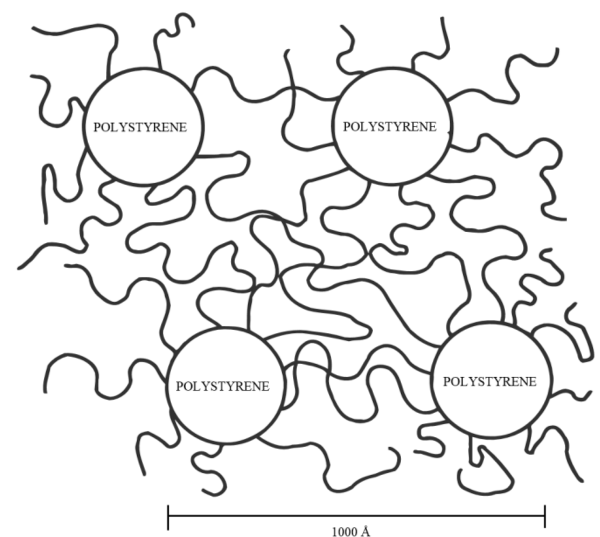
—A—B—B—B—A—B—A—B—A—A— 3

—B—B—B—B—B—A—A—A—A—A— 4

—A—A—A—A—A—A—A—A—A—A— 5 **Graft copolymers**

—B—B—B (grafted at A)   B—B—B— (grafted at A)





styrene-butadiene-styrene (SBS, or PS-PB) block copolymer

- Microphase separate
  - Poly-styrene block forms spheres, but are linked by short butadien chains

http://en.wikipedia.org/wiki/Copolymer

Typical self assembly behavior for linear block copolymers

Block A Block B

Increasing A length / Decreasing B length

Cylinders of A in B

Lamellae

Cylinders of B in A

Spheres of A in B

Ordered Bicontinuous Double Diamond (OBDD) A in B

OBDD B in A

Spheres of B in A

"Nanochemistry: a chemical approach to nanomaterials" by Ozin

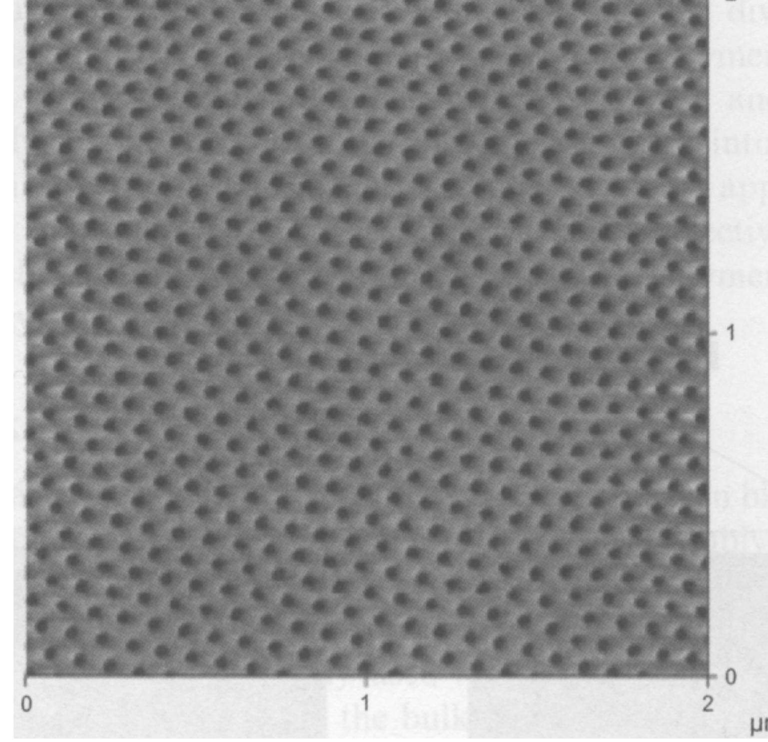
Typical self assembly behavior for linear block copolymers

Nature of patterns	Spheres (SPH) (3D)	Cylinders (CYL) (2D)	Double gyroid (DG) (3D)	Double diamond (DD) (3D)	Lamellae (LAM) (1D)
Space group	Im$\bar{3}$m	p6mm	Ia$\bar{3}$d	Pn$\bar{3}$m	pm
Blue domains: A block					
Volume fraction of A block	0-21%	21-33%	33-37%		37-50%

Block copolymer thin films

- Film applied by drop casting, dip coating, and spin coating.
- Film is then treated to increase the degree of ordering.
- Such as annealing above the order-disorder transition temperature for several days.
    - To increase the speed, anneal at the presence of solvent vapor (toluene...) to swell the film and make the polymer more mobile.

- How to induce alignment
    - directional solidification strategy, such as using a temperature gradient
    - Annealing film in the presence of a gradient in solvent vapor can have similar effect. (see SEM image).



Film ordered by controlled solvent evaporation.

Advanced Material, 16, 226 (2004)

Synthesis: anionic living polymerization

Initiator
Monomer A
Active End
Initiator
Monomer B
Initiator
Quenching
Block A
Block B

Self-assembly of PS-PB di-block copolymer

A B C D

500 nm

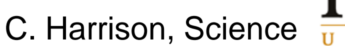
PS: polystyrene
PB: polybutadiene

1,3-butadiene

The most attractive feature of block copolymer self assembly is the extremely high resolution, easily get features down to 10nm.

TEM micrographs of polystyrene-polybutadiene diblock copolymer film masks (a,c) and lithographically patterned silicon nitride (b,d).

C. Harrison, Science



Block copolymer thin films: effect of substrate wetting

Block A is shorter than B
Arranged to minimize surface (interface) energy

Block A Block B

Spin-Coating

B
A
B

A B A

Wetting for B
Parallel cylinders

Wetting for A
Vertical cylinders

Block copolymer self assembly

1. Di-block copolymer self assembly overview.
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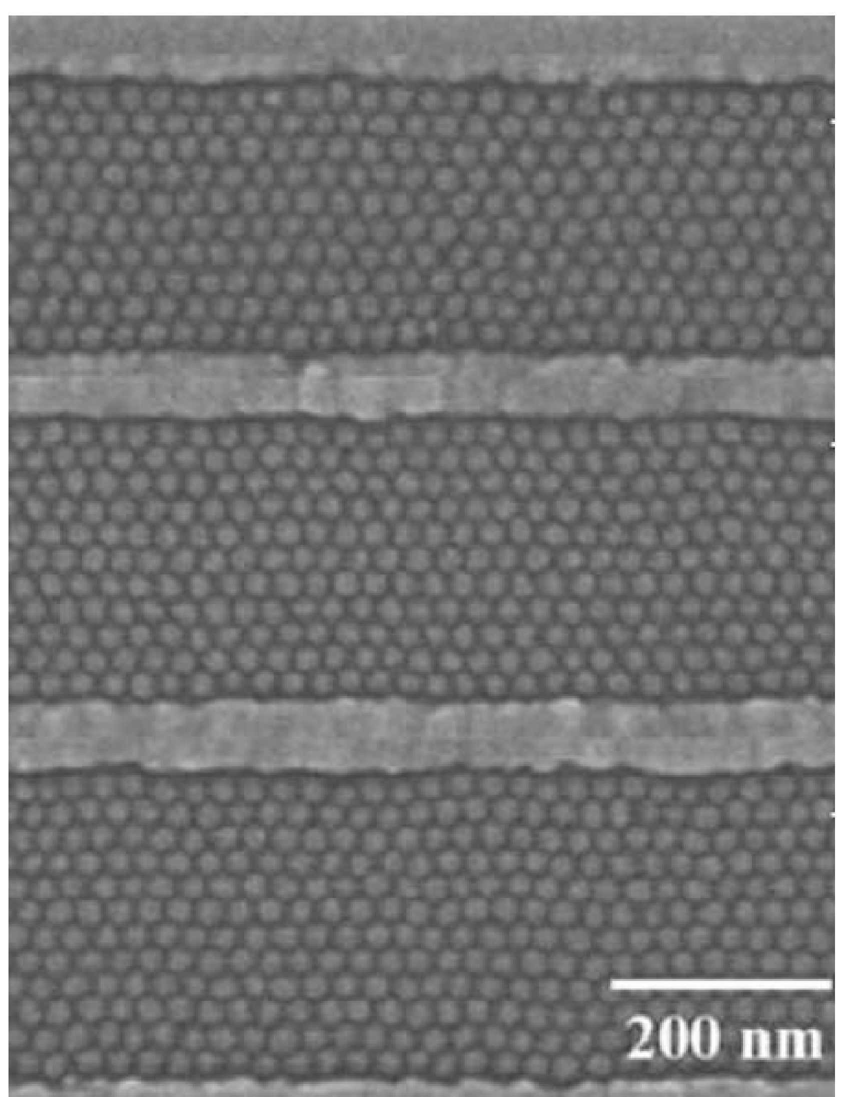
Guided block copolymer self assembly for long range ordering and periodicity

Micro-phase separated block copolymer can be directed/aligned by:

- Electric field
- Shearing force
- Surface control of wettability
- Chemical pattern on surface
- Nano-structured surface
- Spatial confinement by surface relief pattern in substrate and mold
- Void in a range of porous host

Alignment by pre-patterning the substrate



Spherical domains assembled from PS–PFS (polystyrene-polyferrocenyldimethylsilane) block copolymer inside patterned SiO_2 grooves.

The 1.5 wt.% PS-PFS block copolymer in toluene solution was spin-coated onto the grooved substrate and then annealed at 140°C for 48h to obtain a monolayer of spherical PFS domains in a PS matrix within the substrate grooves.

Ross, "Templated self-assembly of block copolymers: effect of substrate topography", Adv. Mater. 15, 1599–1602 (2003).

Alignment by shear force (here for silicon nano-wire fabrication)

(a)

Shear

RuO_4 staining

CF_4 RIE

O_2 descum piranha cleaning

(b)

250 nm

Press

Co-polymer on substrate

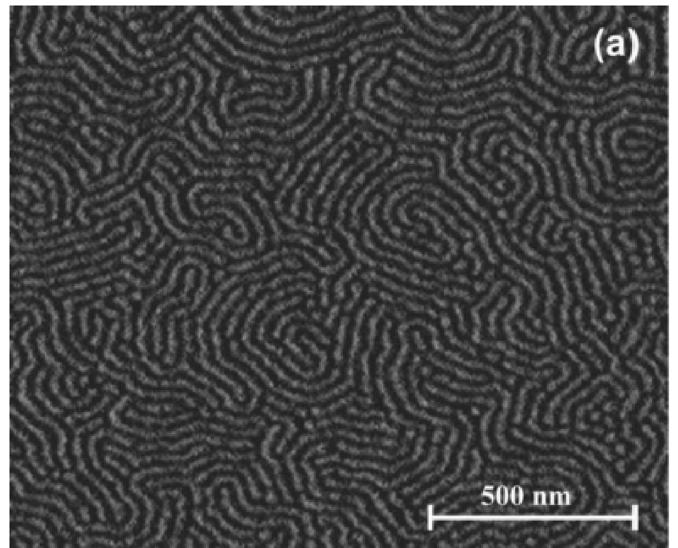
Pull

One way to create shear force.

a) Fabrication process for a Si nano-wire grid polarizer using block copolymer lithography.
b) SEM image of the finished Si nano-wire grid on fused silica.

Here the etch contrast is increased by staining the block copolymer by 2 min exposure to the vapor from 0.5% aqueous RuO_4, which selectively reacts with the PS block and increases its etch resistance, thus permitting Si nanowires of greater aspect ratio to be fabricated.

Alignment by shear force (for silicon nano-wire fabrication)



(b)

500 nm

Pitch=30nm

Tapping mode atomic force microscopy (TM-AFM) phase images of PS–PHMA thin films on top of an α-Si layer on a fused silica substrate:

a) Quiescently annealed

b) Shear aligned.

Glassy PS cylinders are shown as light in a dark rubbery PHMA matrix.

Polystyrene-b-poly(n-hexyl methacrylate) (PS–PHMA) diblock copolymer with a molar mass of 21 and 64 kg/mol for the respective blocks.

Chaikin, "Silicon nanowire grid polarizer for very deep ultraviolet fabricated from a shear-aligned diblock copolymer template", Optics letters, 32(21), 3125-3127 (2007).

Templated self-assembly of block copolymers

$h\nu$

Polystyrene "brushes" by EUV-IL (interference lithography) and surface initiated nitroxide mediated living free radical polymerization

Expose Imaging Layer

Chemically patterned surface

Anneal above T_g

Self-assembled structure

Deposit copolymer film

The PS brush pitch should match that of PS-PMMA self assembly pitch.

Polymerization of block-copolymers on chemically pre-patterned substrates

unpatterned substrate area

Polystyrene-block-methyl meth acrylate (PS-b-PMMA), L_0 = 48nm

Thermodynamics dominates interface widths and domain sizes.

patterned substr. area

When L_s=47.5nm≈L_o=48nm, block copolymer is almost defect free.

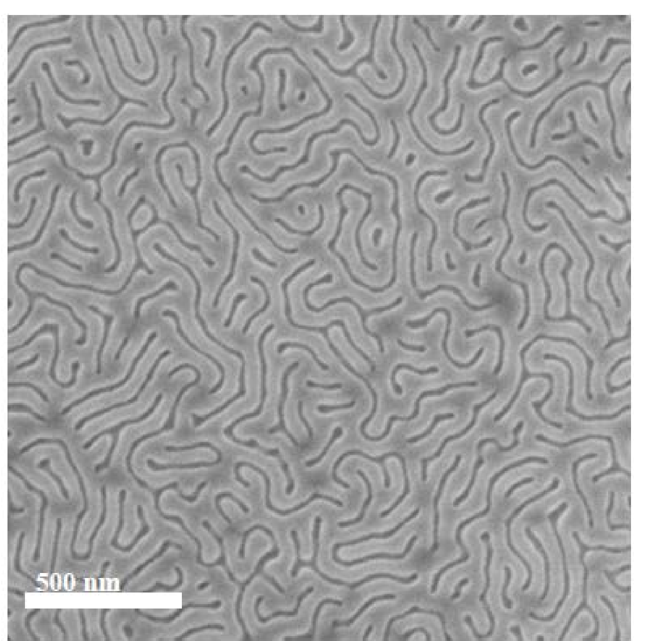
750 nm | 750 nm | 750 nm | 750 nm

L_s = 45 nm | L_s = 47.5 nm | L_s = 50 nm | L_s = 52.5 nm

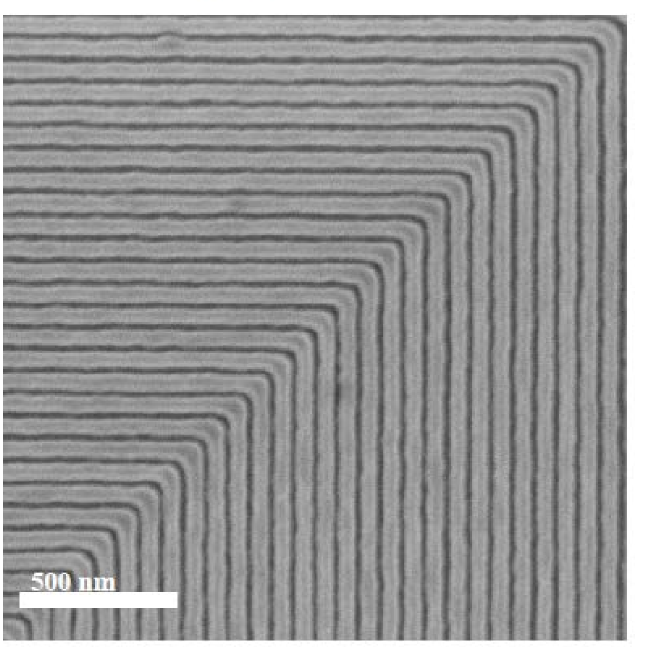
P. F. Nealey, H. H. Solak et al. Nature 424 (2003)

Directed assembly of block copolymer blends into non-regular device oriented structure

Homogeneous Surface



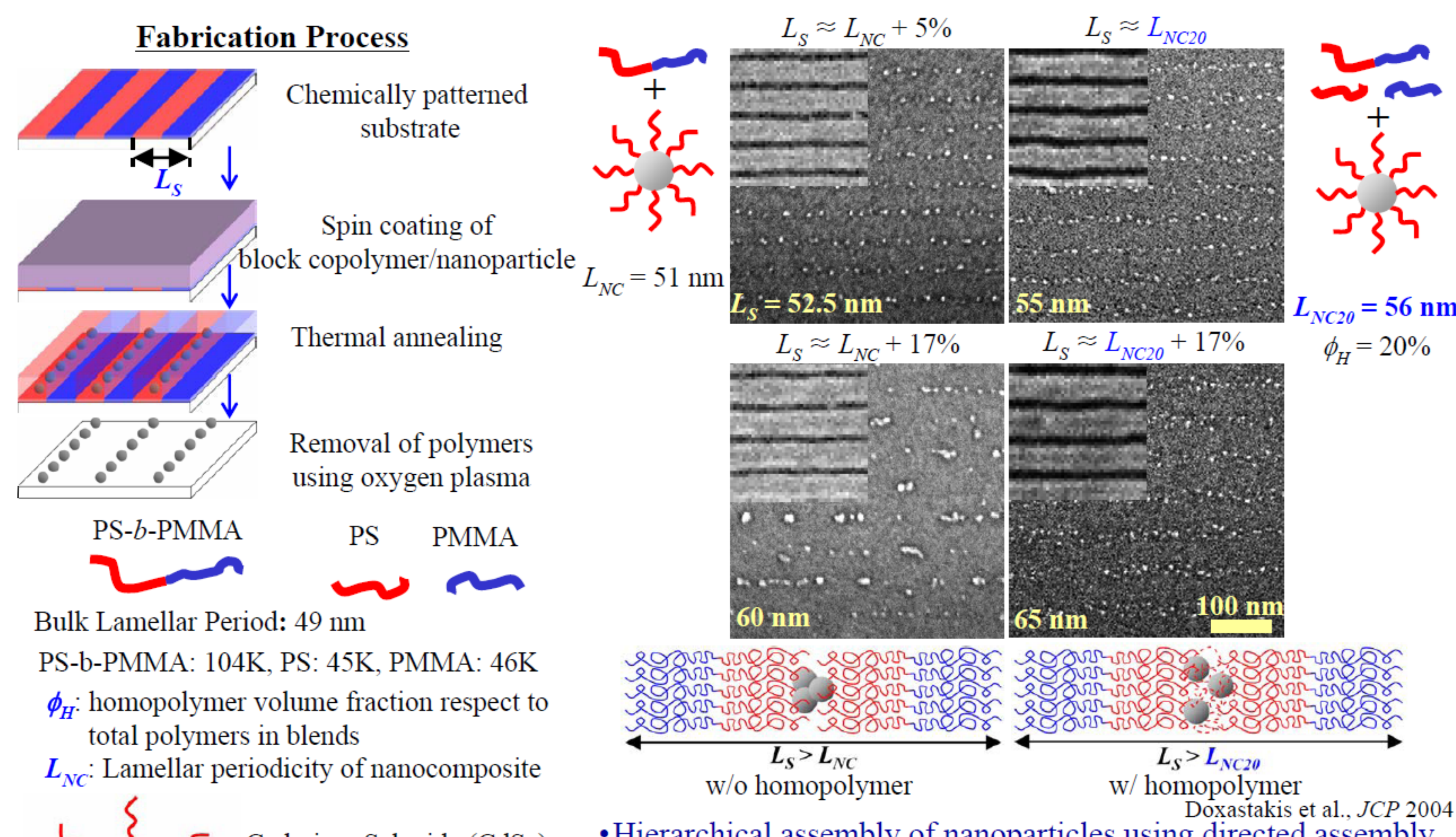
Directed assembly on chemically patterned surface



Block copolymer materials that naturally form simple periodic structures were directed to assemble into non-regular device oriented patterns (here an elbow) on chemically nano-patterned substrates.

Mark P. Stoykovich, Marcus Müller,Sang Ouk Kim, Harun H. Solak, Paul F. Nealey, Science, 308, 1442-1446 (2005).

Directed assembly of nanoparticle filled block copolymer



P=O CdSe O=P C14

Cadmium Selenide (CdSe) capped with tetradecyl-phosphonic acid (TDPA) (8.0 ± 0.4 nm)

- Hierarchical assembly of nanoparticles using directed assembly of block copolymer on chemically patterned substrate.
- Homopolymer addition in block copolymer/nanoparticle system mitigates particle aggregation for the extended block copolymer chain conformation regime.

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Alignment by electric field

Annealed with Electric Field

Annealed without Field

500 nm

Figure 9.7 *TEM micrographs of block copolymer films annealed in the presence of an electric field and without a field, highlighting the electric field alignment near the electrode seen in the bottom left parts of the images.*

“Local control of microdomain orientation in diblock copolymer thin films with electric fields”, Science, 273, 931 (1996)

Block copolymer self assembly

1. Di-block copolymer self assembly overview.
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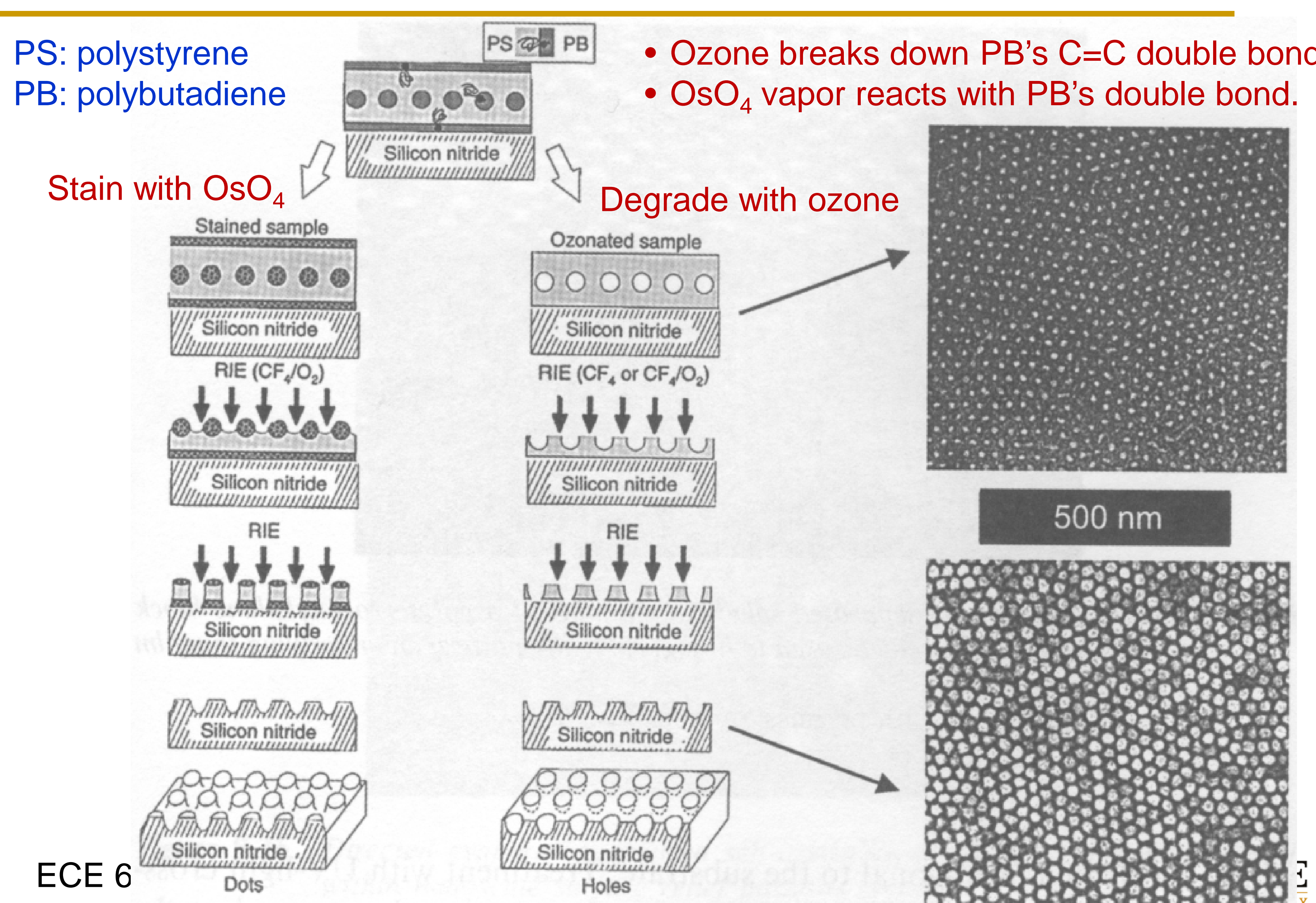
3. Block copolymer lithography.

Block copolymer lithography (i.e. with pattern transfer)

PS: polystyrene
PB: polybutadiene

- Ozone breaks down PB's C=C double bond
- OsO_4 vapor reacts with PB's double bond.



Synthesis of nanowires by wetting

200 nm
As deposited

200 nm
Annealed

200 nm
Repeated deposition and annealing

Silver Evaporation

100 nm
Large area

100 nm
Close-up

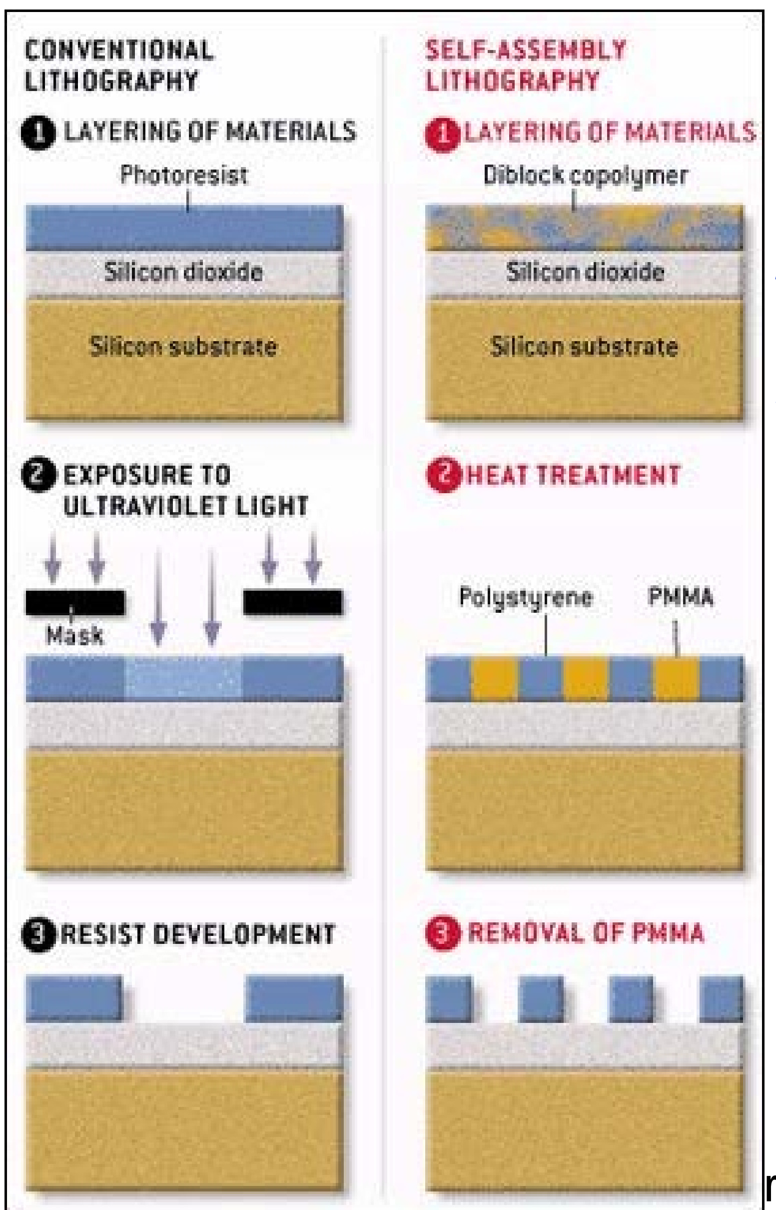
Figure 9.27 *Nanoscale decoration of phase-separated PS-b-PMMA block copolymer film on a silicon nitride substrate by selective wetting and accretion of a vapor deposited metals like gold and silver selectively in the PS phase.*

Wettability masks:
Au and Ag to PS phase
In, Pb, Sn to PMMA phase

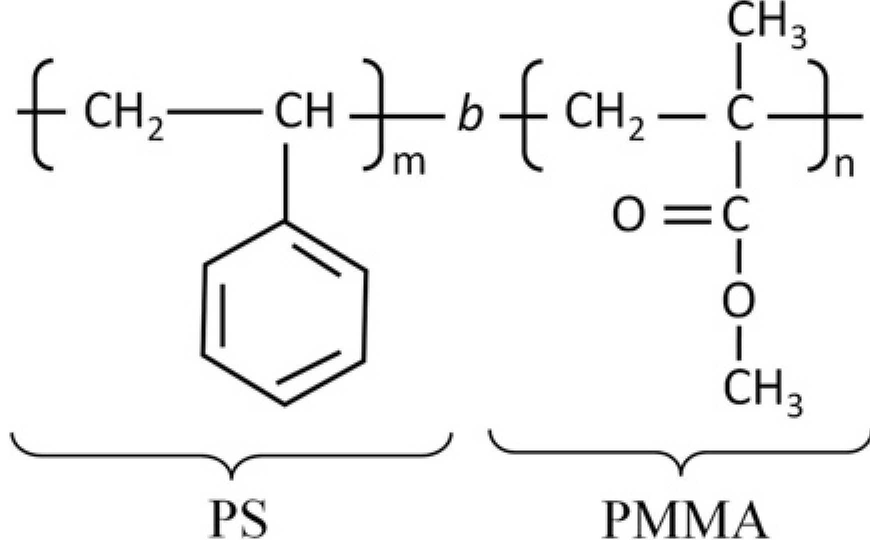
a) Gold metal vapor-deposited onto a preformed PS-b-PMMA template.
b) After annealing at 180°C for 1 min., gold nanoparticles segregate selectively to the PS domains and form chains.
c) Repeated deposition and short-time annealing increases the metal loading, forming continuous conductive nanowires.

Nature, 414, 735 (2001).

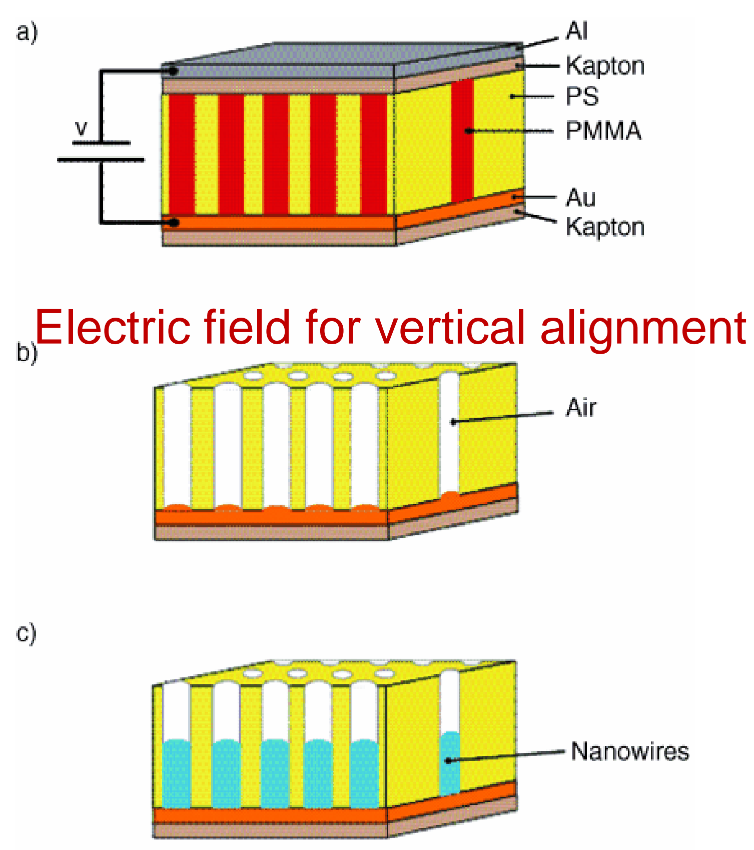
Block copolymer lithography

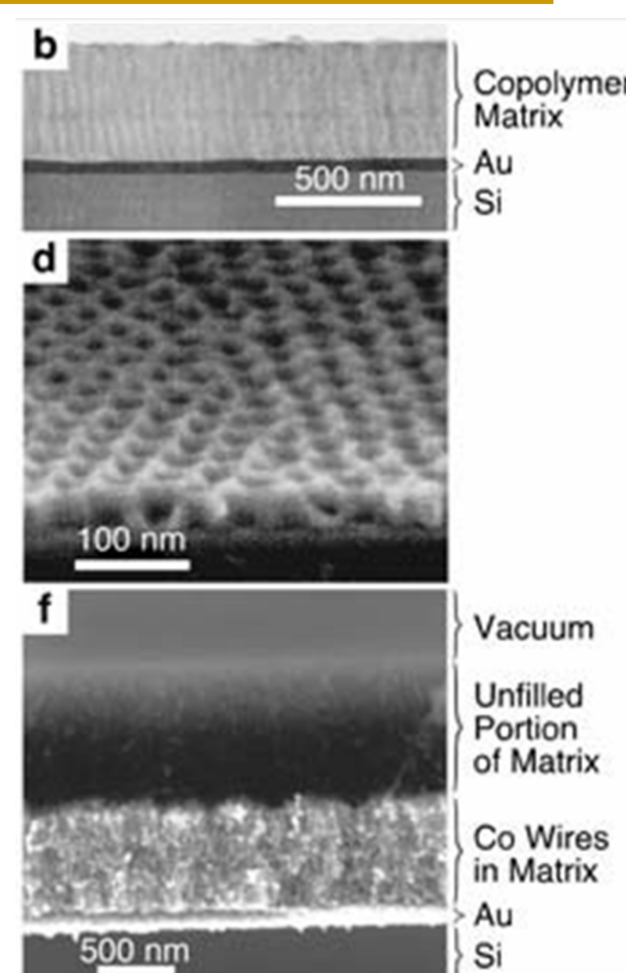


1. After *deep* UV-exposure, polymer chain of PMMA is cut (PMMA is a positive deep UV lithography resist), making it more soluble in solvent.
2. Whereas the polystyrene (PS) chain is cross-linked, making it hard to dissolve by solvent.
3. Therefore, PMMA can be selectively removed by solvents like acetic acid afterwards.



Nanofabrication of vertical nanowires by electroplating

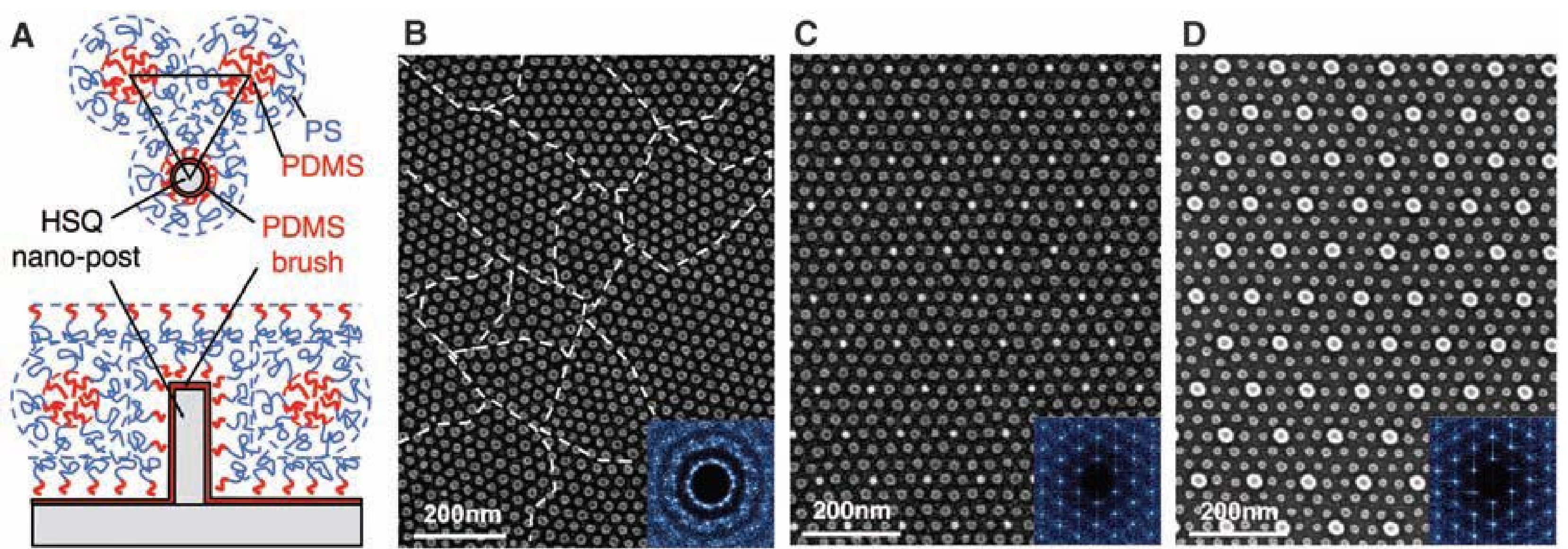




Science, 290, 2126 (2000)

- Aligned by electric field during annealing.
- Styrene 71%, to obtain 14nm PMMA cylinder.
- Deep UV simultaneously degrades PMMA and cross-link PS.
- Acetic acid dissolve PMMA but not cross-linked PS.
- Methanol is added to aqueous plating solution to better wet hydrophobic PS membrane.

Density multiplication (here by 9×) lithography



A. Top-down and side-view schematics showing the arrangement of PS-b-PDMS block copolymer molecules in the region surrounding a single post made from cross-linked HSQ resist (by e-beam lithography). The post and substrate surfaces have been chemically functionalized by a monolayer of short-chain PDMS brush.

B. A poorly ordered monolayer of BCP (block co-polymer) spherical domains formed on a flat surface, that is, without templating. The boundaries between different grain orientations are indicated with dashed lines. The inset is a 2D Fourier transform of the domain positions that shows the absence of long-range order.

C-D. SEM images of ordered BCP spheres formed within a sparse 2D lattice of HSQ

For the moment, this is considered as the most promising route for bit-patterned magnetic recording media fabrication (make the mold for nanoimprint lithography), up to 10Tbits/in^2 for pitch ~8nm.

Ross, "Graphoepitaxy of self-assembled block copolymers on two-dimensional periodic patterned templates", Science, 321, 939-943 (2008).