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Basic Nanotechnology Processes

E SC 212

Unit 4
An Introduction to Basic Pattern Transfer

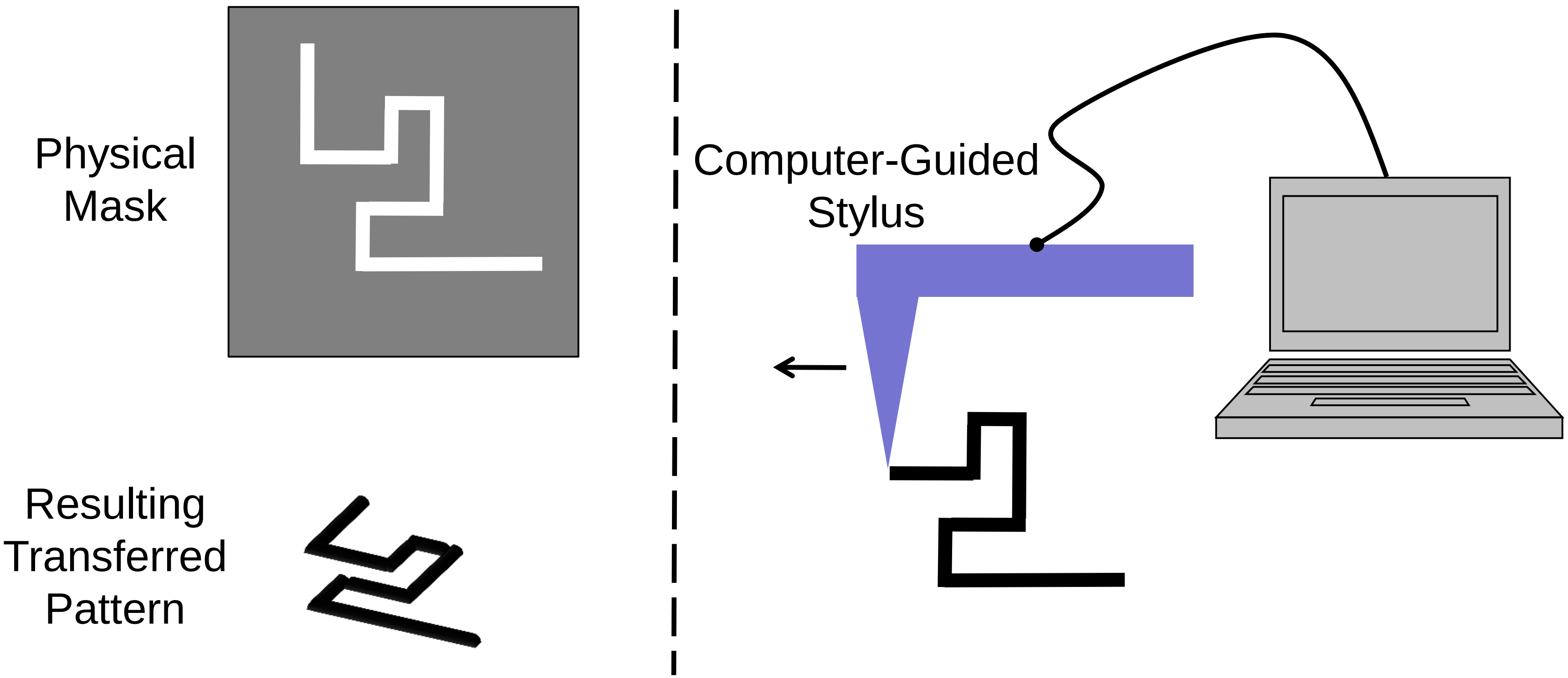
Lecture 1
Pattern Transfer and Lithography Techniques

Outline

- Introduction
- Energy-sensitive pattern transfer
- Dip-pen lithography
- Stamp lithography (micro-contact printing)
- Imprint lithography
- Block copolymer pattern development and transfer

Introduction

- What is pattern transfer?
- Creating a pattern stored in a physical mask or in a computer file onto a surface.



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Introduction

- Why do we need pattern transfer?
- To make structures and devices using the tools of micro- and nano-technology.
- Devices often require patterns, circuits, or well-defined shapes.
- Can’t use macroscopic (conventional, with your own two hands) construction techniques, because the needed features are just too small and dense.

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Pattern Transfer Using Energy Sensitive Chemistry

- Basically, an energy-sensitive chemical is applied to the substrate's surface and exposed to a particular energy source (photons or energetic particles) to produce the desired pattern.
- When the process involves light wavelengths as an energy source, the process is called photolithography.

Photoresists

- Photolithography uses photons to cause a chemical reaction in a film to transfer a pattern into a layer called a photoresist (or just resist for short).
- Photoresists come in two basic varieties:
  - Negative (negative polarity)
  - Positive (positive polarity)

Photoresists

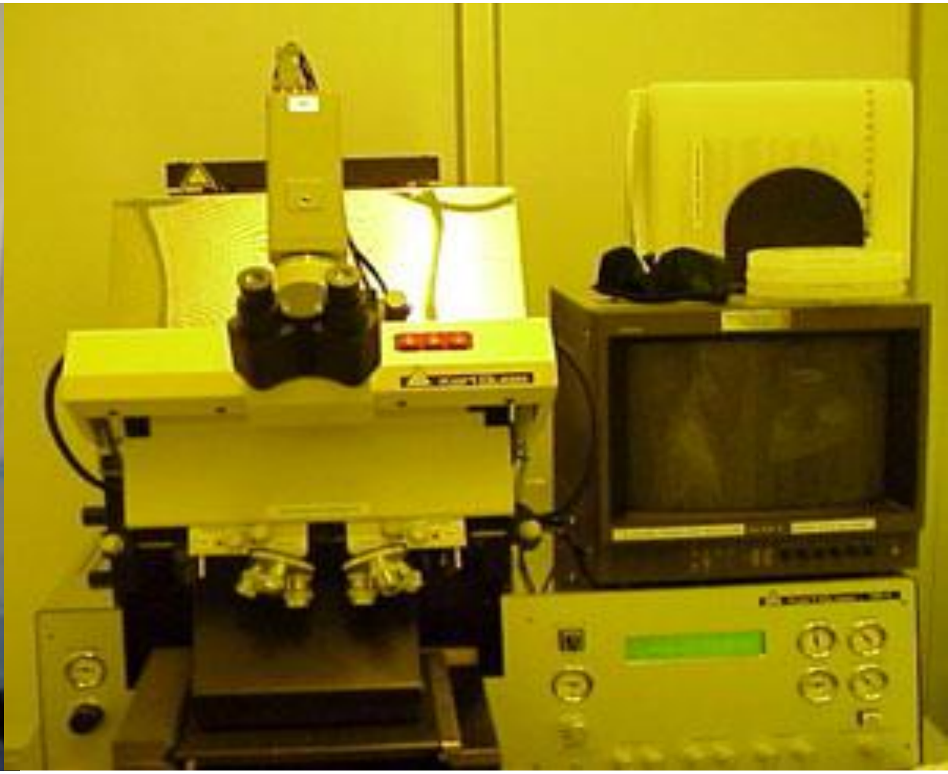
- Negative resist, when exposed to UV light, forms polymer bonds where exposed and becomes insoluble during development;
- Positive resist, upon UV exposure, breaks polymer bonds where exposed and becomes soluble during development;
  - “What shows, goes!”

Contact Photolithography

- Contact photolithography is only one of many types of photo-lithography that uses a **mask** to pattern the substrate’s surface;
  - This method involves a **contact aligner** that clamps the mask and substrate together in a tight seal before exposing the substrate to ultraviolet light energy.
  - Both the Karl Suss MJB3 and MA6 contact aligners are common is small volume manufacturing and research.

Contact Aligners

The Karl Suss MJB3



The Karl Suss MA6

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Nine Basic Steps of Contact Lithography

1) Clean substrate
2) Apply HMDS/Spin/Bake
3) Apply photoresist/Spin
4) Soft bake
5) Alignment/Exposure
6) Develop
7) Quality Check
8) Hard bake

   [pattern transfer: etch, dep., etc.]

9) Resist Removal

Step One: Cleaning Substrate

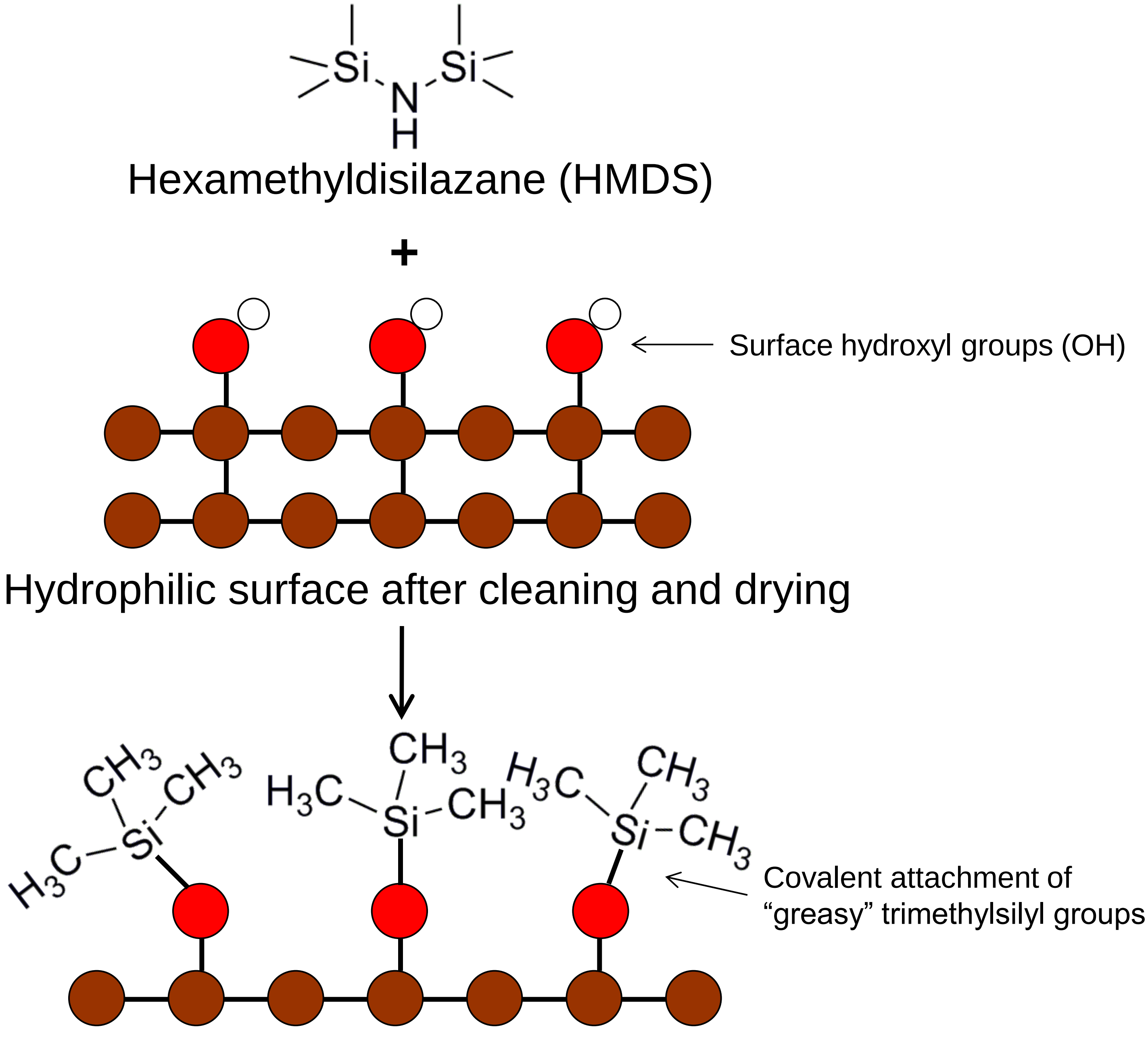
- Before any process, substrates must be free of particles or other contaminants.
- Various cleaning methods were discussed in the contamination lecture, but usually virgin substrates are cleaned with the following:
  - Acetone (removes organics and particles).
  - Isopropanol (removes acetone residue).
  - DI water rinse (removes isopropanol residues).

Step One: Cleaning Substrates

- After the DI rinse, any visible water is removed with the nitrogen gun.
- The substrate is then heated to remove any residual water in what is known as a **dehydration bake**.
  - Industry uses sophisticated ovens with carefully controlled temperature settings to remove water.
  - For research purposes, placing substrates on a hotplate at a temperature of at least 105^{o}C for a few minutes will suffice.

Step Two: HMDS Application

- Hexamethyldisilazane (HMDS) is used as a **primer**.
  - This chemical promotes the adhesion of photoresist, by displacing any water left behind on the substrate’s surface after the dehydration bake, and reduces surface tension.
  - HMDS *primes* the substrate’s surface by adding an organic layer (hydrocarbons) to which photoresist, being mainly organic, can easily attach.
- Following the HMDS spin, an activation bake is performed for 15 sec at 105 °C.
- This bake ensures the removal of remaining solvents.



Hydrophobic surface after priming with HMDS

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Step Three: Photoresist Application

- For example, Shipley 1800 series positive resist (http://www.shipley.com/), can be purchased by desired thickness:
  - Shipley 1805,1813, and 1827.
- The 1800 refers to the series number, the last two numbers refer to the nominal thickness (in microns) of the resist layer as a function of time and spin speed.

Step Three: Photoresist Application

- When applied properly…
  - 1805 = 0.5 microns
  - 1813 = 1.3 microns
  - 1827 = 2.7 microns

- 1813 resist has a thickness of 1.3 microns when…
  - Spun-on at 4,000 RPM
  - For 40 seconds
  - With a 1,000 RPM/sec ramp rate

Step Three: Photoresist Application

- For example, Shipley 1800 series resist can use a static spin application
- The substrate is placed on a vacuum chuck, several cubic centimeters of resist are placed in the center of the substrate and allowed to reach a desired diameter
- The chuck then spins, spreading the resist and spinning off the excess.

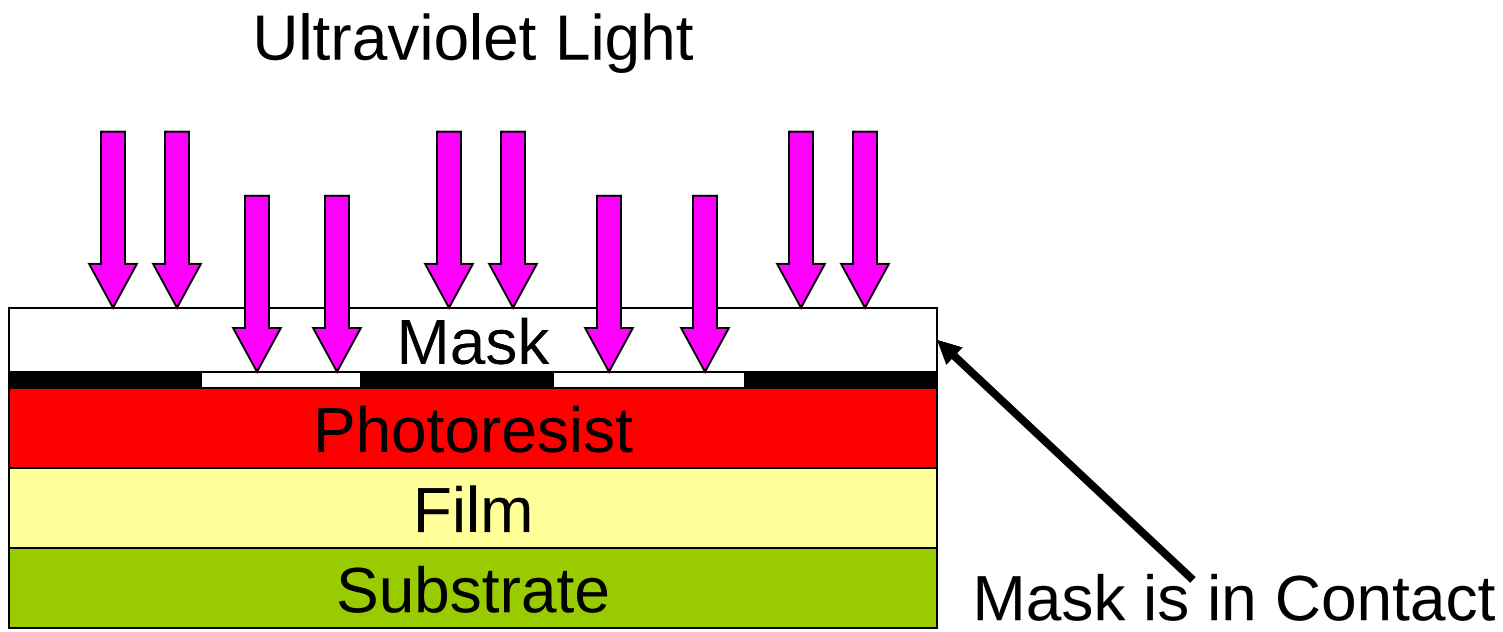
Step Four: Soft Bake

- The purpose of the soft bake is to drive out solvents from the photoresist.
  - We usually bake for 90 seconds at 105 °C, at this point, the resist is still "soft."
- Driving out the solvents serves three purposes:
  - Prevent exposure interference.
  - Improve adhesion
  - Prevents the substrate from sticking to the mask.

Step Five: Alignment/Exposure

- A typical lithography mask is made of high-quality quartz with chrome coated on one side.
  - Due to diffraction, it is important that the chrome side of the mask be in contact with the substrate to insure proper pattern transfer.
- The mask must be as contaminant and defect-free or the pattern will not be correctly transferred.
- The pattern produced on the substrate can only be as good as the pattern on the mask.

Exposure



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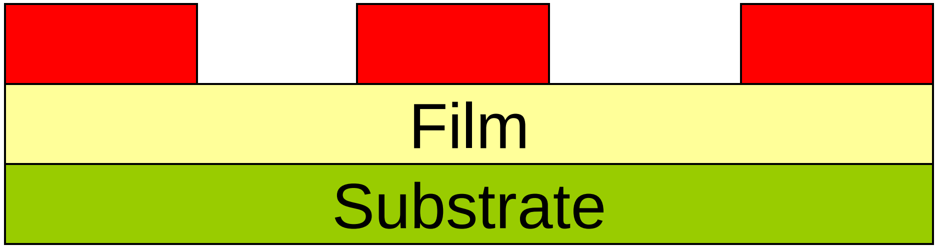
Step Five: Alignment/Exposure

- The specifics of contact lithography have been discussed previously.
  - There are many other methods of lithography, that will be discussed later in the course.
- Shipley 1800 resists are sensitive to UV light, specifically 365 and 405 nm wavelengths.
  - The MJB3 lamp uses a mercury vapor bulb to emit these wavelengths.
- Typically Shipley 1813 requires an exposure time of about 6 seconds @ about $14 mW/cm^2$.

Step Six: Develop

- Sensitive substrate materials using positive photoresist requires the use of a nonionic solution of **tetramethylammonium hydroxide** (TMAH), followed by a DI water rinse.
  - Shipley’s commercial developer is CD-26.
  - MF-312 can also be used but must be diluted 1:1 with DI water to be the same concentration as CD-26.
  - Usually, samples are developed for 55 seconds

Development



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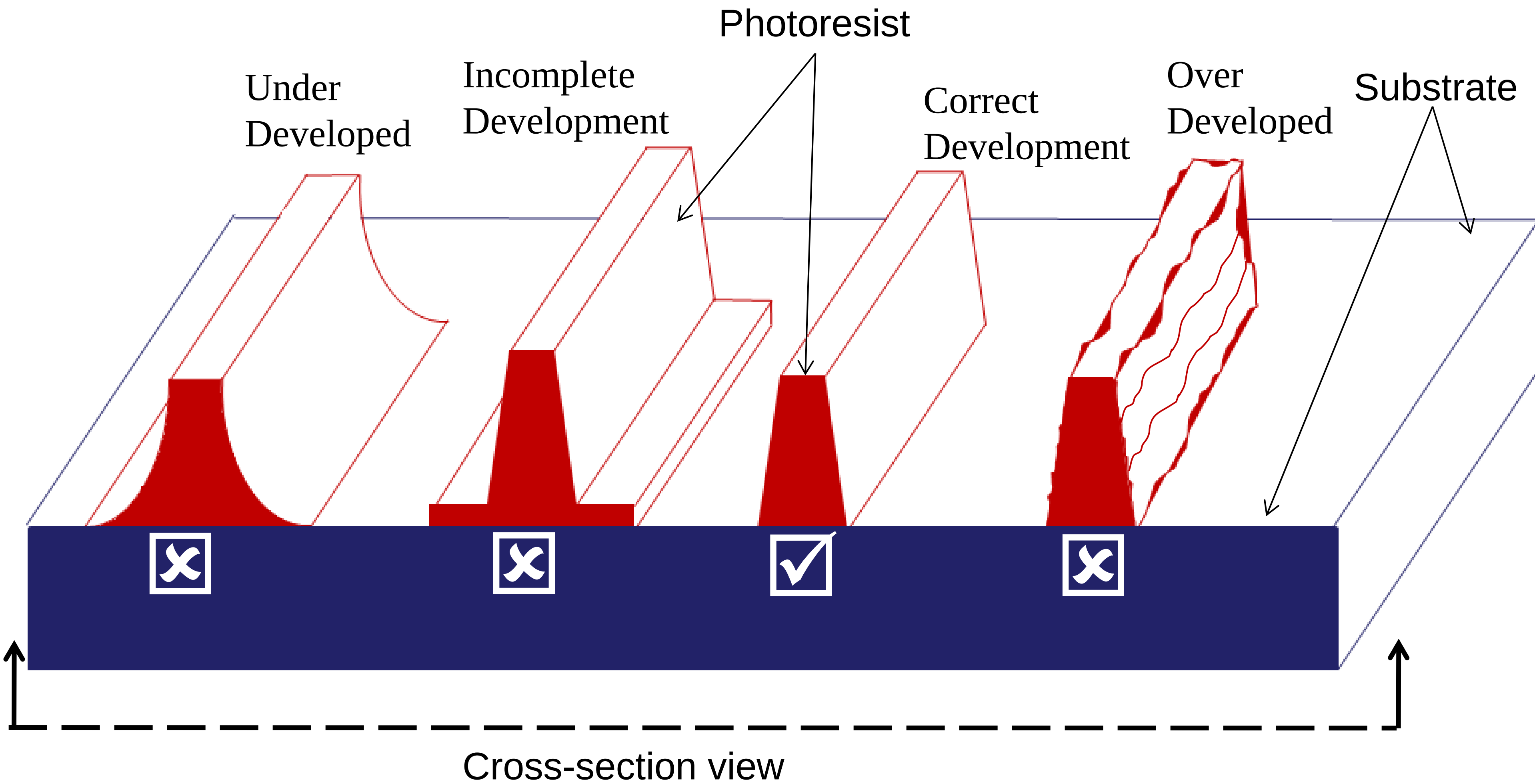
Step Seven: Quality Check

- After development, an optical inspection of the photoresist film should be performed.
- Check the shape of resist formations under the light microscope to determine if development and exposure times were adequate.
- Resist can be easily removed and reapplied if undesirable defects are found.

Quality Check



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Step Eight: Hard bake

- If the pattern looks good, the next step is to **hard bake** the photoresist. This step is optional, but serves three purposes:
  - Further promote adhesion.
  - Drive out more solvents.
  - Engineer the sidewalls.
- Hard bake times will vary.
- Shipley 1813 is typically baked for 1-5 minutes at 120°C.

Step Nine: Remove Photoresist

- After a desired processing step is complete, the photoresist is no longer needed and must be removed;
  - This can be accomplished by using wet chemistries or plasma.

Wet Resist-Removal Chemistries

- Piranha etch and Nanostrip are excellent resist removers (strippers) for non-metallized surfaces and can remove positive or negative resists.
- Since metals are vulnerable to oxidation, three types of specialized chemistries can be used;
  - Organic strippers
  - Solvent/amine strippers
  - Specialty wet strippers

Dry Stripping

- Resist can be removed via an oxygen plasma, by a process known as **ashing**.
  - Plasma creates highly reactive oxygen radical ozone O_3 which oxidizes the organic resist to gases that can be removed from the chamber by a vacuum pump

$$C_xH_y\text{(resist)} + O_2 \text{ plasma} \rightarrow CO\text{(gas)} + CO_2\text{(gas)} + H_2O$$

Beam Lithography

- E-beam lithography
- Ion beam lithography

What is the wavelength of an electron vs. UV-light?

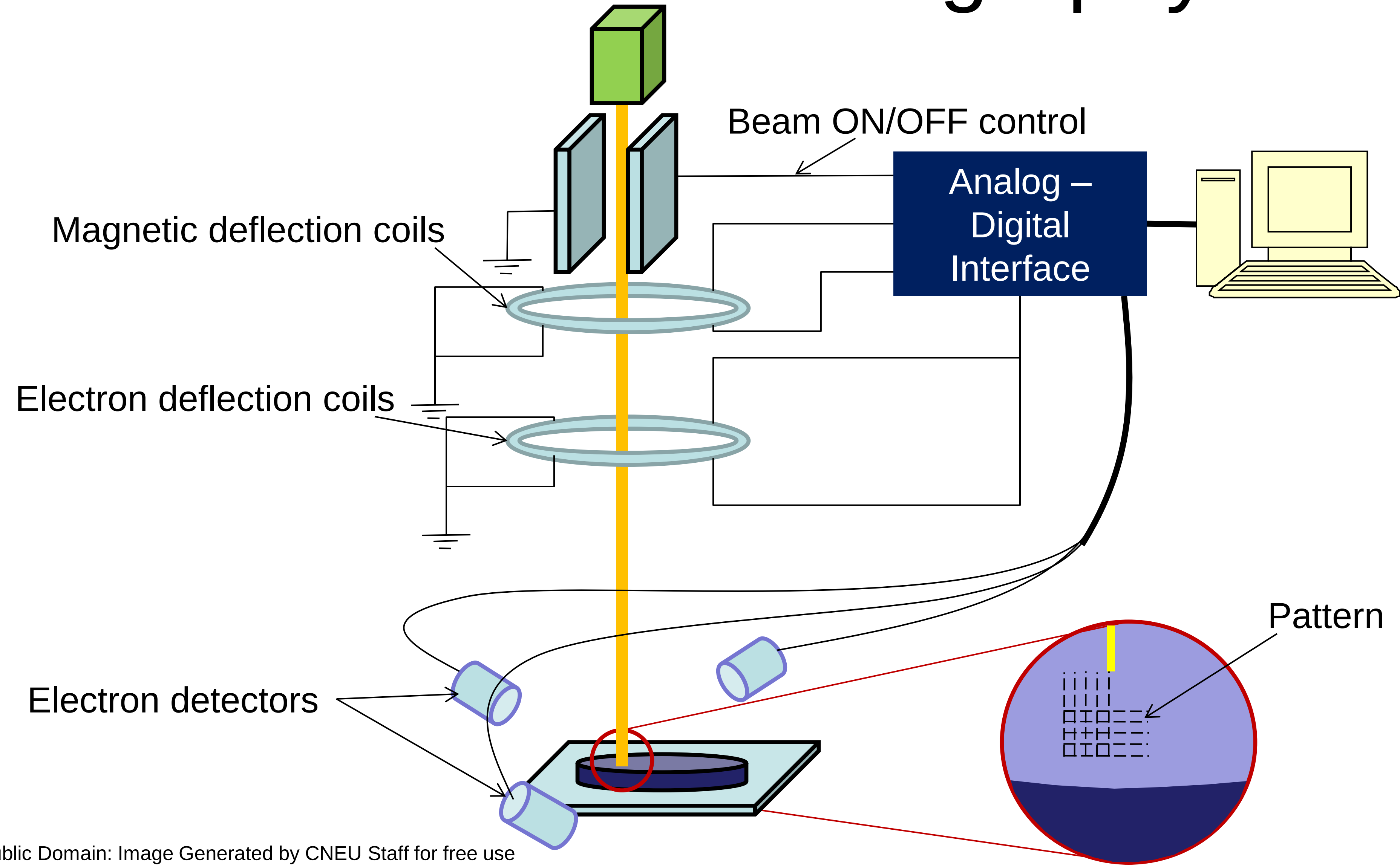
Electron Beam Lithography

- This is a non-optical system, consisting of an electron source that produces a small diameter spot and a “blanker” capable, of turning the beam on and off.
- Exposure must take place in a vacuum to prevent air molecules form interfering with the beam.
- The beam passes through two electrostatic plates capable of directing the beam on the mask or substrate.
- Uses a beam of electrons to transfer a pattern to an e-beam resist.

Electron Beam Lithography

- E beam lithography does not use a mask or reticle, instead this system employs a *direct write* technique (there is no physical mask).
  - The pattern initially resides in computer files.
  - The steering and blanking is controlled by a computer with the substrate pattern stored in its memory (CAD design stage).
  - The beam is rastered, so it is an inherently slow process.

Electron Beam Lithography



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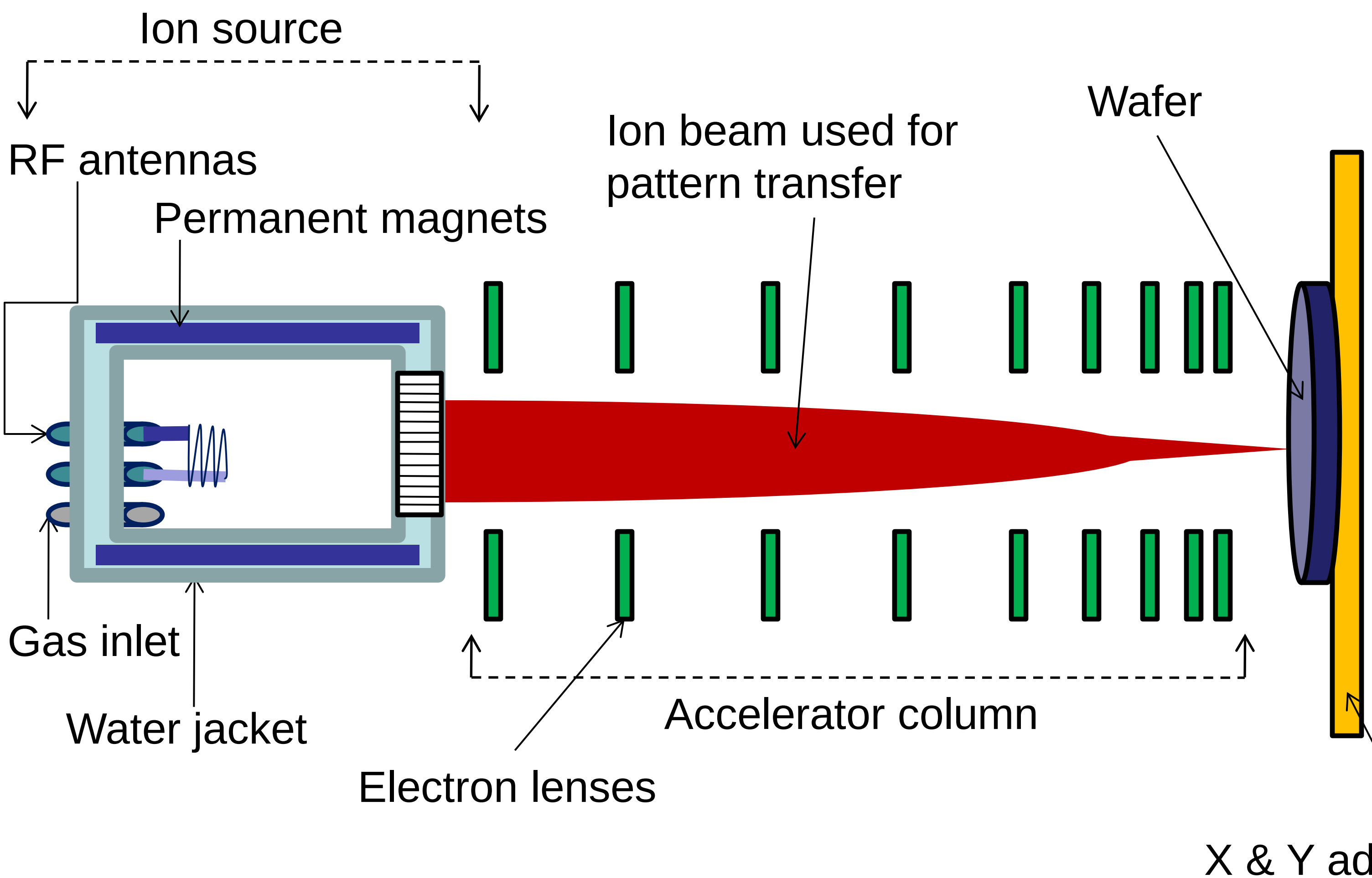
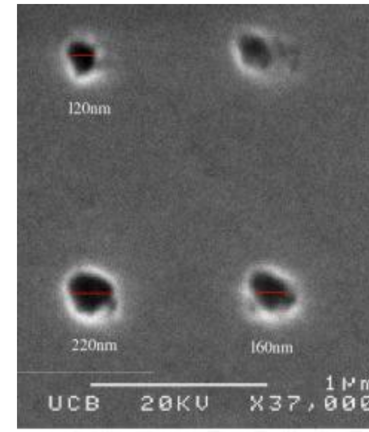
Ion Beam Lithography

- Uses a Focused Ion Beam (FIB) instead of an electron beam.
- The ion beam rasters across a substrate coated with a sensitive coating.
- No mask is used, a computer program controls the rastering.

Ion Beam Lithography





120 nm features achieved in PMMA resist using ion beam lithography

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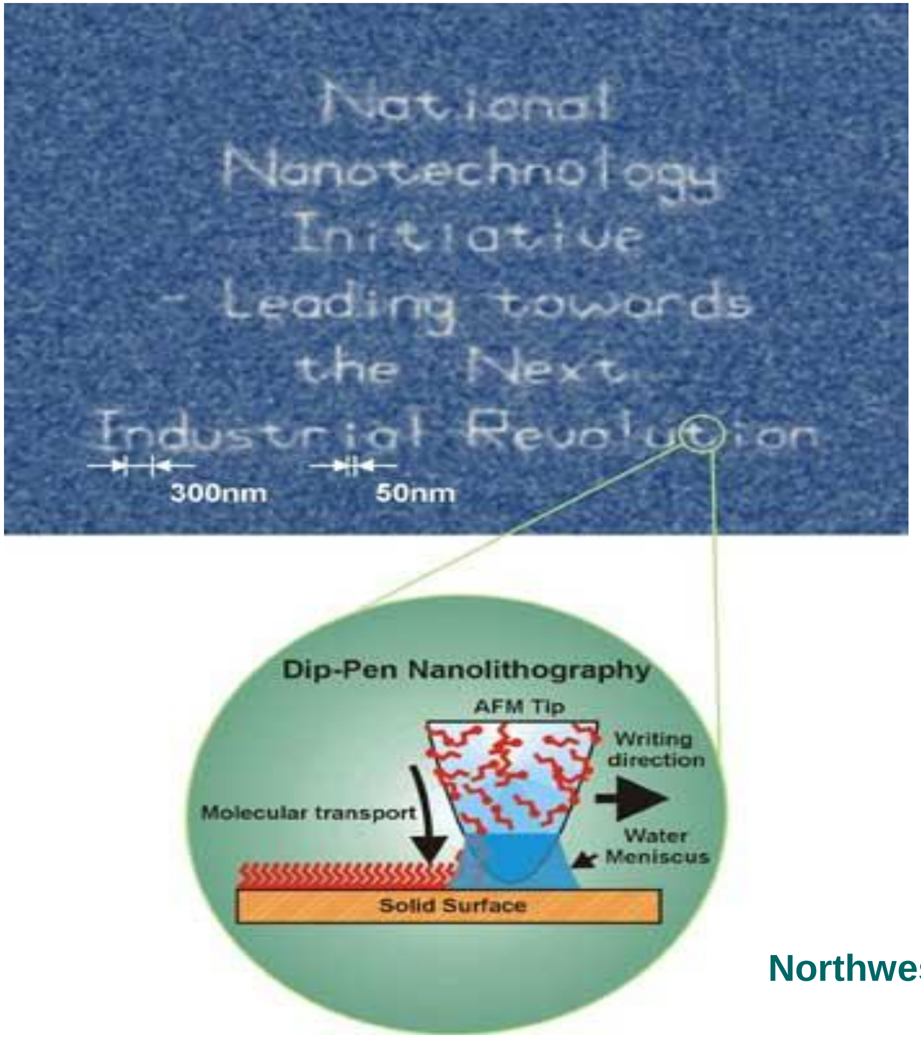
Dip-Pen Lithography

- Use a probe tip to write alkanethiols onto a surface.
  - Tip has a hole in it. “Ink” (e.g., thiols) is pumped through this hole like ink.
- Very slow process
  - Slower than e-beam because probe tip must be moved.
- Writes ~50 nm thick.

Dip-Pen Lithography



Writes sub-100 nm features

Moving the tip is SLOW

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Northwestern University Center for Nanofabrication and Molecular Assembly

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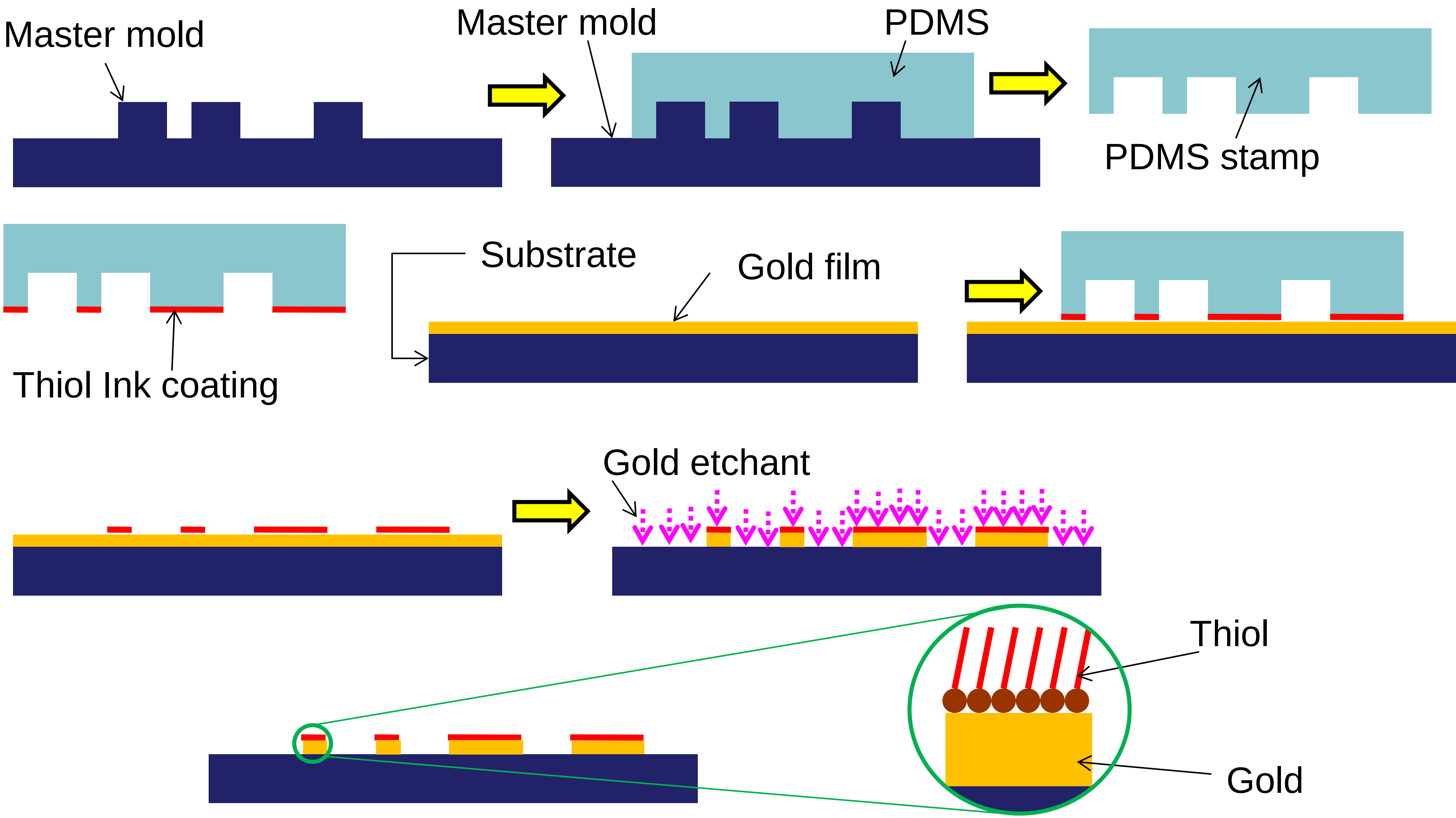
Stamp Lithography

- Printing with a stamp.
- Stamp made with photo, e-beam, etc lithography
- The stamp is used to carry and 'ink.'
- Can achieve feature sizes from microns to 50 nm.

Luesebrink, H. *Nanoimprint lithography: the semiconductor I ndustry and beyond*. Microlithography world Vol 15 No. 1 Feb 2006

Stamp Use


Master mold
Master mold
PDMS
PDMS stamp
Substrate
Gold film
Thiol Ink coating
Gold etchant
Thiol
Gold

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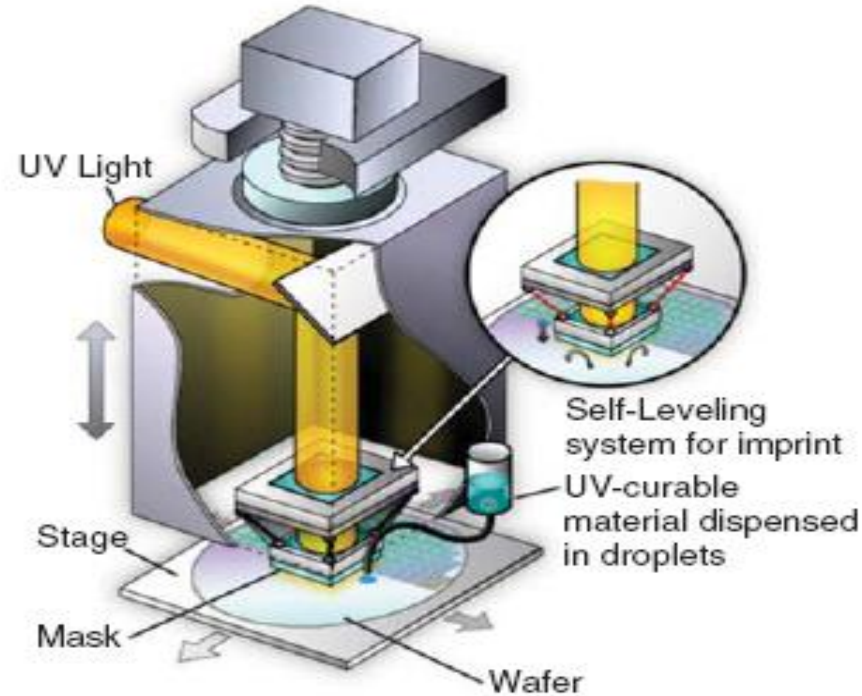
Imprint Lithography



Imprint pattern into a “resist”

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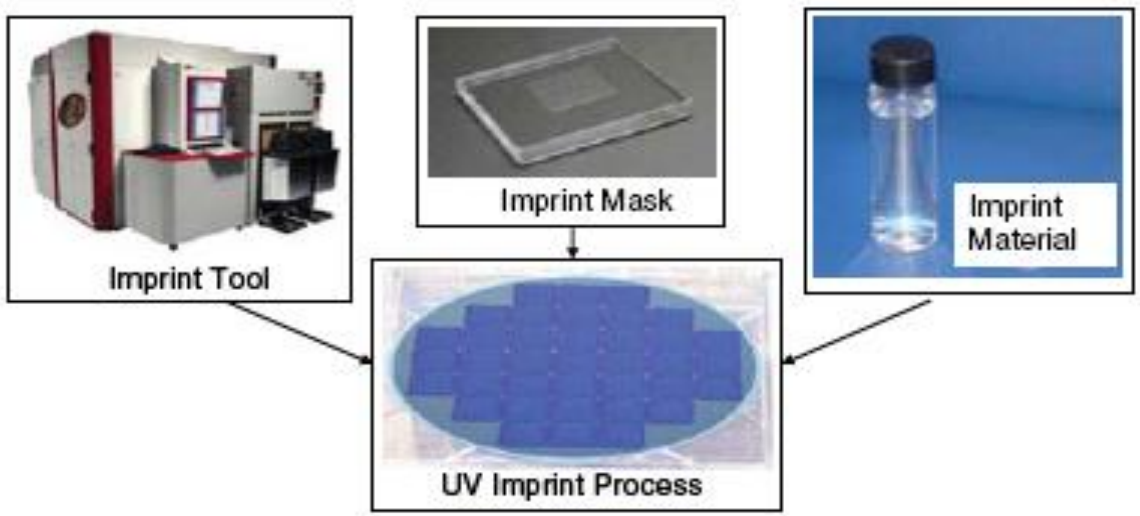
Imprint Lithography Process



. Building blocks of the ultraviolet (UV) imprint process: tool, mask, and material.

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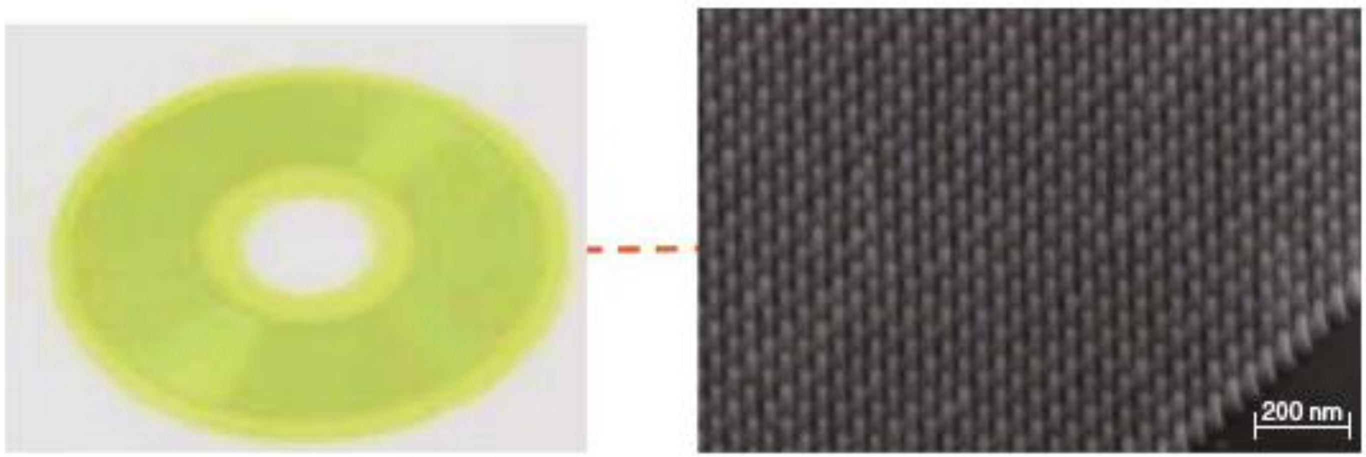
A Use of Imprint Lithography



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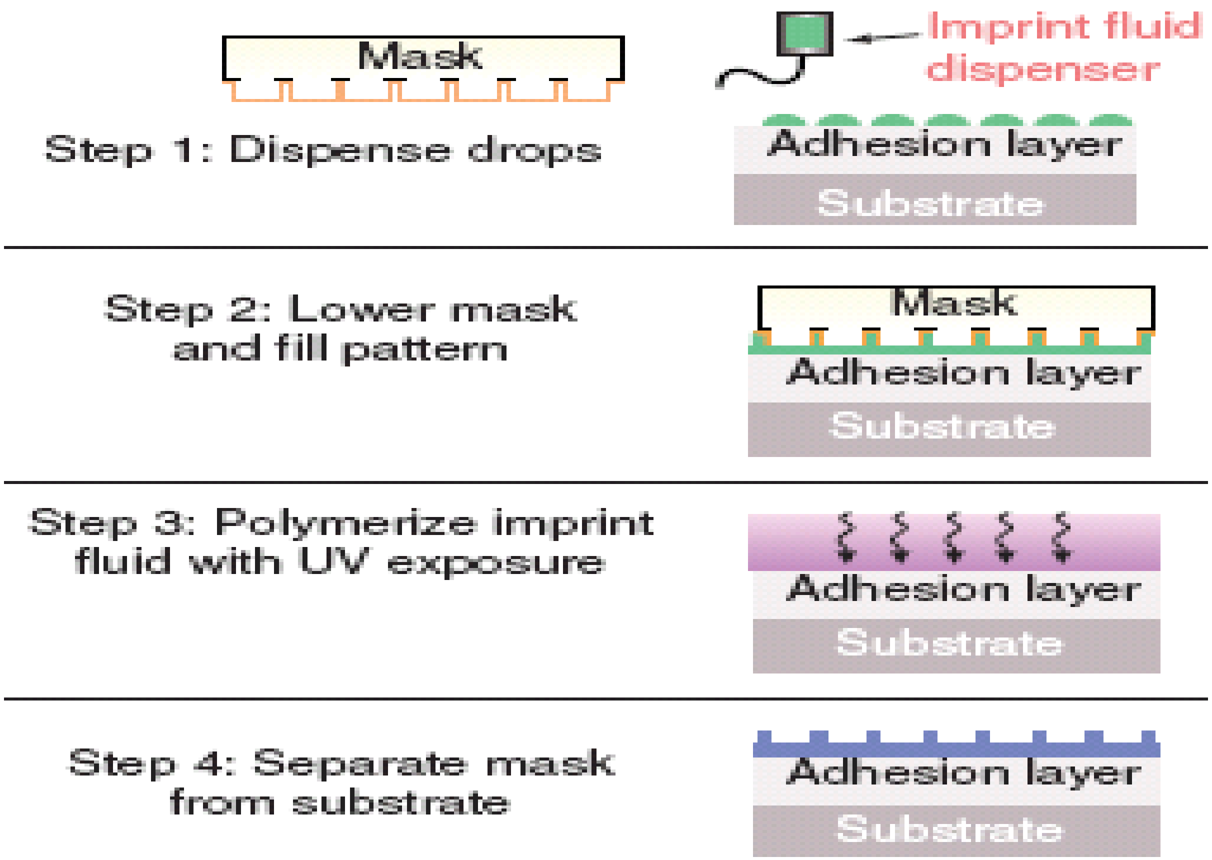
Step-and Flash
(A variation of imprint lithography)



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Block Copolymer Pattern Transfer

What are block copolymers?

1. Long organic molecules.
2. Diblock copolymers have 2 different polymer blocks covalently bound to each other.
3. Each block has a unique chemical composition.
4. The blocks are chosen, so that they want to separate from the other block like oil and water (hydrophobic and hydrophilic).

Block Copolymers

<u>Basic processing:</u>

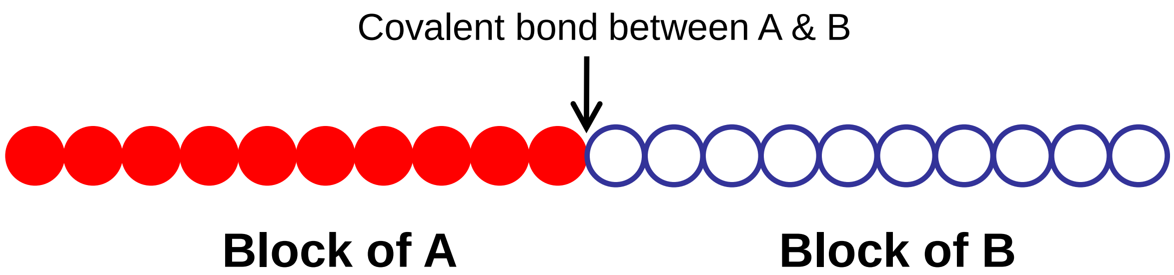
1. Dissolve block copolymer in an organic solvent (toluene or PGMEA).
2. Spin cast a thin film onto a neutralized surface.
3. Anneal block copolymer film in a vacuum oven to promote self-assembly.
4. Result = nano-patterned film on top of substrate.
5. Further steps are possible to selectively degrade or strengthen one block versus the other.

Block Copolymers

<u>Advantages:</u>

- Inexpensive compared to other types of lithography.
- No complex equipment need; just a spin coater and a vacuum oven.
- Can form nano-patterns over very large areas (whole wafers) in several simple steps.
- Pattern self-assembles.

More About Block Copolymers



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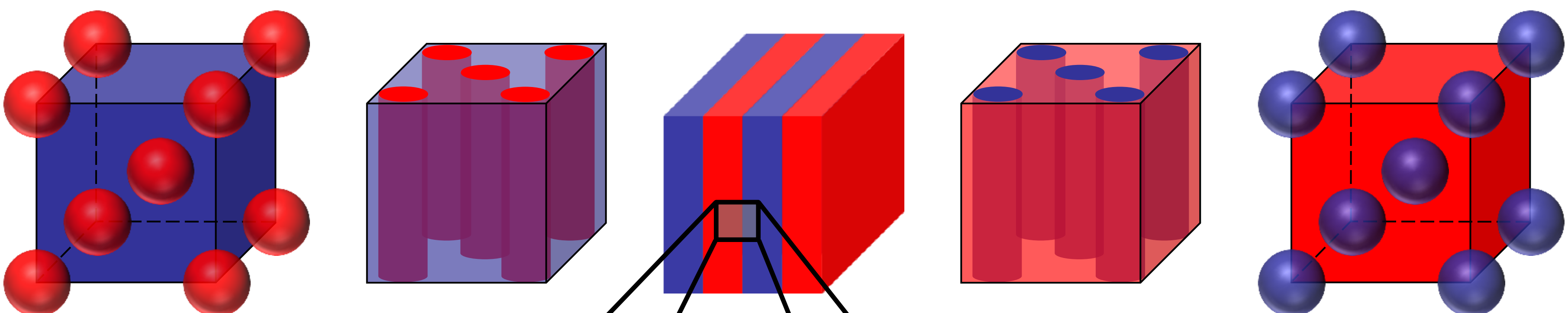
- If A and B do not like each other, they behave like oil and water.
- Phase separation: A only wants to be with A, and B only wants to be with B.
- But, the A block is covalently (permanently) attached to the B block.
- Blocks can phase separate but cannot move very far away from each other.
- However, the length of many useful block copolymers is in the nanometer range.

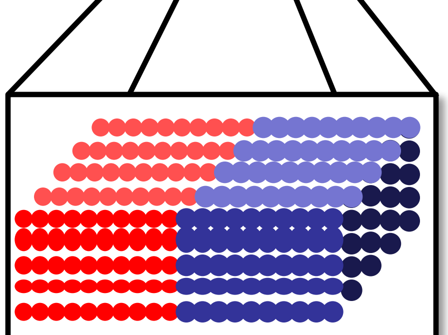
Phase separation of the blocks creates patterns on the nano-scale.

Block Copolymer Phases

Increasing Length of A → **← Increasing Length of B**

20:80	30:70	50:50	70:30	80:20
Spheres of A	**Cyl of A**	**Lamellae**	**Cyl of B**	**Spheres of B**





Minimization of surface area between two incompatible phases

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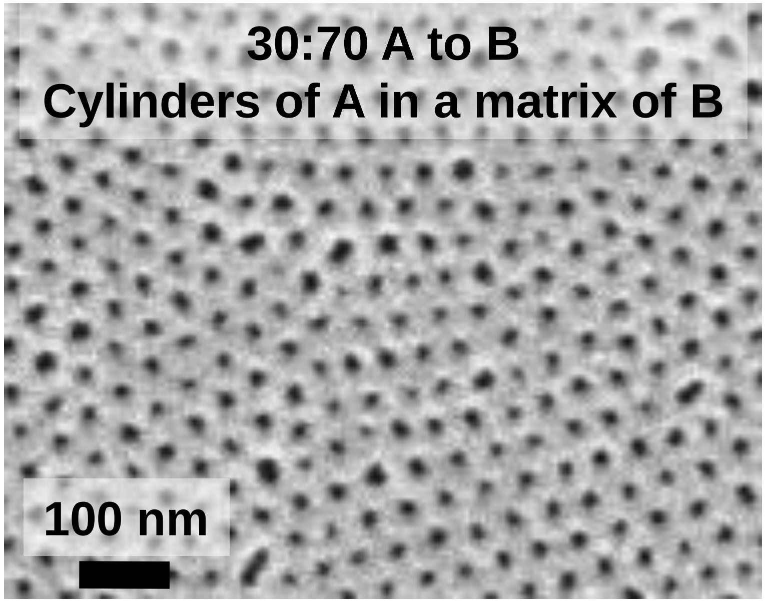
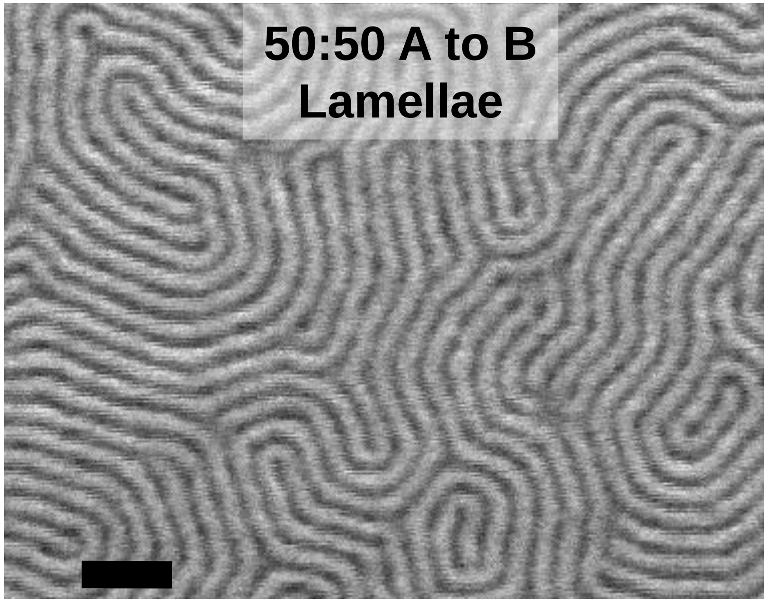
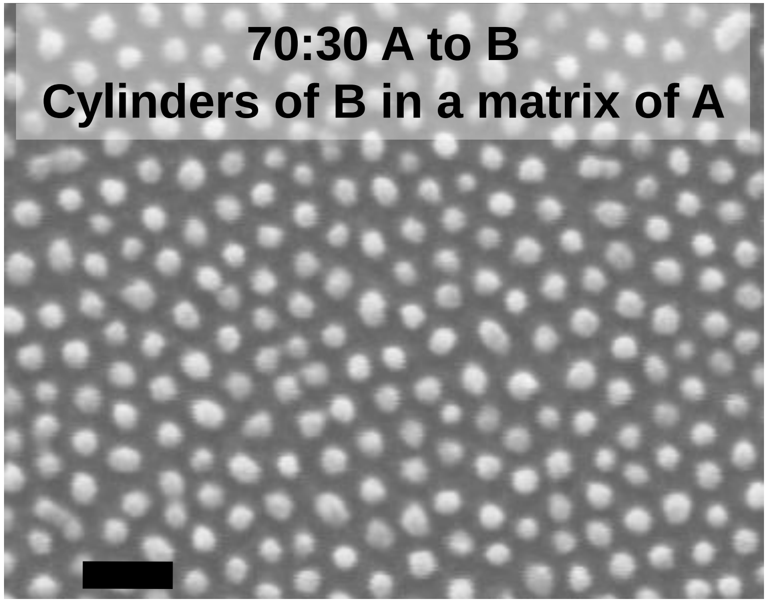
Images of Block Copolymers







Increasing size of A block

Decreasing size of B block

Overall size (A + B)
remains constant

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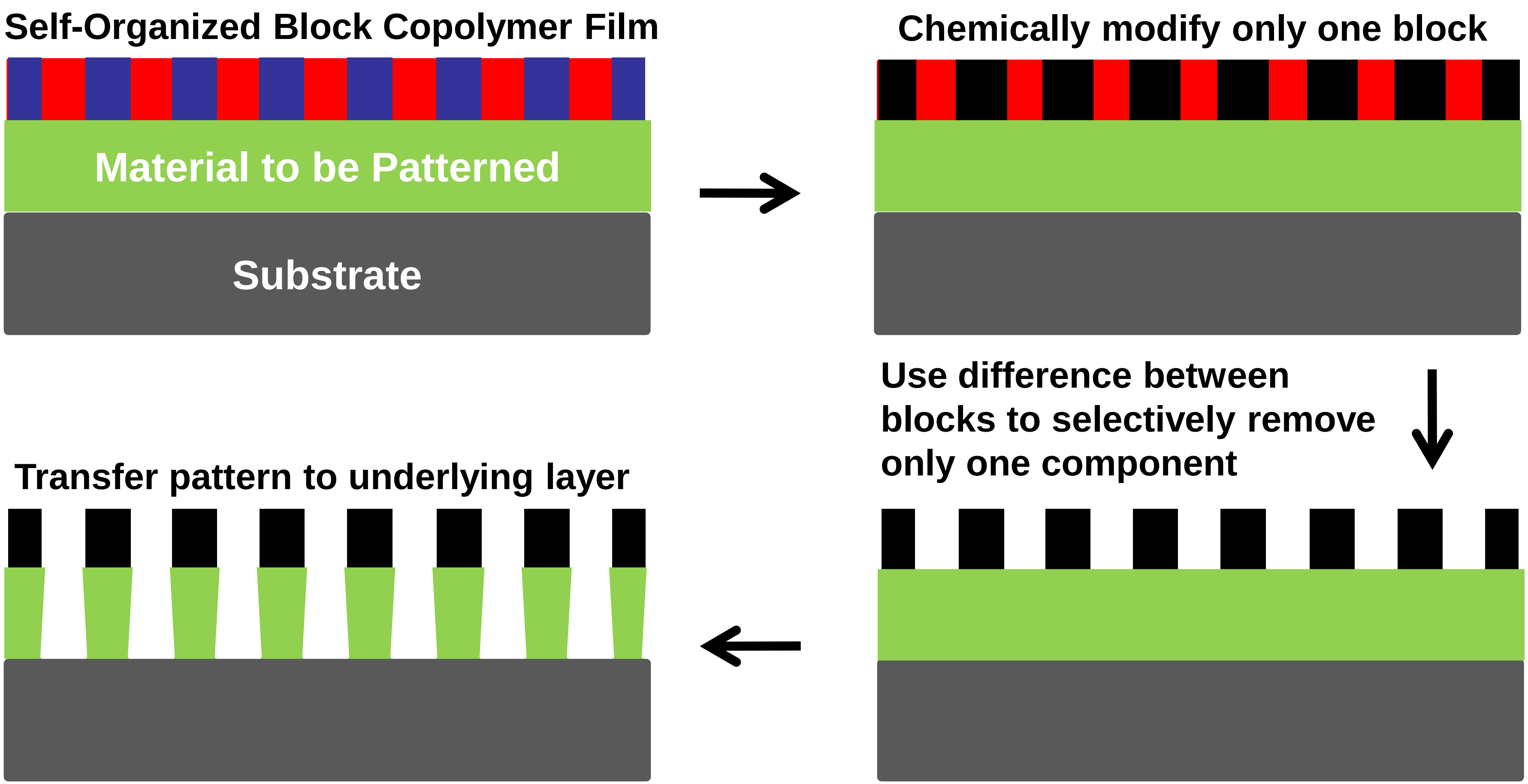
Examples of Block Copolymers

- Polystyrene-*block*-poly(methyl methacrylate): PS-*b*-PMMA
- Polystyrene-*block*-poly(ethylene oxide): PS-*b*-PEO
- Poly(2-vinylpyridine)-*block*-polydimethylsiloxane: P2VP-*b*-PDMS

…and many, many more!

Nano-Pattern Development and Transfer Using Block Copolymers



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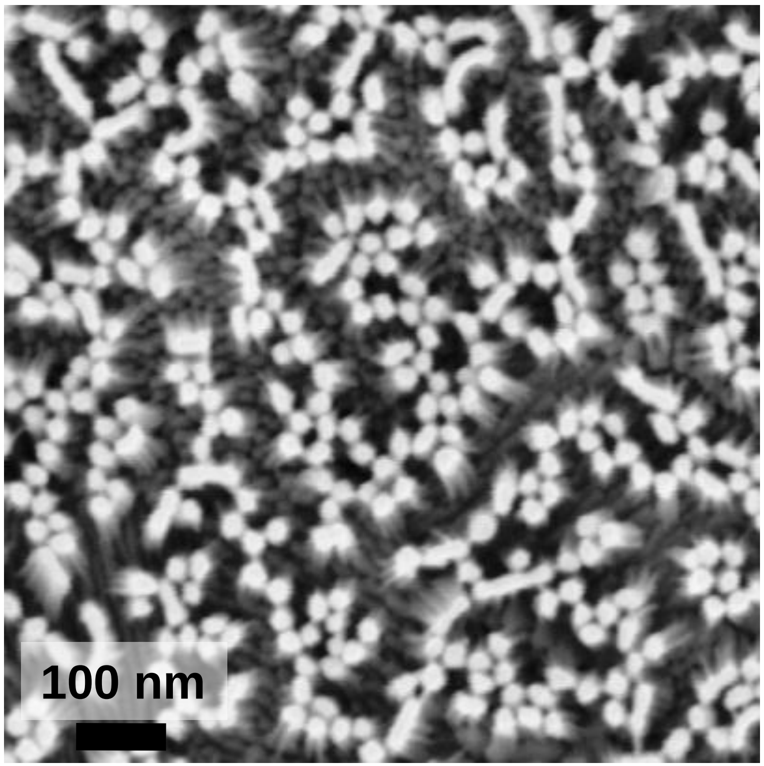
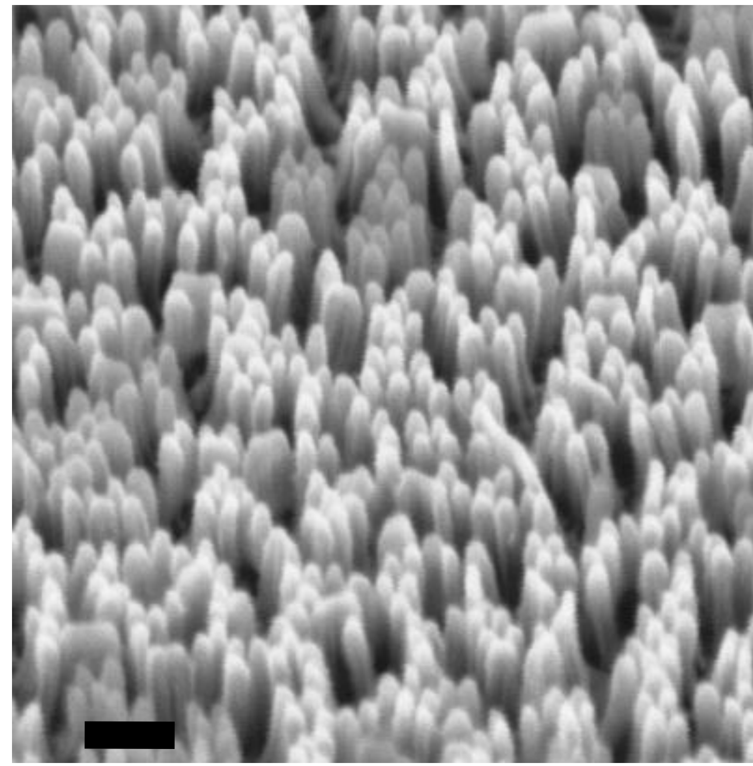
Images of Nano-Structures

Top View



Side View



Notes: Some of the unique issues that must be addressed at the nano-scale can be seen here in the top view. Nano-rods that have been produced have tended to coalesce into bundles. Possible causes: (1) van der Waals interaction, (2) Casimir effect. Generally, this coalescing must be avoided.