Nano Sensors

PhD/ MTech/ BTech
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L-T-P [C]: 3–0–0 [3]

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Lecture 34-35 dated 15th Apr 2025

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Lithography using self assembly:
- block co-polymer self assembly,
- porous anodized aluminum oxide and
- nano-sphere lithography

1. Di-block copolymer self assembly overview.
2. Guided (directed, aligned) self assembly.
3. Block copolymer lithography.
4. Anodized aluminum oxide (AAO) overview.
5. Nanofabricating using AAO template

- These are three most important self-assembly techniques, widely used for nanofabrication, with numerous publications each year.
- Basically, for those who don't have access or don't like too much EBL, FIB or imprint, they can often use self-assembly fabrication to demonstrate their idea.
- The most significant advantage of self-assembly is low cost.
- The biggest limit: only periodic pattern can be created, usually without long range ordering.

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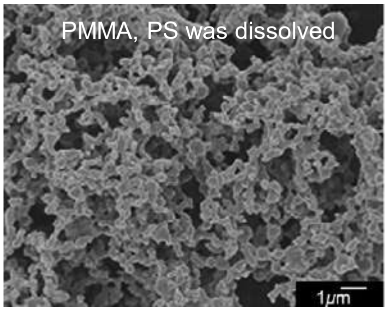
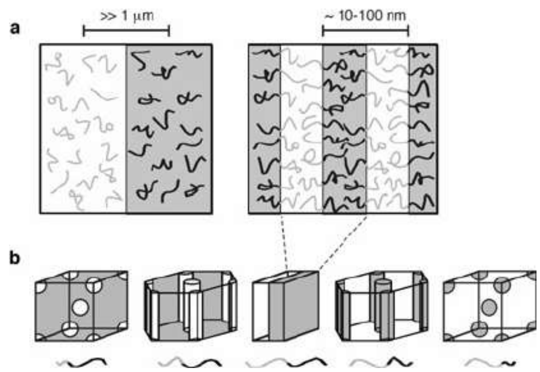
Phase separation of block copolymers

Phase separation of a blend of PMMA and PS homo-polymer





1. A mixture of PMMA (M_w=93.9 kg/mol) and polystyrene (PS, M_w=194.9 kg/mol) (PS/PMMA=70/30, w/w) is dissolved in tetra-hydrofuran (THF) to form a 5 wt% solution.
2. Polymer film was made by spin-cast the solution on glass slide.
3. Exposure to cyclohexane at 70°C to dissolve PS.

a) A blend of two **incompatible** homo-polymer separates into distinct phases on a large scale (left), whereas block copolymers micro-phase separate into periodic domains (right).
b) Basic morphologies obtained by different block copolymer compositions.

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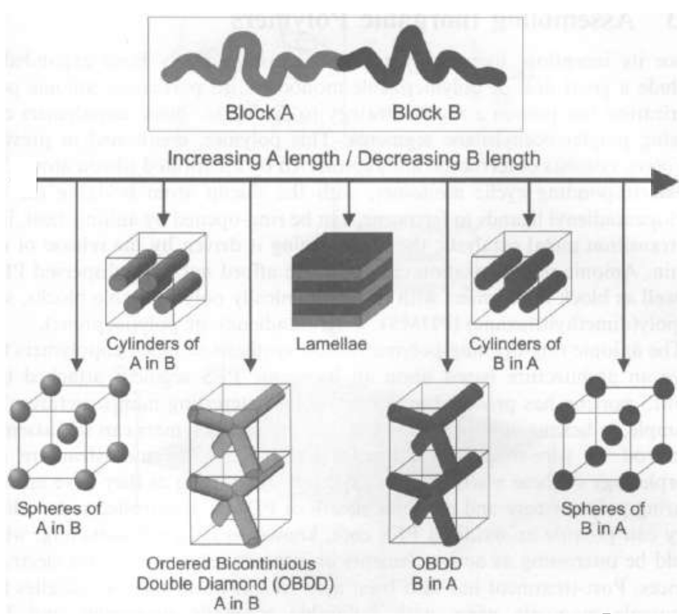
Typical self assembly behavior for linear block copolymers



"Nanochemistry: a chemical approach to nanomaterials" by Ozin

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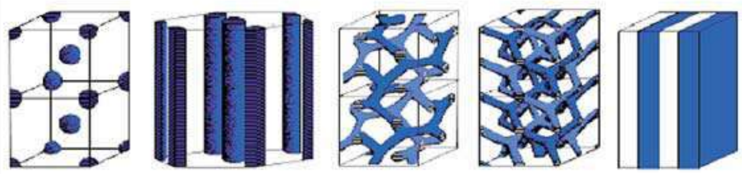
Typical self assembly behavior for linear block copolymers

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 self-assembly study is started in the bulk phase, as shown above; whereas thin film is desired for nanofabrication and device application.
- When film thickness is well controlled, **hole**/ **pillar array** or **line array** **pattern** can be created.

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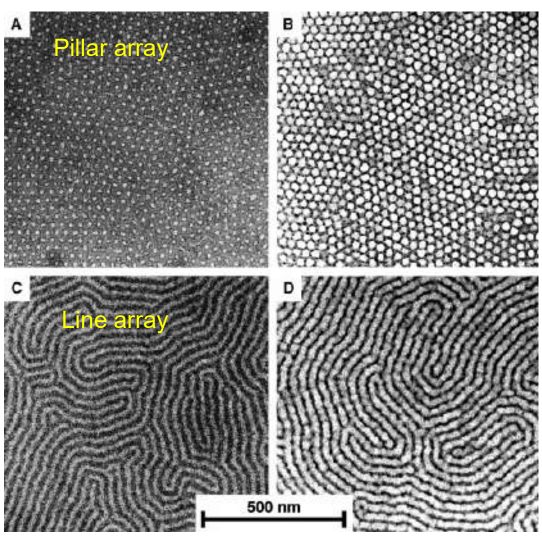
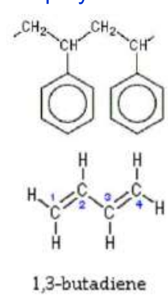
One example: self-assembly of PS-PB di-block copolymer



PS: polystyrene
PB: polybutadiene



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

TEM images of PS-PB diblock copolymer film masks (a, c) and lithographically patterned silicon nitride (b, d).

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C. Harrison, Science

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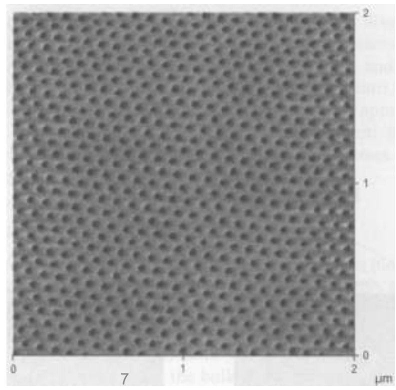
Block copolymer thin films

- 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.
- Or annealing in the presence of solvent vapor (toluene...) to swell the film and make the polymer more mobile.

- One way to achieve alignment is through directional solidification strategy
- Such as using a temperature gradient – the film is heated to above order-disorder transition and cooled in the presence of such gradient; so that the ordered phase nucleates at the cool end that serves as a template and orient the rest of the film.
- Annealing film in the presence of a gradient in solvent vapor has similar effect.



Film ordered by controlled solvent evaporation.

Advanced Material, 16, 226 (2004)

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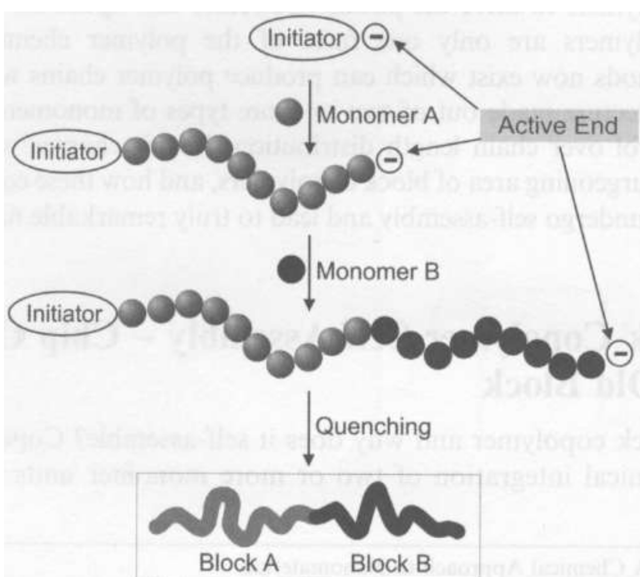
Synthesis: anionic living polymerization



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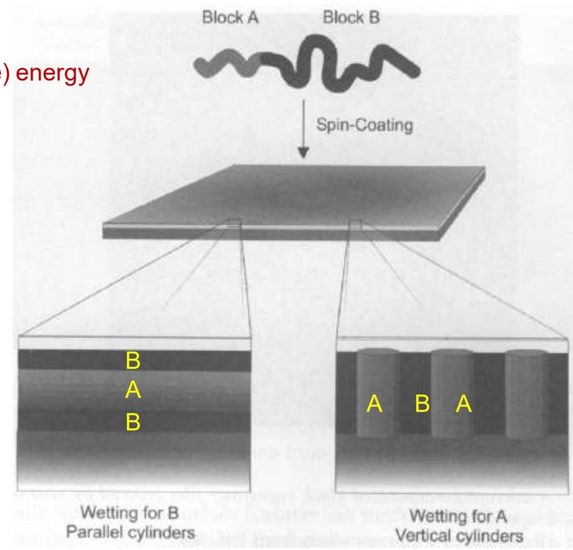
Block copolymer thin films: effect of substrate wetting

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



A forms cylinders embedded in B

(left) will result in line array (grating) pattern
(right) will result in hole/pillar array pattern

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Lithography using self assembly: block co-polymer self assembly, porous anodized aluminum oxide and nano-sphere lithography

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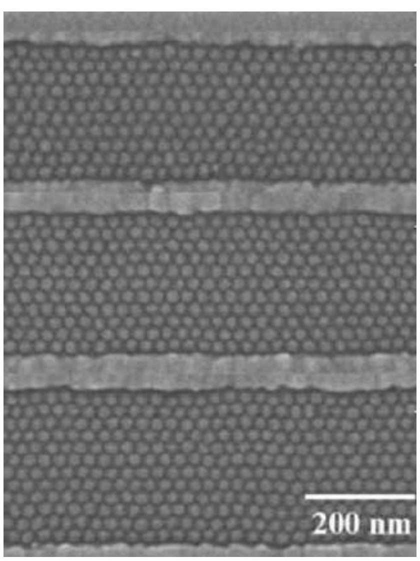
Guided block copolymer self assembly for long range ordering and periodicity

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

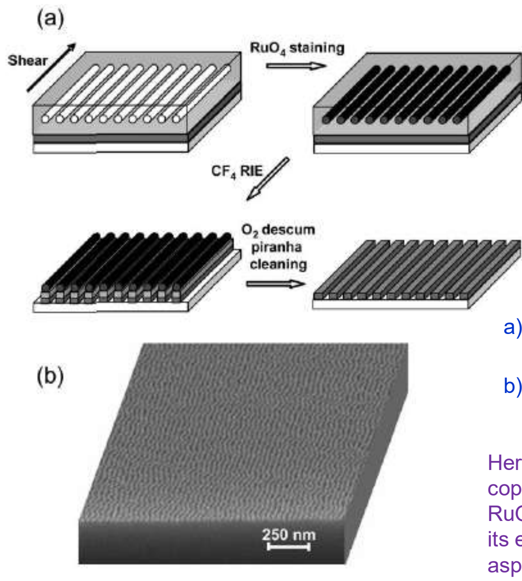


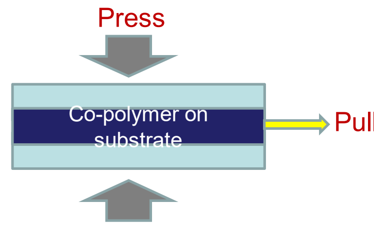
Spherical domains assembled from PS–PFS (polystyrene-polyferrocenyldimethylsilane) block copolymer inside patterned SiO_2 grooves.

The 1.5 wt.% PS-PFS block copolymer in toluene solution was spin-coated onto the grooved substrate and then annealed at 140^{o}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)



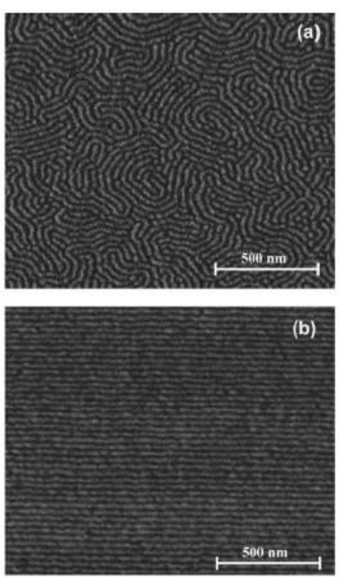


One way to create shear force.

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)



Pitch=30nm

Tapping mode AFM *phase* images of PS–PHMA thin films on top of an α-Si layer on a fused silica substrate:

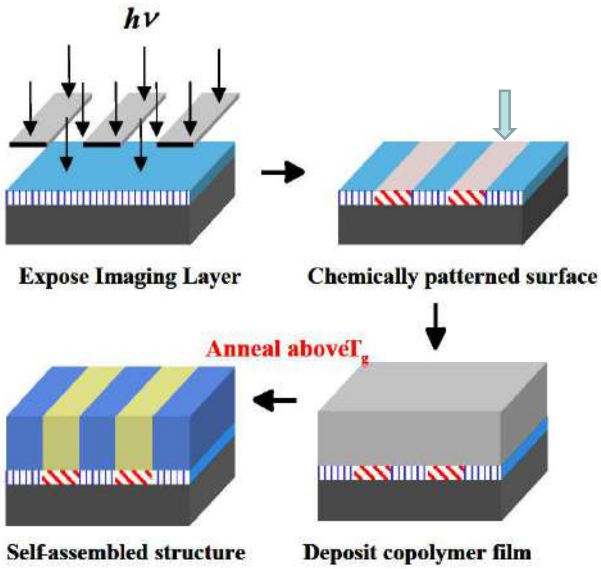
a) Quiescently annealed
b) Shear aligned.

Glassy (hard) PS cylinders are shown as light in a dark rubbery (soft) 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



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

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

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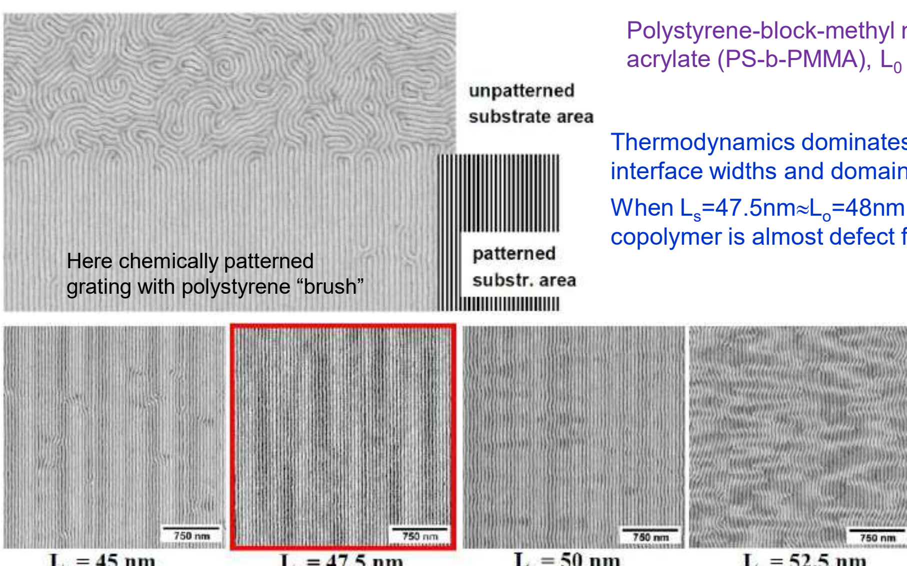
Polymerization of block-copolymers on chemically pre-patterned substrates



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

Thermodynamics dominates interface widths and domain sizes.

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

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

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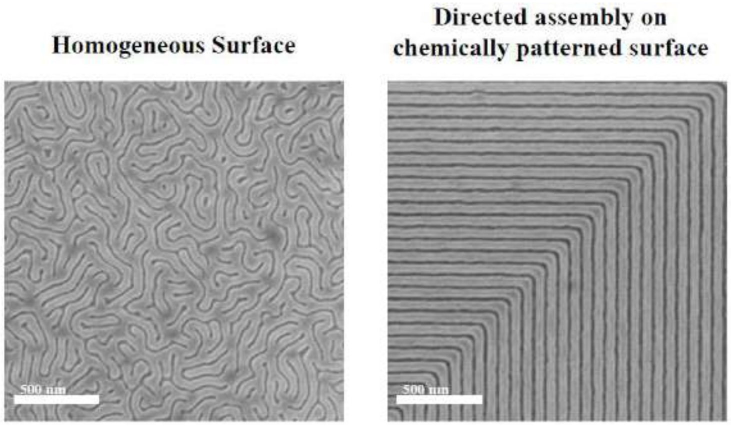
Directed assembly of block copolymer blends into non-regular device oriented structure



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).

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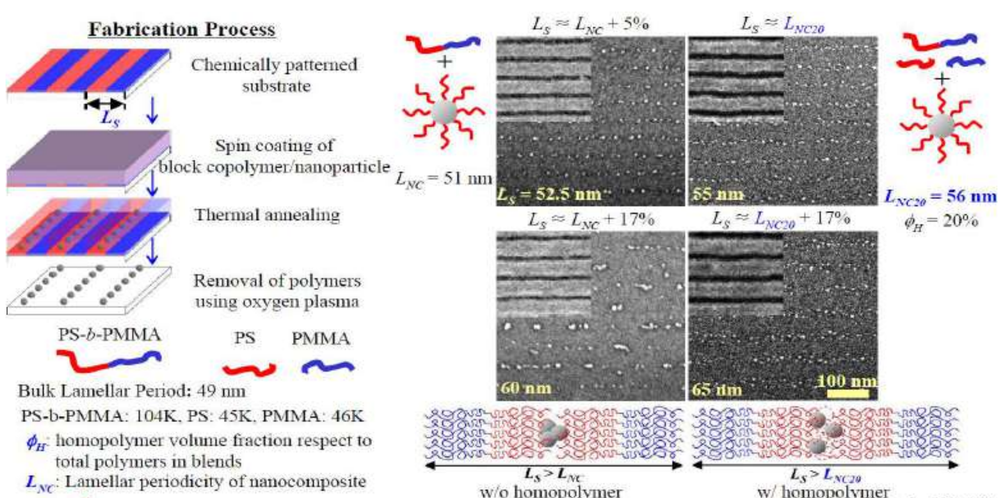
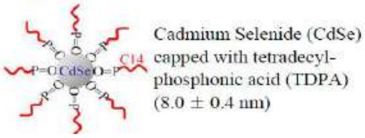
Directed assembly of nanoparticle filled block copolymer





- 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

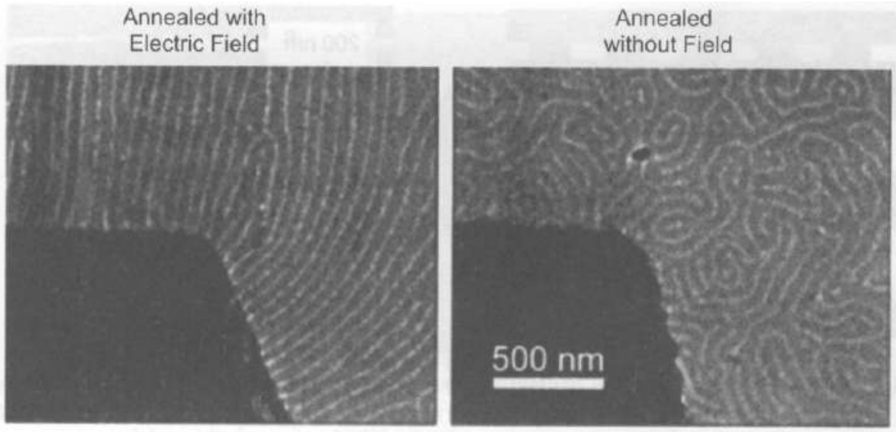

Figure 9.7 *TEM micrographs of block copolymer films annealed in the presence of an electric field and without a field, highlighting the electric field alignment near the electrode seen in the bottom left parts of the images.*

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

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Lithography using self assembly: block co-polymer self assembly, porous anodized aluminum oxide and nano-sphere lithography

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Block copolymer lithography (add pattern transfer)

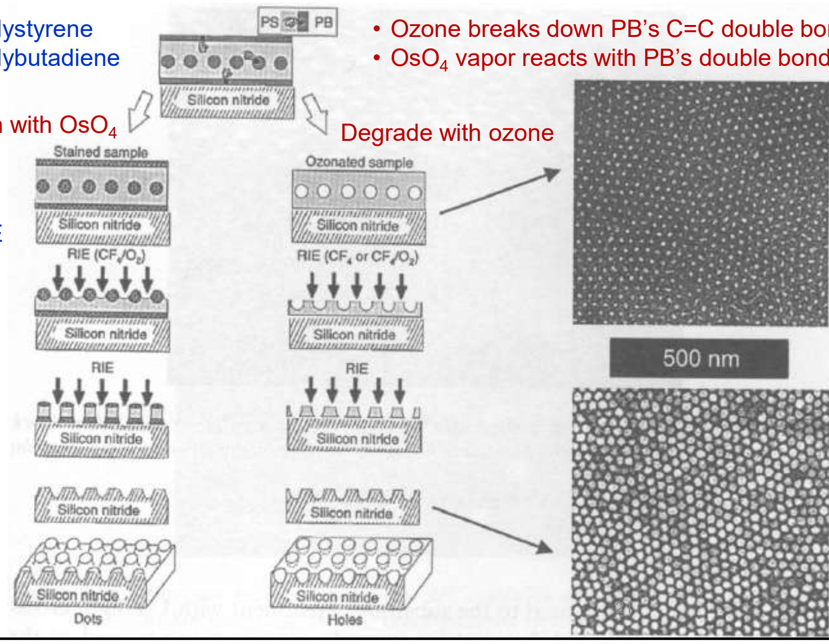
PS: polystyrene
PB: polybutadiene

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

Stain with OsO_4

Degrade with ozone

O_s is a hard RIE mask



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Synthesis of nanowires by wetting

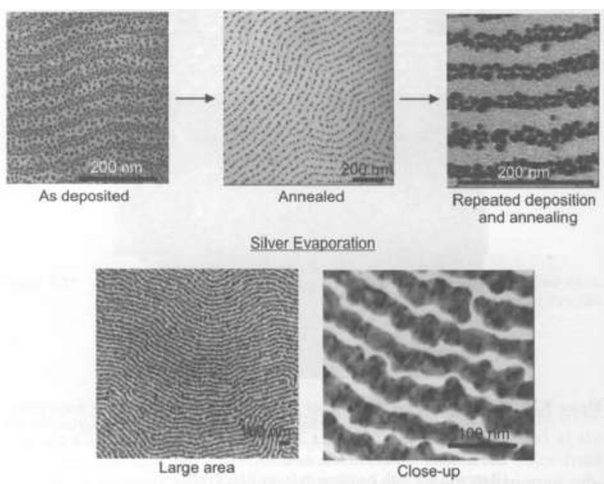

Figure 9.27 *Nanoscale decoration of phase-separated PS-b-PMMA block copolymer film on a silicon nitride substrate by selective wetting and accretion of a vapor deposited metals like gold and silver selectively in the PS phase.*

Wettability masks:
Au and Ag go to ("wet") PS phase
In, Pb, Sn go to PMMA phase

a) Gold (or Ag) 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.

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Nature, 414, 735 (2001).

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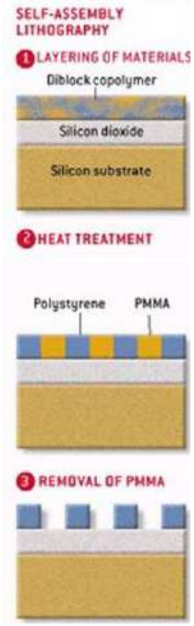
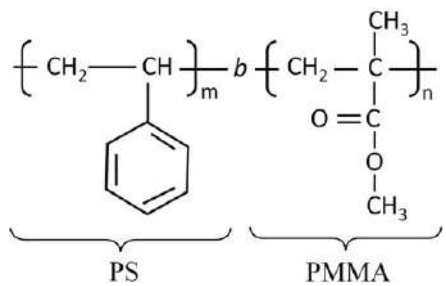
Block copolymer lithography using PMMA-PS



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.

(PMMA chain can also be broken by UV light at λ=365nm, but need very long time exposure, ~1 h at 40mW/cm^2 intensity)



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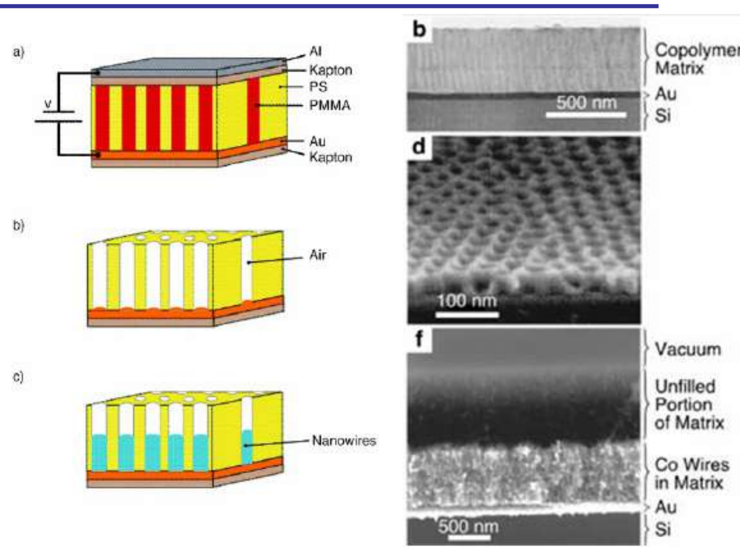
Nanofabrication of vertical nanowires by electroplating

Electric field is for vertical alignment of self-assembly

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



Science, 290, 2126 (2000)

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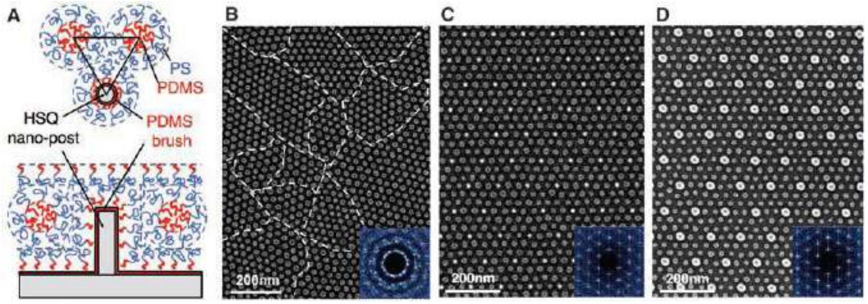
Density multiplication (here by 9×) lithography



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 (without template guidance). 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.

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

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Lithography using self assembly: block co-polymer self assembly, porous anodized aluminum oxide and nano-sphere lithography

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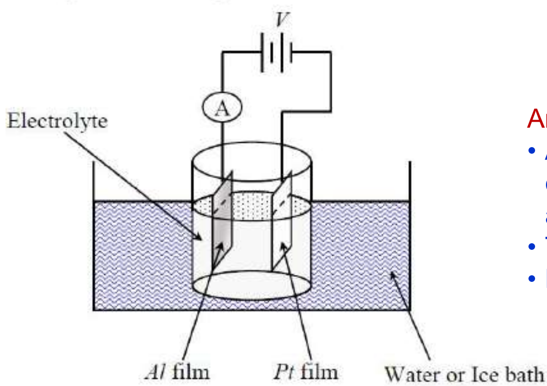
Aluminum anodization setup

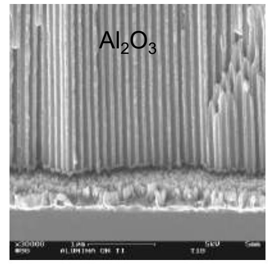
Anodization Reaction :

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2 \quad [\Delta G = -8.65 \times 10^5 J]$$

Experiment Setup :



Porous anodized aluminum



Anodization:

- A direct current is passed through an electrolytic solution where the Al sheet is used as the anode.
- Two processes: dissolving and oxidation
- Naturally formed triangular pore arrays

Electrolyte:
Oxalic acid, phosphoric acid, sulfuric acid …

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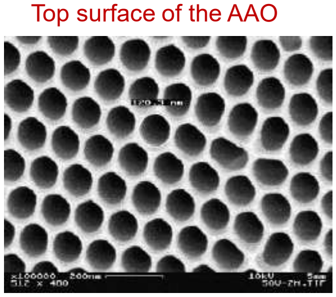
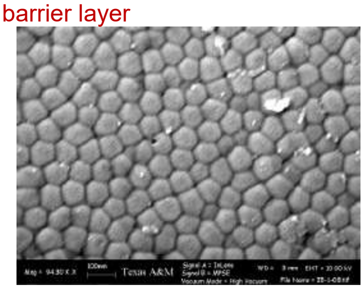
Porous Al_2O_3 membranes

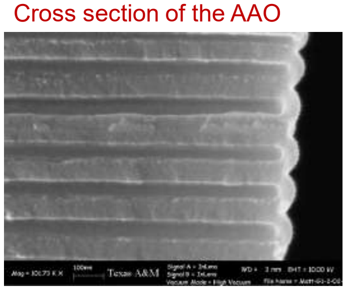
Top surface of the AAO



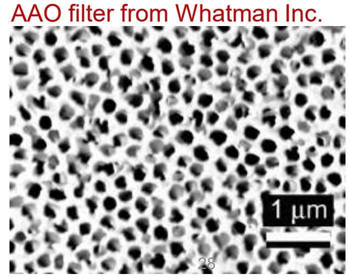
Bottom surface of the AAO showing the barrier layer



Cross section of the AAO



AAO filter from Whatman Inc.



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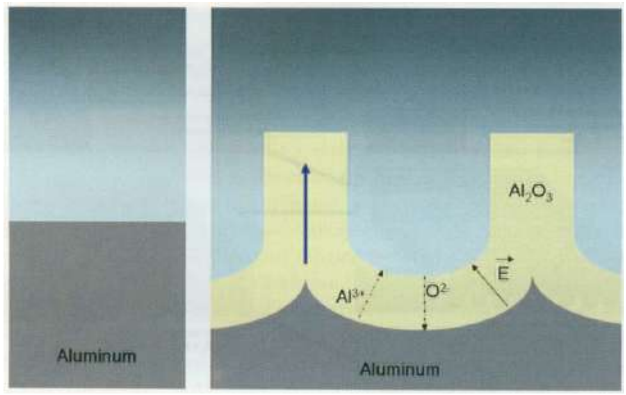
Nano-pore formation mechanism



- Two types of electrical current due to 1) oxide growth, 2) its dissolution.
- The barrier has to be thin to be “transparent” for anions OH^- and O^{2-}.
- These ions interacts with Al^{3+} ions, which can also move under electric field.
- The wall is “pushed” upward by the continuous anodization at the oxide/Al interface.
- Other mechanisms have also been reported.

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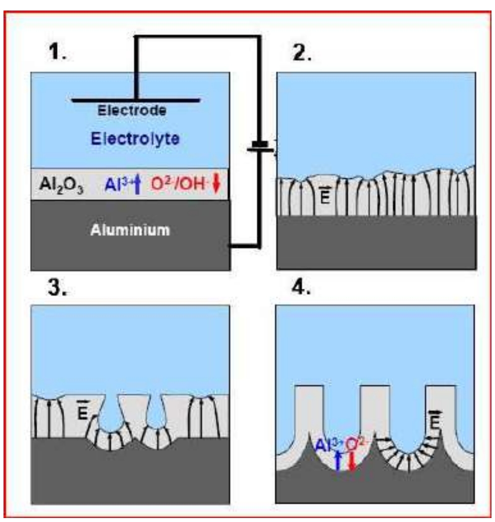
Nano-pore formation mechanism



Schematic diagram of the pore formation at the beginning of the anodization.

1. Formation of barrier oxide on the entire area.
2. Local field distributions caused by surface fluctuations.
3. Creation of pores by field-enhanced or/and temperature-enhanced **dissolution**. Some pores stop growing due to competition among pores.
4. Stable pore growth.

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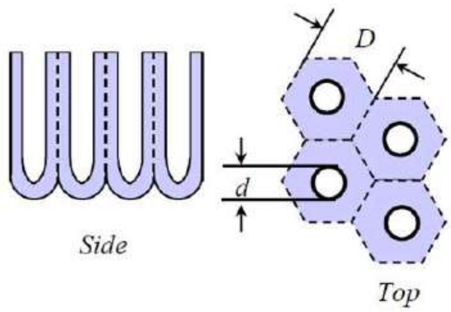
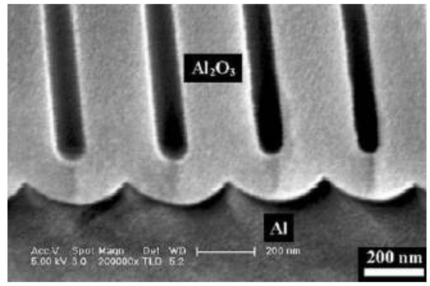
Pore dimensions



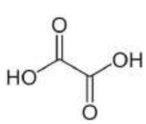


Controlling parameters: voltage, electrolyte, temperature and time.
Cell size D ~ 2.5×V (nm), V is voltage with a unit volt.
Pore size d ~ V (nm), depends on pH; but pore can be enlarged in acids.

Common acids for AAO

Table 1. Lists the array of geometrical parameters as a function of the anodization conditions.

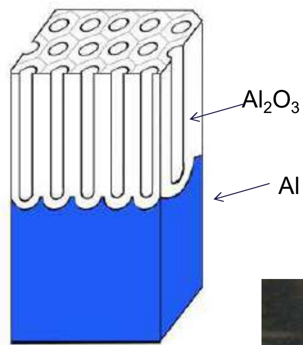
Electrolyte	Interpore Distance, D_{int}	Inner Wall Thickness, D_{inner}	Pore Diameter, D_P	Porosity
H_2SO_4 25 V 0.3 M	66.3 nm	7.2 nm	24 nm	12%
$(COOH)_2$ 40 V 0.3 M	105 nm	9.1 nm	31 nm	8%
H_3PO_4 195 V 0.1 M	501 nm	54 nm	458.4 nm	9%

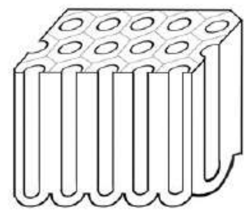


Oxalic acid

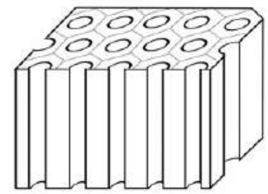
- Sulfuric acid generally gives smallest pore diameter and largest pore density.
- Standard deviation of pore diameter usually is within 10%.

AAO membrane production

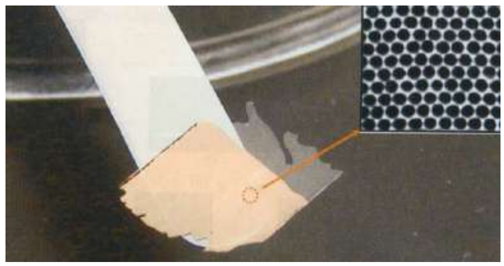




Wet-etch Al
(using $HgCl_2$)



Etch barrier



Free standing ~10μm-thick AAO membrane, with Au plated for better viewing contrast.

Commercial membrane: thickness ~60μm, pore size down to 20nm (one side only!)
Application: filter, as template for nano-wire production.

Chemistry involved in nanofabrication using AAO

- Removing Al without attacking AAO: saturated $HgCl_2$
  $Al + HgCl_2$-----Al^{3+} + Hg, room temperature

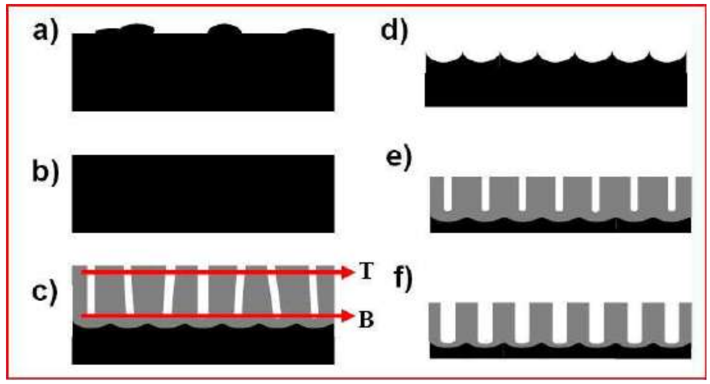
- Removing AAO without attacking Al: It is not easy for Al to dissolve in H2CrO4 aqueous.
  $6\%H_3PO_4 + 1.8\%H_2CrO_4$, 60^oC, 2h

- Removing the barrier layer at the bottom without attacking too much the AAO pores.
  $5\%H_3PO_4$, 30^oC, 30min

Two-step anodization process to improve periodicity

Stages of the formation of self-ordered alumina:

a) Annealing at 500^{o}C for 3h to increase grain size;
b) electro-polishing in a solution of 1/4 $HClO_4$ + 3/4 C_2H_5OH for 4 min at 8V with agitation;
c) first anodization;
d) selective dissolution of the formed oxide layer;
e) second anodization under the same conditions as the first anodization; and
f) if needed, isotropic etching in 1M phosphoric acid at 30^{o}C to widen the pores.



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Pre-pattern Al surface can also improves periodicity

Al is pre-patterned by FIB

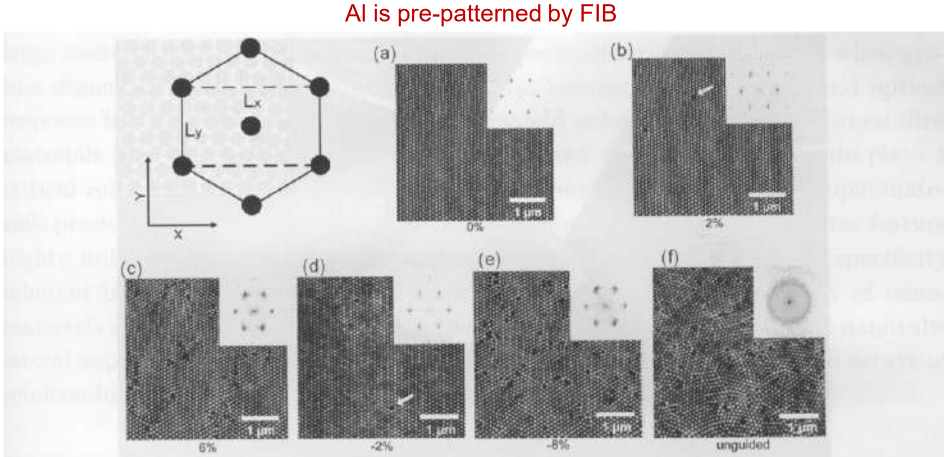

Figure 3. Diagram of an unit cell of the lattice followed by AFM images of the barrier with lattice mismatch = (a) 0%, (b) 2%, (c) 6%, (d) −2%, (e) −8% and (f) a self organized structure with insets showing the 2D power spectra of the corresponding regions of the 10 micron AAO films. White arrows in (b) and (d) indicate point defects in the lattice. [Reproduced with permission from APL 84, No 14 (2004) Pg 2510.]

"Order–disorder transition of anodic alumina nanochannel arrays grown under the guidance of focused-ion-beam patterning", page 2509-2511.

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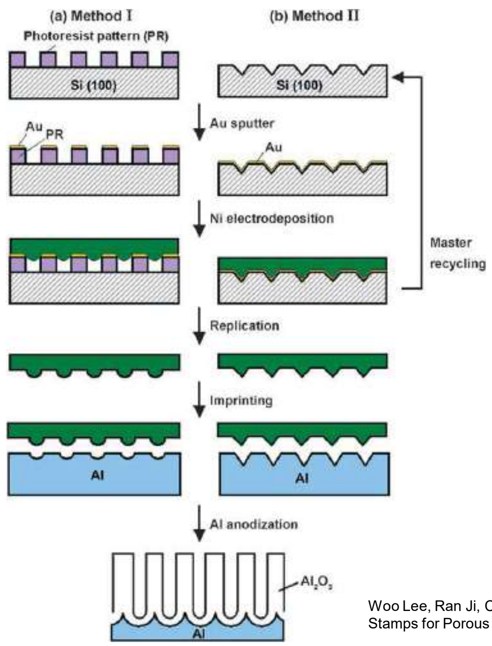
Pre-pattern Al surface using imprint with a Ni mold



Imprint pressure order 1000atm!!
(regular imprint into resist 20atm)

Schematic diagram of the fabrication of ideally ordered anodic alumina using Ni imprint stamps that can be replicated from:

a) a resist pattern (method I).
b) a silicon pattern (method II).

Woo Lee, Ran Ji, Caroline A. Ross, Ulrich Gçsele, and Kornelius Nielsch, "Wafer-Scale Ni Imprint Stamps for Porous Alumina Membranes Based on Interference Lithography", Small, 2006.

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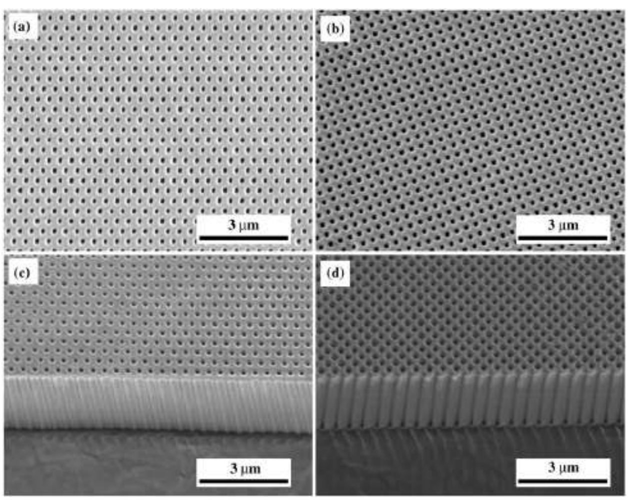
Ideally ordered AAO by imprint pre-pattering Al



SEM images of long-range-ordered anodic alumina with a) hexagonal and b) square arrangements of nano-pores. c,d) Oblique views of the cross sections.

From same group, "Fast fabrication of long-range ordered porous alumina membranes by hard anodization", Nature Materials, 2006.

No other way can get such a high aspect ratio periodic pattern.

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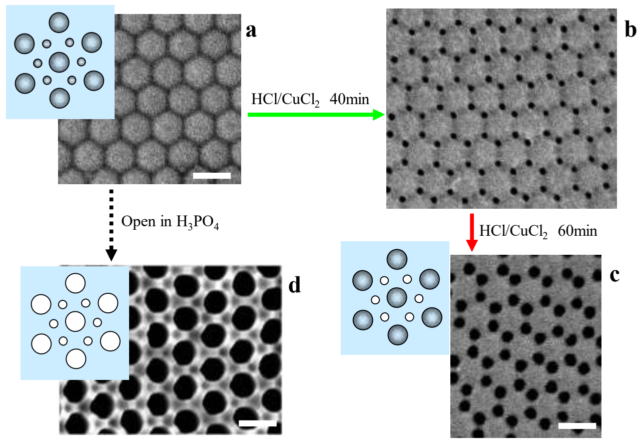
Novel structure of AAO film

Anodization using 0.8 M H_2SO_4 + 0.1 M $Al_2(SO_4)_3$ solution. Addition of $Al_2(SO_4)_3$ allows higher current density/voltage, which leads to this new structure. A discovery by "accident".



SEM of AAO with novel structure. (a) View of bottom, just removing the Al substrate in a mixed solution of $HCl/CuCl_2$ (immersing for 20min); (b) extending the immersing time till 40 min, small pores appear; (c) extending the immersing time till 60 min; (d) after immersing in 5% H_3PO_4, the normal nano-pores are opened, surrounded by six small pores. The scale bar is 100nm.

Shiyong Zhao, Arthur Yelon and Teodor Veres. "Novel structure of AAO film fabricated by constant current anodization" Adv. Mater. 19(19), 3004, 2007.

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Lithography using self assembly: block co-polymer self assembly, porous anodized aluminum oxide and nano-sphere lithography

1. Di-block copolymer self assembly overview.
2. Guided (directed, aligned) self assembly.
3. Block copolymer lithography.
4. Anodized aluminum oxide (AAO) overview.
5. Nanofabricating using AAO template.

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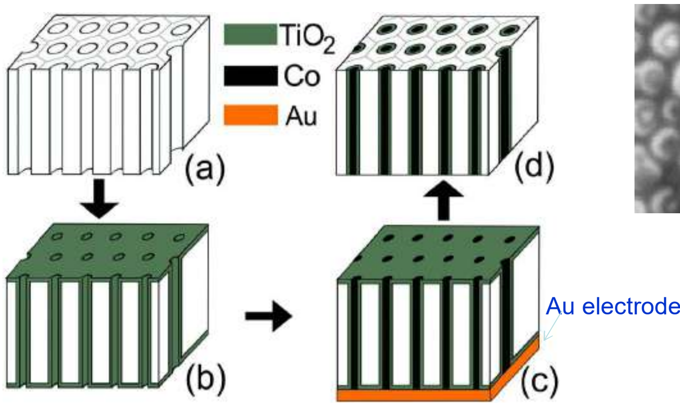
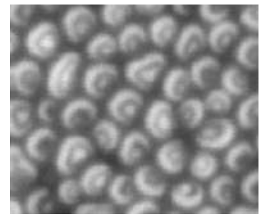
Shrink pore diameter by isotropic coating onto AAO

- The pore spacing and the pore diameter are coupled to each other and determined by the applied voltage of anodization.
- Pores are easy to enlarge using subsequent wet etching after anodization.
- It is more challenging to shrink the pore size.





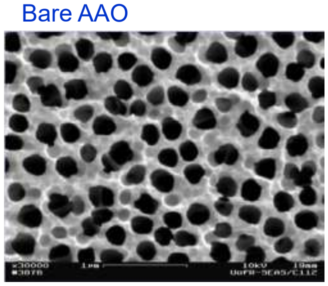
Co nanowires in TiO_2 nanotubes

TiO_2 is coated by isotropic sol–gel deposition technique

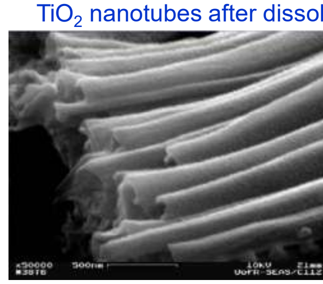
Z. Ye, H. Liu, I. Schultz, W. Wu, D. G Naugleand I. Lyuksyutov, Nanotechnology 19, 325303 (2008).

Deposition of TiO_2 nanotubes using Sol-Gel method

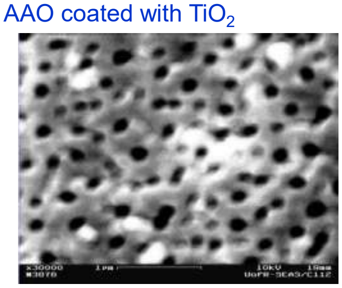
Bare AAO



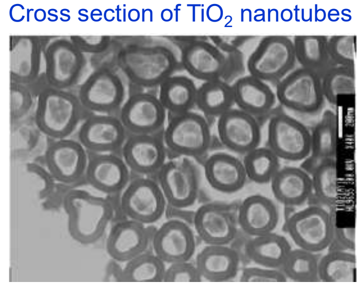
TiO_2 nanotubes after dissolving AAO



AAO coated with TiO_2

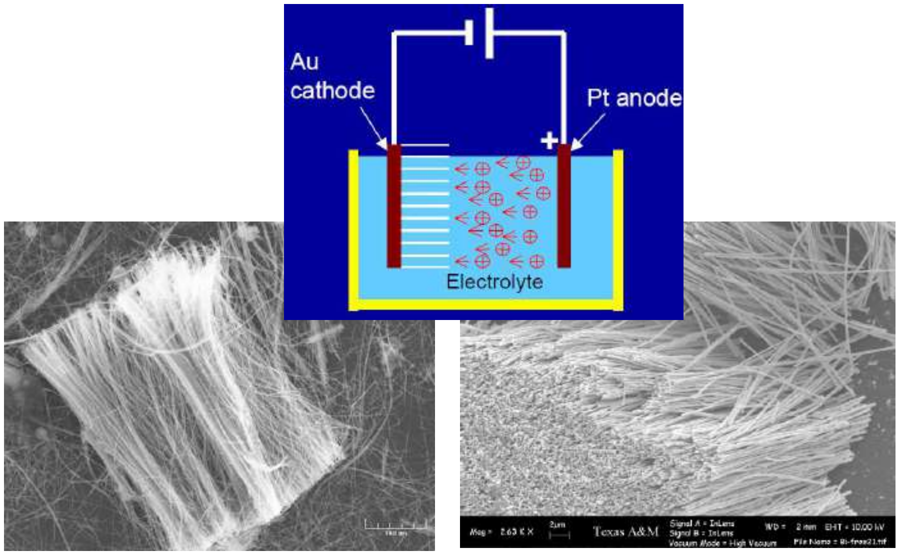


Cross section of TiO_2 nanotubes



Recipe: $TiF_4 + H_2O \rightarrow TiO_2 + HF$ at 60°C and pH = 2

Electroplating of nanowires



Aspect ratio: 50µm/60nm ~800
This extremely high aspect ratio is hard to achieve by lithography plus etching

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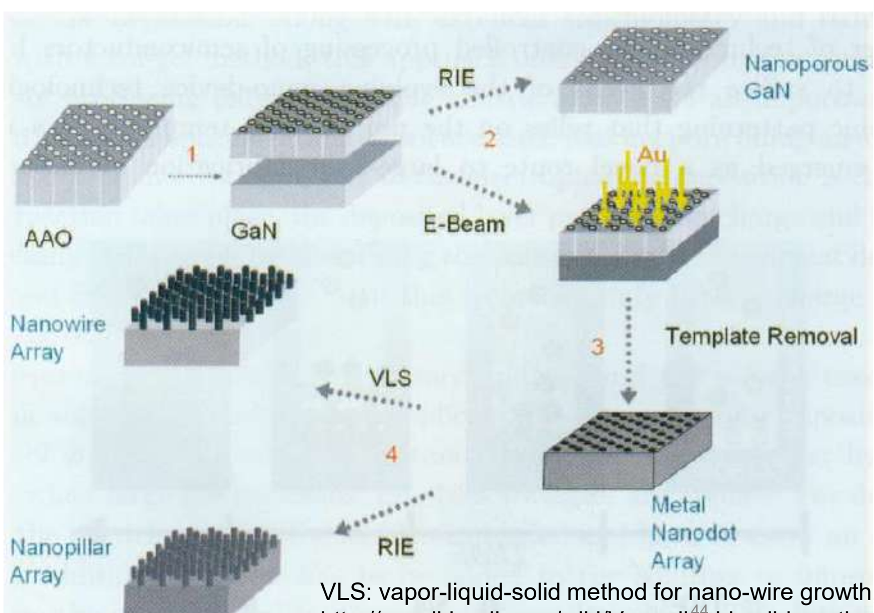
Other nanofabrication routes using AAO



VLS: vapor-liquid-solid method for nano-wire growth, see
http://en.wikipedia.org/wiki/Vapor-liquid-solid_method

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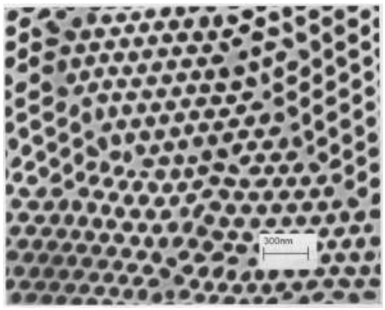
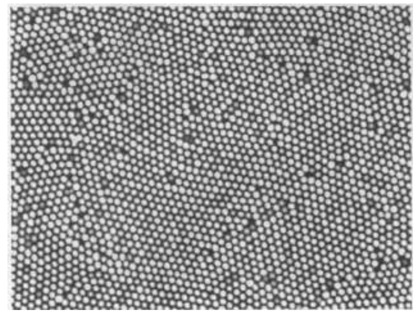
Patterning GaN using AAO



Nano-pore array in GaN by RIE using AAO as mask



Nano-pillar array in GaN by metal liftoff using AAO, followed by GaN RIE.

Grow carbon nanotube into AAO pores

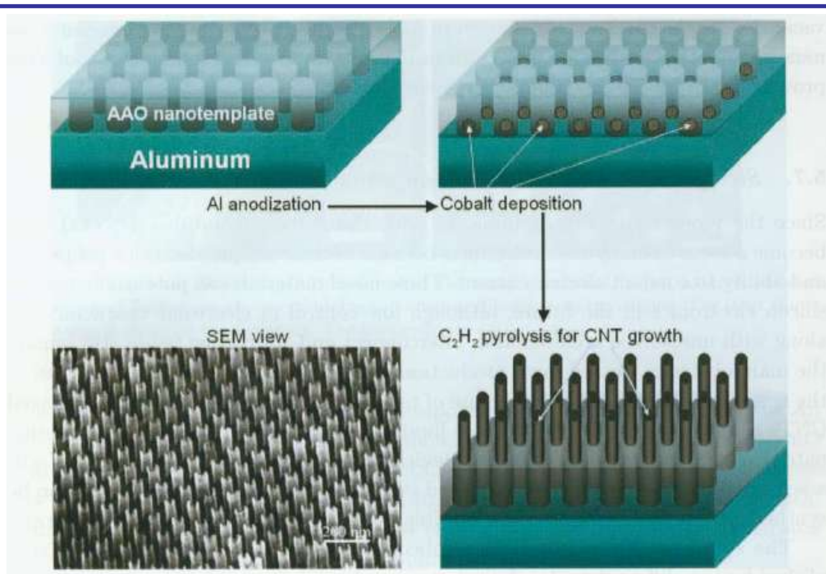
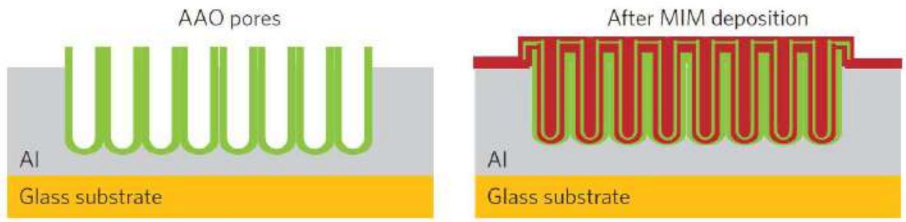
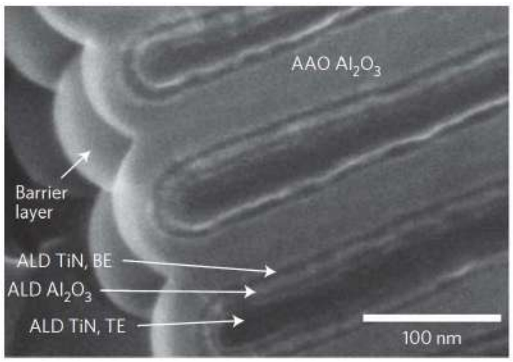


Figure 17. Schematics of catalyst-assisted CNT growth in AAO templates. Below, left a top view SEM image of CNT array is presented. Reprinted with the permission of [C. Papadopoulos, A. Rakitin, J. Li, A. S. Vedeneev, and J. M. Xu, Phys. Rev. Lett. 85, 3476-3479 (2000)].

Nanotubular super-capacitor for energy





MIM: metal-insulator-metal

here TiN ("metal"), Al_2O_3 and TiN, all deposited by atomic layer deposition (ALD).

Due to the enormous interface area, the capacitance is huge (C $\propto$ area), with peak (discharge) power up to 10^6 W/kg.

Energy stored = ½ $CV^2 \propto C$.

"Nanotubular metal–insulator–metal capacitor arrays for energy storage", Nature Nanotechnology, 2009.

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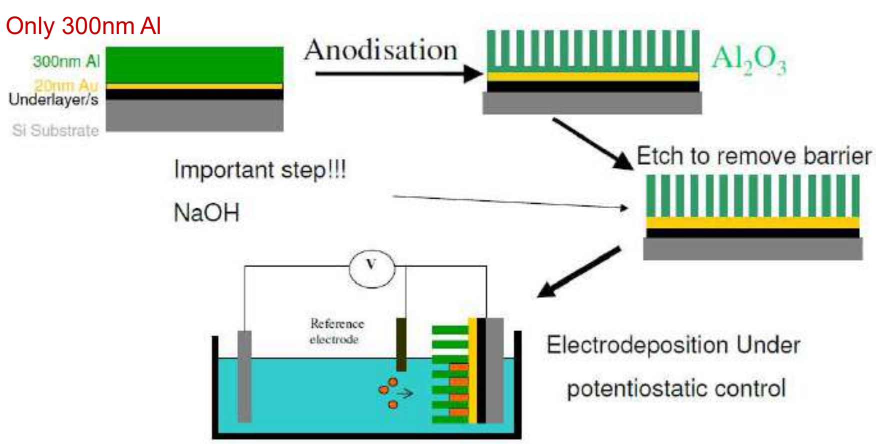
AAO on wafers

- Al foils are interesting but limited. It is not microfabrication compatible.
- Al films on wafers are. AAO on flat surface may be used for data storage with high density.



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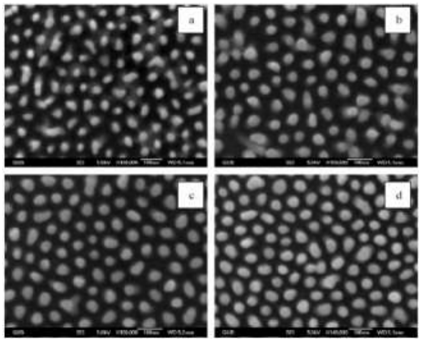
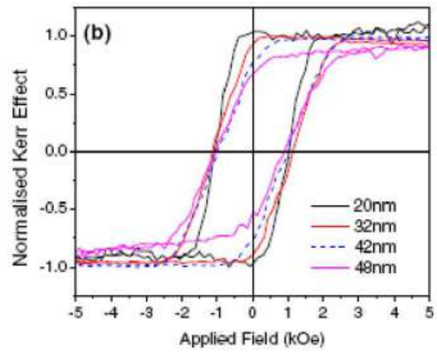
Magneto-optics of Ni nanowires

Pitch ~70nm





Challenges for AAO using thin Al film:

- The deposited Al is usually not as pure as Al sheet due to oxidization or (cross-) contamination during film deposition. (Al atom is so reactive)
- Al film is usually too thin for two-step anodization, thus poor periodicity.
- Electrochemical polish would also be extremely difficult to control for thin films.

Nanotechnology 17 5764 (2006)

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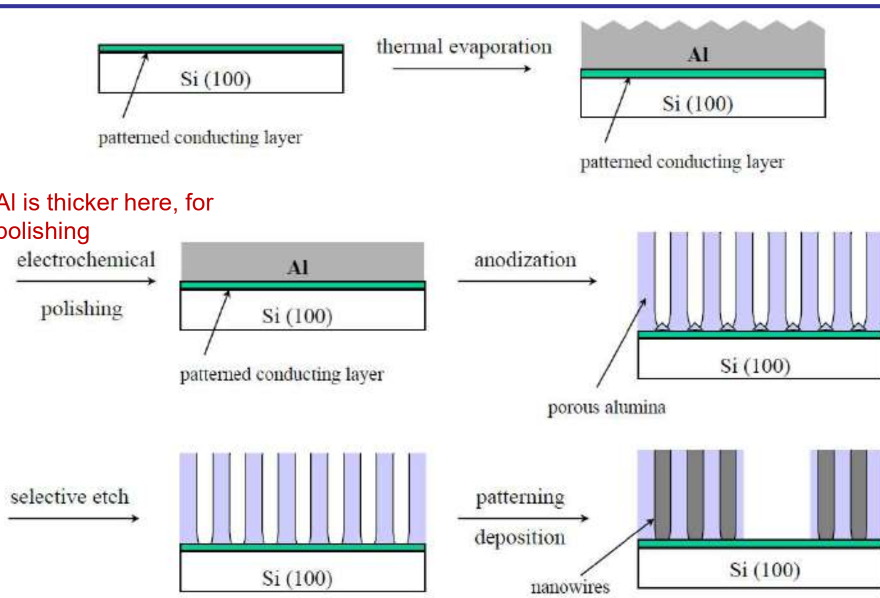
Thicker alumina templates on silicon wafers

Al is thicker here, for polishing



M. Dresselhaus, MIT

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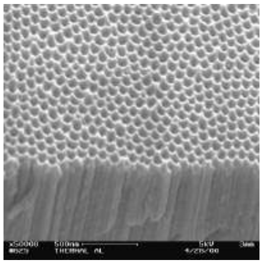
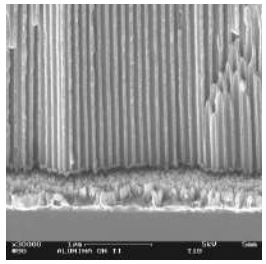
Nano-wire by alumina template
(results using the steps in previous slide)

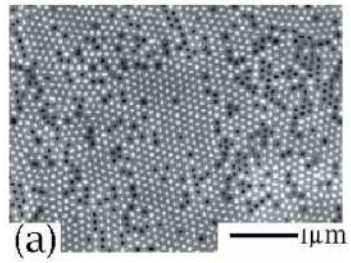
Pore oblique view



Cross-section (ϕ~100nm)



Filled with nano-wire



Here Al film is >2µm.

Some pores are not filled by metal

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End of AAO based nano-patterning