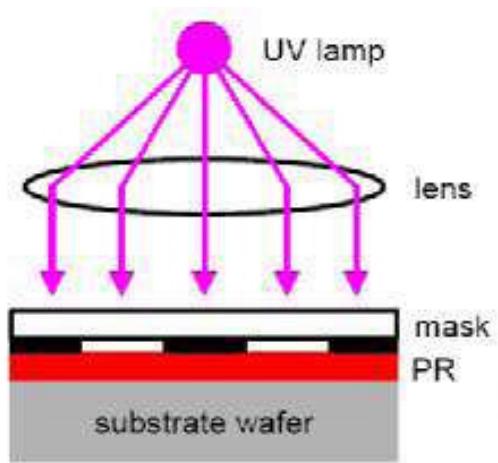


Photolithography and resolution enhancement techniques (RET)

1. Photolithography and resolution limit
2. Immersion lithography
3. Off-axis illumination (OAI)
4. Phase-shift mask (PSM)
5. Optical proximity correction (OPC)
6. Double processing

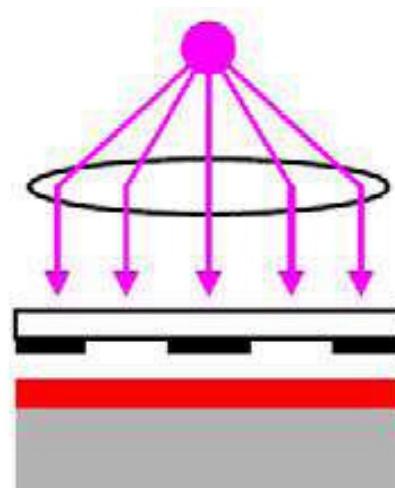
Optical lithography

Contact aligner



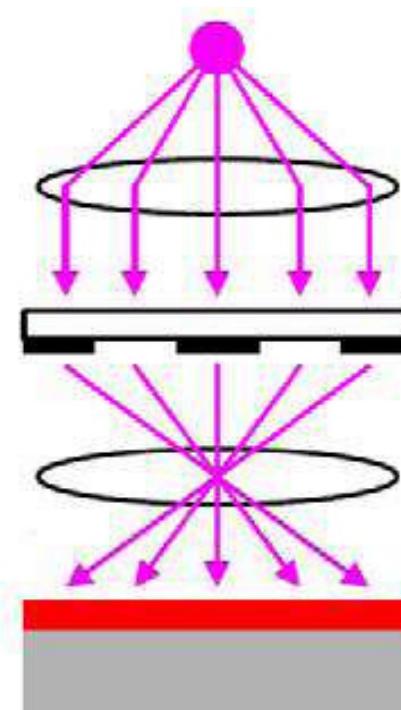
Mask in contact with
photo-resist film
(Gap=0 μm)

Proximity aligner



Gap (order 10μm)
between mask
photoresist

Projection aligner



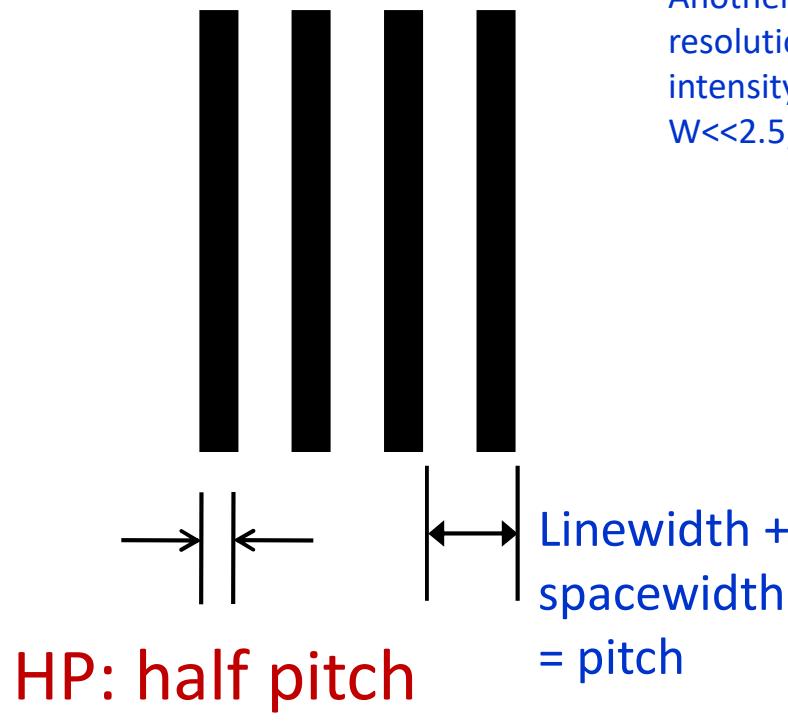
Like photography, imaging

Resolution: $\frac{3}{2} \sqrt{\lambda(g + t/2)}$
(g=gap, t=resist thickness)

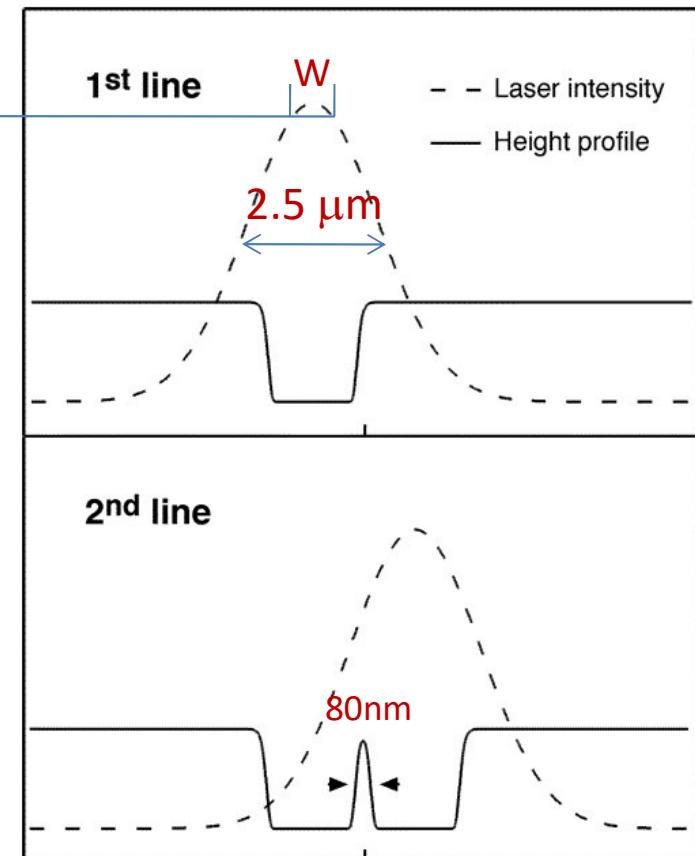
Contact and proximity is for research (simple, cheap equipment, but mask wear).
Projection for IC production, long mask life, image reduction (4×).

It is easy to make small, but difficult to make dense

- To put a lot of transistors on a chip, they need to be close to each other.
- Pitches are limited by physics – minimum line-widths are not!
- The IC term for lithography is “half pitch”, though “resolution” is still used.



Another way for high resolution: threshold intensity here will give $W << 2.5 \mu\text{m}$.

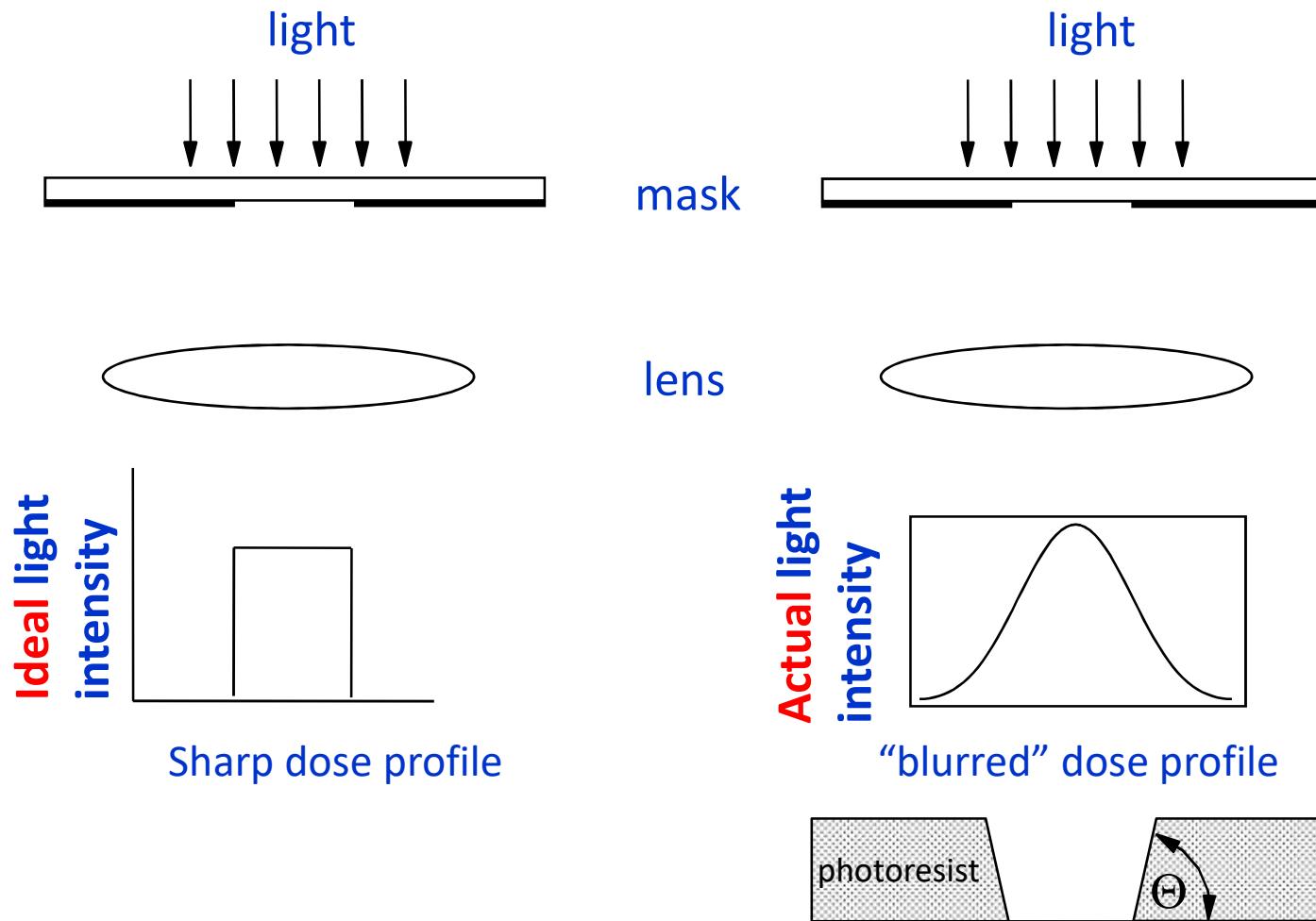


Is this positive or negative resist?

Nano. Lett. 6(10), 2358(2006)

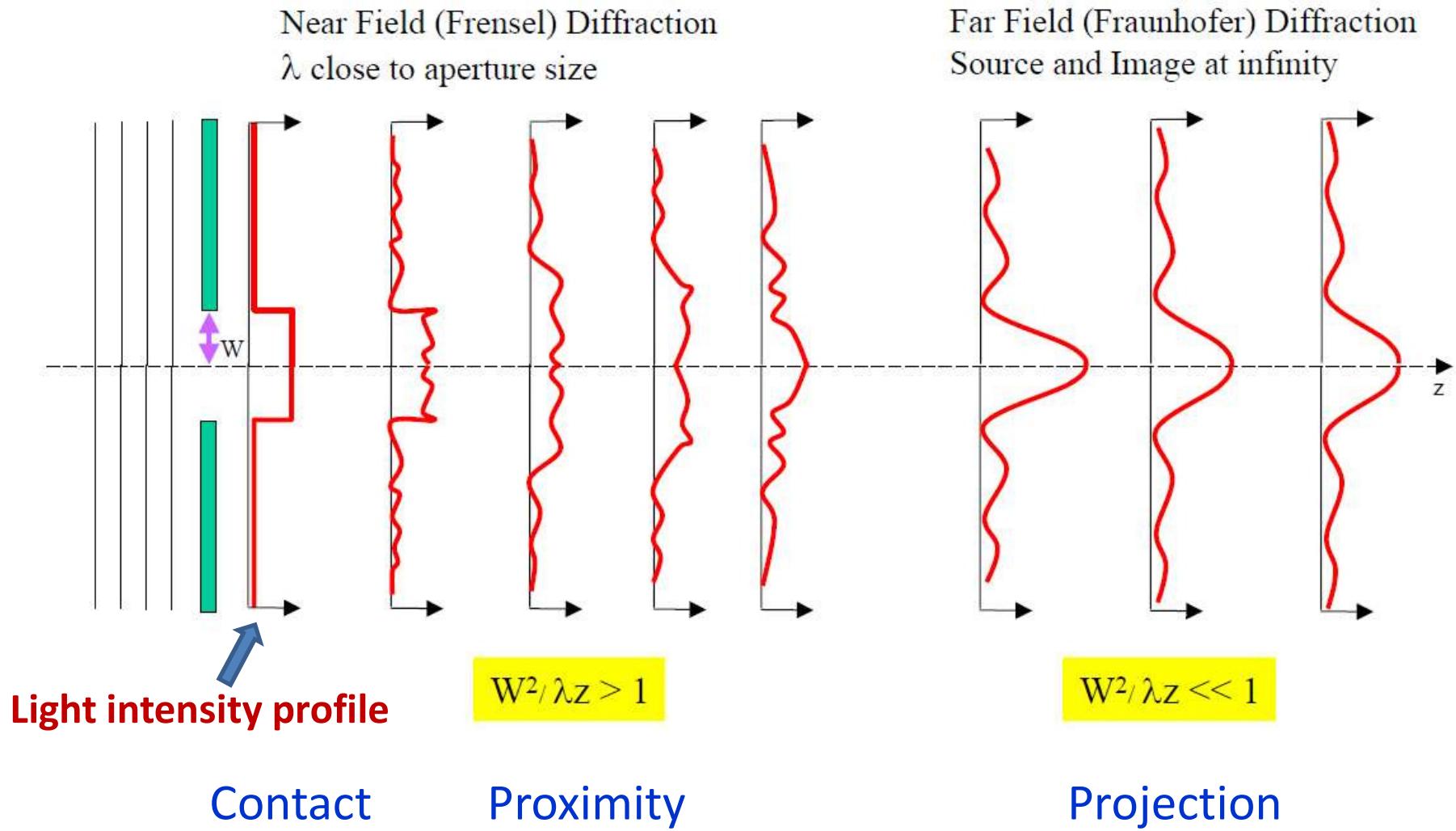
2.5 μm laser beam can pattern 80nm line-width!
But it won't be able to pattern a grating with pitch $< 2.5 \mu\text{m}$.³

What is hard about nanolithography?

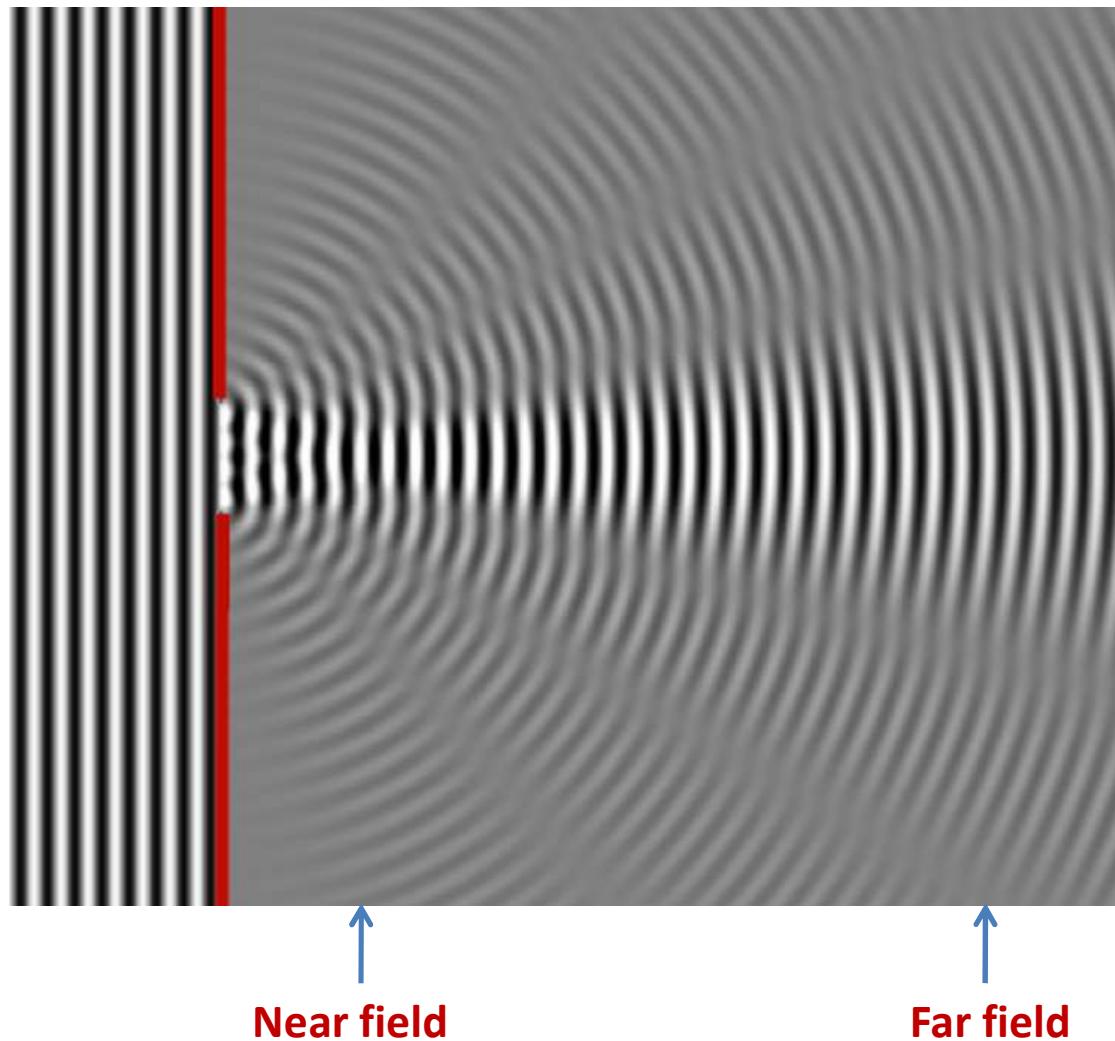


Final profile is determined by MTF and resist contrast

Fresnel & Fraunhofer diffraction (from an aperture)



Fresnel & Fraunhofer diffraction (from an aperture)



The HP (half pitch, ~resolution) is limited by diffraction of light.

Light diffraction through a small circular aperture (Airy disk)

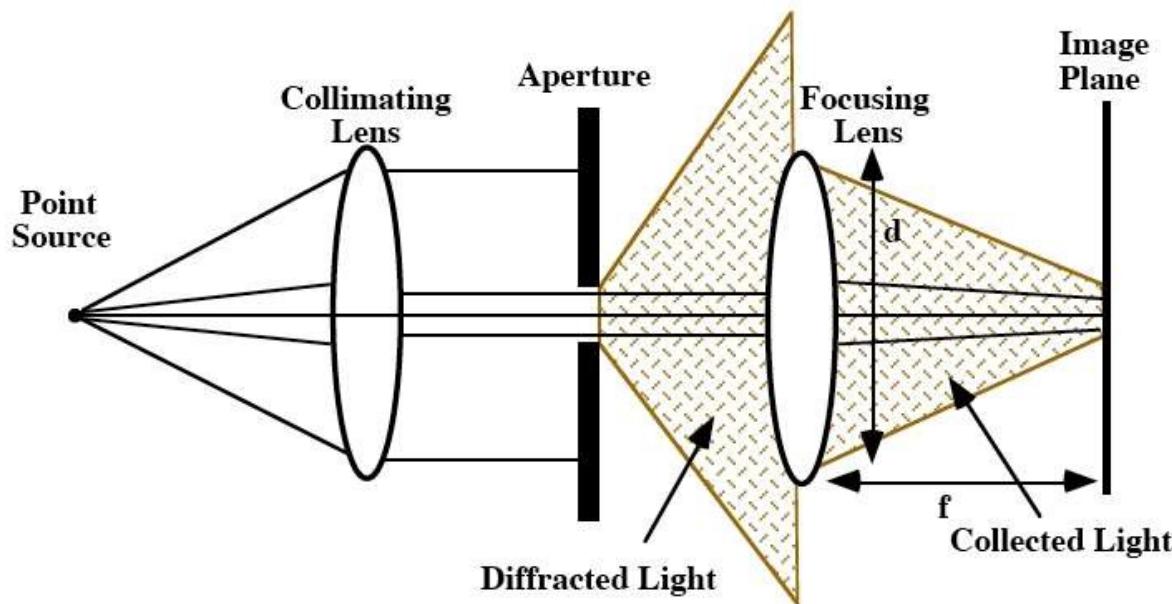
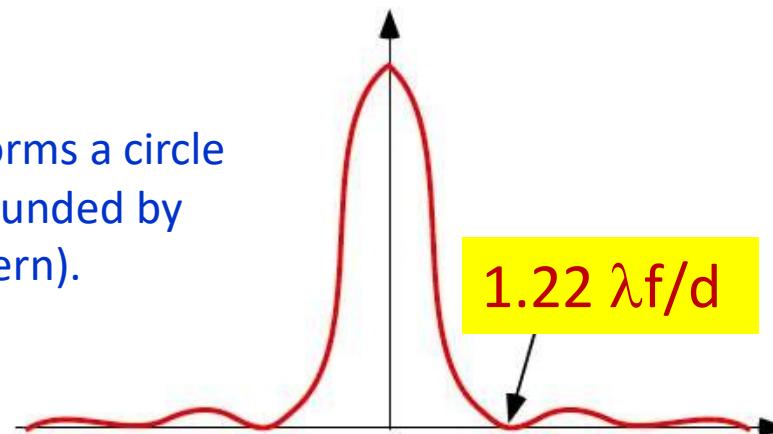
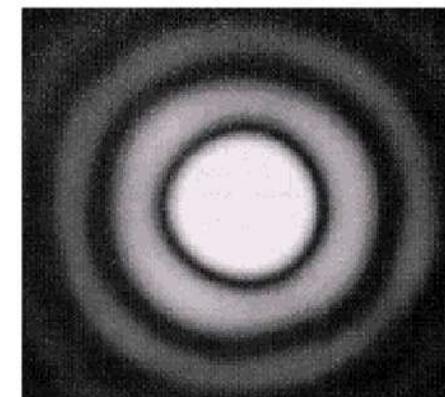


Image by a point source forms a circle with radius $1.22\lambda f/d$ surrounded by diffraction rings (Airy pattern).

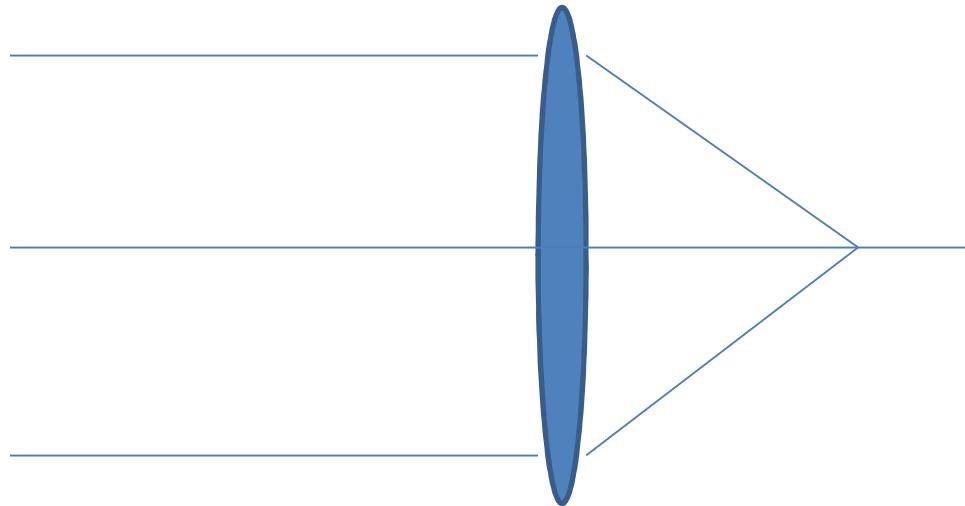


Airy pattern

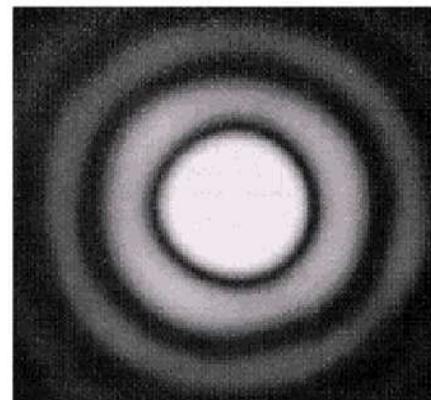


For resolution, we care about the minimum feature size (or half pitch) on the resist surface, and the object that forms this image is less important.

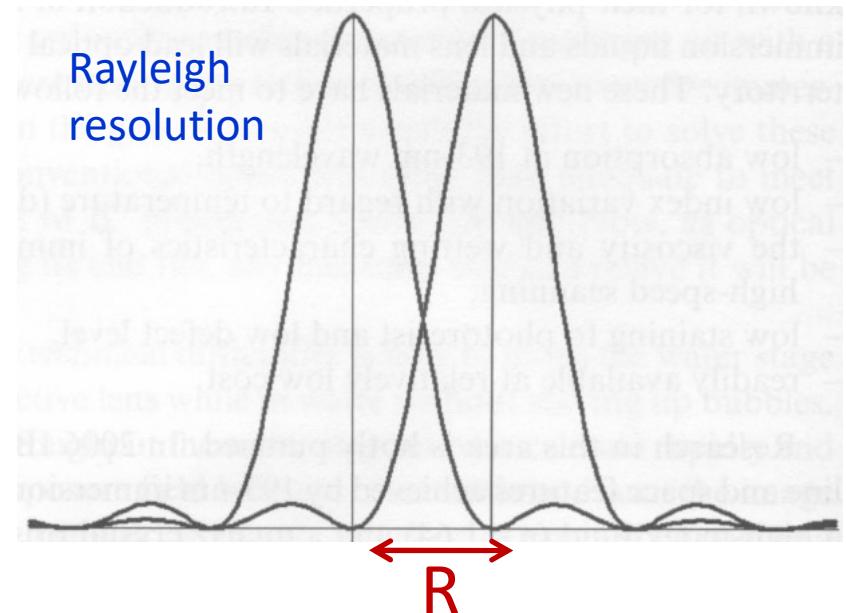
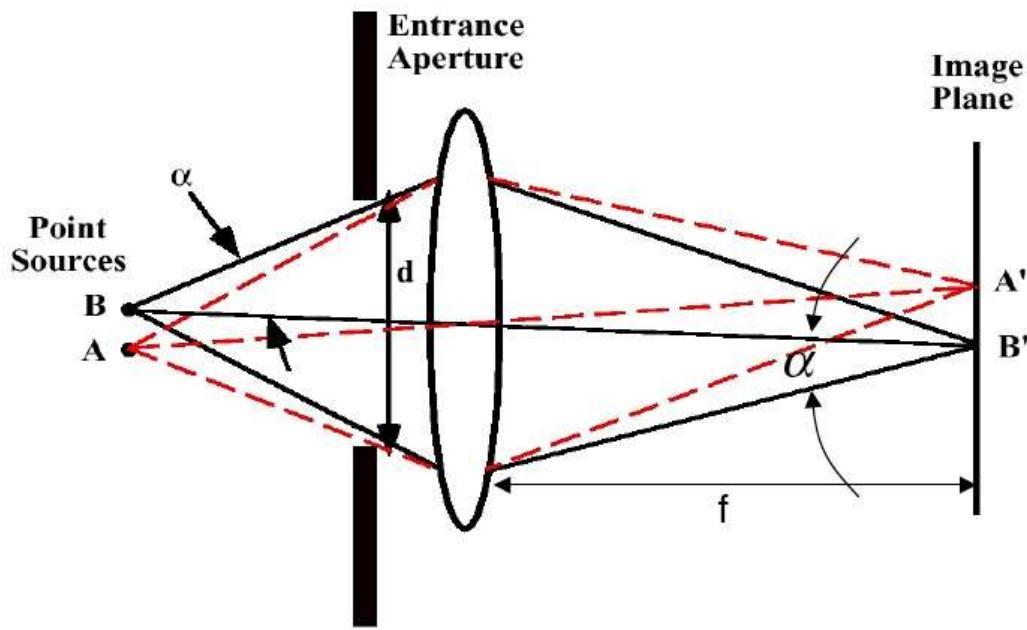
A plane wave goes through a lens will be focused to the focal point, and the actual light intensity profile at the focal point is below:



Airy pattern



Rayleigh resolution criteria (for circular aperture)



$$R = \frac{1.22 \lambda f}{d} = \frac{1.22 \lambda f}{n(2f \sin \alpha)} = \frac{0.61 \lambda}{n \sin \alpha} = \frac{0.61 \lambda}{NA}$$

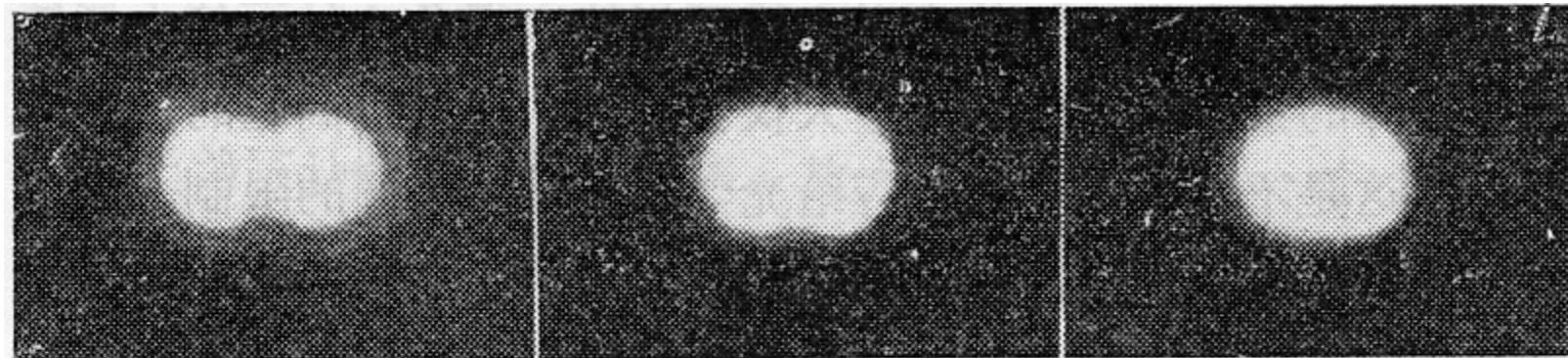
NA= $n \cdot \sin \alpha$, numerical aperture

NA: the ability of the lens to collect diffracted light

In fact, image plane is not the same as focal plane.

For $\frac{1}{4}$ reduction, image plane is $5/4 \times f$ (mask plane is $5 \times f$).

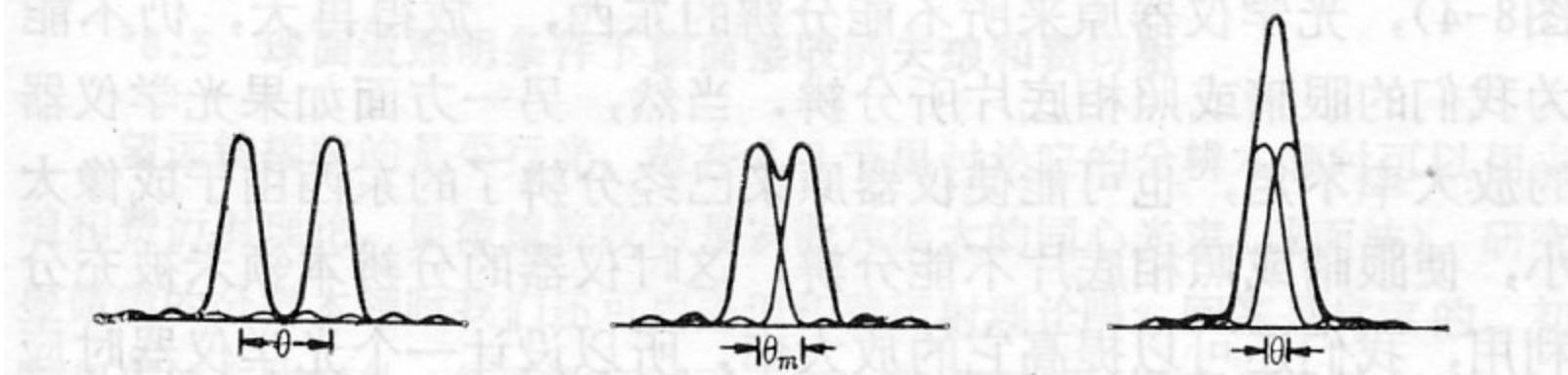
Rayleigh resolution criteria (for circular aperture)



Well-resolved

Just resolved

Not resolved



Generalized resolution (half pitch)

$$R = k_1 \frac{\lambda}{NA}$$

k_1 represents the ability to approach physical limits depending on:

- Lenses: aberrations.
- Resists: contrast.
- Equipment and process control in manufacturing.

To increase resolution: reduce λ and k_1 , increase NA;

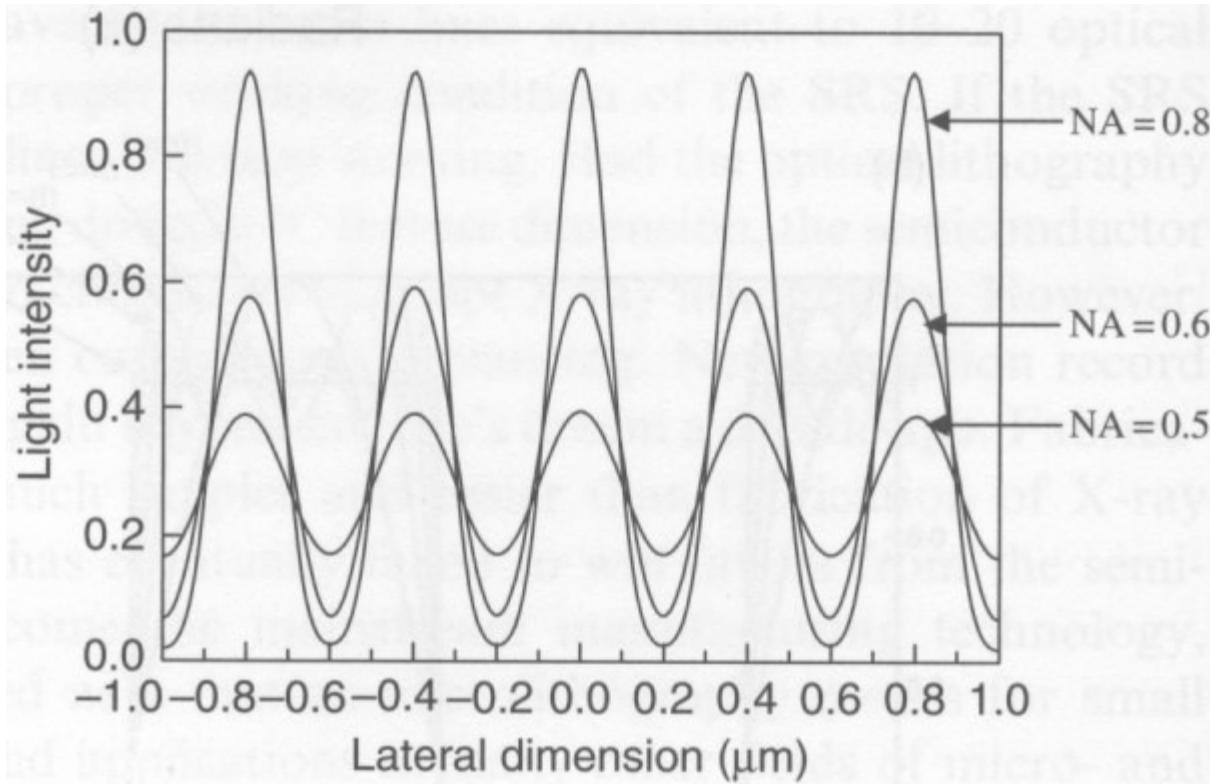
But this also reduces depth of focus.

Depth of Focus or Depth of Field (DOF):

$$DOF = k_2 \frac{\lambda}{(NA)^2}$$

For a camera, a small lens/small NA (like a cell phone) has very deep depth of focus.

NA: its influence on optical imaging by numerical simulation

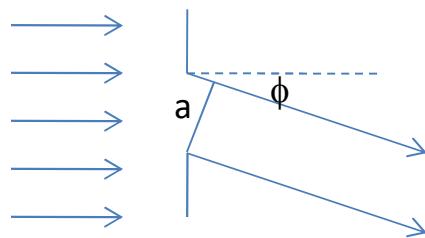
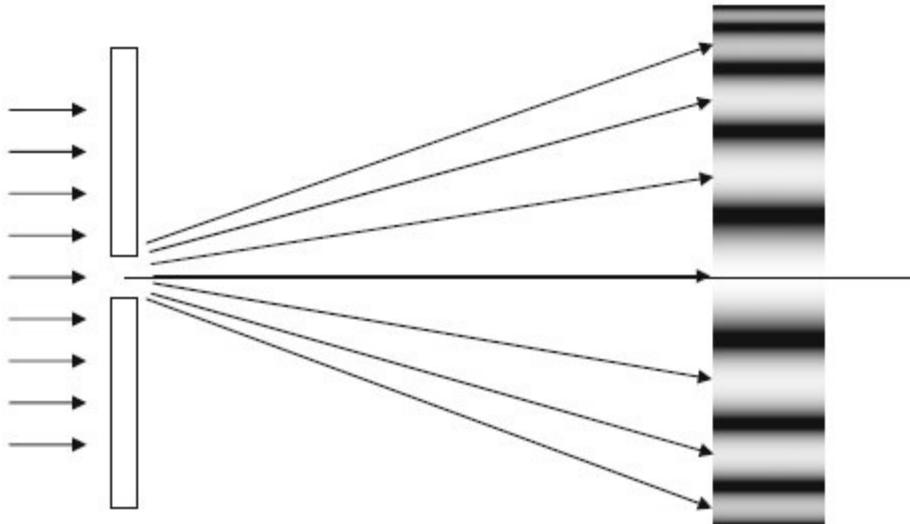


1.6 μm pitch grating photo-mask imaged through a projection optical system at $\lambda=248\text{nm}$.

Increase NA:

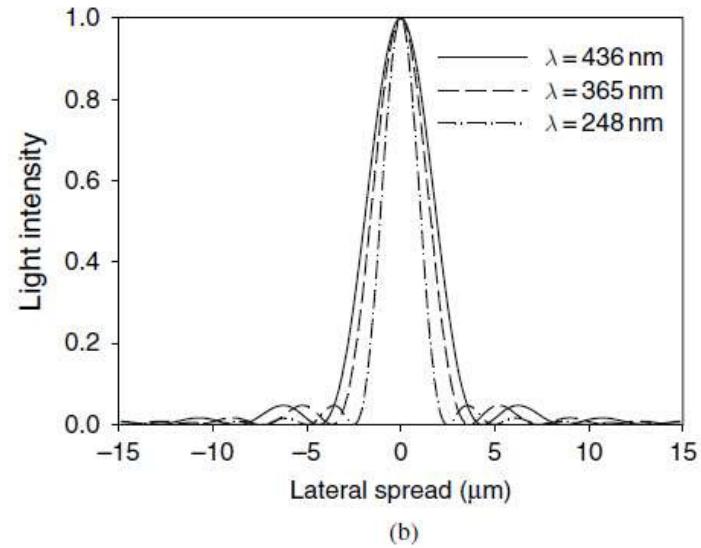
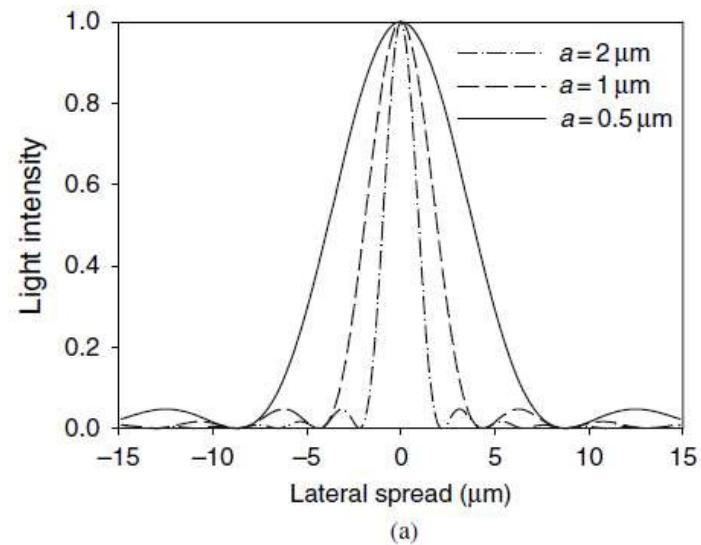
- Resolve better the line image (higher image contrast)
- Gives brighter image (higher image intensity).

Diffraction from a slit



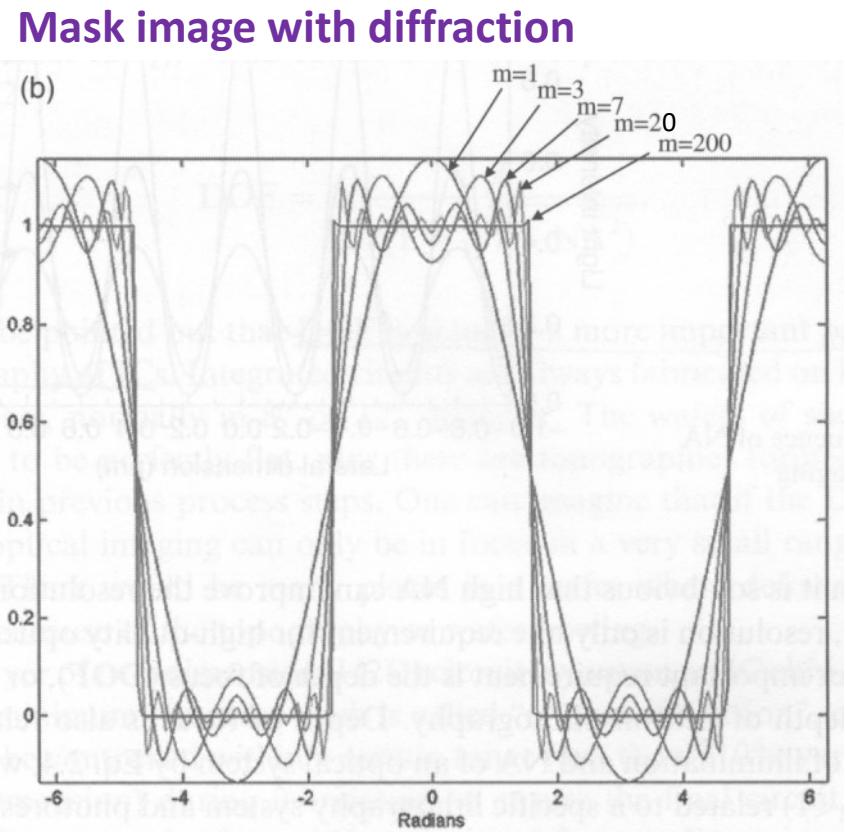
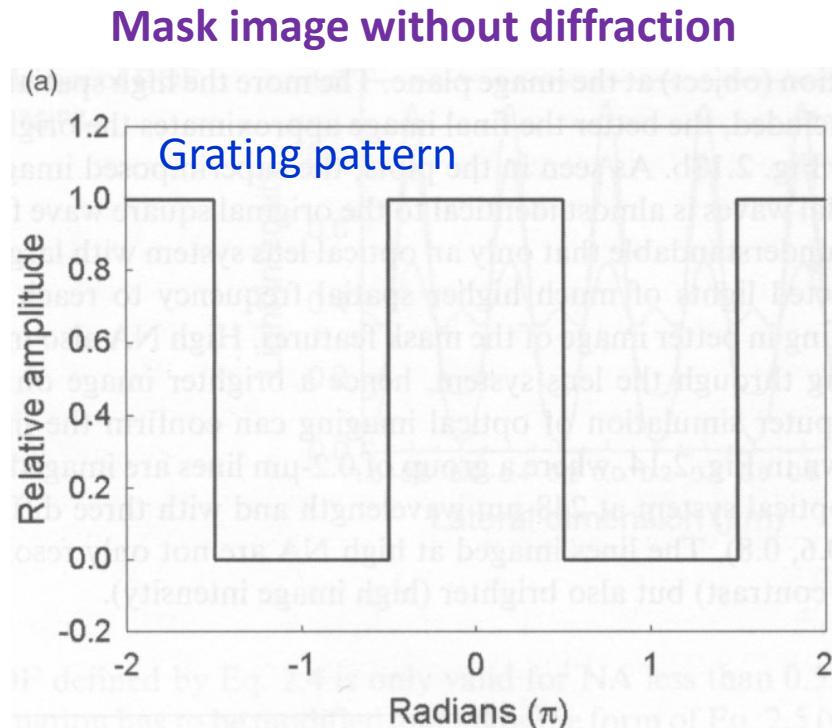
Minimum when
 $a \cdot \sin\phi = m\lambda$, or
 $\sin\phi = m\lambda/a$
 $m=1, 2\dots$

If put a lens in-between, resolution
(similar to Rayleigh resolution criteria)
 $R=0.5\lambda/\sin\alpha=0.5\lambda/NA$ (i.e. for slit, $k_1=0.5$)

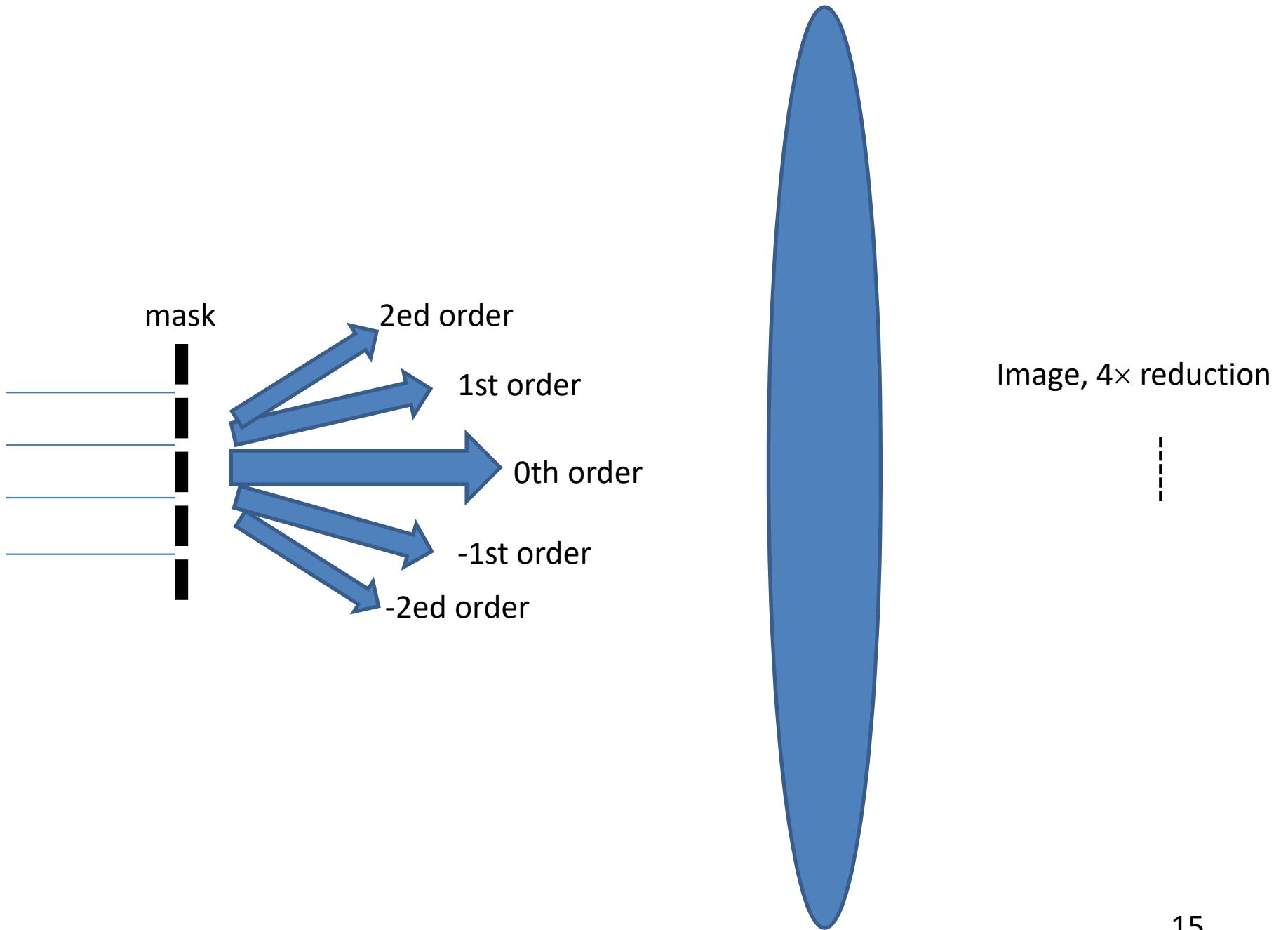


Light intensities of three single-slit diffractions:
(a) at 436-nm wavelength; and (b) for 1 μm slit width.

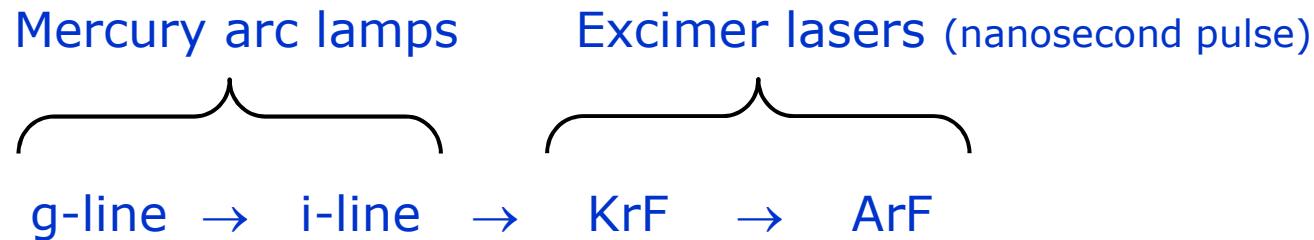
NA: effect of including increasing numbers of diffracted orders on the image of a periodic slit array



- For smaller NA (smaller $\sin\alpha$), fewer diffracted orders (smaller m) will be collected to form the image, so the details of the slit (sharp corners) are lost.
- **When talking about resolution, we need at least $m=1$.**
- The way to increase resolution is to increase the NA of the lens (and reduce λ).



Increase resolution by reducing λ



436 nm → 365 nm → 248 nm → 193 nm

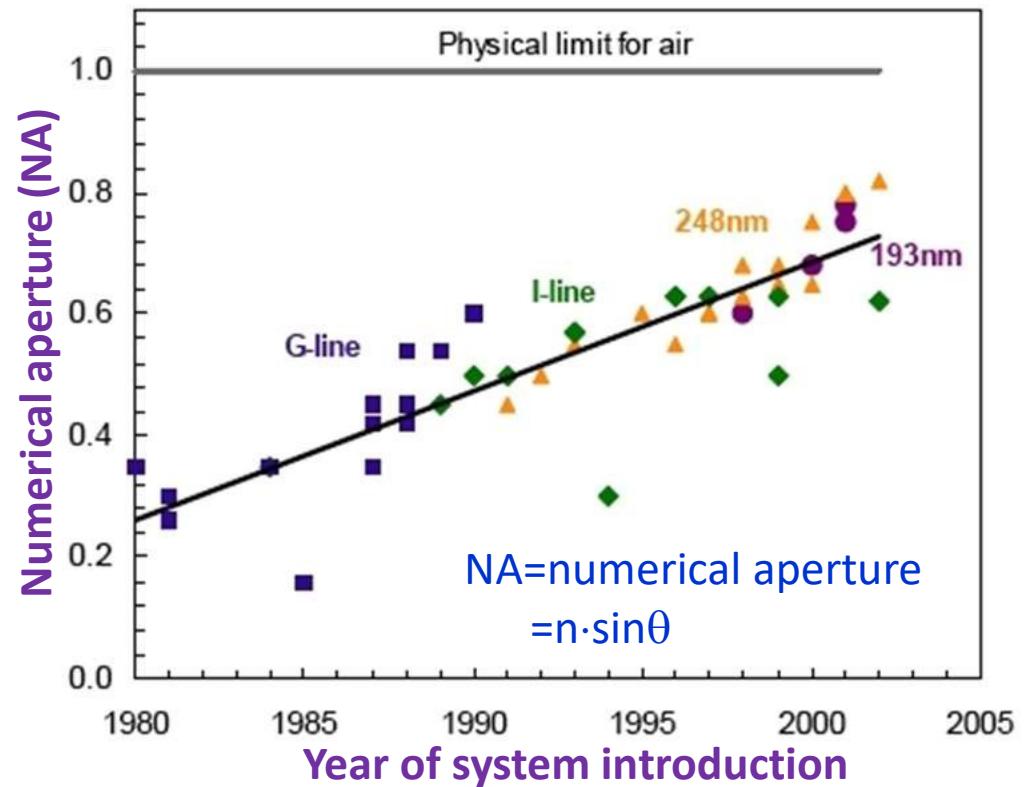
1 —————→ 0.44×

	$R \gg \lambda$	$R > \lambda$	$R \sim \lambda$	$R \ll \lambda$
Minimum feature size (nm)	7000–1000	1000–350	350–180	180–32
Lithography wavelength (nm)	436 (G-line)	365 (I-line)	248 (DUV)	193 (DUV)

Increase resolution by increasing numerical aperture NA to approach 1

- The physical limit to NA for exposure systems using air as a medium between the lens and the wafer is 1.
- The practical limit is somewhere ~ 0.93 (collecting angle $\alpha=68^\circ$, huge lens $\sim 500\text{kg}$).
- One issue for large NA is polarization of illumination light near Brewster's angle.
- Therefore, the resolution limit for 193nm exposure systems:

$$R = \frac{k_1 \lambda}{NA} \leq \frac{0.25 \times 193}{0.93} = 52\text{nm}$$



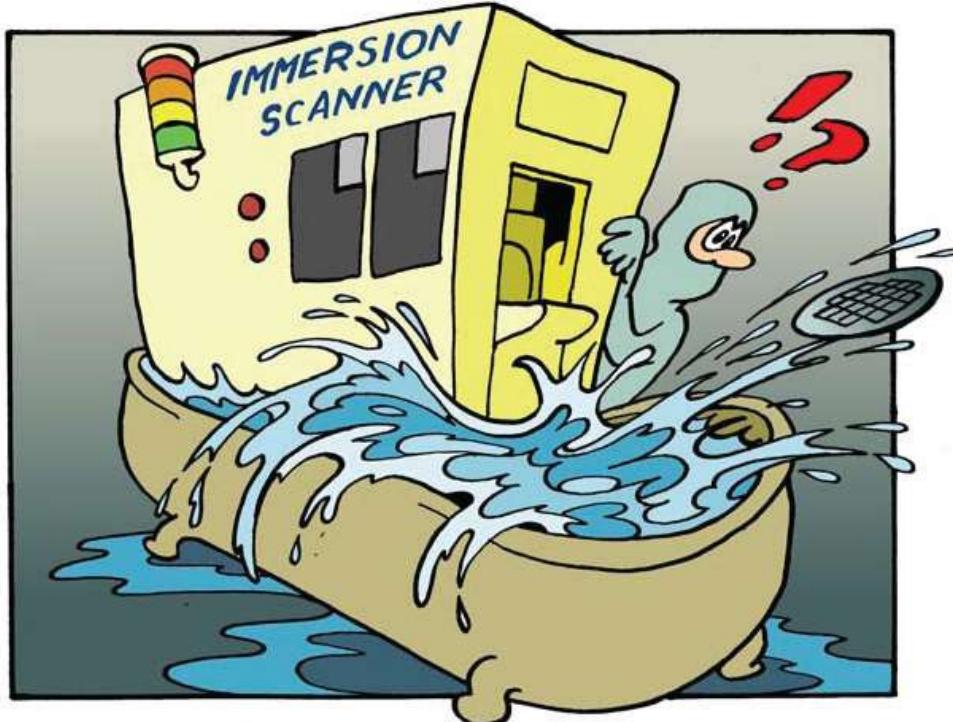
Photolithography and resolution enhancement techniques (RET)

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Increase resolution by increasing NA to beyond 1: immersion lithography

- Very simple idea. Indeed, immersion is NOT new for optical imaging: oil immersion in optical microscope has been used for a century.
- But Immersion lithography is highly complex, and was adopted by semiconductor industry only recently (since 2004).

From research idea



to development



Immersion lithography has been considered as impractical at the beginning.

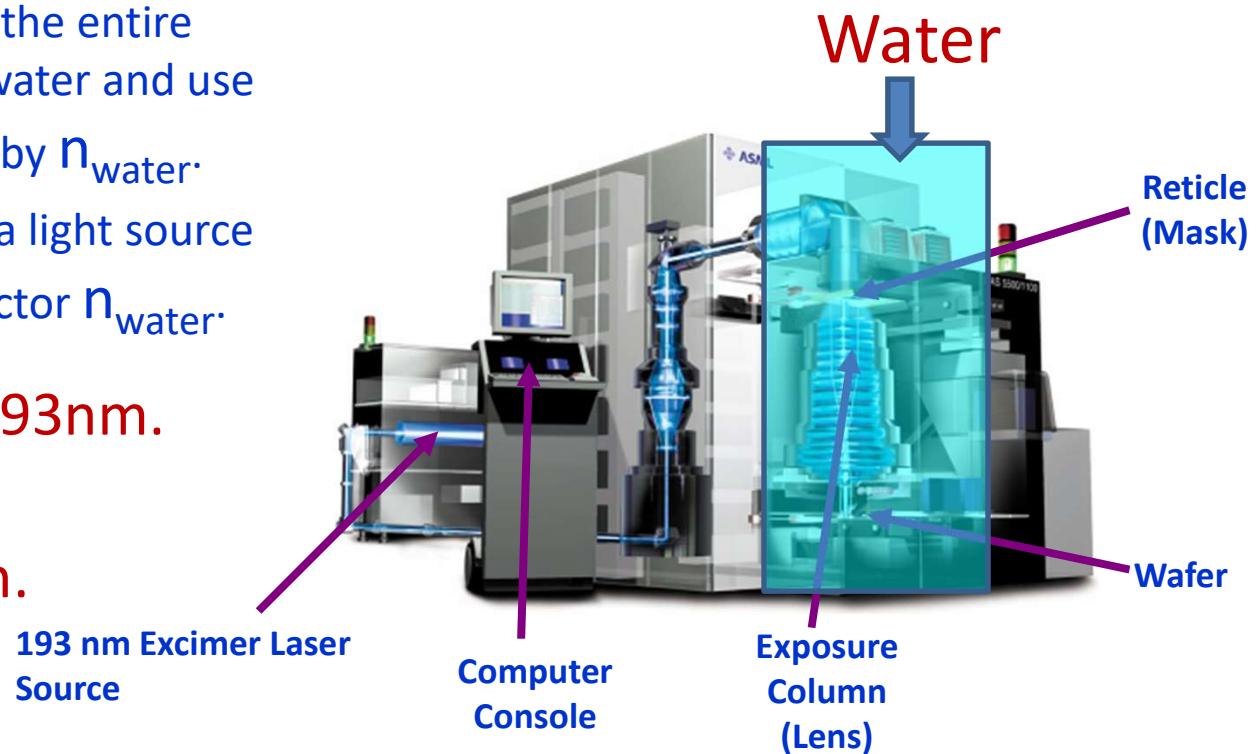
“Total” immersion

$$R = k_1 \frac{\lambda}{NA} = k_1 \frac{\lambda}{n \sin \theta} = k_1 \frac{\lambda / n}{\sin \theta} = k_1 \frac{\lambda'}{\sin \theta}$$

In principle, one can put the entire exposure system inside water and use lens having n multiplied by n_{water} . This is equivalent to use a light source having λ reduced by a factor n_{water} .

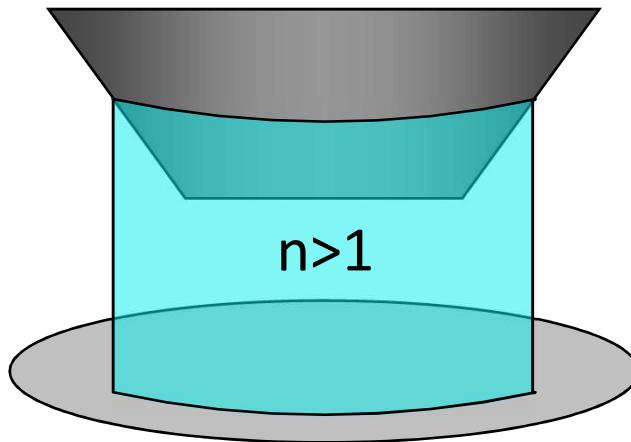
$n_{\text{water}} = 1.44$ at 193nm.

So λ : 193 → 134nm.

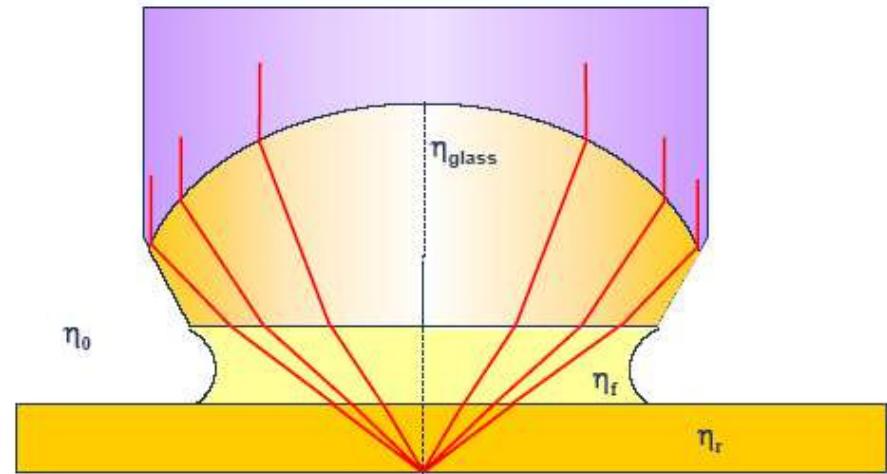


However, total immersion is not practical, and is not necessary.

Immersion between projection lens and wafer



Snell's law : $NA = \eta_0 \sin \theta_0 = \eta_f \sin \theta_f = \eta_r \sin \theta_r$



The medium between the lens and the wafer must:

- Have low optical absorption at 193nm
- Be compatible with photoresist and the lens material
- Be uniform and non-contaminating

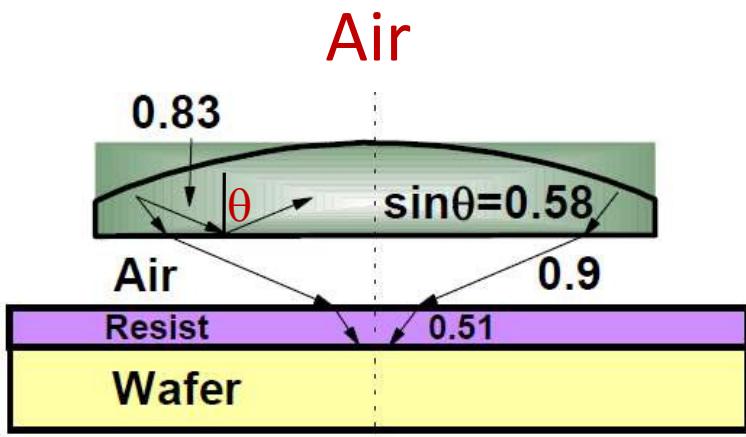
$NA = n \times \sin \alpha \propto n$
Can be >1 for $n > 1$

Surprisingly, ultrapure water meets all of these requirements:

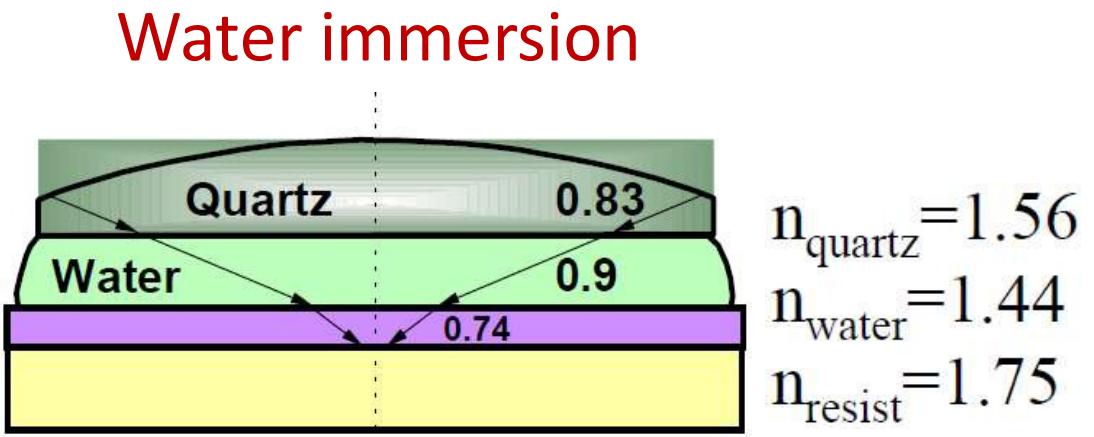
$n = 1.44$, absorption of $<5\%$ at working distances of up to 6mm, compatible with photoresist and lens, non-contaminating in its ultrapure form.

Why immersion lithography increases resolution?

Fundamentally, light is a carrier of information on the mask. When more light is collected, more information is collected, leading to higher resolution – can resolve denser line array pattern.



For NA=0.9, inside lens
 $\sin\theta=0.9/1.56=0.58$ ($\theta=35.5^\circ$)
Total internal reflection for
 $\sin\theta>1/1.56=0.64$ ($\theta=39.8^\circ$)



Inside lens $\sin\theta=1.44 \times 0.9/1.56=0.83$ ($\theta=56^\circ$)
So light, which is internally total-reflected for air, can now be collected to form image in the resist.

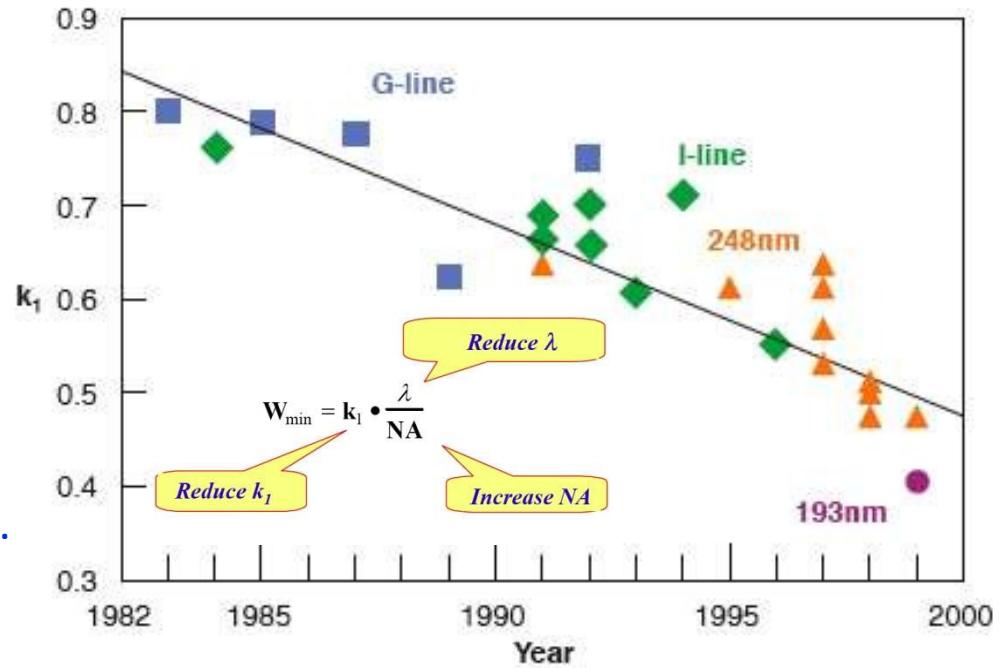
Collect light up to $\theta=35.5^\circ$;

NA=0.9 in air; NA=1.44×0.9=1.3 in water

Collect light up to 56° (angle inside lens)

Photolithography - k_1

- k_1 is a complex factor of several variables in the photolithography process such as:
 - Quality of the photoresist
 - Use of resolution enhancement techniques (RET)
 - Off-axis illumination (OAI)
 - Phase shift masks (PSM)
 - Optical proximity correction (OPC).
- The practical lower limit for k_1 is thought to be about 0.25 (for single exposure).



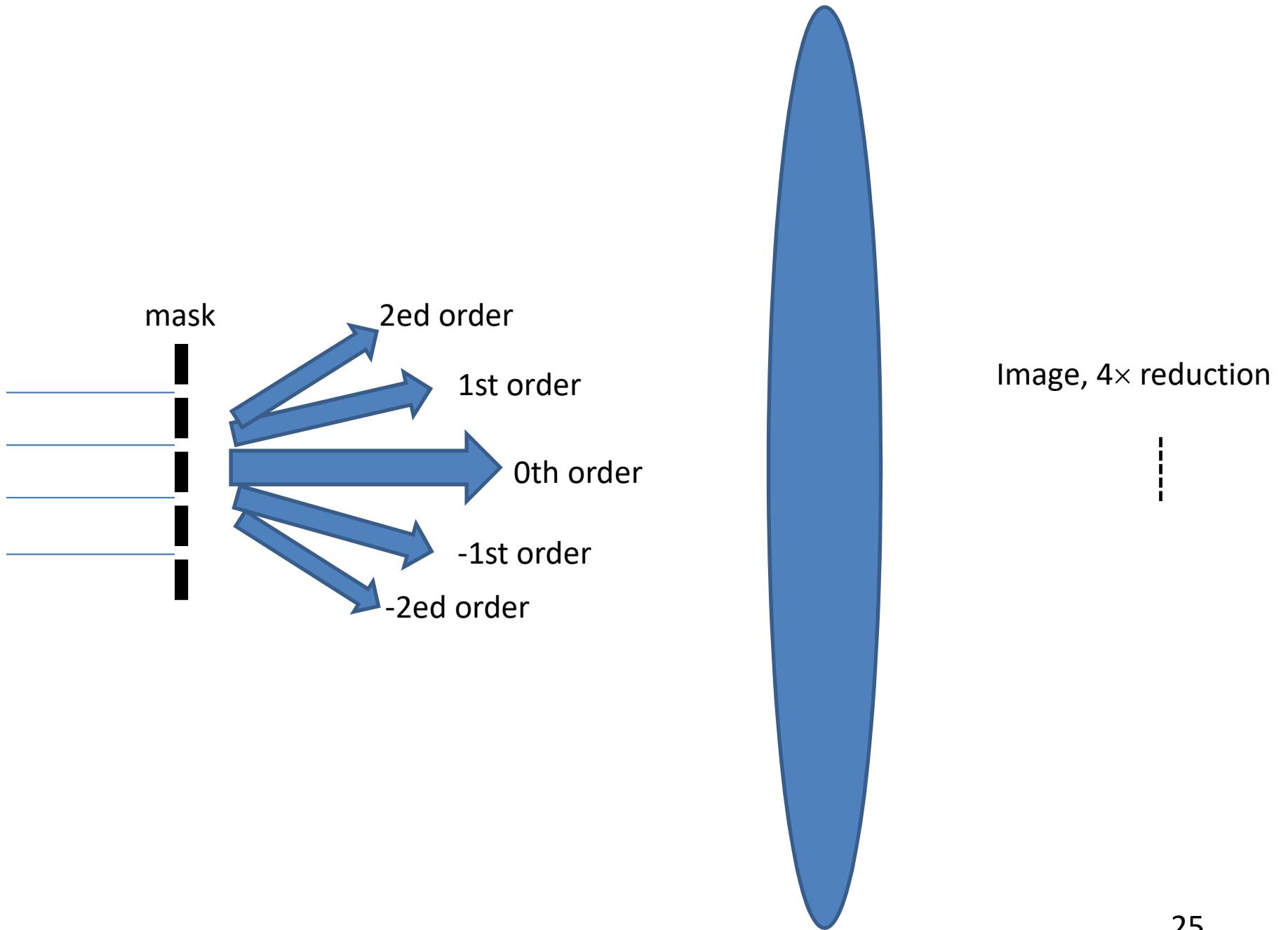
Reduction of k_1 factor until 193-nm optical lithography was introduced.

Table 2.4 Summary of resolution enhancement techniques

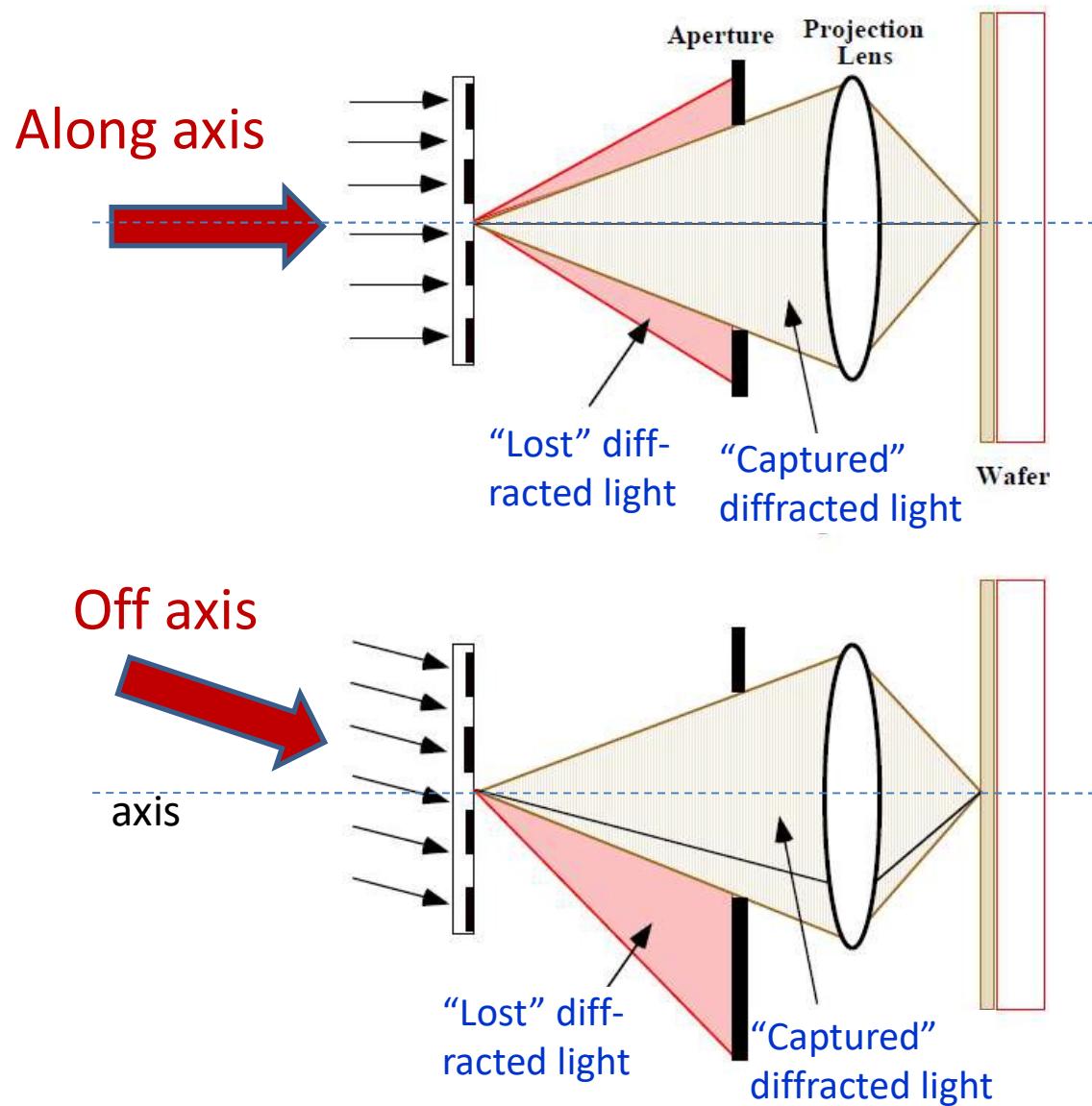
Components of optical lithography	Innovations to reduce k_1 factor
Illumination optics	Off-axis illumination (OAI): annular, quadrupole, or programmable
Photomask	Phase-shifting masks (PSMs), optical proximity correction (OPC)
Photoresist layer	Top surface imaging (TSI), antireflective coating (ARC), double exposure or double patterning

Photolithography and resolution enhancement techniques (RET)

1. Photolithography and resolution limit
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6. Double processing



Off-axis illumination (OAI)



Off-axis illumination

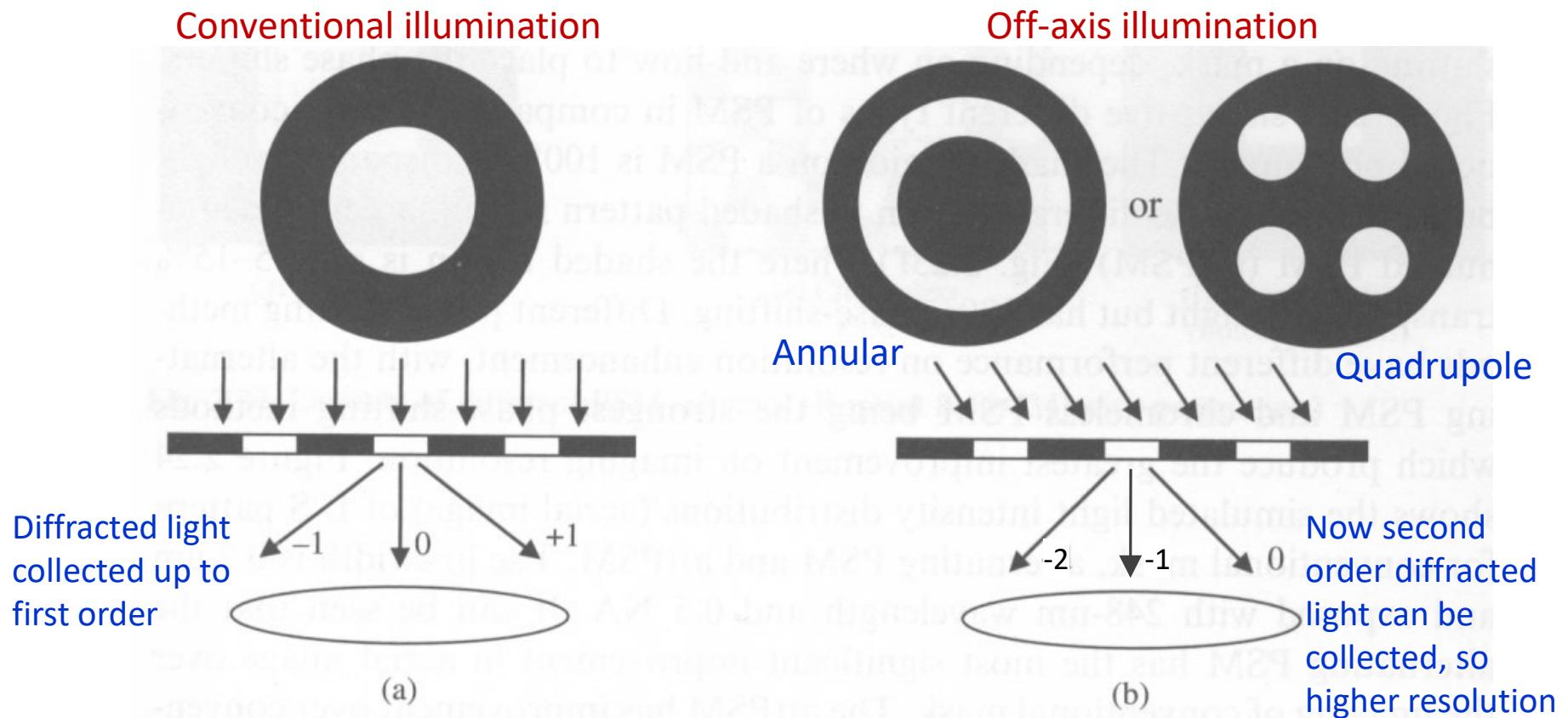


Fig. 2.21 Comparison of conventional and off-axis illumination schemes: (a) conventional aperture (b) off-axis apertures (annular or quadrupole)

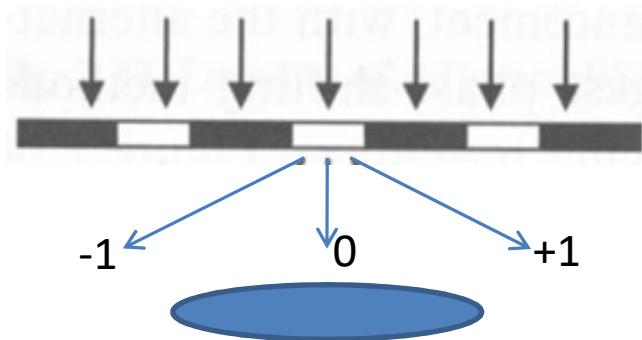
Quadrupole: most effective for line/space pattern (depends on line orientation, best for vertical or horizontal line/space pattern), less for isolated features.

Annular OAI: less resolution enhancement, but orientation independent.

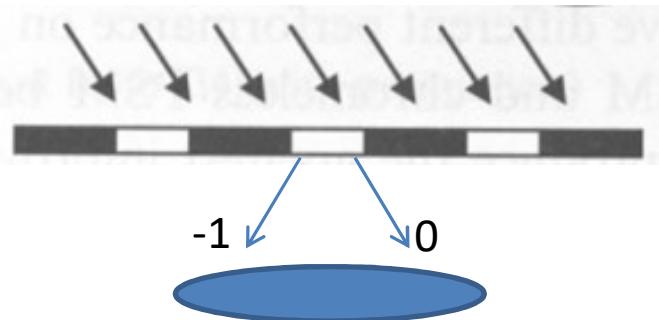
Easiest and cheapest RET, state-of-art OAI apparatus are programmable for each set of masks.

Off-axis illumination (OAI)

Fig. 2.21 (previous slide) is misleading. In IC industry, only $m=0$ and $+1$ (or -1) order diffracted light is collected. No need of second order.



For small lens (small NA) without OAI, only 0 order is collected to form image on the resist. Uniform exposure across the wafer (no grating pattern, "DC" signal only).

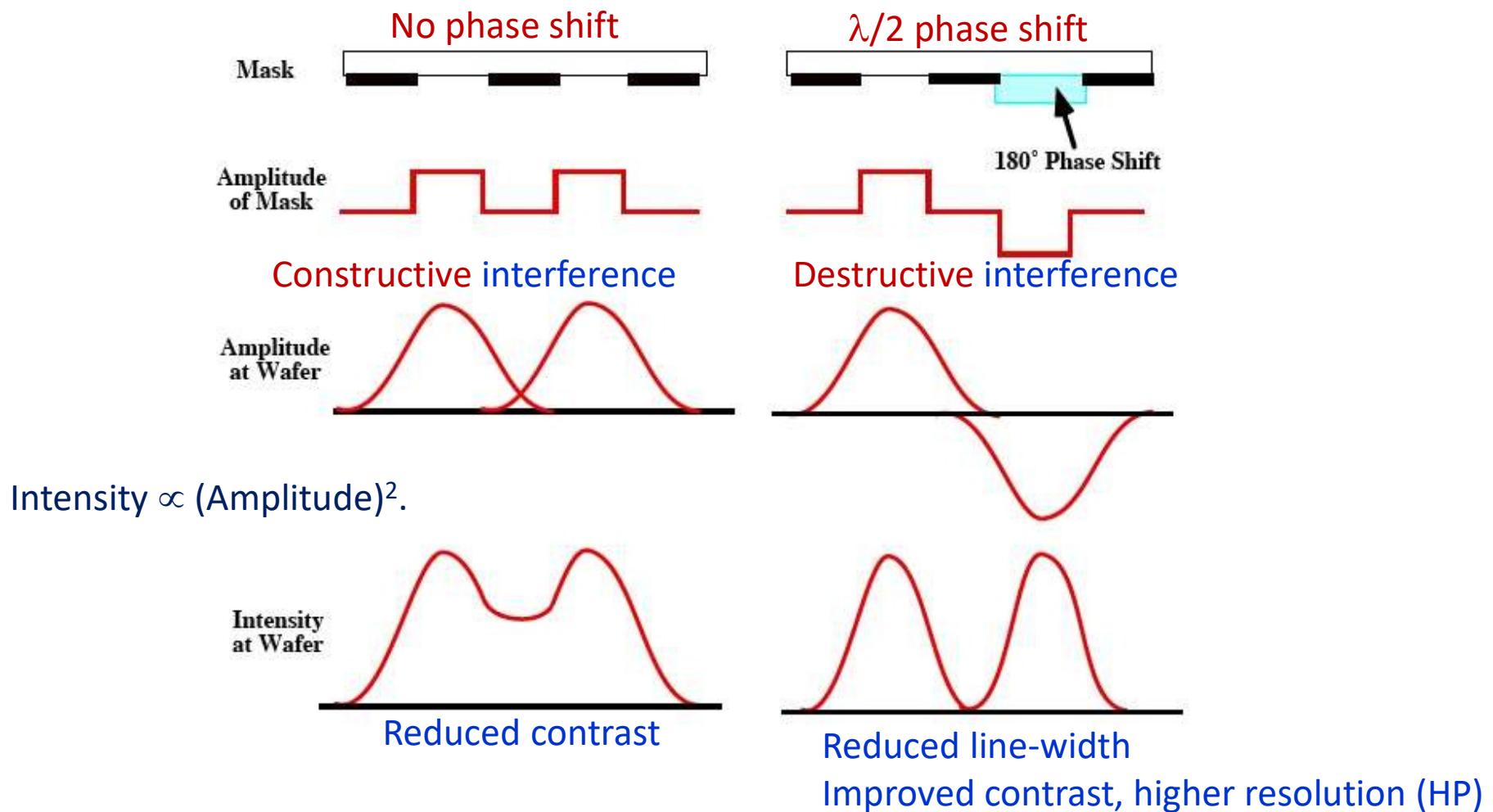


For small lens but with OAI, now both 0 and -1 order is collected.
-1 order carries the information of the grating. The exposure profile in the resist will be sinusoidal.

Photolithography and resolution enhancement techniques (RET)

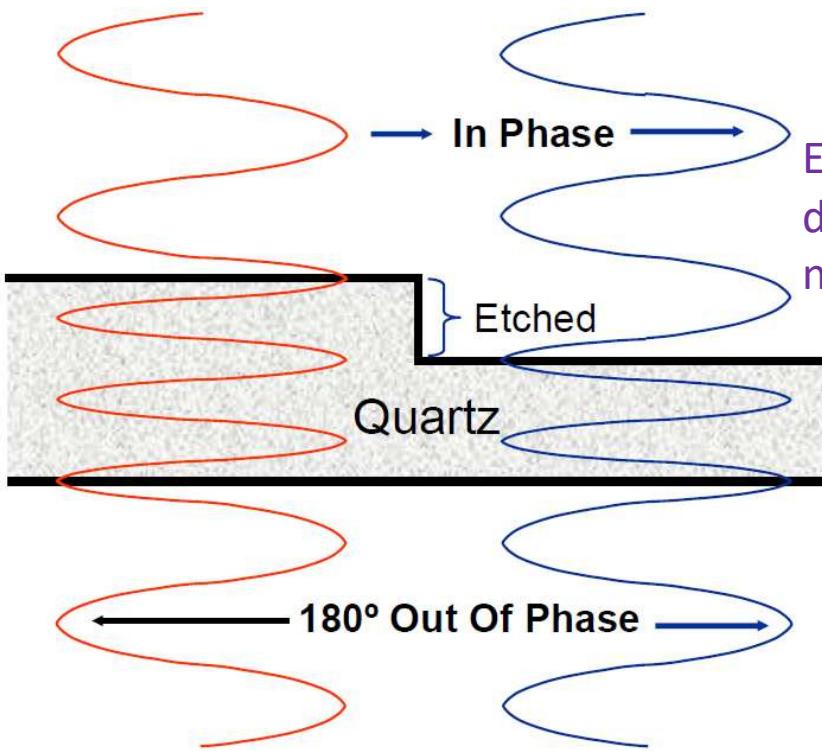
1. Photolithography and resolution limit
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Phase shift masks (PSM)



- PSM changes the phase of light by 180° in adjacent patterns, leading to destructive interference rather than constructive interference.
- Improves contrast of aerial image on wafer. Making k_1 smaller.

Phase shift masks fabrication



Etch depth:
 $d=(\lambda/2)/(1.56-1)=172\text{nm}$
 $n(\text{quartz})=1.56$

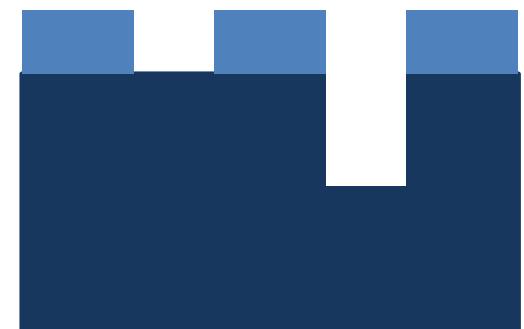
Standard mask

Chrome



Phase-shift
mask

0° 180°

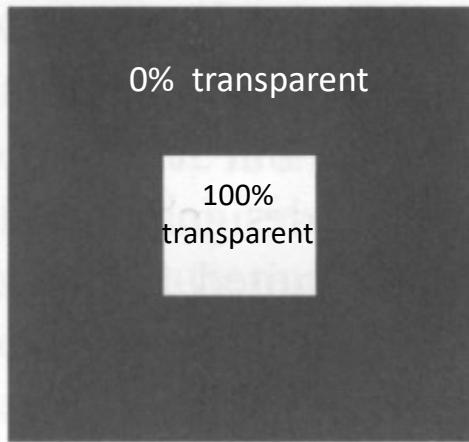


Quartz etched to induce shift in phase

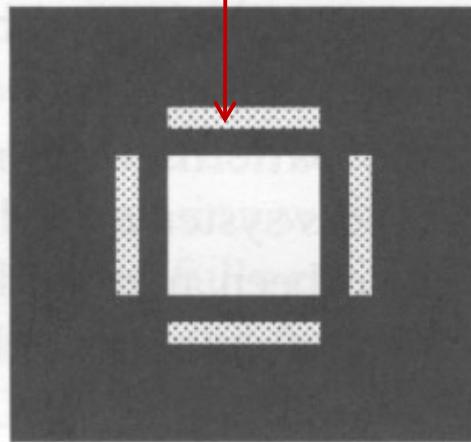
- Need two patterning steps with accurate alignment.
- Fabrication cost 10× that of binary mask.

Different phase-shift mask schemes

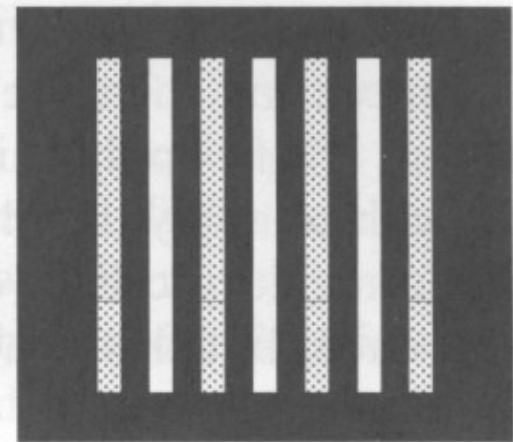
Shaded region: 100% transparent, but 180° phase shift



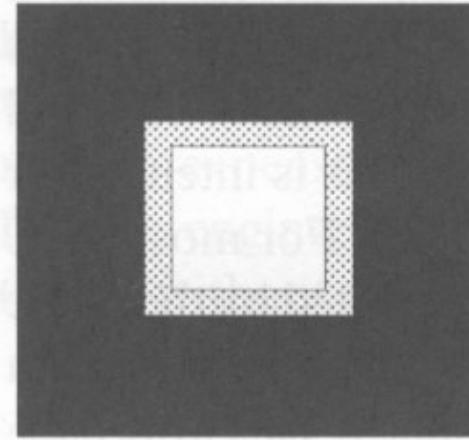
(a) Binary mask
(conventional)



(b) Auxiliary PSM
(scattering bars PSM)

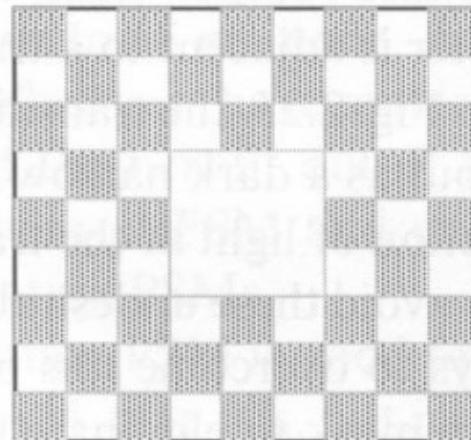


(c) Alternating



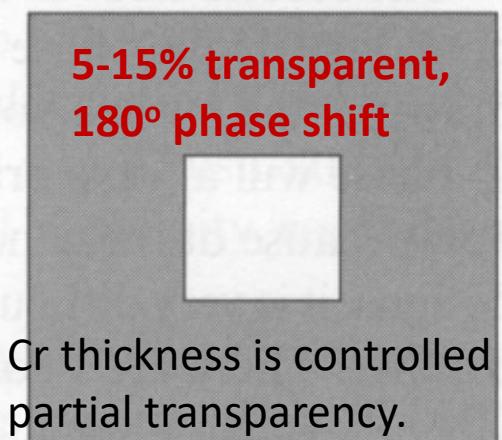
(d) Rim PSM

Similar to (b) (auxiliary PSM)



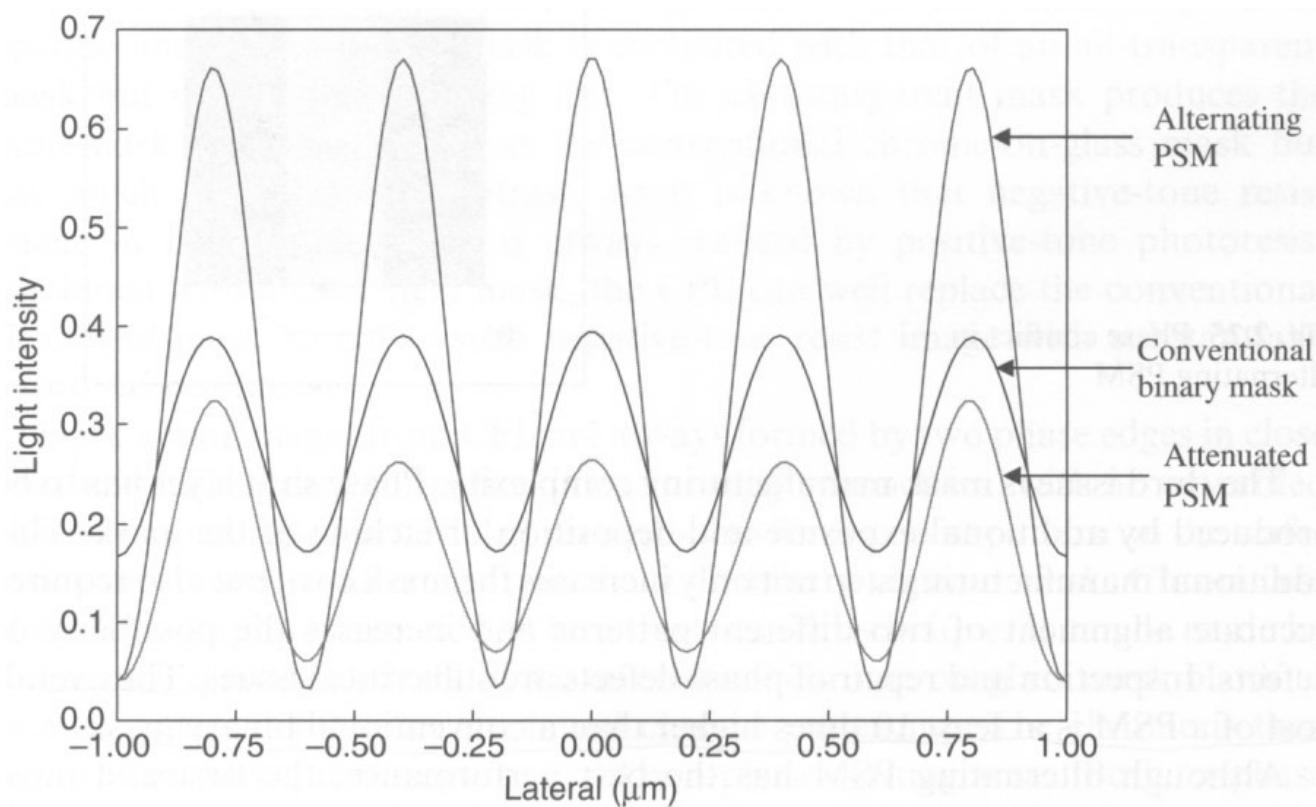
(e) Chromeless
PSM

No Cr metal: 100% transparent everywhere

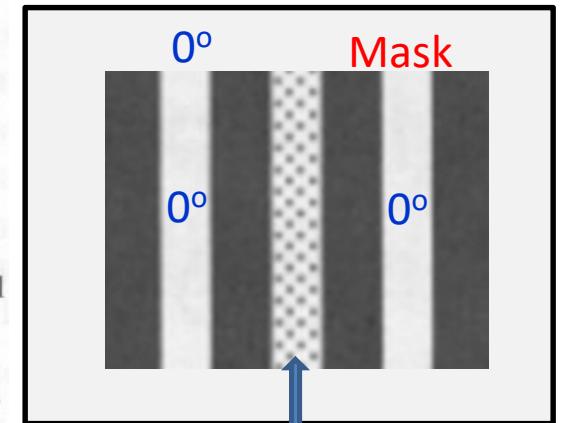


(f) Attenuated PSM
(Embedded PSM)

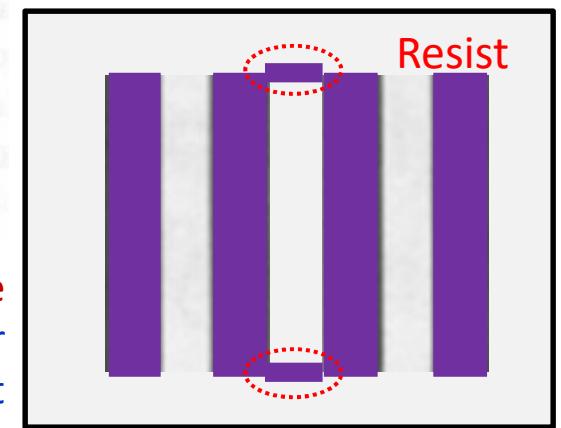
Comparison of binary, alternating and attenuated PSM



Phase conflict



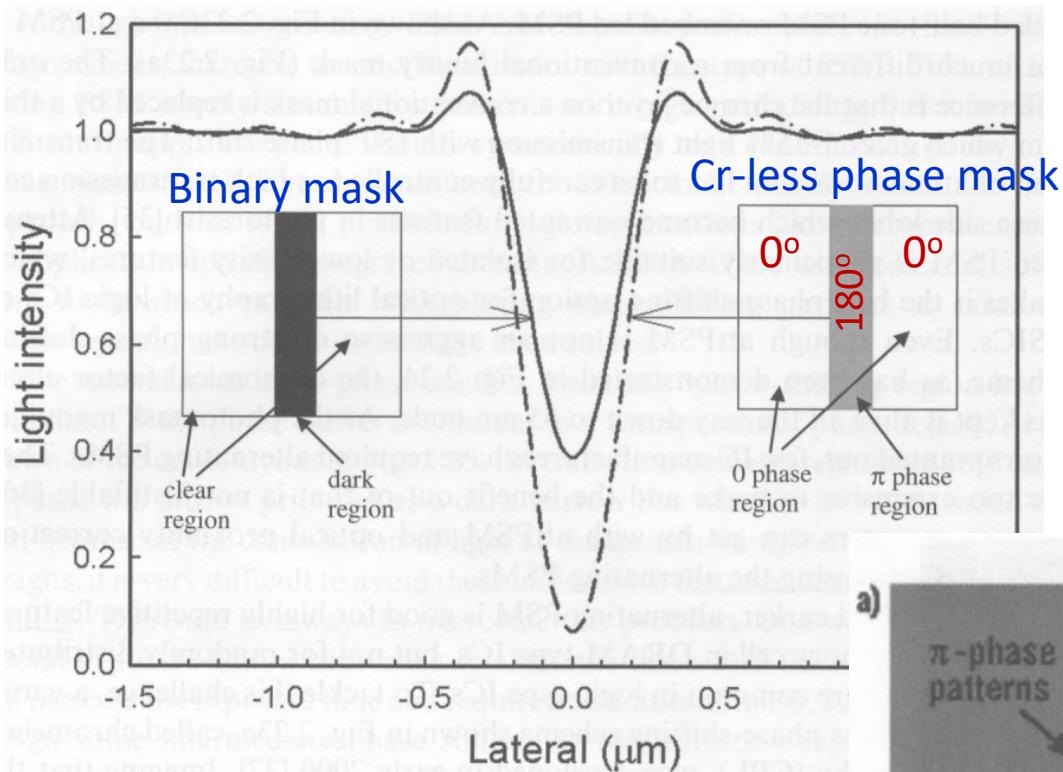
Positive resist after development



Alternating PSM gives highest contrast, but

- It is good only for periodic structures (memory cell), not for random patterns (CMOS).
 - Phase conflict may happen → undesired dark regions at the boundary of 0° and 180° phase.
- In reality, the attenuated PSM is most widely used.

Chromeless phase lithography (CPL)



Comparison of CPL with conventional binary mask

CPL has better image contrast, thus higher resolution.

Is this a positive or negative resist?

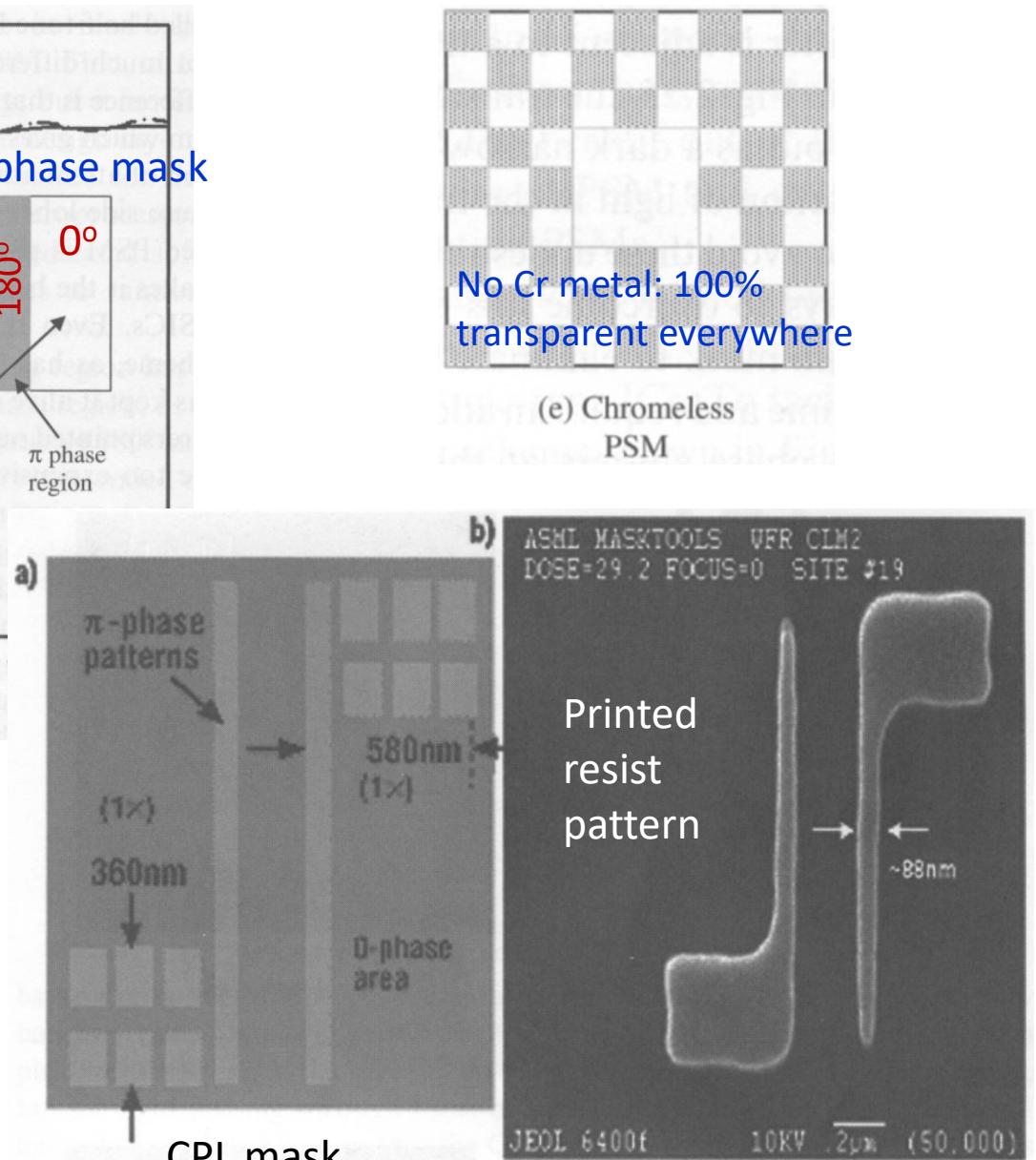


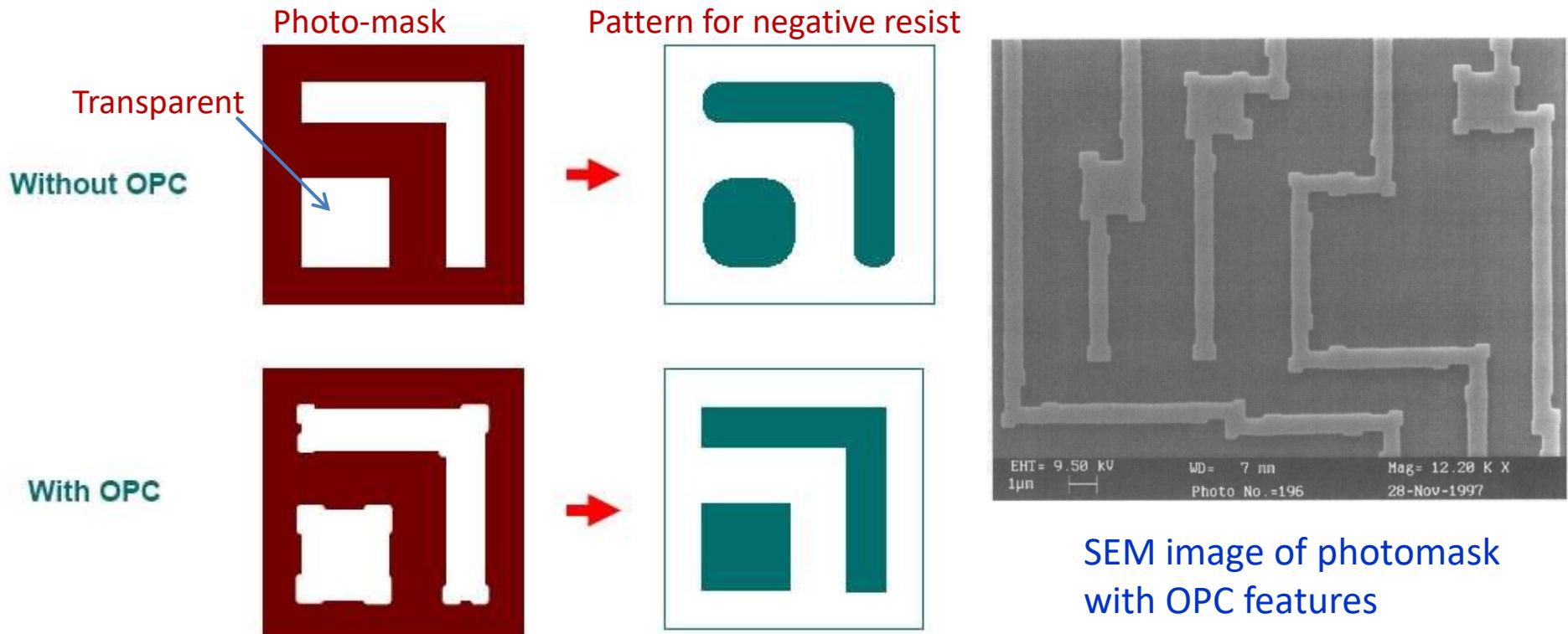
Fig. 2.27 CPL mask and printed resist patterns (Reprint from [38] with permission)

Photolithography and resolution enhancement techniques (RET)

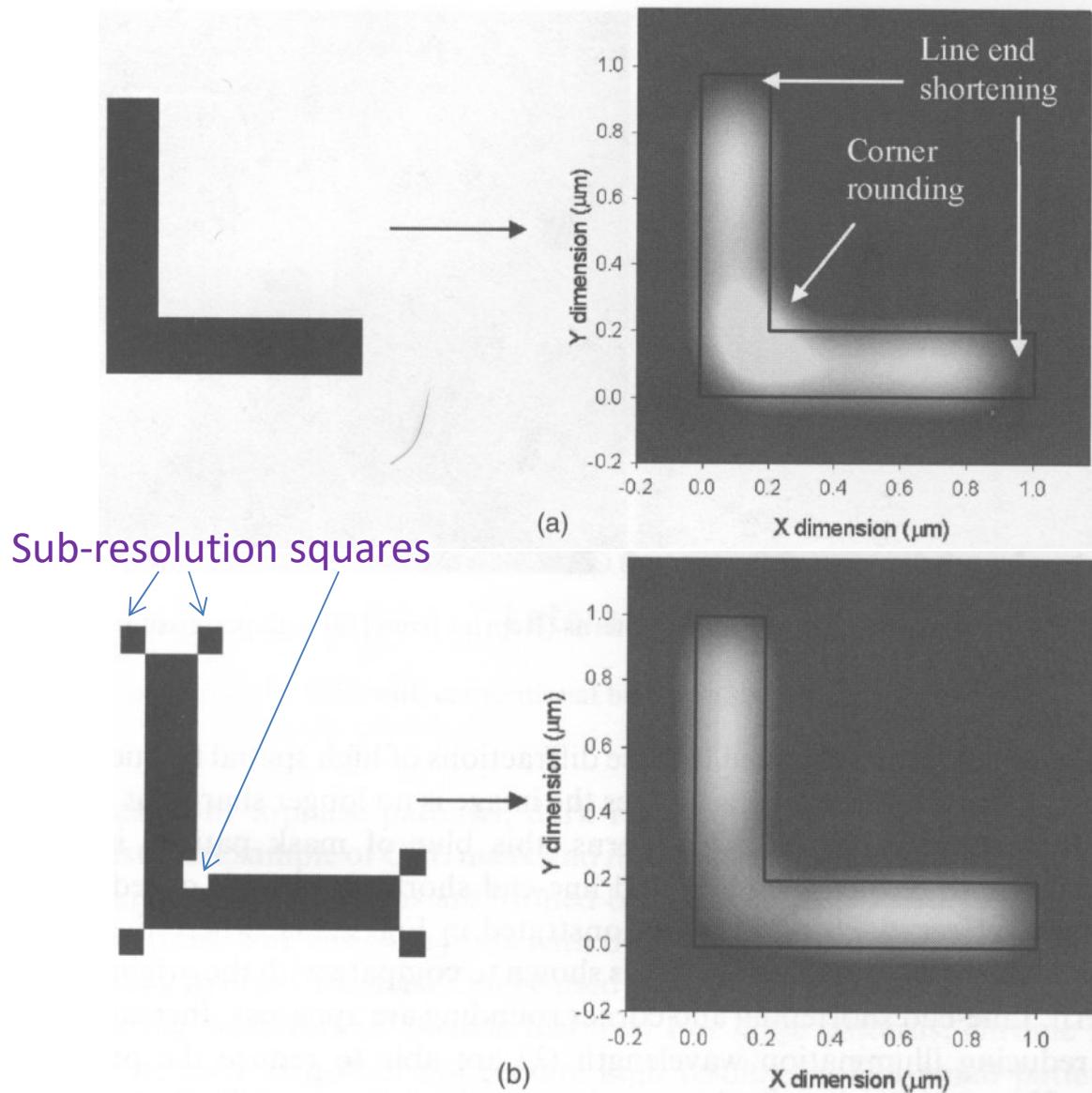
1. Photolithography and resolution limit
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Optical proximity correction (OPC)

- Presence or absence of other features nearby (proximity) will affect the optical behavior.
- Sharp features are lost (corners become rounded), because higher spatial frequencies are lost due to diffraction.
- These effects can be calculated and can be compensated for.
- This improves the resolution by decreasing k_1 .



Optical proximity effect and its compensation by adding/taking away sub-resolution features



Optical proximity effect result in corner rounding and line-end shortening.

Optical proximity correction: modifies the mask design to restore the desired pattern.

The sub-resolution features won't appear in the resist (since it is *sub-resolution*, too small to be resolved/to show up).

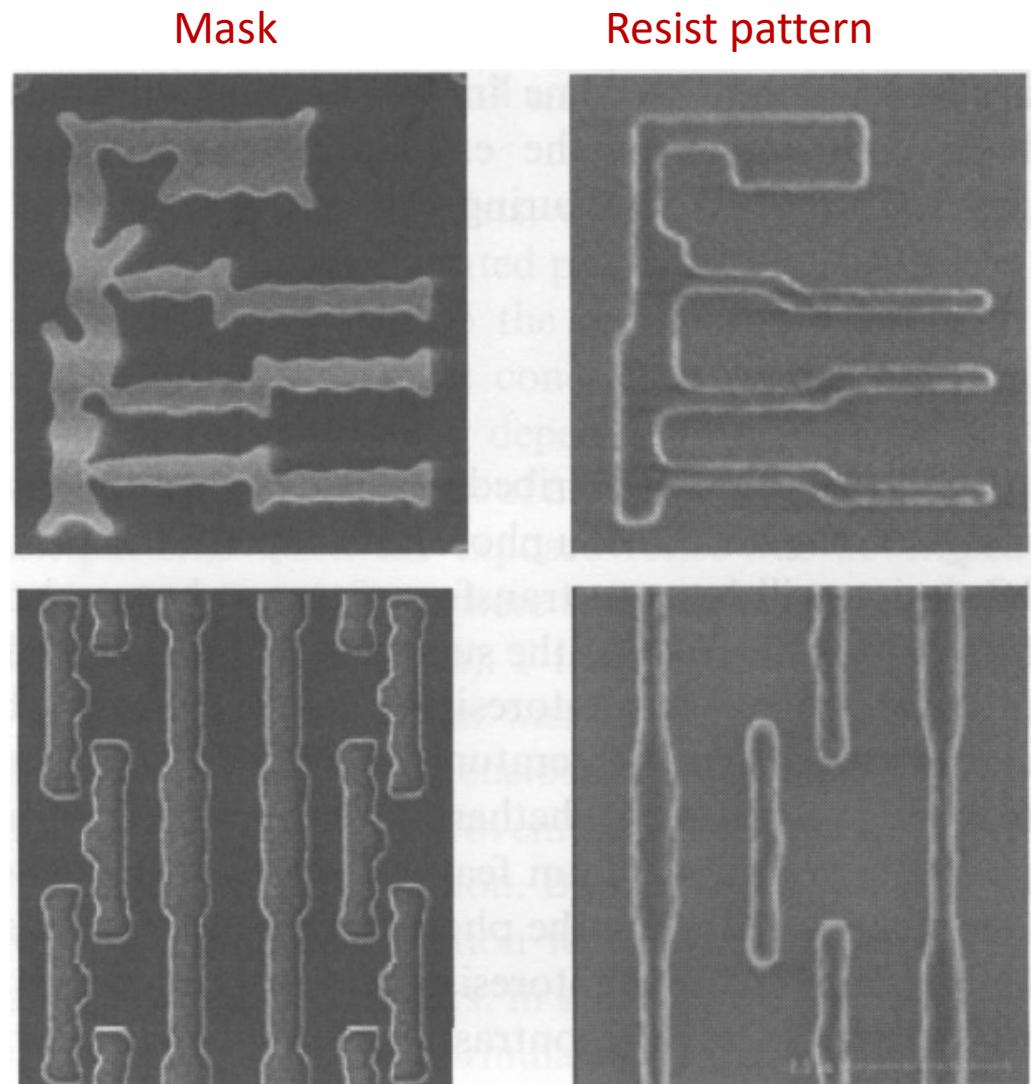
Inverse lithography technology (ILT) (ultimate solution for OPC)

- Design the photomask by working out how an ideal image is generated. I.e. working **backwards** to find the “perfect” mask that can generate the ideal image.
- Very complicated math, data file for such a mask ~1000GB.

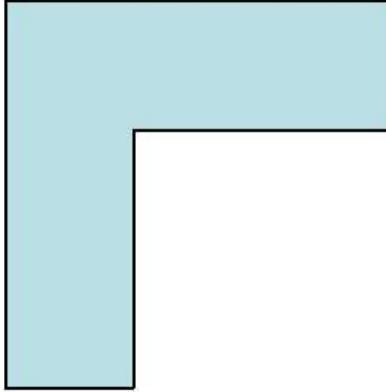
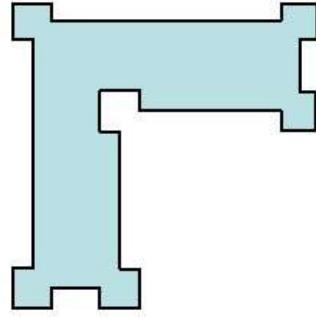
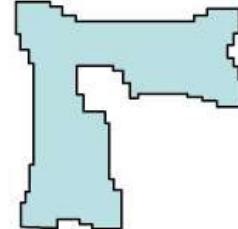
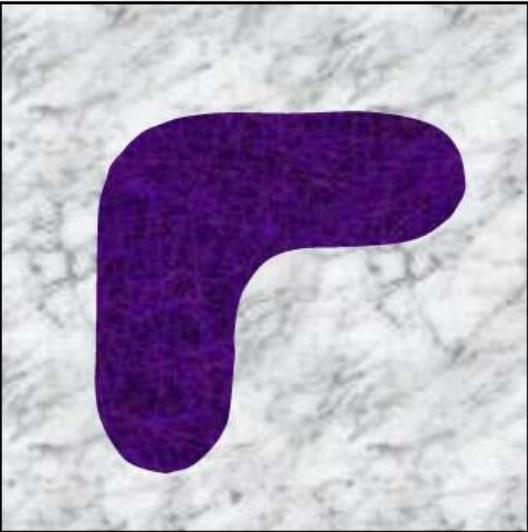
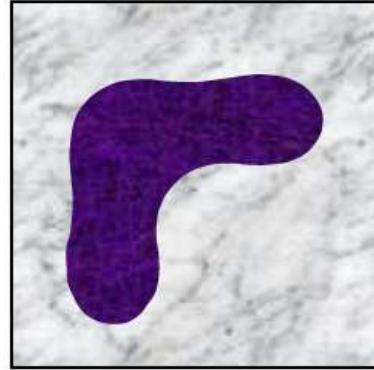
In ILT, every pixel of the mask is optimized, lots of calculation. For less aggressive OPC, only feature edges/corners need to be considered for modification.

Top: aggressive ILT mask.

Bottom: non-aggressive OPC mask.



Optical proximity correction (OPC): summary

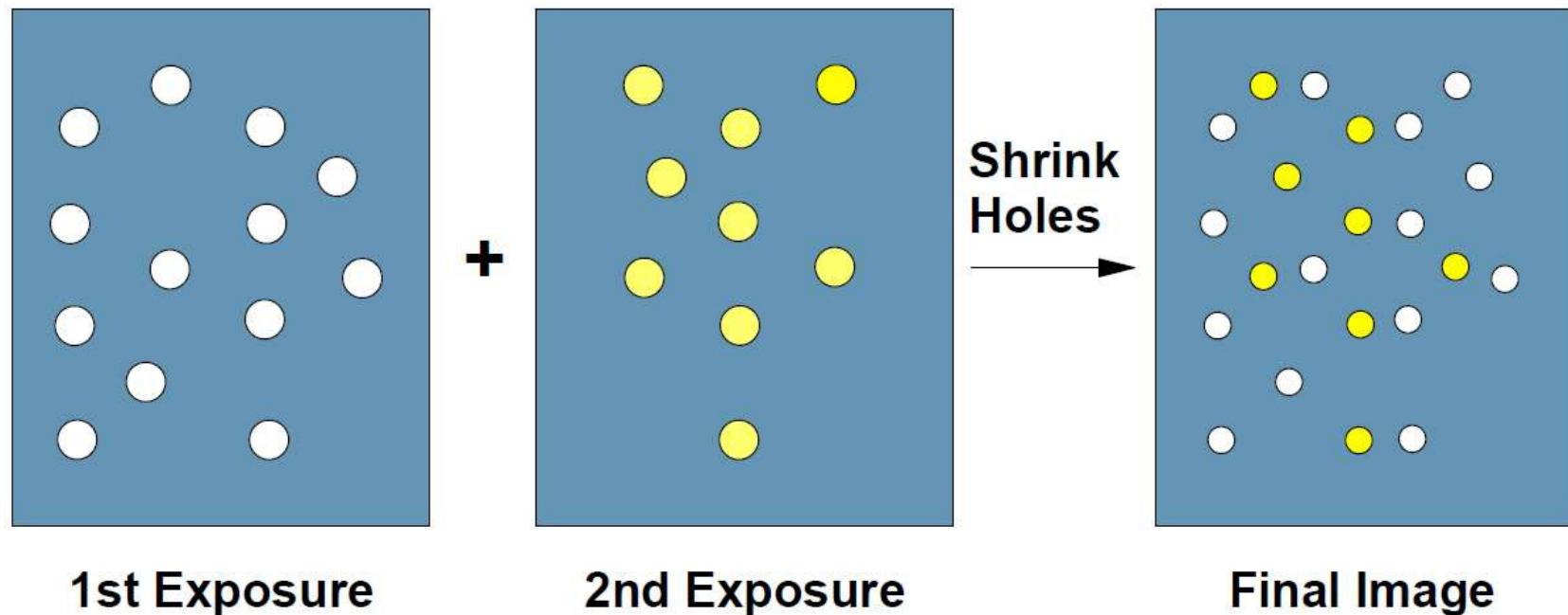
	180nm Conventional mask	Rule-based OPC	<i>Model-based OPC</i>
Mask			
Wafer			
Rule-based OPC improves 130nm			<i>Model-based OPC enables 100nm</i> (now 14nm)

Photolithography and resolution enhancement techniques (RET)

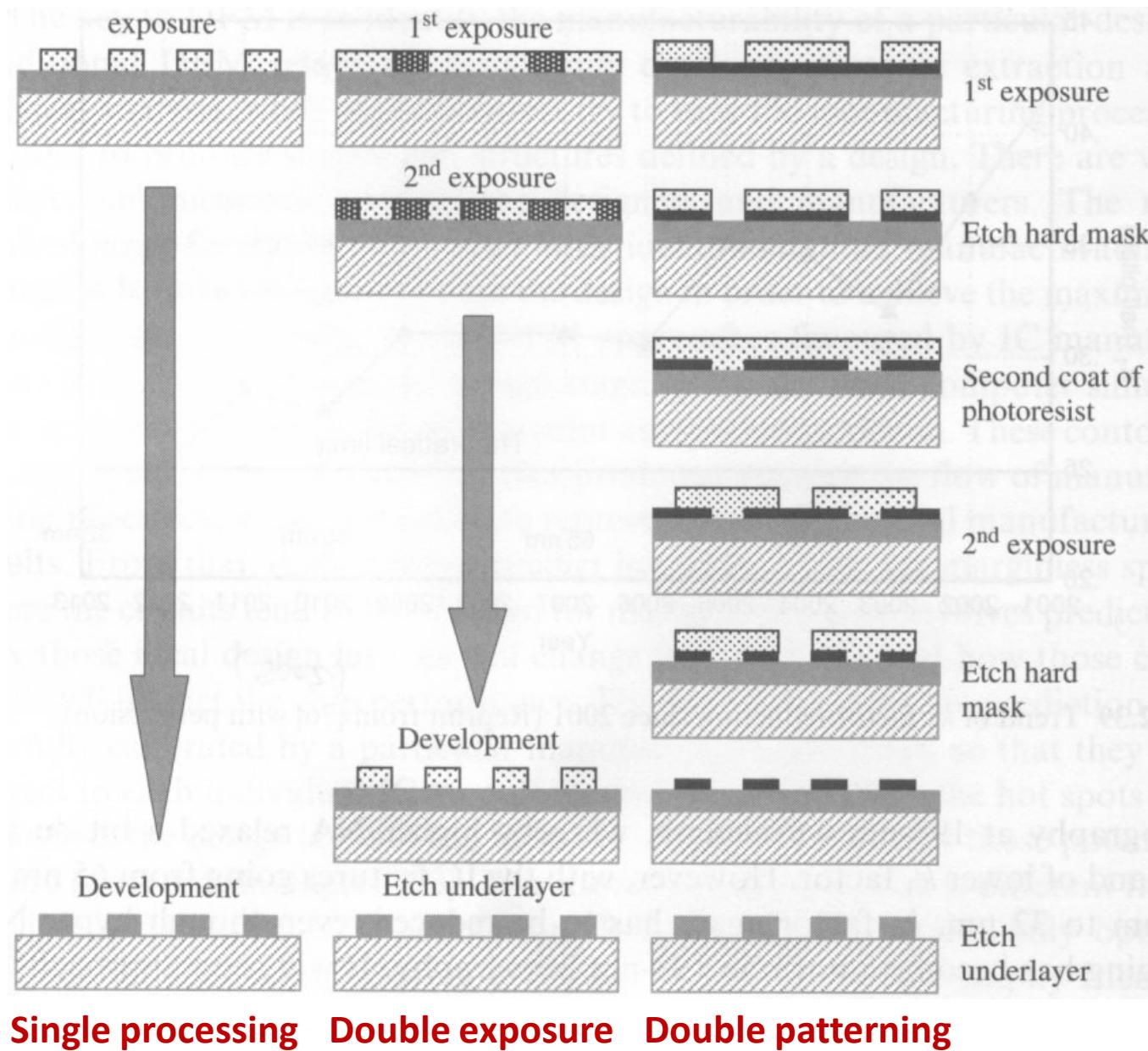
1. Photolithography and resolution limit
2. Immersion lithography
3. Off-axis illumination (OAI)
4. Phase-shift mask (PSM)
5. Optical proximity correction (OPC)
6. Double processing

Pitch splitting to improve resolution (half pitch)

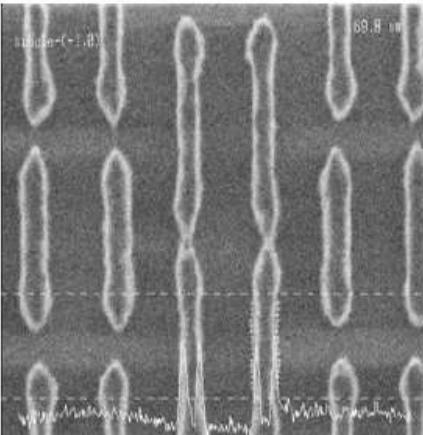
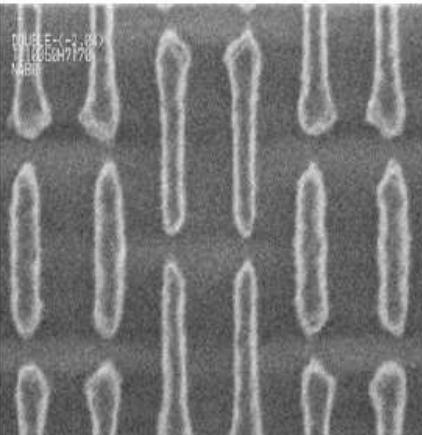
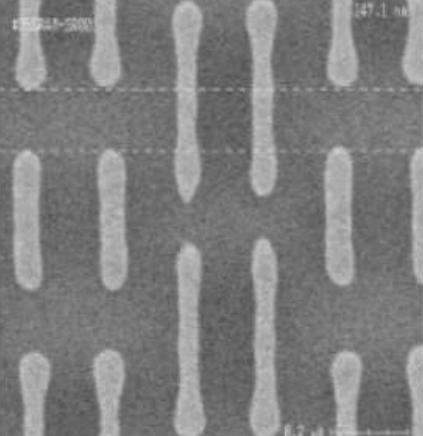
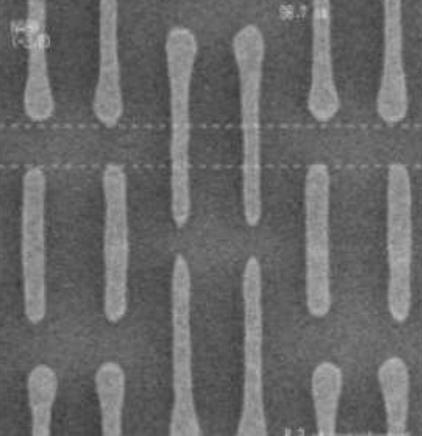
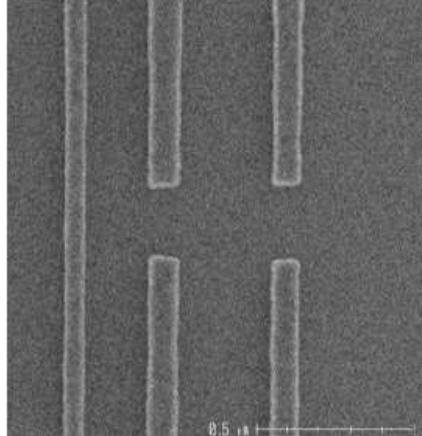
- Divide patterns on a mask into two masks, resulting in larger separation between features.
- Expose the resist twice using the two masks. (double exposure)
- For complete separation of cross talk, two exposures and two pattern transfers by etching is carried out. (double patterning)
- Finally, feature sizes are trimmed back (optional).



Double processing (double exposure and double patterning)

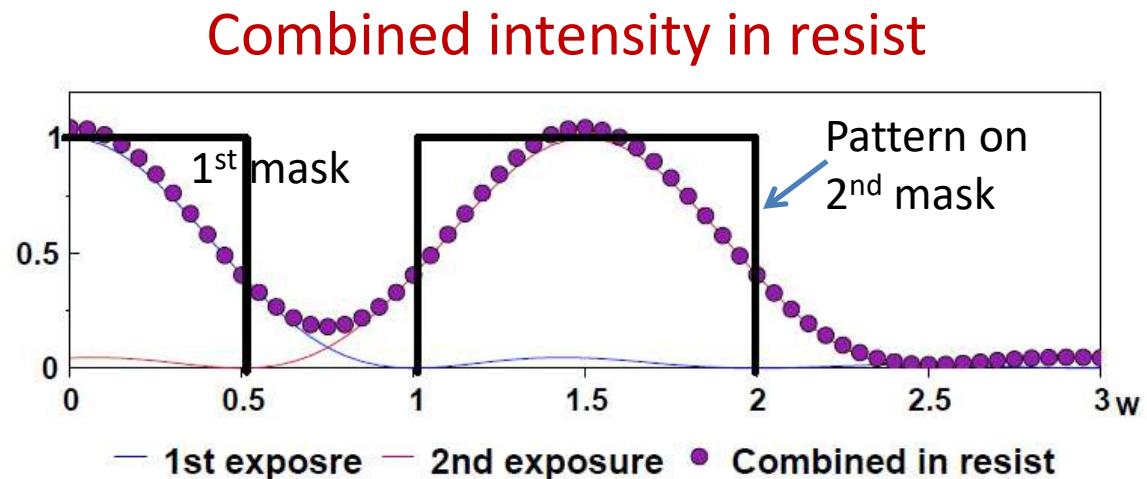


Comparison: single exposure, double exposure, double patterning

	Single exposure	Double exposures in resist	Double exposures through etch.
Resist			
After resist development			
After etch into sub-layer			

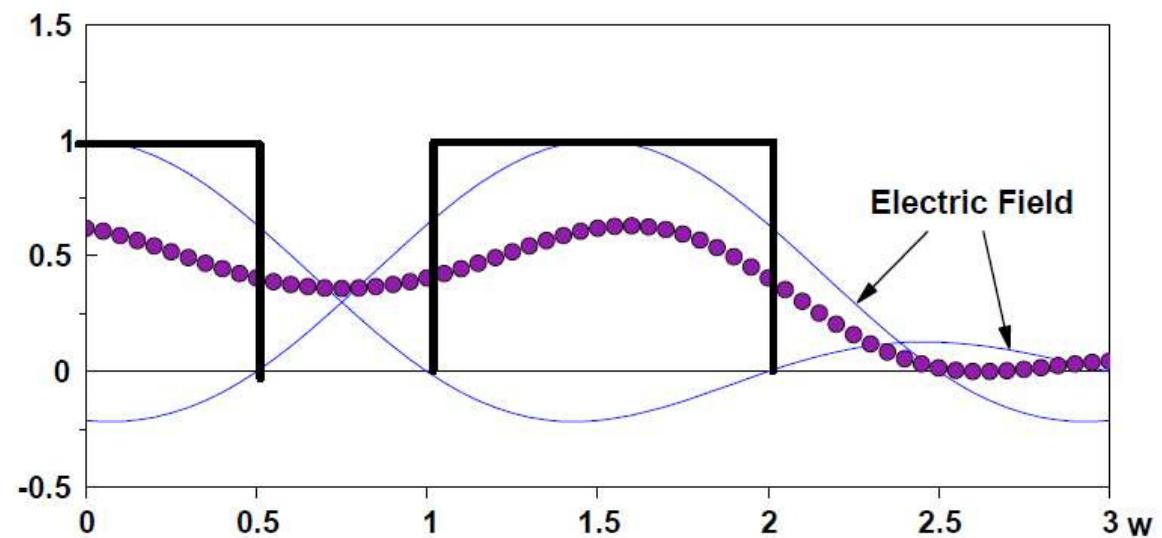
Why double exposure has higher resolution than single exposure?

Incoherent combination of light with *double* exposure.
(Intensity= $E_1^2+E_2^2$)

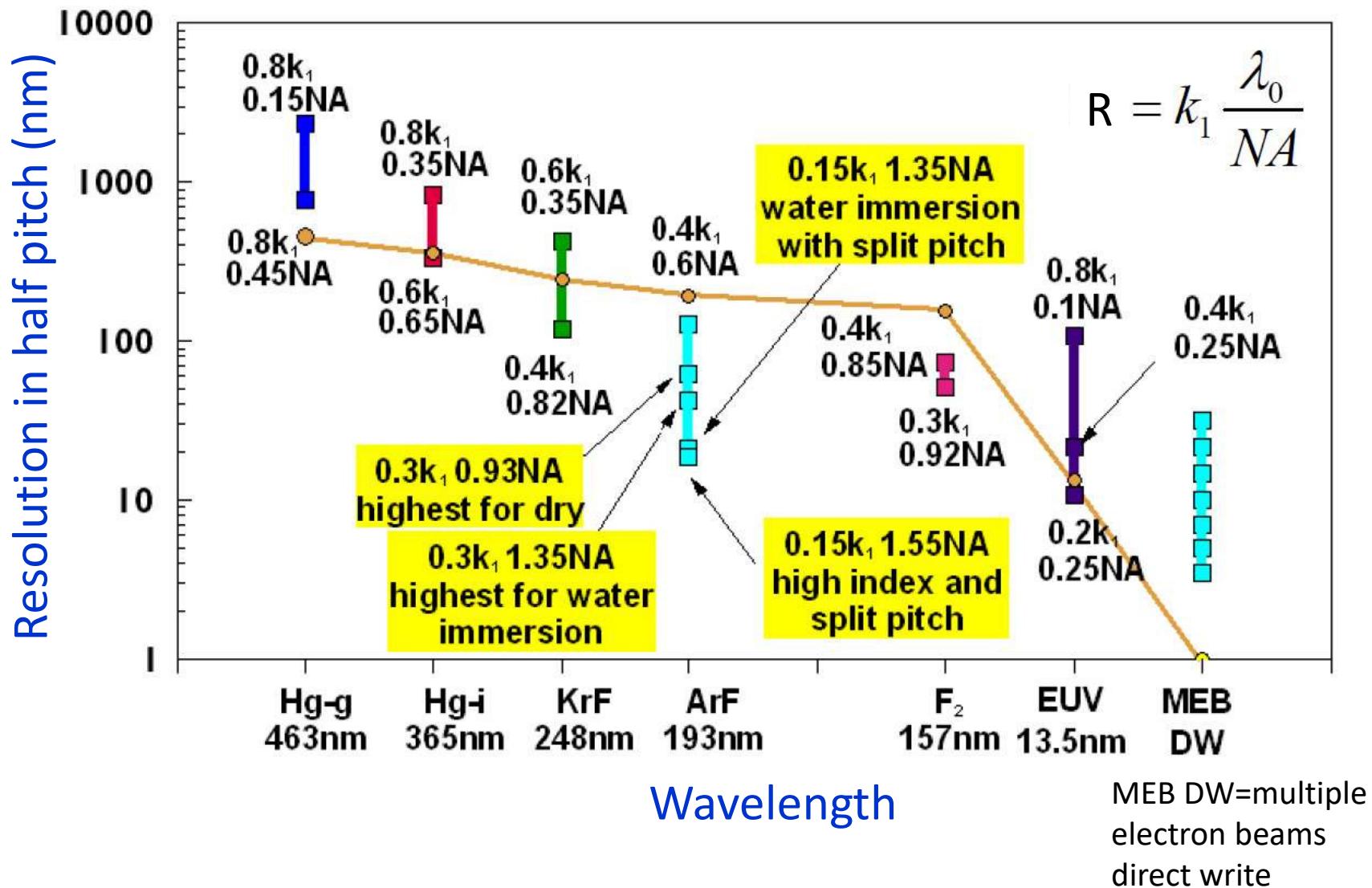


Coherent combination with *single* exposure.
(Intensity in gap= $(E_1+E_2)^2 > E_1^2+E_2^2$
Intensity drops in the pattern area)

In IC industry partial coherence is used that is better than coherence for high resolution, but still worse than incoherence.

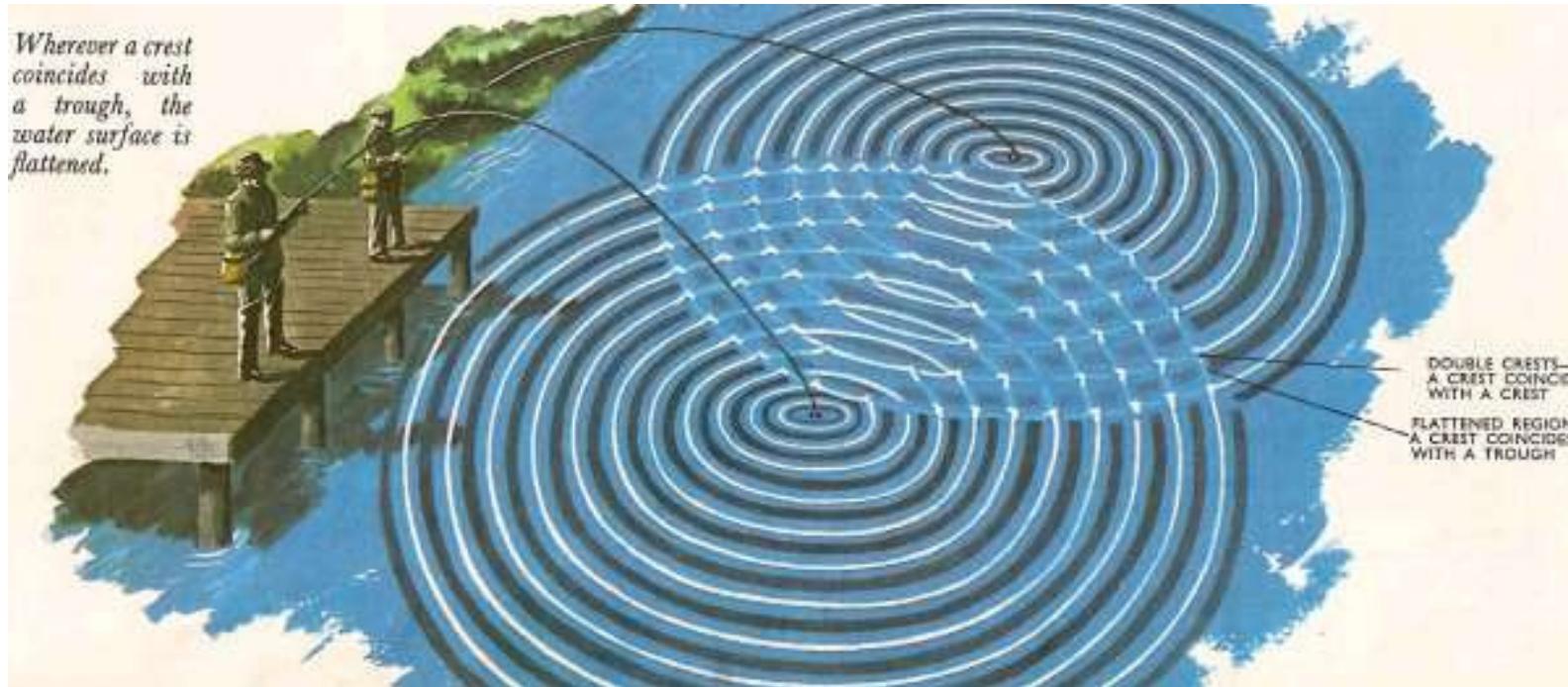


Resolution of exposure tools



Other photon-based lithographies

1. Interference lithography
2. Phase-mask lithography
3. Laser beam direct writing and micro-mirror array lithography
4. Two-photon lithography



Interference lithography: overview

Intensity modulation in the region of the overlapping of two or more *coherent* beams.

Advantages:

- Simple and fast, no photomask or lenses.

Disadvantage:

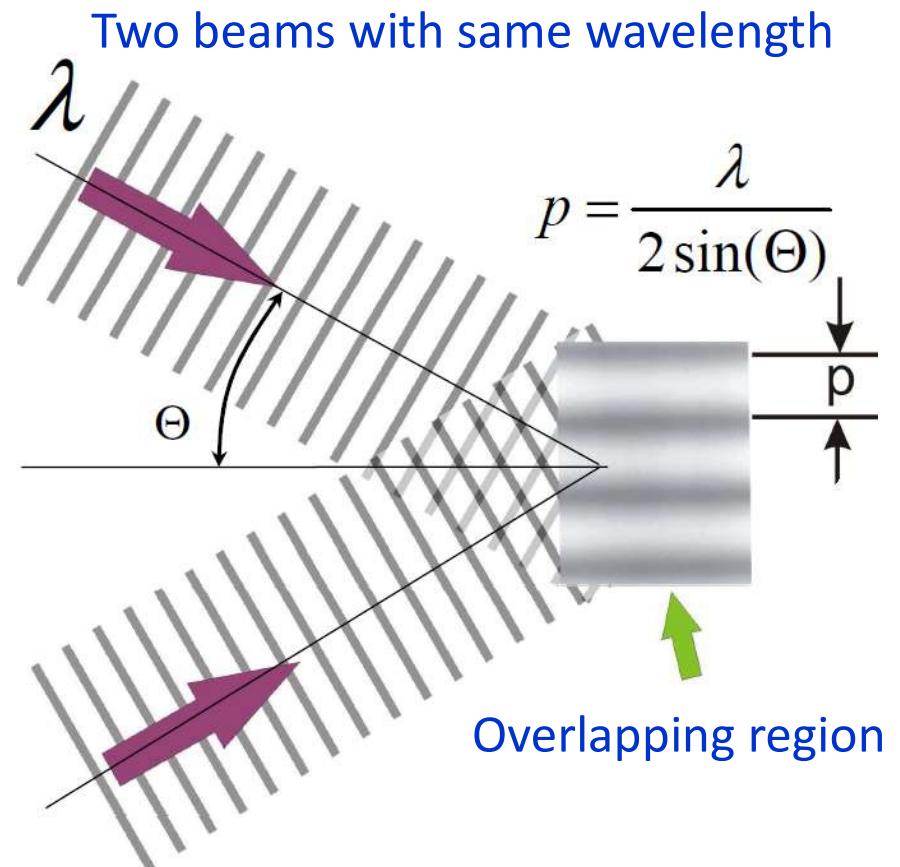
- Difficult to create anything other than a periodic structure.

Requirements:

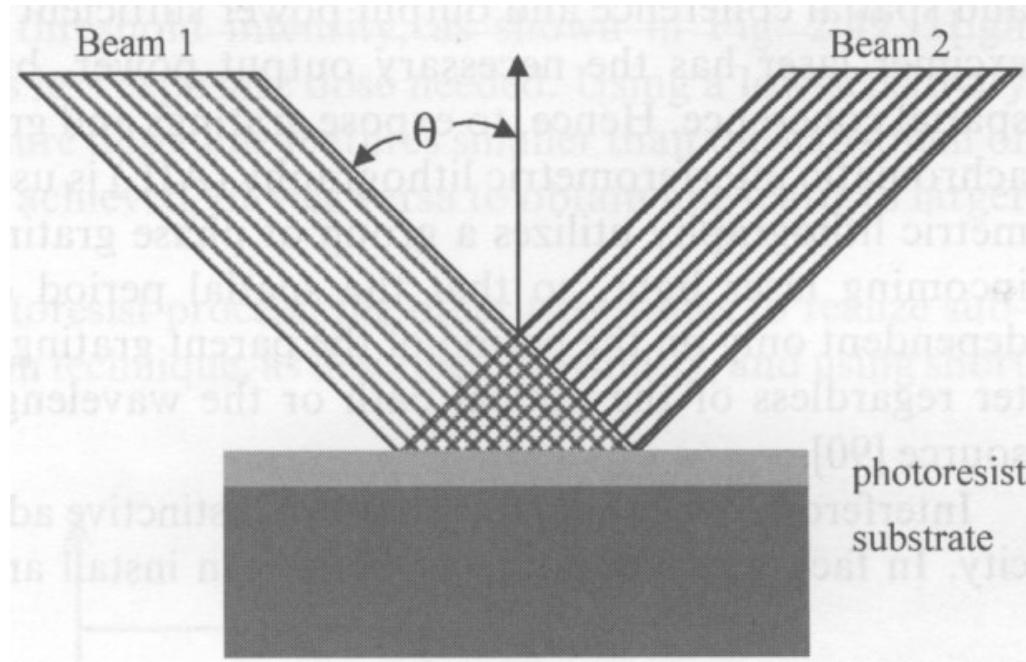
- High spatial and temporal coherence of the light source.

Applications:

- Guided wave optics.
- Distributive-feedback or distributed Bragg-reflector lasers.
- Sub-wavelength optical elements.



Interference lithography: grating pitch



Light intensity on photoresist:

$$I(x) = 2|E^2| [1 + \cos(2kx \sin \theta)]$$

$$k = \frac{2n\pi}{\lambda}$$

For E-field in plane (i.e. E parallel to resist surface).

$$I(x) = 2|E^2| [1 + \cos 2\theta \times \cos(2kx \sin \theta)]$$

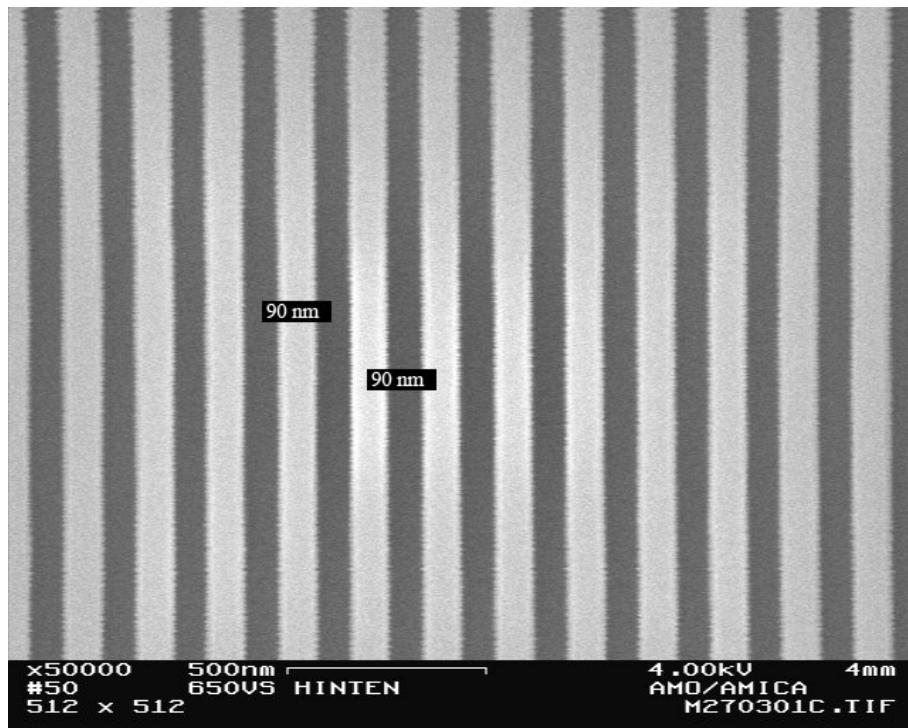
For E-field out of plane (not parallel).

$$\text{Pitch } P = \lambda/2n\sin\theta > \lambda/2 \text{ (for } n=1\text{). (i.e. } 2kP\sin\theta=2\pi\text{)}$$

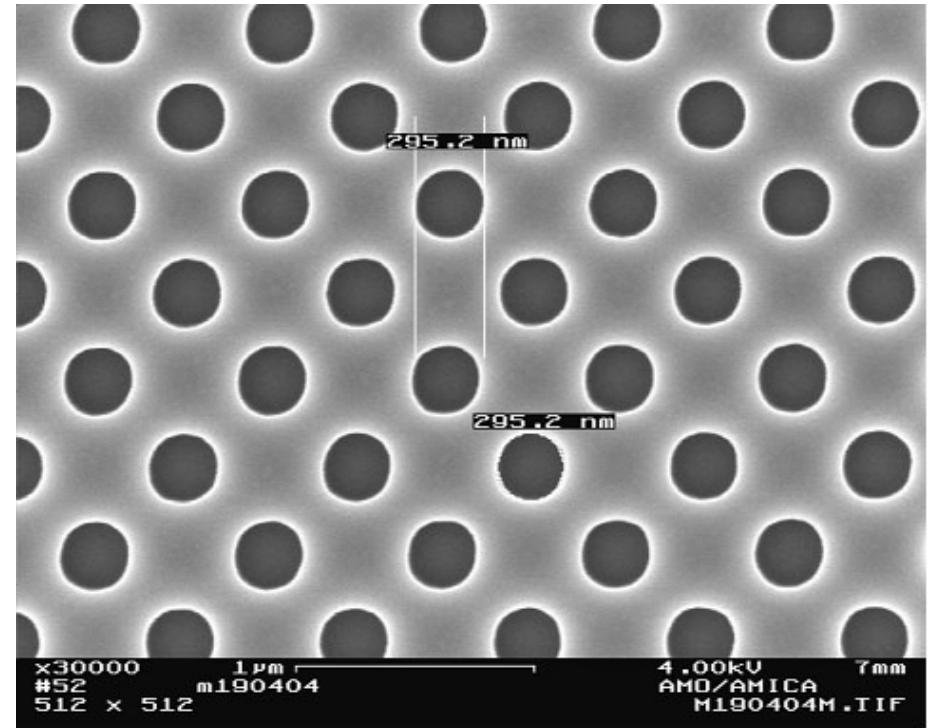
For E-field out of plane, no interference for $\theta=45^\circ$ since now the two E-fields are perpendicular.

1D and 2D structures by interference lithography (IL)

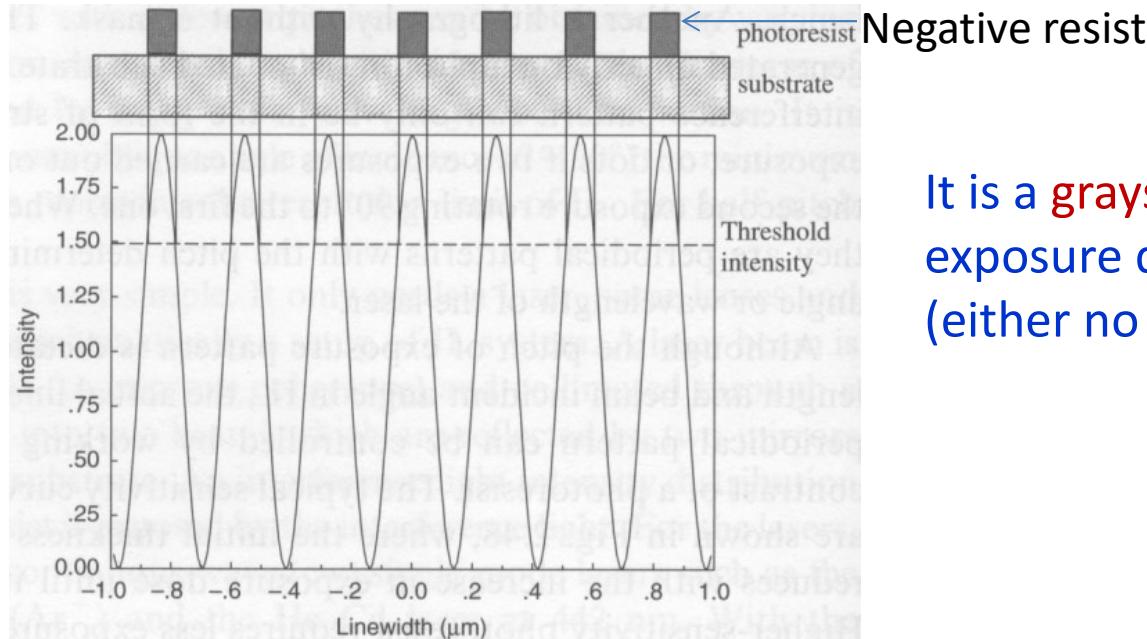
Grating of 200nm pitch by 2-beam IL



Hole array by 4-beam IL
(or two exposures at orthogonal directions)



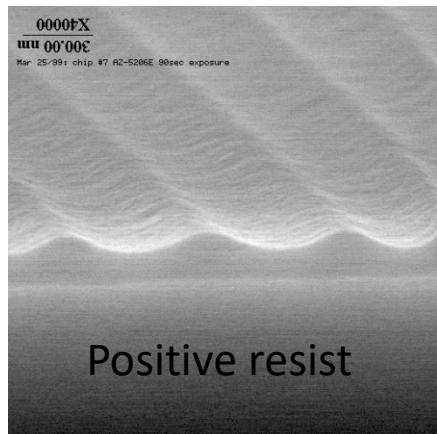
Feature size control by tuning exposure dose



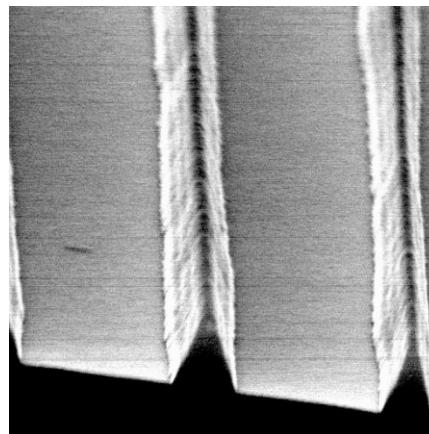
Profile in resist

It is a **grayscale lithography** (sinusoidal exposure dose profile); not binary (either no exposure or full exposure).

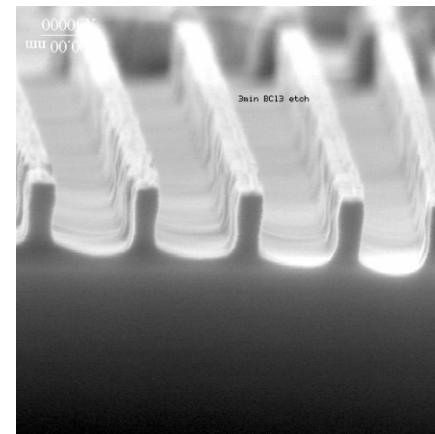
Profile in substrate after pattern transfer by etching



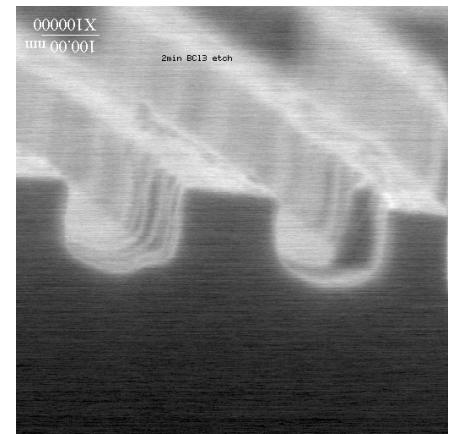
underexposed



overexposed

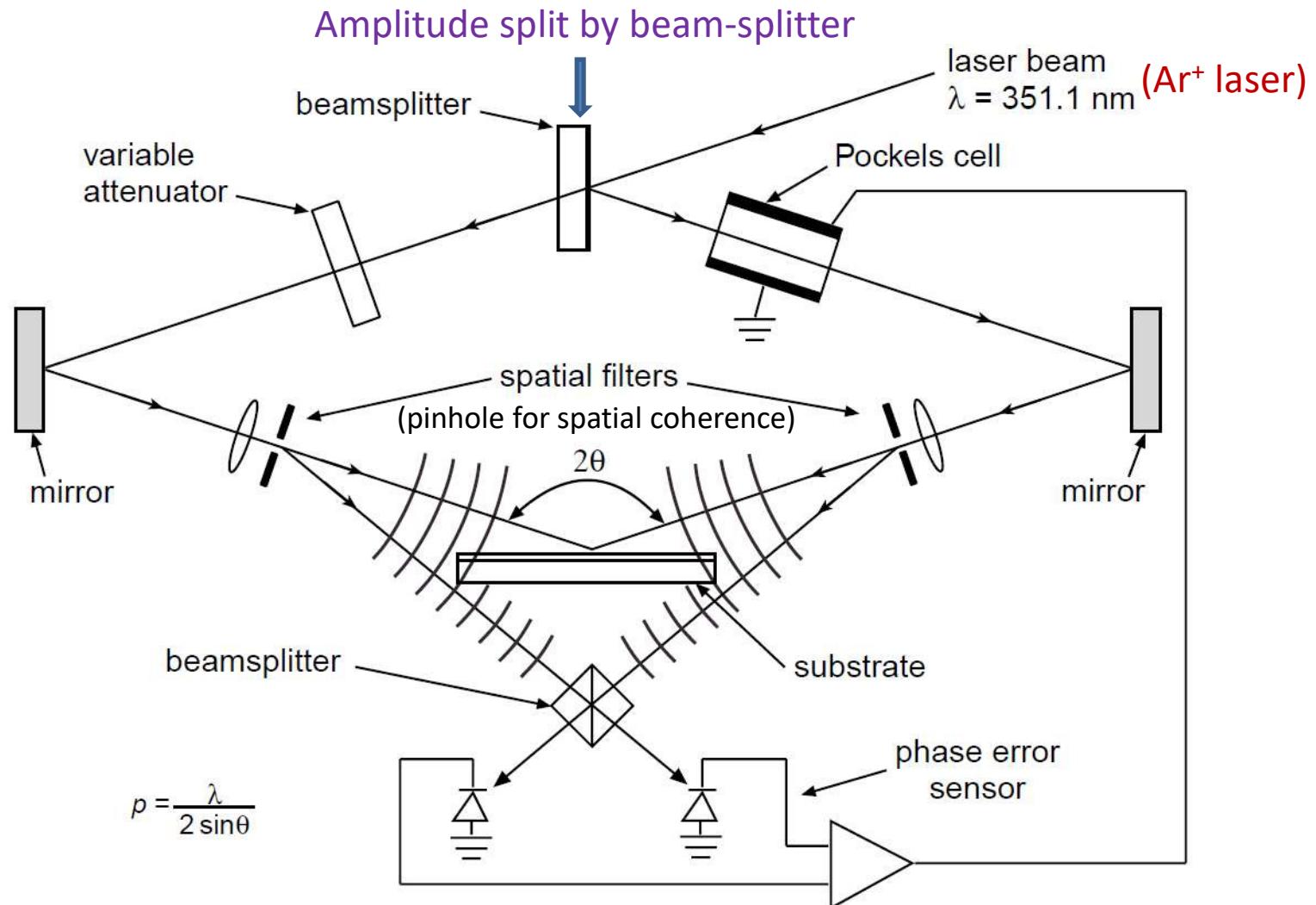


20% duty cycle
(line-width=20% pitch)



50% duty cycle
(equal line/space)

Optical setup: *amplitude* split interference lithography



It is very challenging to expose large area with target pitch close to $\lambda/2$. During exposure the system must be mechanically and optically stabilized to sub-wavelength precision.

Optical setup: wave-front split interference lithography

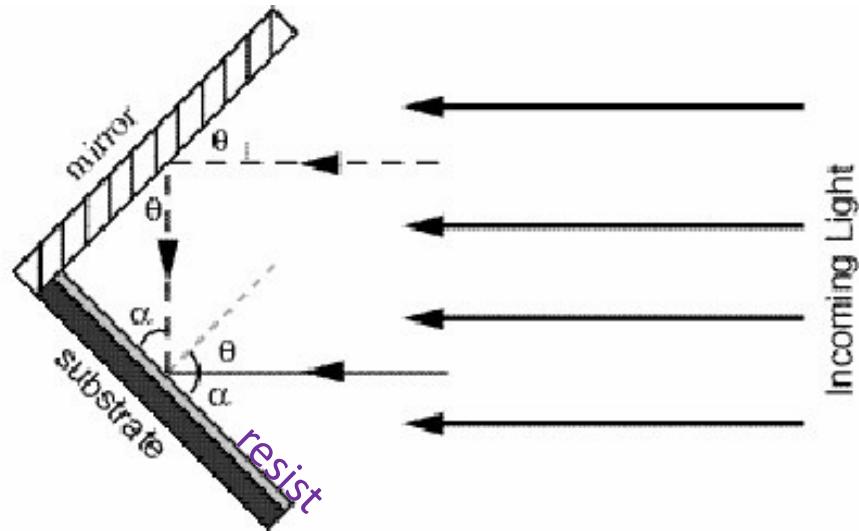
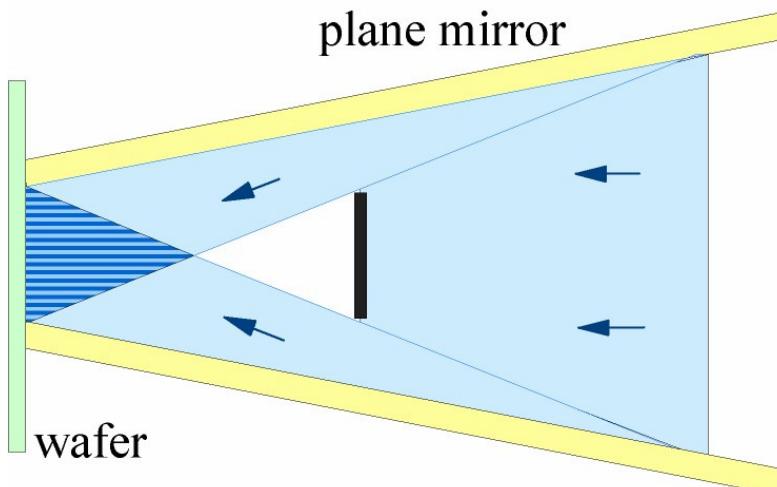


Figure 3.2) Basic Lloyd's mirror configuration

Lloyd's mirror:

- Easy to tune the pitch, simply by rotating the mirror/substrate.
- Only one optical branch, so more tolerant to environmental perturbations.
- But more defects are found due to dusts/contaminations on the mirror.

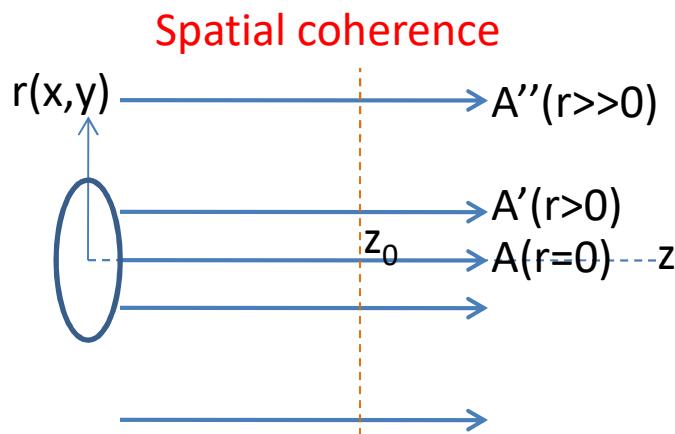


Another type of wave-front split IL setup using two mirrors. Better than Lloyd (above) in that Lloyd setup will have problem if mirror is not 100% reflective.

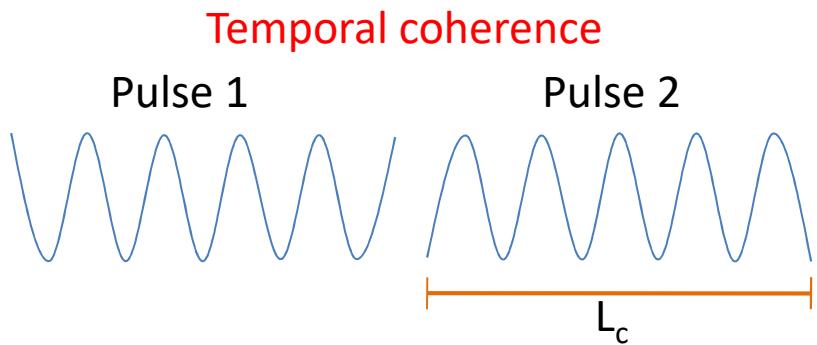
Temporal and spatial coherence

For plane wave, $E=E_0\cos(k \cdot r - \omega t - \varphi)$, here k and $r(x, y, z)$ is vector.

For ideal plane wave (100% coherent), φ (phase) is constant, independent of r (position) and t (time). But in reality, $\varphi = \varphi(r, t)$

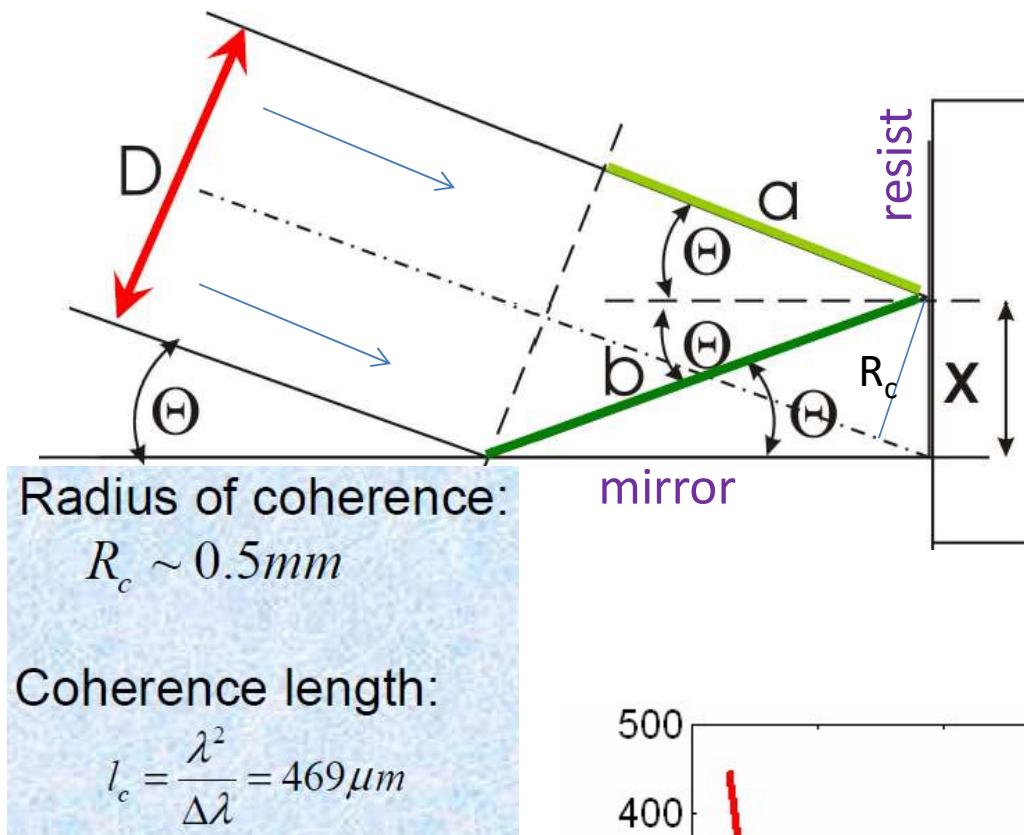


At any z -value z_0 , if the phase difference between sub-beam A and A' is small, namely $\Delta\varphi = \varphi(A') - \varphi(A) \ll 2\pi$, we can then consider φ as constant, and the two beam can interfere with well defined periodic interference pattern. But for large r such as point A'' , $\Delta\varphi = \varphi(A'') - \varphi(A)$ is no longer negligible, then the interference between sub-beam A and A'' become unpredictable, so no well defined periodic pattern. The r value at which $\Delta\varphi$ is still negligible is the coherence radius.



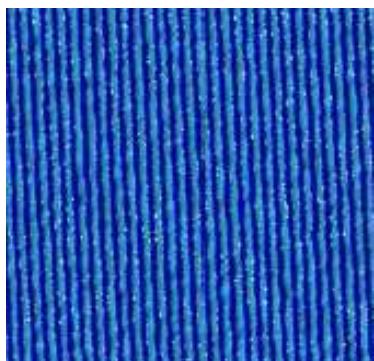
For pulse 1, $\varphi = \varphi_1$ (constant); for pulse 2, $\varphi = \varphi_2$. φ_1 and φ_2 is irrelevant to each other, so the interference pattern between pulse 1 and pulse 2 will be unpredictable. That is, to obtain predictable periodic interference pattern, the optical path difference between the two beams/"arms" must be $|L_2 - L_1| < L_c$. (or the "arrival time" must be $\Delta t = |L_2 - L_1| / c < L_c / c$ = pulse duration, so the term "temporal")

Coherence limitations to the pattern area: one example

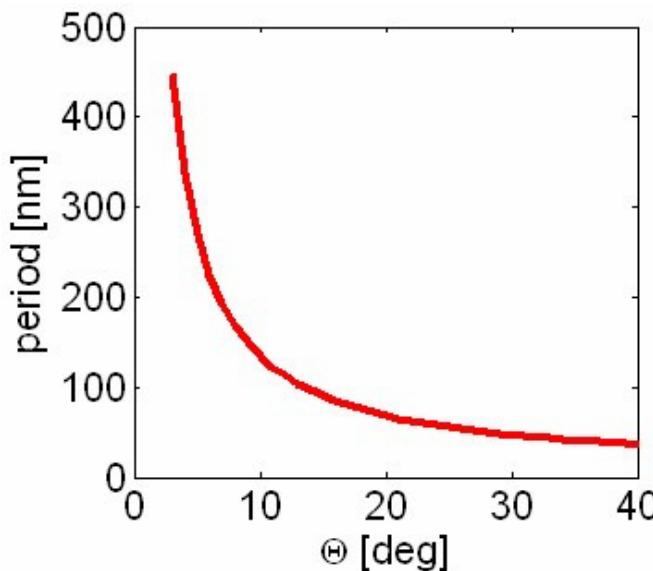


Coherence length:

$$l_c = \frac{\lambda^2}{\Delta\lambda} = 469\mu\text{m}$$



Period 95nm



- Spatial coherence:

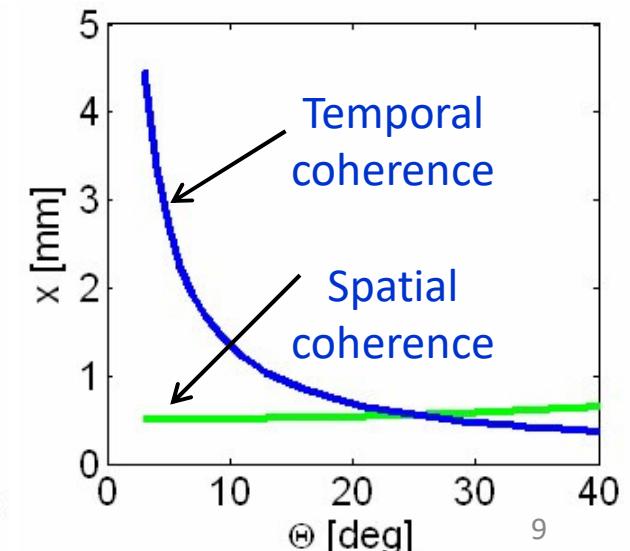
Requirement: $D \leq 2R_c$

$$x = \frac{R_c}{\cos(\Theta)}$$

- Temporal coherence:

Requirement: $b - a \leq l_c$

$$x = \frac{l_c}{2\sin(\Theta)}$$



Interference lithography using incoherent light source

At $\lambda < 257\text{nm}$ (frequency doubled Ar⁺ laser), no good coherent source with high output power exists.

Phase grating can be used to relax/eliminate coherence requirement.

$$p \sin \theta = \frac{\lambda}{n}, \sin \theta = \frac{\lambda}{np}$$

$$P = \frac{\lambda}{2n \sin \theta} \equiv \frac{p}{2}$$

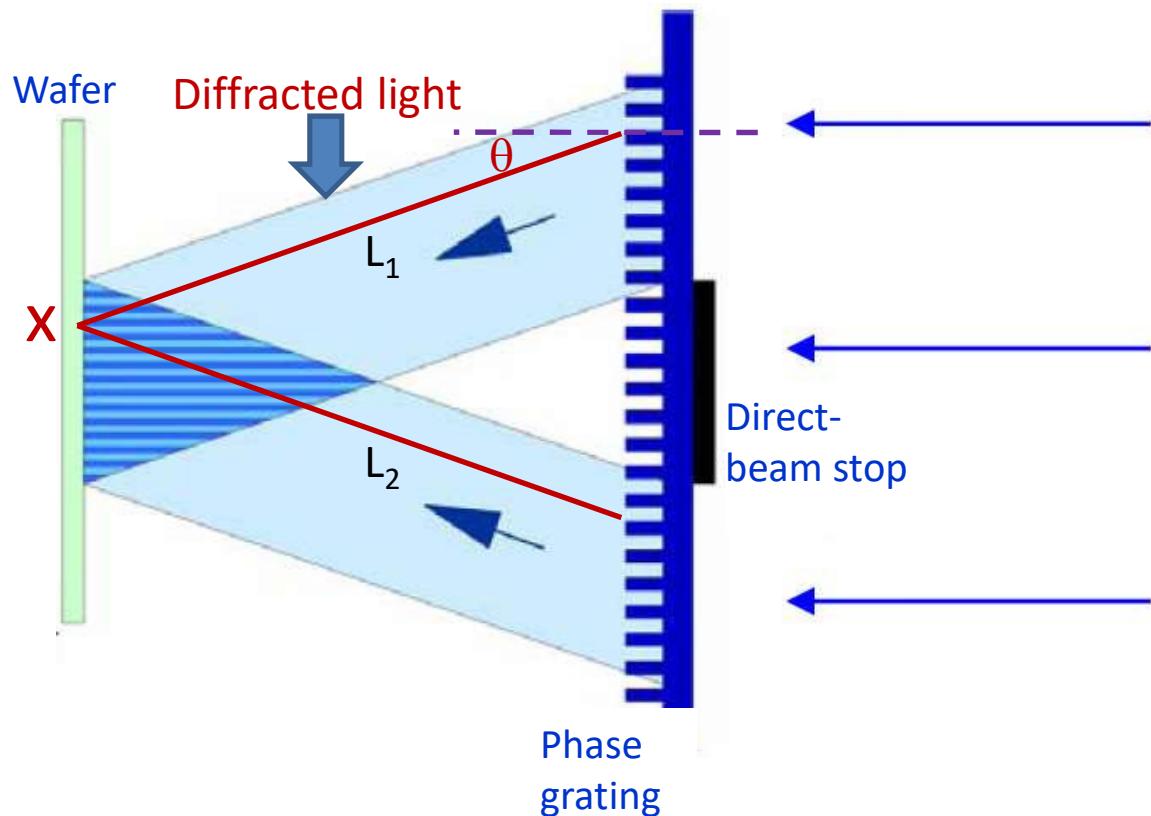
(n is refractive index)

p is pitch of phase grating.

P is pitch of grating on wafer.

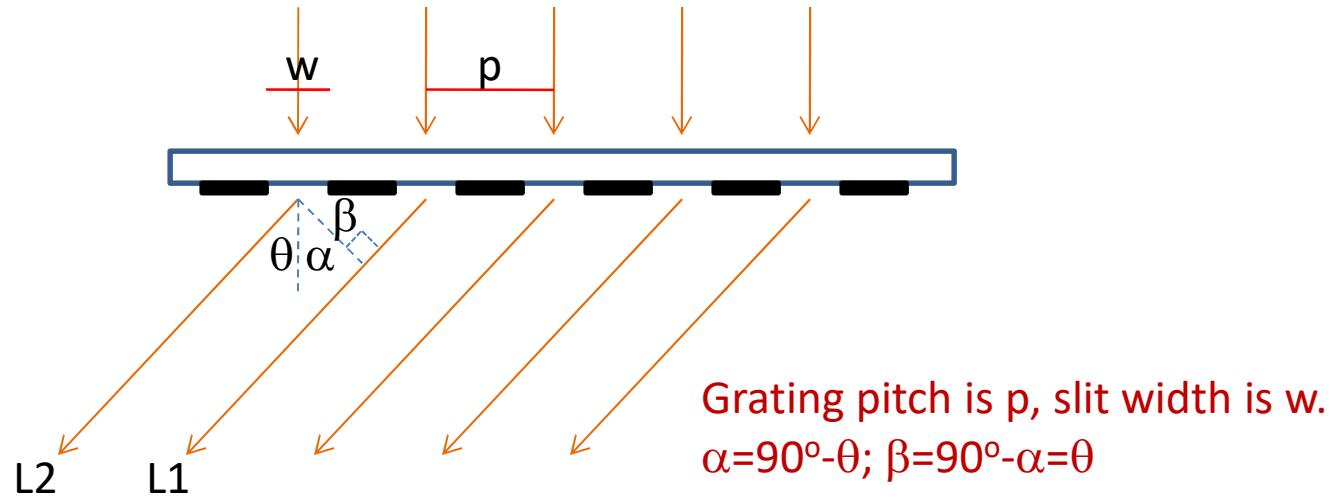
$P \equiv p/2$, independent of λ .

(but must $\lambda < np$)



For an arbitrary position X on the wafer, the two beams have the same optical path ($L_1 = L_2$), so no need of temporal coherence (spatial coherence is still needed).

Light diffraction through a grating (periodic slit array)



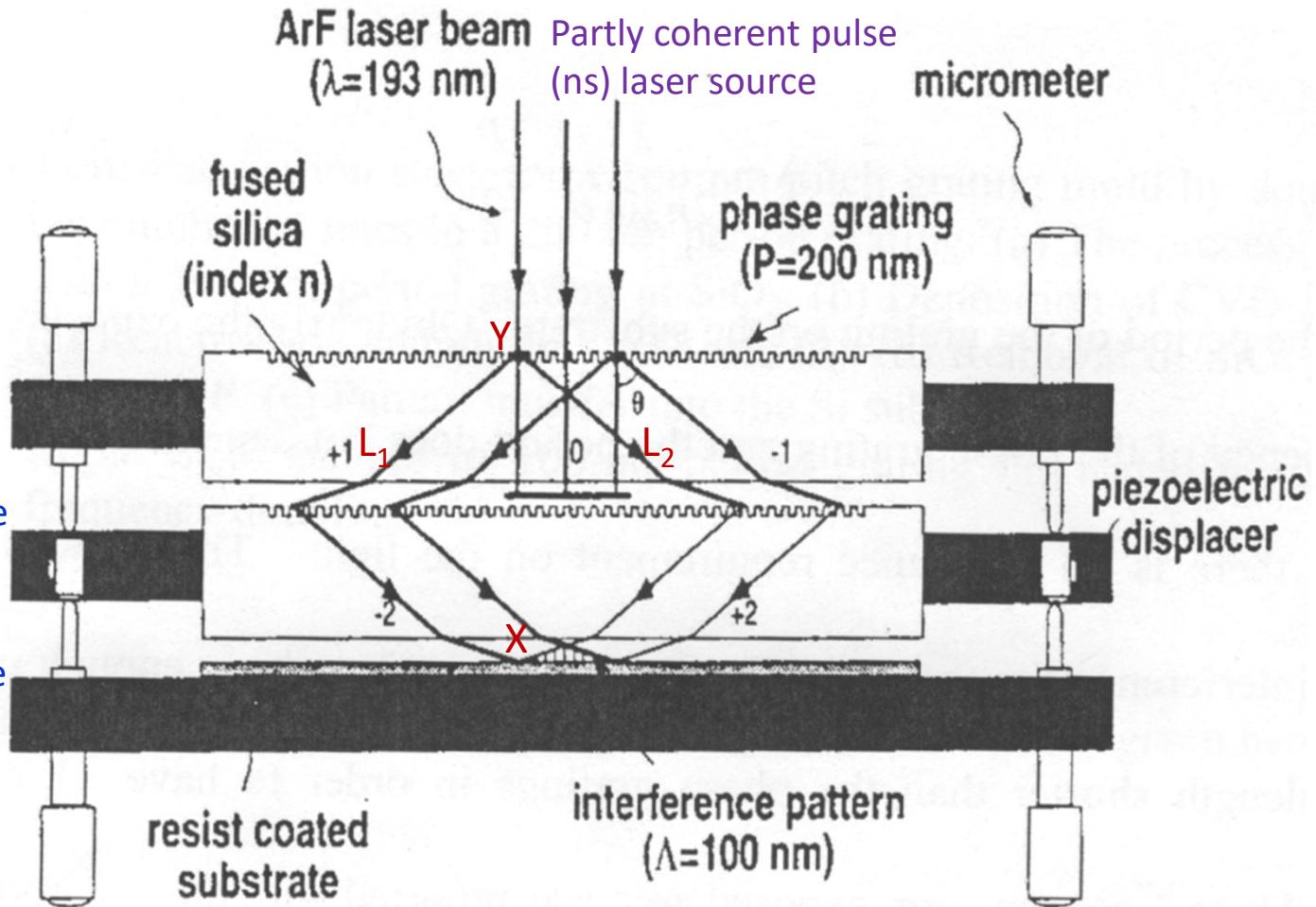
When two adjacent sub-beams $L_2-L_1=m\lambda$, $m=0, \pm 1, \pm 2, \pm 3\dots$, the diffracted light has high intensity (bright), since the sub-beams are all “in-phase”. m is called the order of diffraction.

For -1 order (here “-” means diffract to the left side), $L_2-L_1 = -psin\beta = -psin\theta=-\lambda$, so $sin\theta=\lambda/p$. Here p is the period of the grating, assume refractive index $n=1$.

Achromatic interference lithography

For any point X on the wafer, not only the optical path $L_1=L_2$ (so no need of temporal coherence); but also the two beams come from the same source location Y (so no need of spatial coherence).

In addition, the laser source doesn't need to be monochromatic (i.e. very narrow $\Delta\lambda$), so the name "achromatic".



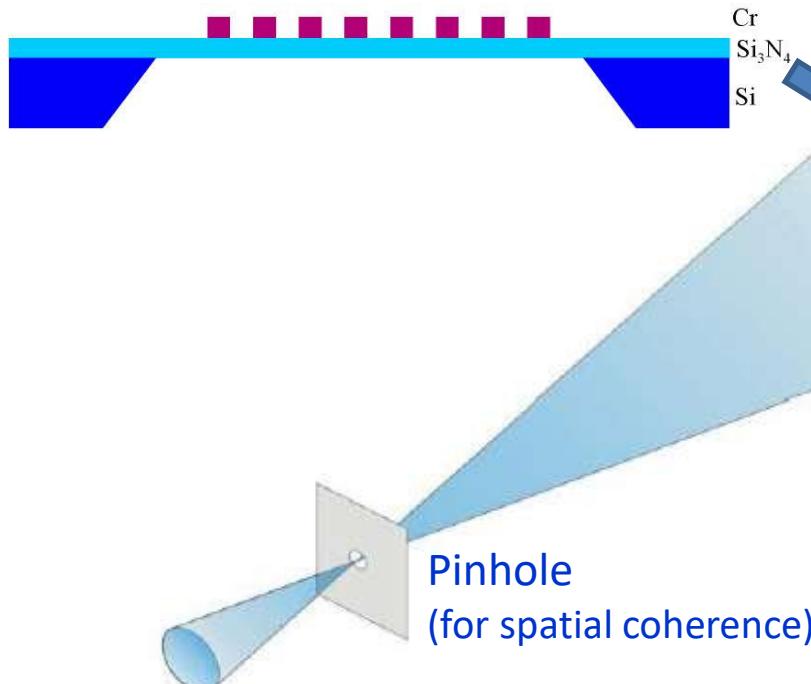
$$\sin \theta = \lambda / (nP)$$

$$\Lambda = \lambda / (2n \sin \theta)$$

$$\Lambda = P/2$$

Scale down the pitch: EUV interference lithography at $\lambda=13.5\text{nm}$ (EUV: extreme UV, also called soft x-ray)

Diffraction phase grating
membrane mask fabricated
by e-beam lithography



Resist coated
substrate

Lithographic performance:

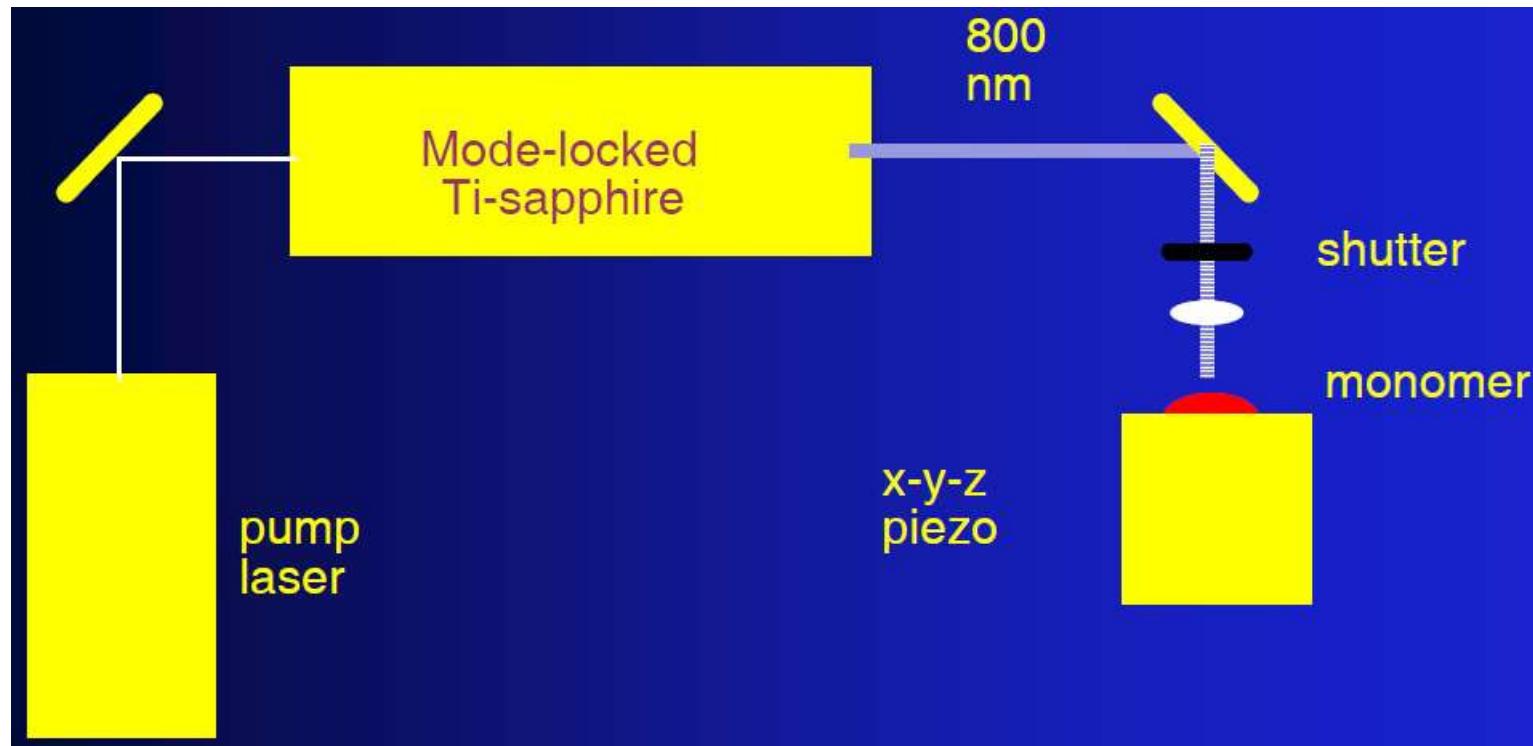
- Resolution: 25-50 nm period(!!)
- Minimum features: 3.5nm(!!)
- Exposure area: up to mm's
- Substrate size: up to 8" wafers (scan stage)
- Exposure time: 5-30 secs
- Throughput: 1 wafer/hour (for 100 fields)

Other photon-based lithographies

1. Interference lithography
2. Phase-mask lithography
3. Laser beam direct writing and micro-mirror array lithography
4. Two-photon lithography

Two photon absorption photolithography

Photo-polymerization only occurs in small volumes corresponding to the focal spot of a laser beam where the intensity is high enough to produce absorption of two photons.

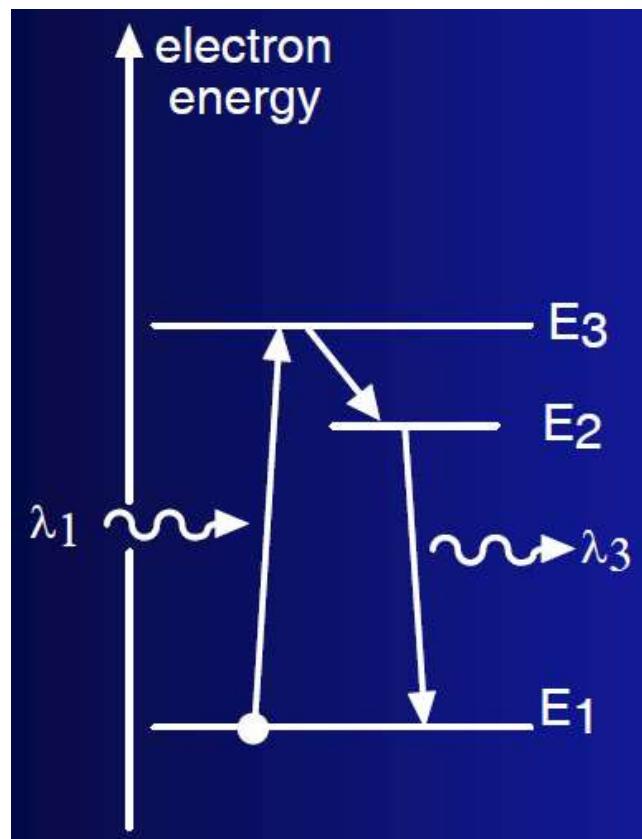


Two photon absorption to create photon with λ close to $800/2=400\text{nm}$ (UV light), which can expose (cure or crosslink) the monomer resist.

Absorption of light of one and two photons

Normal optical absorption
(α has units of cm^{-1})

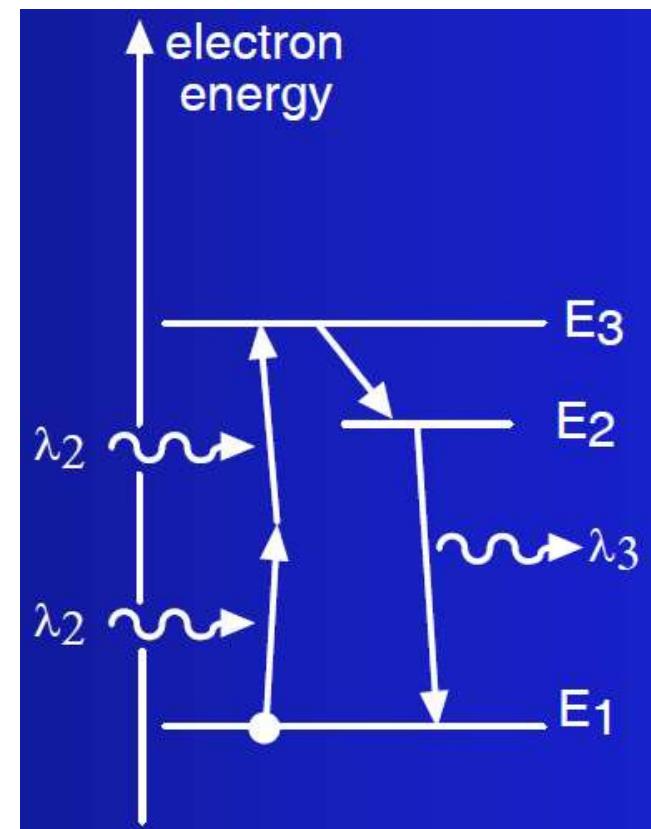
$$\frac{dI}{dx} = -\alpha I, I(x) = I_o e^{-\alpha x}$$



One-photon absorption and
luminescence $\lambda_1 < \lambda_3$

Two-photon (non-linear) absorption
(β has units of cm/Watt)

$$\frac{dI}{dx} = -\beta I^2, I(x) = \frac{I_o}{1 + I_o \beta x}$$



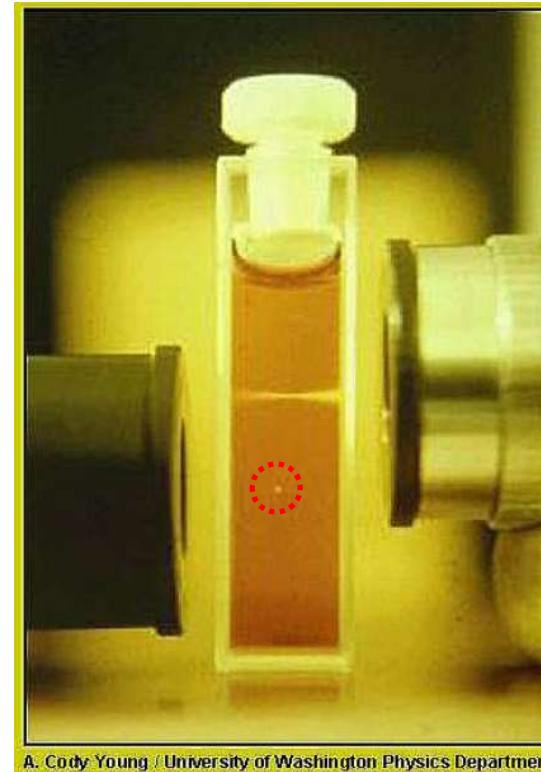
Two-photon absorption and
luminescence $\lambda_2 = 2 \lambda_1 (> \lambda_3)$

Two photon excitation (or luminescence)

Upper beam from right:
luminescence from one-photon
absorption at $\lambda=400\text{nm}$.

Lower beam from left:
luminescence from two-photon
absorption at $\lambda=800\text{nm}$.

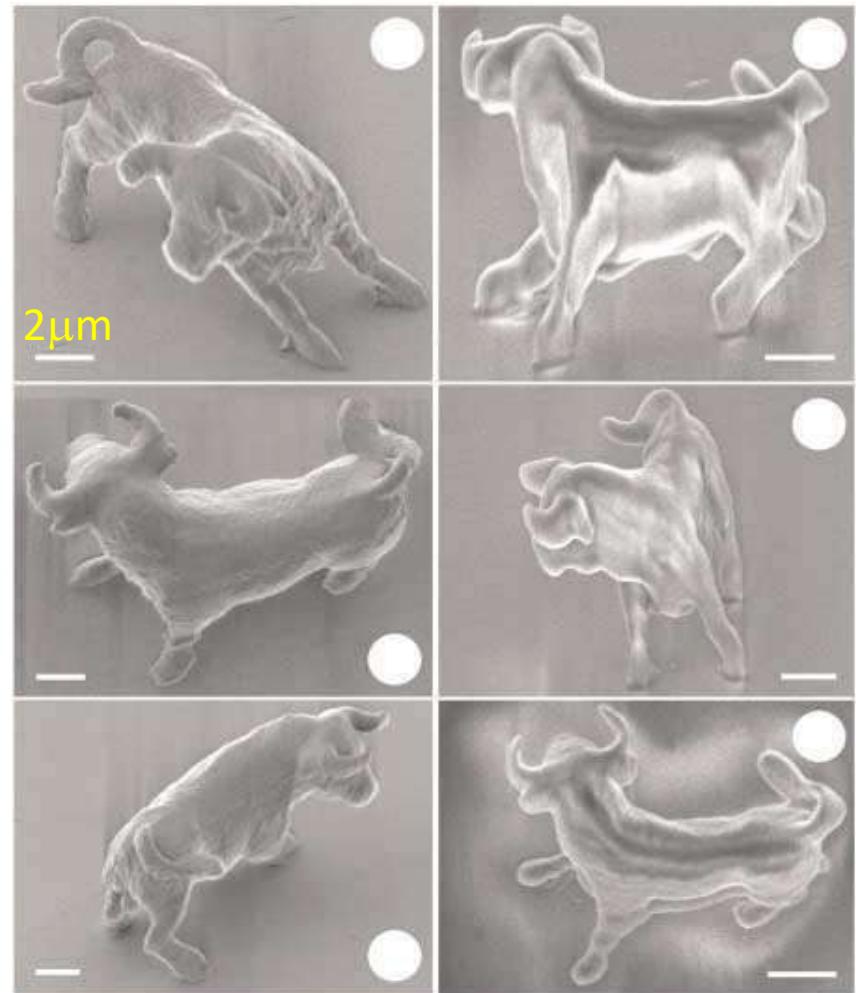
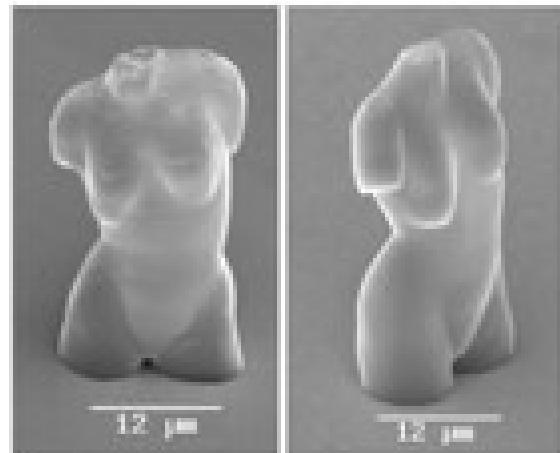
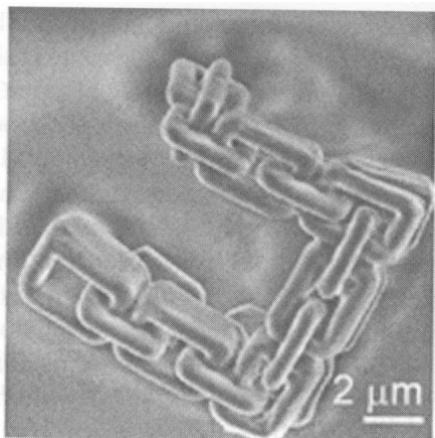
- Absence of out-of-focus absorption.
- The infrared excitation light suffers less scattering.



- Two-photon excitation arises from the simultaneous (10^{-18} seconds) absorption of two photons in a single quantized event.
- Fluorescence emission (at λ_3) varies with the *square* of the excitation intensity.
- The photon density must be approximately one million times required to generate the same number of one photon absorptions.
- Only the focal point of mode-locked pulsed lasers (very high peak power) can have such photon density.

Two photon photolithography (2PP): examples

Chain with smallest feature size 120nm



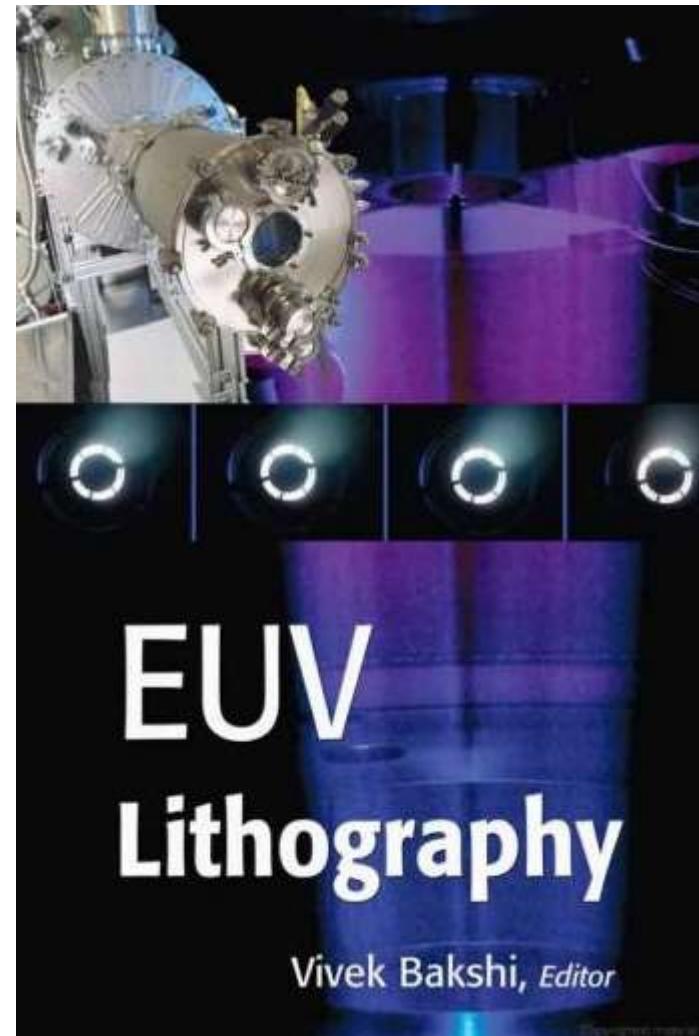
A titanium sapphire laser operating in mode-lock at 76 MHz and 780 nm with a 150-femtosecond pulse width was used for exposure.

Extreme UV (EUV) lithography

1. Overview, why EUV lithography?
2. EUV source (hot and dense plasma).
3. Optics (reflection mirrors).
4. Mask (absorber on mirrors).
5. Resist (sensitivity, LER, out-gassing).
6. Contamination control.

Textbook page 16-20. You can read the book by Vivek if you want to learn more.

http://books.google.ca/books?id=91XeKLC9MUEC&pg=PA393&lpg=PA393&dq=Elemental+absorption+at+13.5nm&source=bl&ots=u2vsBa2dgr&sig=a1JKcj0vE6Gx7X-6m_zUR9CT5k&hl=en&ei=QZsQSpTVKZS8M5aT2FI&sa=X&oi=book_result&ct=result&resnum=1#PPR7,M1

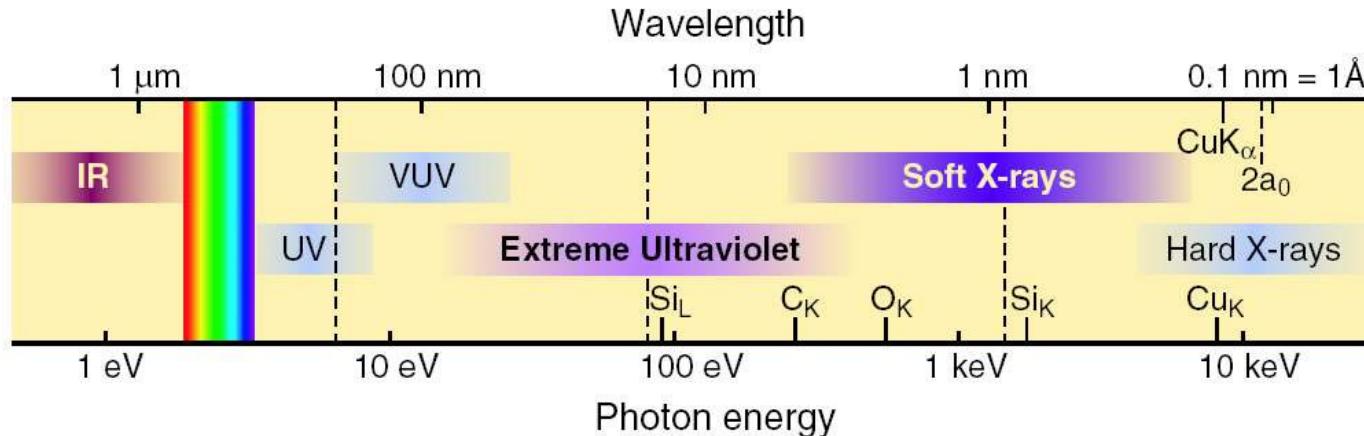


NE 353: Nanoprobing and lithography

Instructor: Bo Cui, ECE, University of Waterloo; <http://ece.uwaterloo.ca/~bcui/>

Textbook: Nanofabrication: principles, capabilities and limits, by Zheng Cui

Electromagnetic spectrum



- Visible is $400 - 700\text{nm}$ (1.7 to 3eV)
- UV down to about 170 nm ($\sim 7\text{eV}$)
- VUV- Vacuum UV (starts where N_2 is absorbing) then there is FUV (far UV) & EUV
- EUV/soft x-ray, $2-50\text{nm}$
- 47nm is the λ for the Ne-like-Ar X-ray Laser (capillary discharge laser).
- But for EUV lithography, it is at $\sim 13.5\text{nm}$ (92eV).

Current 193nm deep UV (DUV) lithography: mask material

- Photo-masks today are made from fused silica (amorphous SiO₂).
- Fused silica has a number of advantageous properties.
 - Chemical stability.
 - Transparency for ultraviolet light.
 - No intrinsic birefringence (i.e. refractive index is polarization independent).
 - A low coefficient of thermal expansion.
- A low coefficient of thermal expansion: 0.5ppm/°C.
 - If a mask changes temperature by 0.1°C, then the distance between two features separated by 50mm will change by 2.5 nm.
 - This change in registration can be absorbed into overlay budgets, after reduction by 4× (i.e. pattern on resist misaligns by 2.5/4=0.6nm, OK).

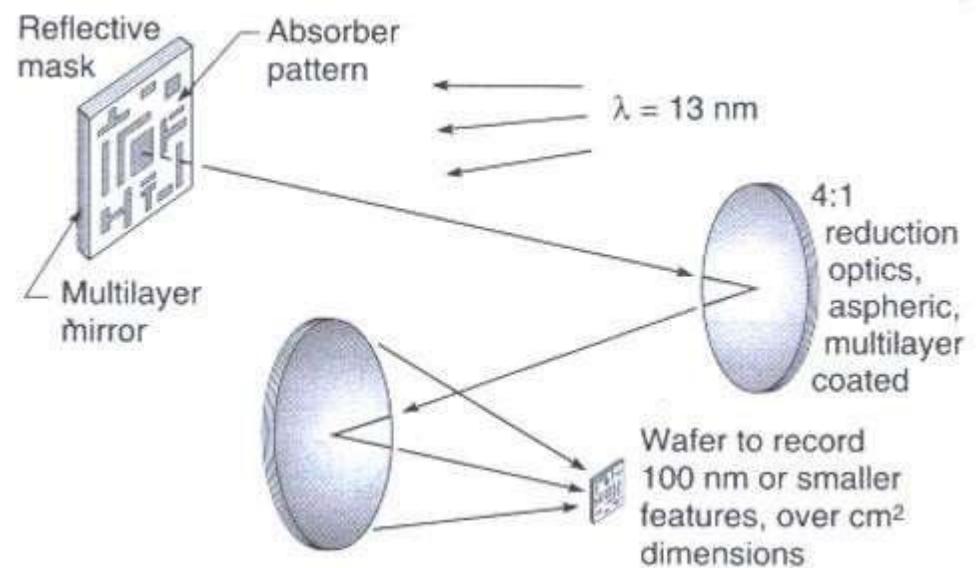
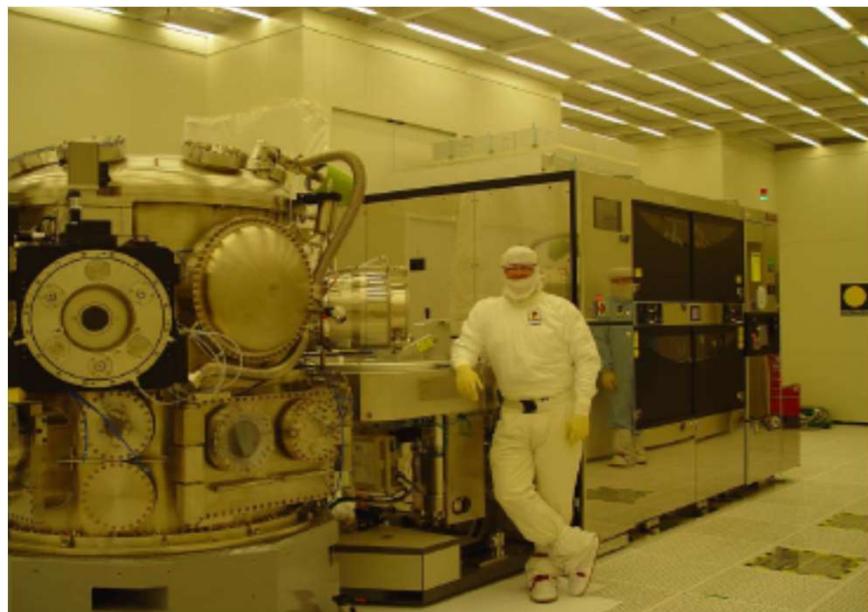
Why not the next excimer line (157nm)?

Why not a stop at 157nm?

- Fused silica and atmospheric oxygen become absorptive by 157nm, so even incremental decreases in wavelength (by only 36nm) start to require a major system modification: vacuum exposure, use CaF₂ as lens material (resist materials also different).
- CaF₂ has a crystalline structure (not “glassy/amorphous” like fused silica), with significant birefringence (i.e. light propagation through the lens depends on the polarization relative to crystalline orientation).
- The coefficient of thermal expansion of CaF₂ is 19ppm/°C, versus 0.5ppm/°C for fused silica.
- The 2.5nm of mask registration error for fused silica now becomes nearly 100nm (25nm after $\frac{1}{4}$ reduction, still too high).
- Below 157nm, no excimer laser line has the required output power.
- The development of EUV lithography further makes 157nm lithography unnecessary.

EUV lithography (EUVL) characteristics

- EUV radiation is strongly absorbed in virtually all materials, even gases, so EUV imaging must be carried out in a near vacuum.
- There is no refractive lenses usable - EUVL imaging systems are entirely **reflective**.
- But EUV reflectivity of individual materials at near-normal incidence is very low, so “distributed Bragg reflectors” are used.
- The best of these reflectors function in the region between 11 and 14nm (Si/Mo material)



Extreme UV (EUV) lithography

1. Overview, why EUV lithography?
2. EUV source (hot and dense plasma).
3. Optics (reflection mirrors).
4. Mask (absorber on mirrors).
5. Resist (sensitivity, LER, out-gassing).
6. Contamination control.

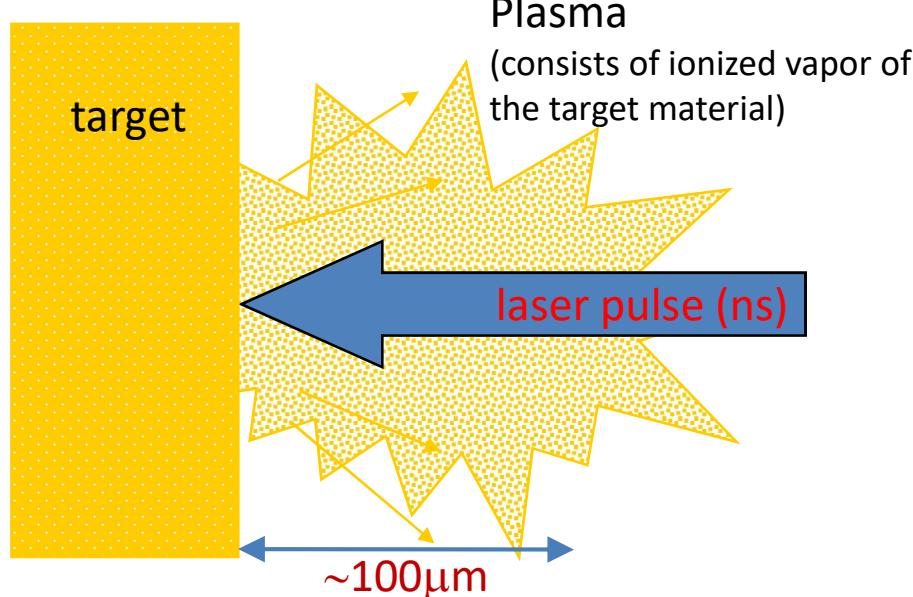
EUV @13.5nm plasma radiation source

Light sources must match the wavelengths at which Mo/Si multi-layers have high reflectivity.

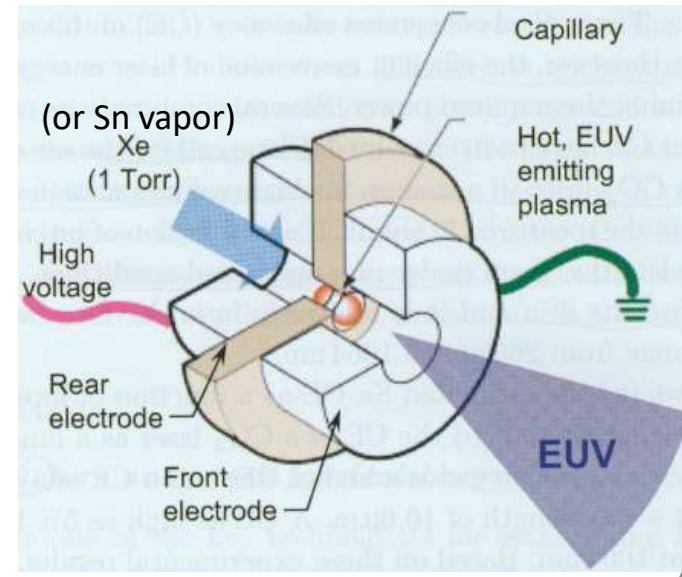
The only viable source for 13.5nm photons is a hot and dense plasma
(synchrotron radiation also creates EUV, but very expensive and huge size.)

- Powerful plasma: temperature of up to 200,000°C, atoms ionized up to +20 state.
- Emit photons by (e - ion) recombination and de-excitation of the ions.
- Plasma must be pulsed: pulse length in pico- to nanosecond range
- Plasma is produced by powerful pulsed laser or electric arc (discharge) of up to 60000A peak current.

Laser Produced Plasma (LPP)



Discharge Produced Plasma (DPP)



Plasma radiation source for 13.5nm: Sn

Plasma: ionized gas, similar to the plasma used for reactive ion etching (RIE). But in regular RIE, only <10% gas molecules are ionized; here all ions are ionized, and to a high ionization state (up to Sn^{20+}).

Since the mass of electron is << that of ion, electrons transfer little of its energy to ions upon collision. As a result, electrons and ions are not in thermal equilibrium in a plasma, with electrons much “hotter” than ions.

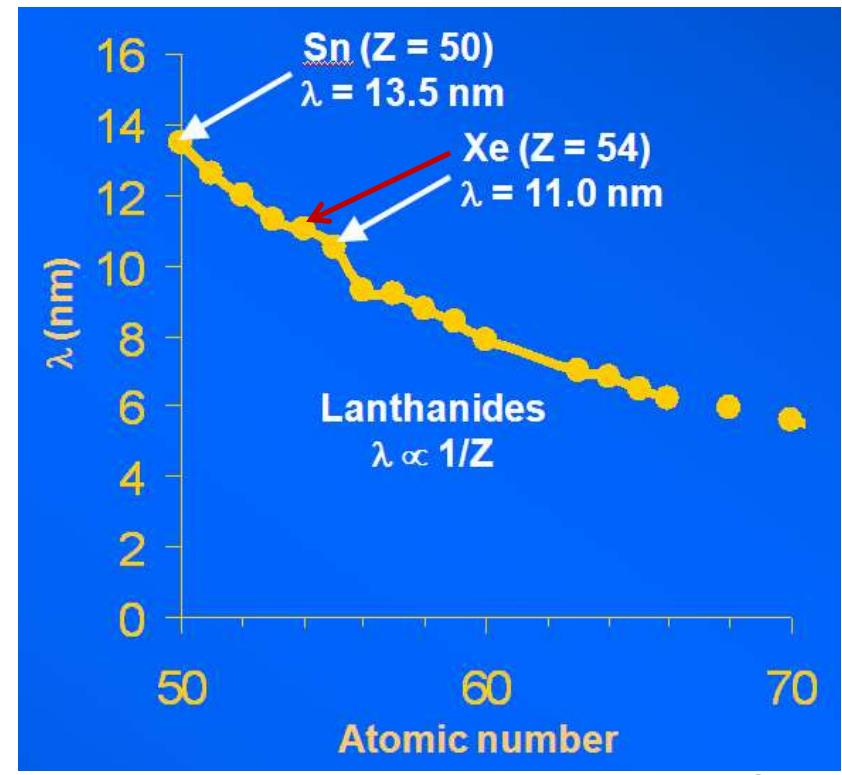
Laser produced Sn plasma

Target, Z=50 [Kr]5s ² 4d ¹⁰ 5p ²	Sn
Laser wavelength, λ	1.064μm
Laser flux, ϕ	$1 \times 10^{11} \text{ W/cm}^2$
Electron temperature, T_e	48.8eV
Electron density, n_e (300K is 26meV, 1eV is $1.15 \times 10^4 \text{ K}$)	$9.88 \times 10^{20} \text{ cm}^{-3}$

Ion distribution:

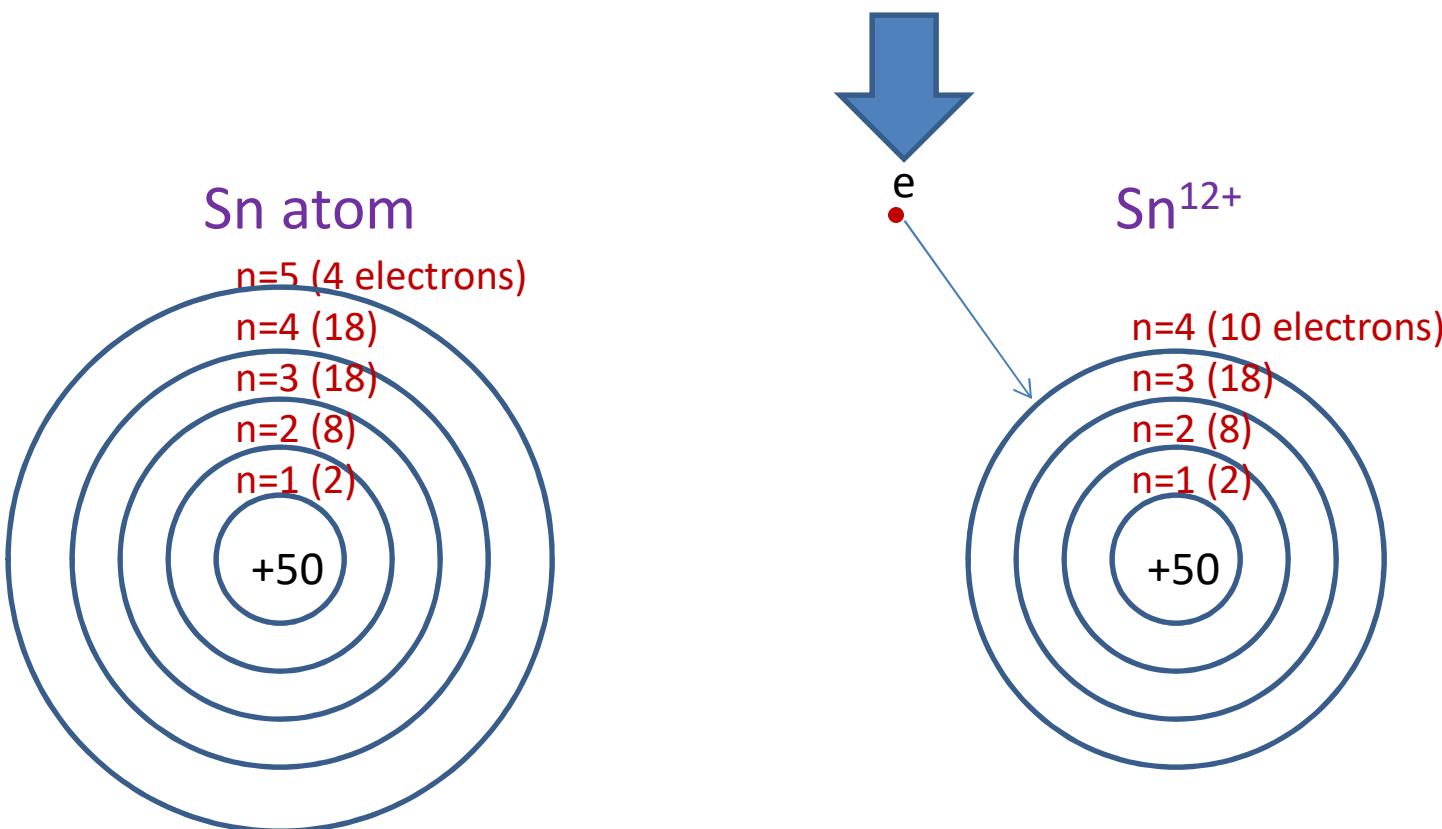
Sn X	0.046
(Sn^{10+})	(4.6%)
Sn XI	0.243
(Sn^{11+})	(24.3%)
Sn XII	0.306
Sn XIII	0.330
Sn XIV	0.068

Emission peak wavelength (nm) versus atomic number



Why need ionization state >10 to produce EUV?

Energy level $E=-13.56 Z^2/n^2$ (eV). For this “free” electron, it “sees” $Z=50-38=12$ positive charges. So when it jumps to the $n=4$ level, it should emit a photon with energy $13.56 \times 12^2/4^2 = 122, which is the same order as 92eV for 13.5nm wavelength.$

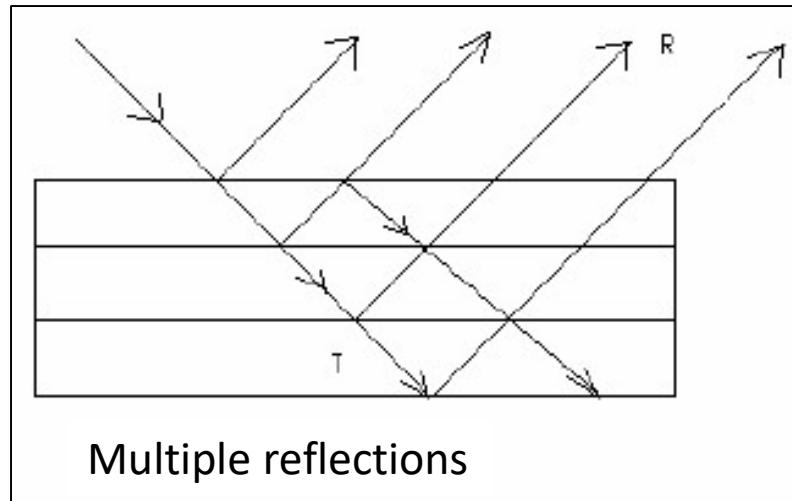


Extreme UV (EUV) lithography

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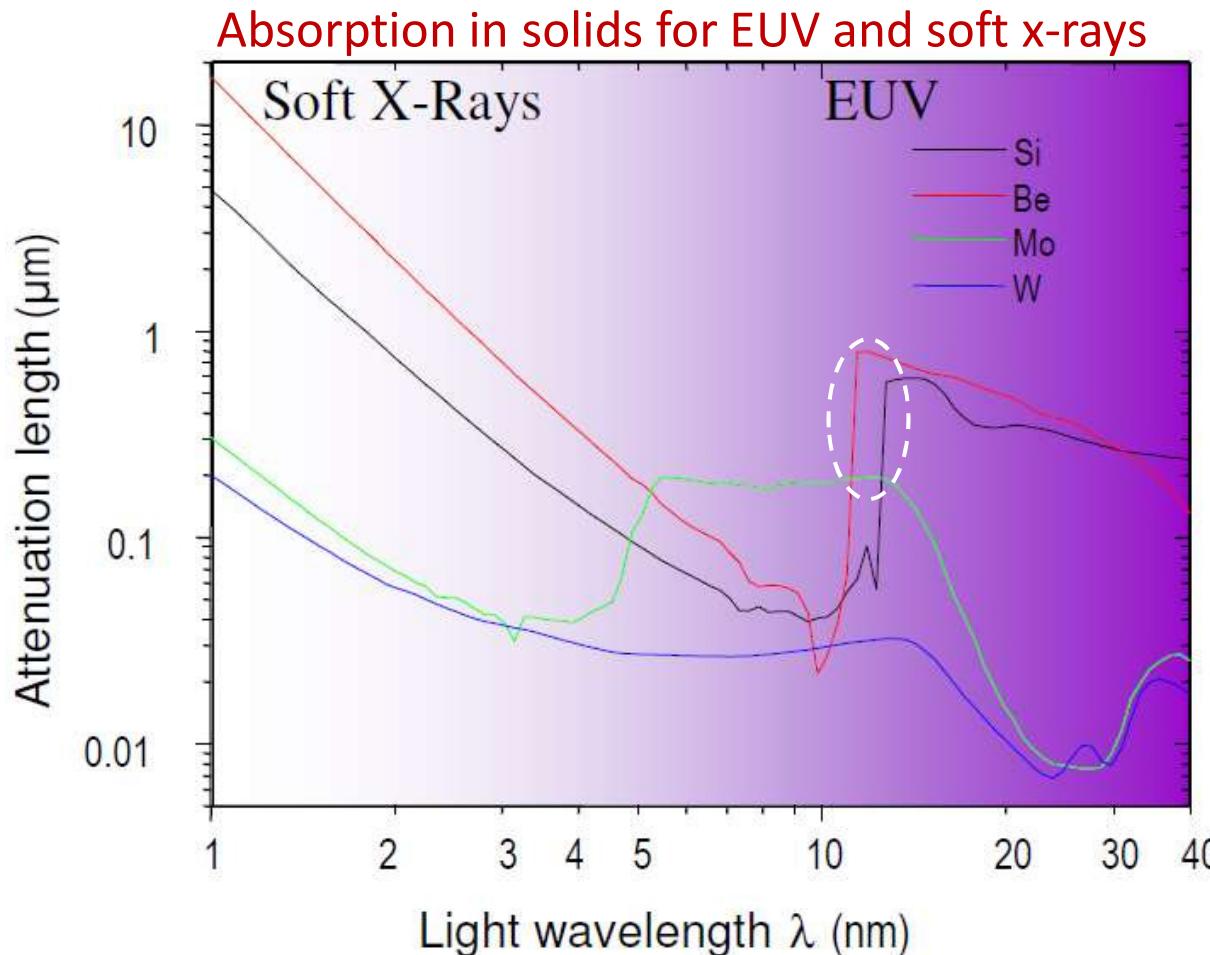
Optics for EUV lithography (EUVL): overview

- All solids, liquids, and gasses absorb 13.5nm photons, so no longer refracting/transparent lens. (A beam of EUV light is absorbed in 100nm - thick of H₂O)
- EUVL uses mirrors coated with multiple layers of molybdenum and silicon that can reflect 70% light.
- The other 30 percent is absorbed by the mirror.
- Without the coating, light would be almost totally absorbed by the mirror (almost no reflection).



If the thicknesses and compositions of all films are carefully controlled, the reflected light will *constructively interfere*, resulting in the brightest possible reflection.

Why Si/Mo and 13.5nm?



For high reflection, the absorption should be low (i.e. attenuation length should be large). So Mo, Si, Be are good candidates at ~10-15nm.

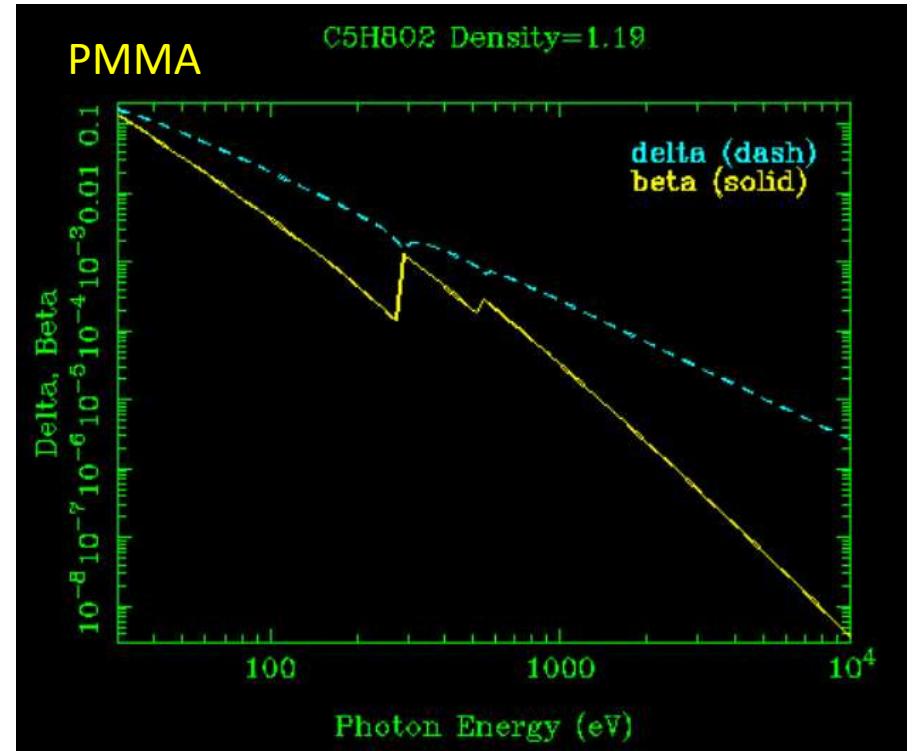
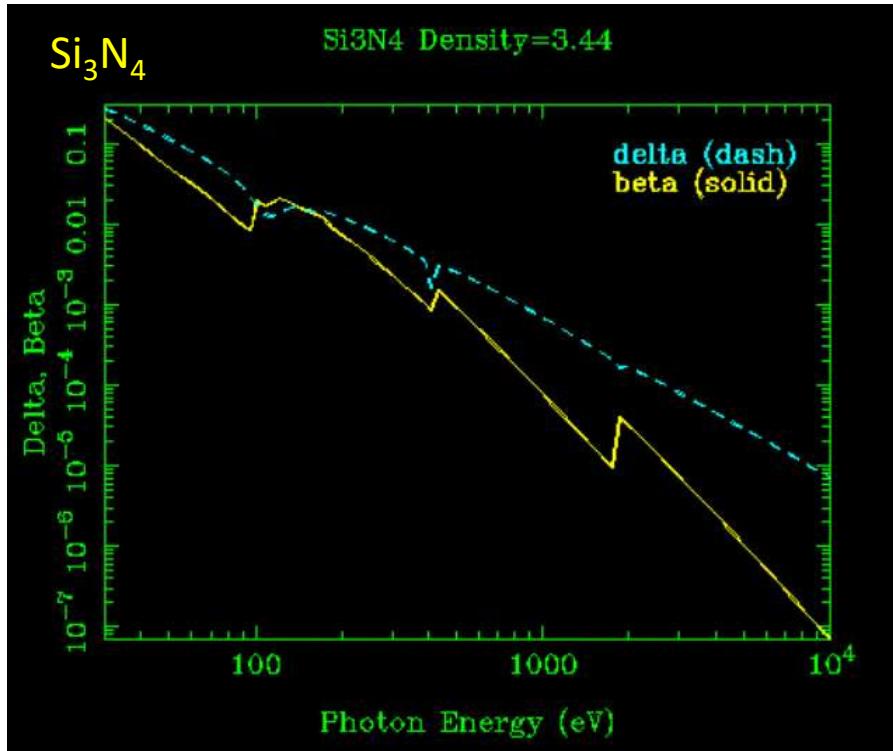
$$I = I_0 e^{-\alpha t} = I_0 e^{-t/\mu}$$

t : depth into the material
 α : absorption coefficient
 μ : attenuation length

- Mo/Si ~40 layer pairs give ~70% reflectance where Mo and Si are most transparent.
- Mo/Be is higher (at $\lambda=11\text{nm}$) but narrower $\Delta\lambda$; and more importantly, Be is toxic.

Refractive index at EUV

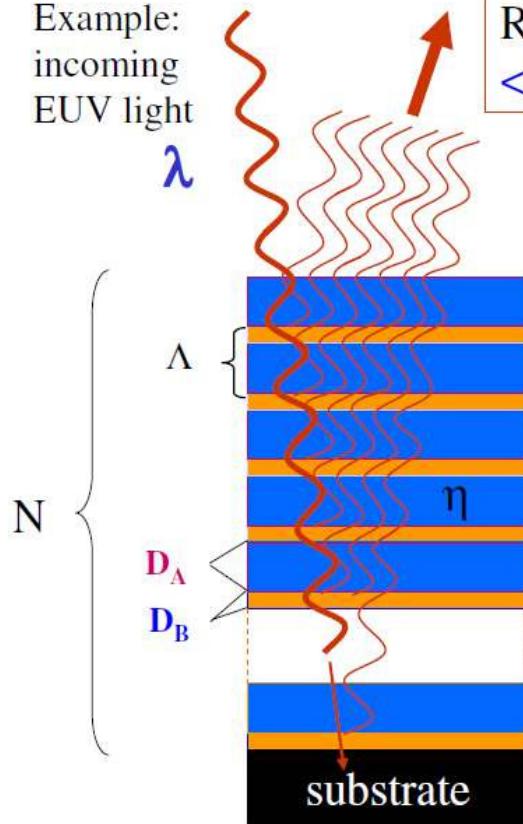
$n=1-\delta-i\beta$ ($\delta, \beta \ll 1$), n is close to 1, so low reflection



- Refractive index is very closer to 1.0 for shorter wavelength (higher photon energy). So no “optics” for x-ray ($>>100$ eV).
- For $\lambda=13.5$ nm, photon energy = 92eV, so δ, β is not negligible (>0.01), making reflective optics possible.
- Amplitude reflection $r=(n_1-n_2)/(n_1+n_2)$ for normal incidence at each interface.
- r has order of $0.01/2$, or order 1% at each reflection. Need many interfaces to achieve high total reflection. E.g., 50 layers will give order 50% reflection.

Multilayer EUV mirrors – Bragg reflectors

Example:
incoming
EUV light



Reflected EUV EM-waves "in phase"
<1% per interface → ~70% in total

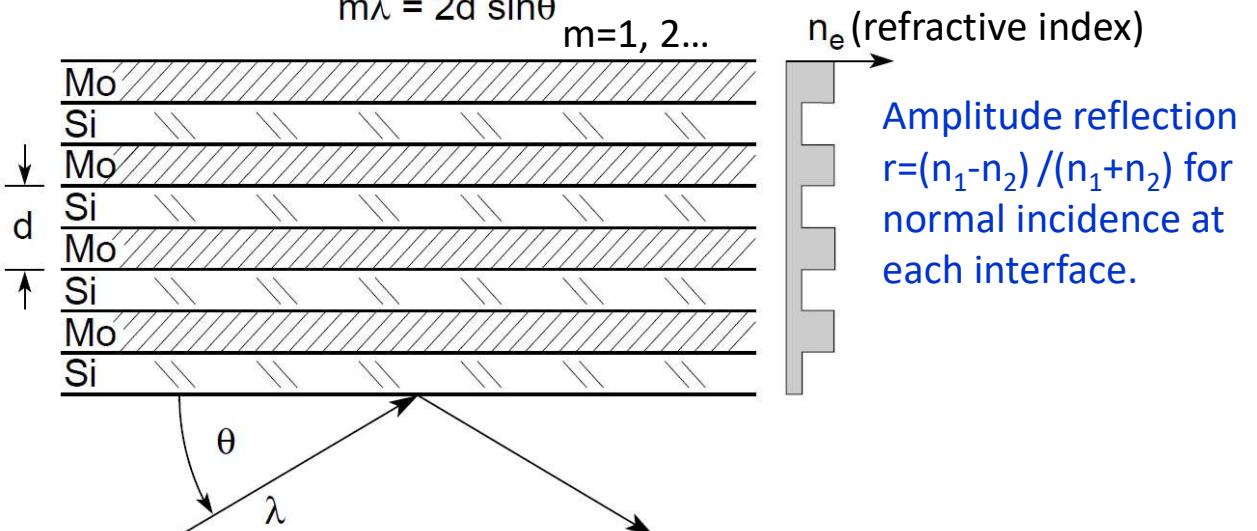
$$\Lambda = D_A + D_B = \text{bi-layer period}$$

$$\lambda = \text{radiation wavelength}$$

The period $\Lambda \approx \frac{1}{2}$ wavelength (for normal incidence)

Layer thicknesses $\approx \frac{1}{4}$ wavelength

$$m\lambda = 2d \sin\theta \quad m=1, 2\dots$$

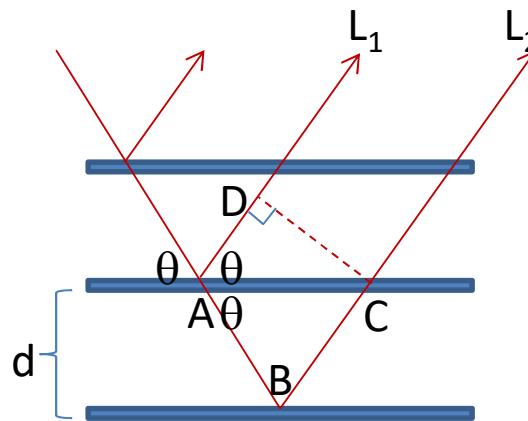


- For normal incidence, if $D_A \sim D_B$, then each layer $\sim \lambda/4 = 3.4\text{nm}$ for $\lambda = 13.5\text{nm}$.
- Since the angle of incidence changes across the mirror, so do the required Mo/Si layer thicknesses.
- Acceptable surface roughness: 0.2nm RMS, corresponding to a phase shift error of 10° .

Bragg reflectors

Assume one layer is much thinner, and refractive index of the thicker layer is $n \approx 1$.

For maximum reflection, the “sub-beam” must be all “in phase”, namely the optical path difference $n(L_2 - L_1) \approx L_2 - L_1 = m\lambda$ (m is integer)



$$L_2 - L_1 = (AB + BC) - AD$$

$$AB = BC = d / \sin \theta$$

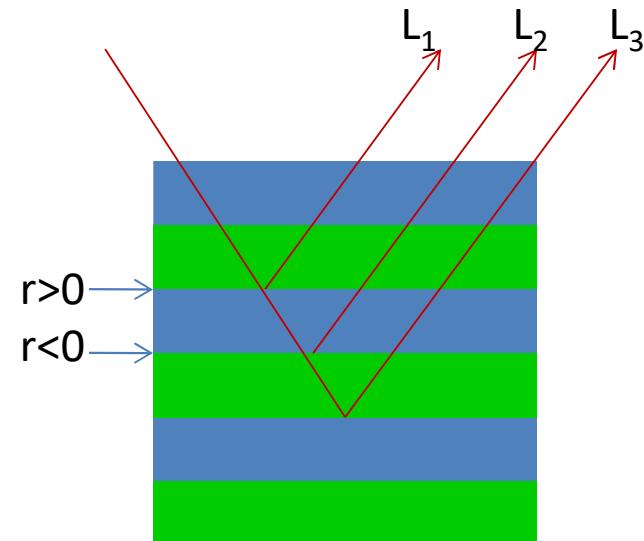
$$AD = AC \cos \theta; (AC/2) \tan \theta = d; \text{ so } AD = 2d(\cos \theta)^2 / \sin \theta$$

$$L_2 - L_1 = 2d / \sin \theta - 2d(\cos \theta)^2 / \sin \theta = 2d \sin \theta = m\lambda$$

This is the same equation as x-ray diffraction for materials analysis, where d is the crystal lattice constant.

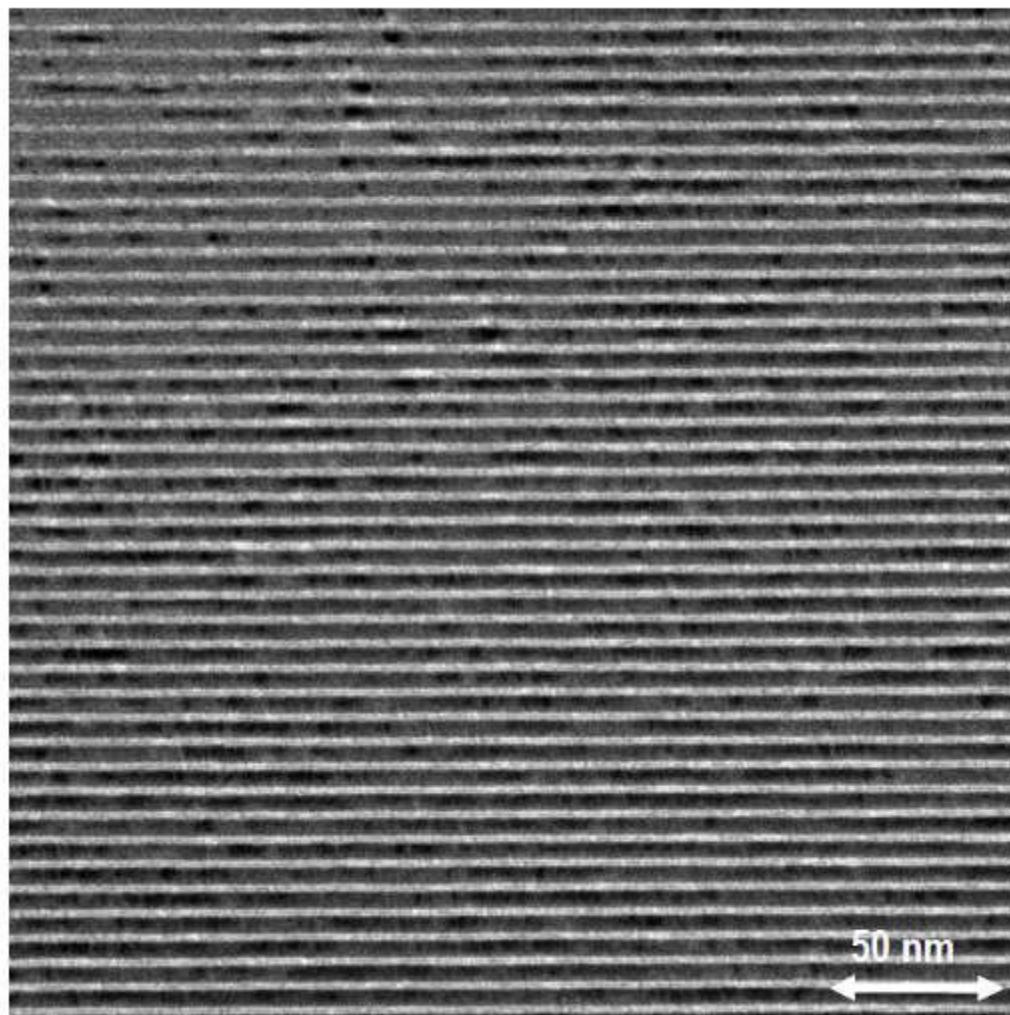
For the case that the two layers have similar thickness, if $L_3 - L_1 = \lambda$, then $L_2 - L_1 = \lambda/2$. So it seems that the net reflection should be zero.

“Fortunately”, the reflectivity $r = (n_1 - n_2) / (n_1 + n_2)$ has opposite sign at the two interfaces, which means there is a “half wave loss” (equivalent to an extra optical path of $\lambda/2$ or $-\lambda/2$) at the interface where $r < 0$. As a result, equivalently $L_2 - L_1 = \lambda$ or 0.



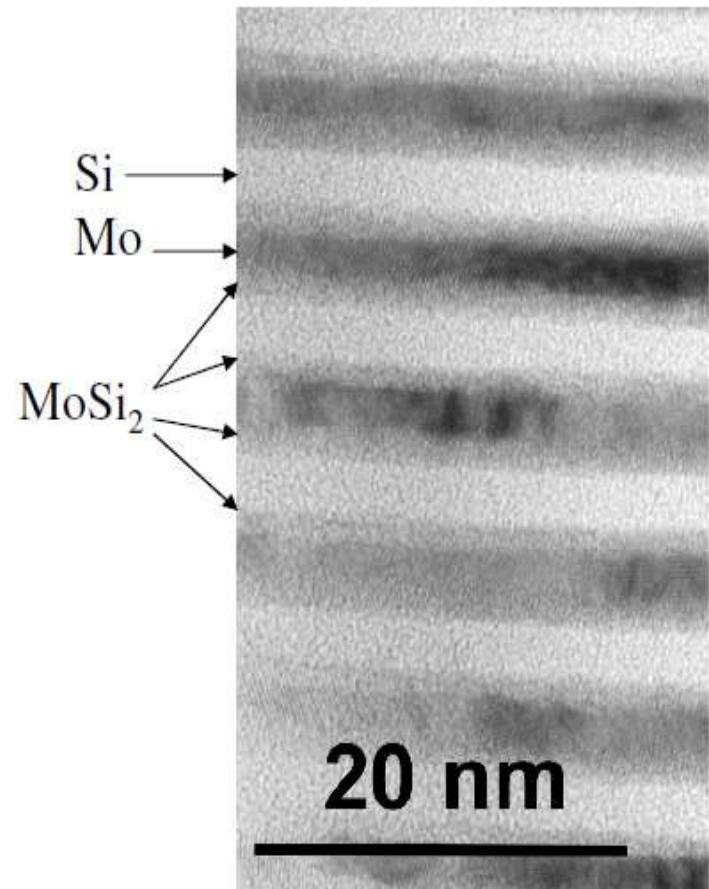
TEM images of EUV mirrors

TEM of a Mo/Si EUV mirror, N=50, $\Lambda=6.8$ nm

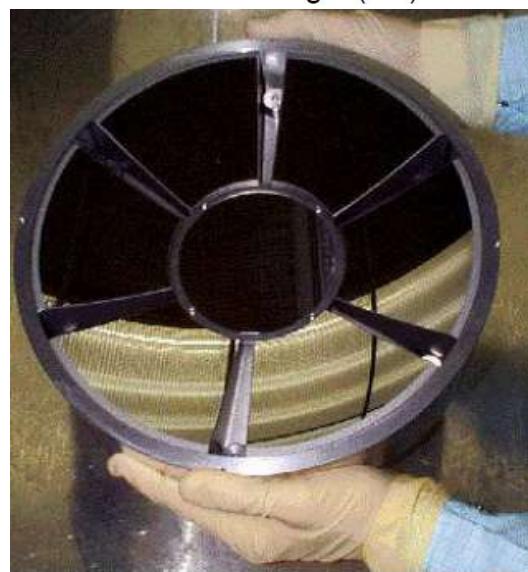
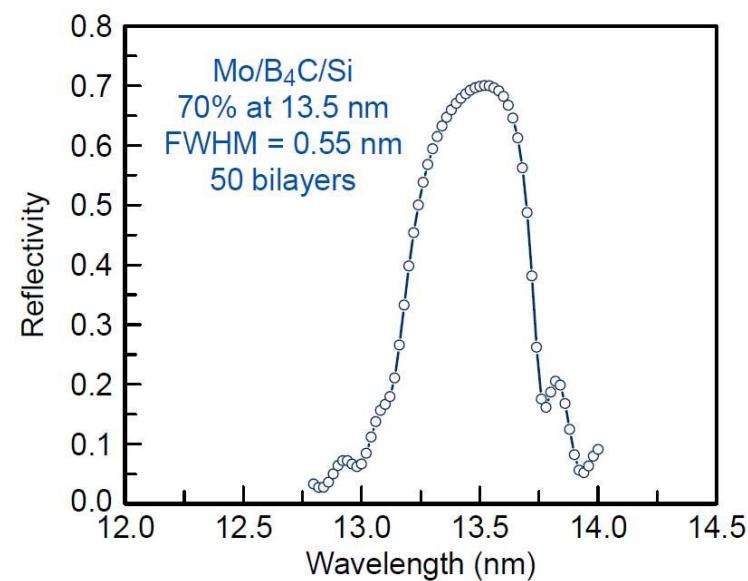


Deposited by magnetron sputtering

HR TEM reveals interfacial MoSi_2



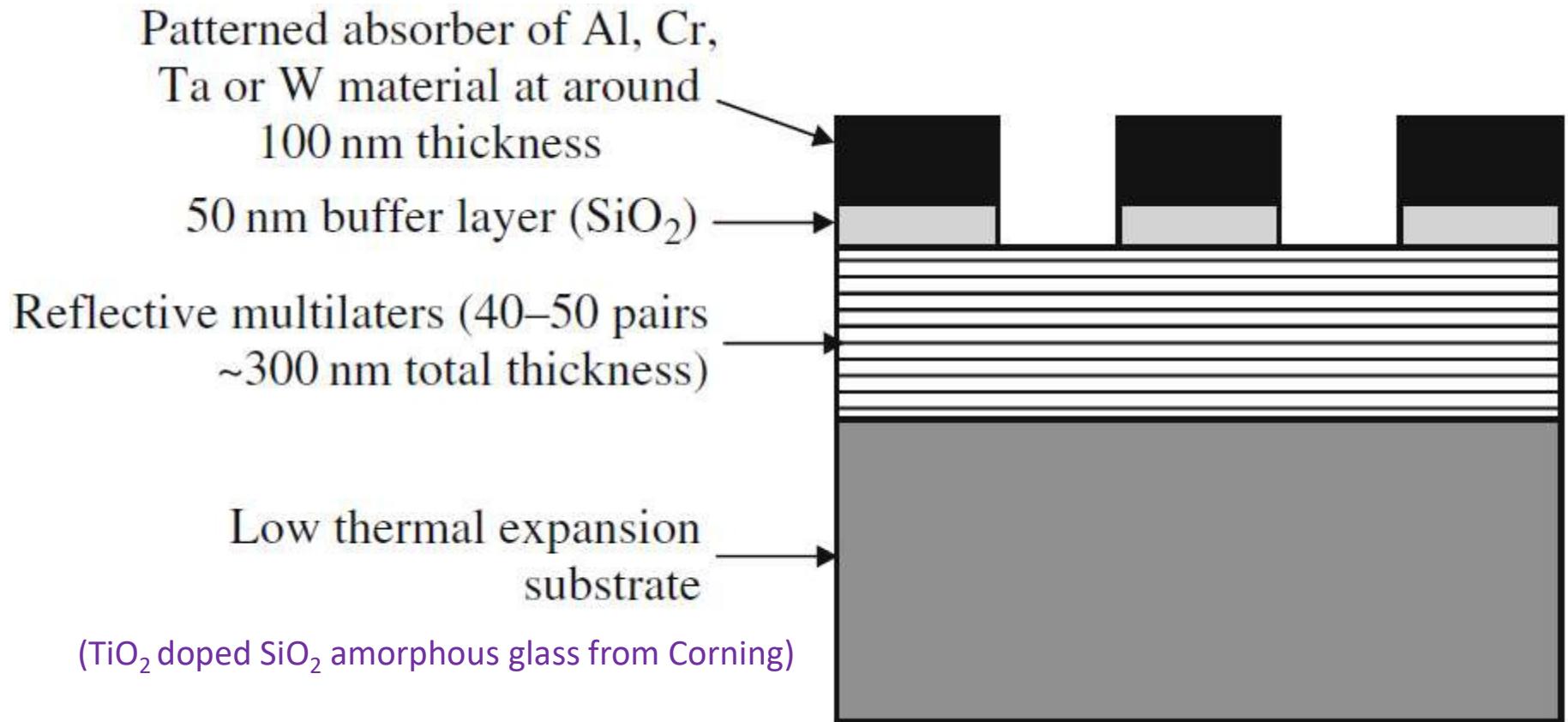
Photos of EUV mirrors



Condenser optic



Mask for EUV lithography



In principle, one can use a transmission mask (like common photolithography) by putting the absorber pattern on a thin (sub-100nm, thus transparent) membrane, but such mask is not robust.

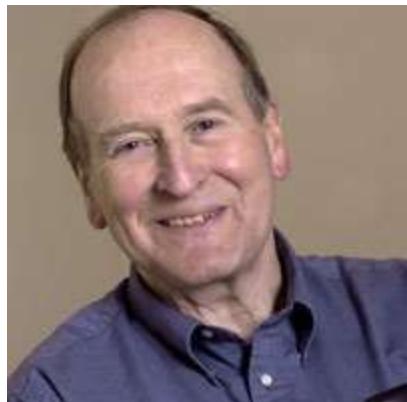
There can also be a capping layer (11nm Si) above the multilayer, to protect the multilayer during the following mask-making processes.

X-ray lithography (XRL)

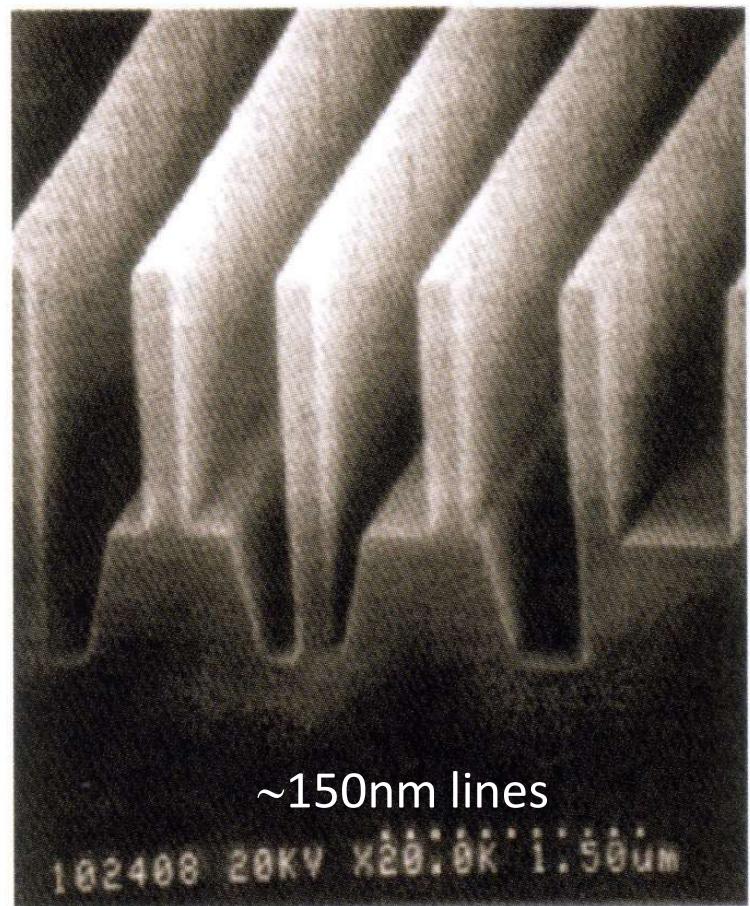
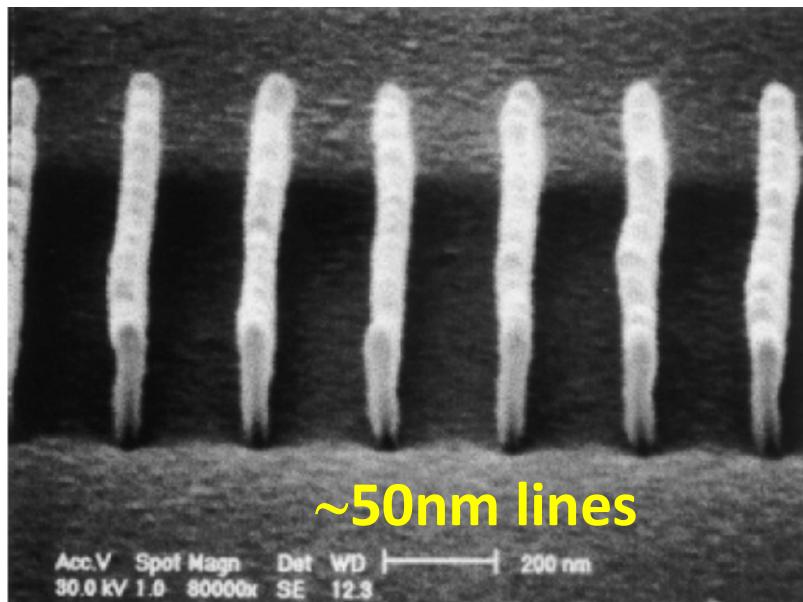
1. Overview and resolution limit.
2. X-ray source (electron impact and synchrotron radiation).
3. X-ray absorption and scattering.
4. X-ray lithography resist (PMMA and SU-8).
5. X-ray lithography mask (absorber on membrane).
6. LIGA process (for high aspect ratio metal structure).
7. Zone plate for focused x-ray beam array lithography.

High resolution resist structures by x-ray lithography

D. L. Spears and H. I. Smith, "High resolution pattern replication using soft x-rays", Electronic Letters, 8, 102 (1972).



H. I. Smith (MIT)

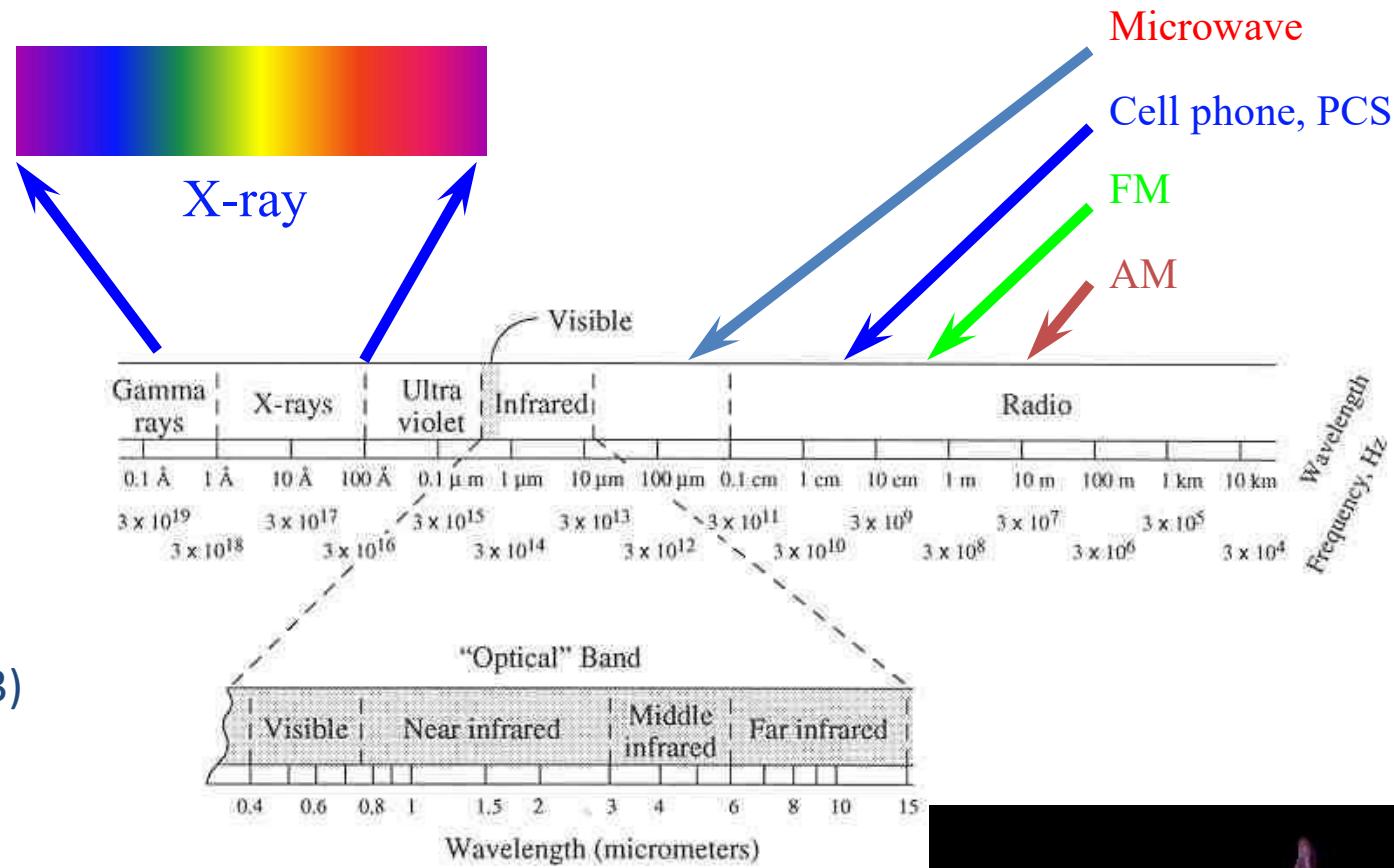


R. Waser (ed.), Nanoelectronics
and Information Technology

What is X-ray?



Wilhelm Conrad
Roentgen (1845-1923)

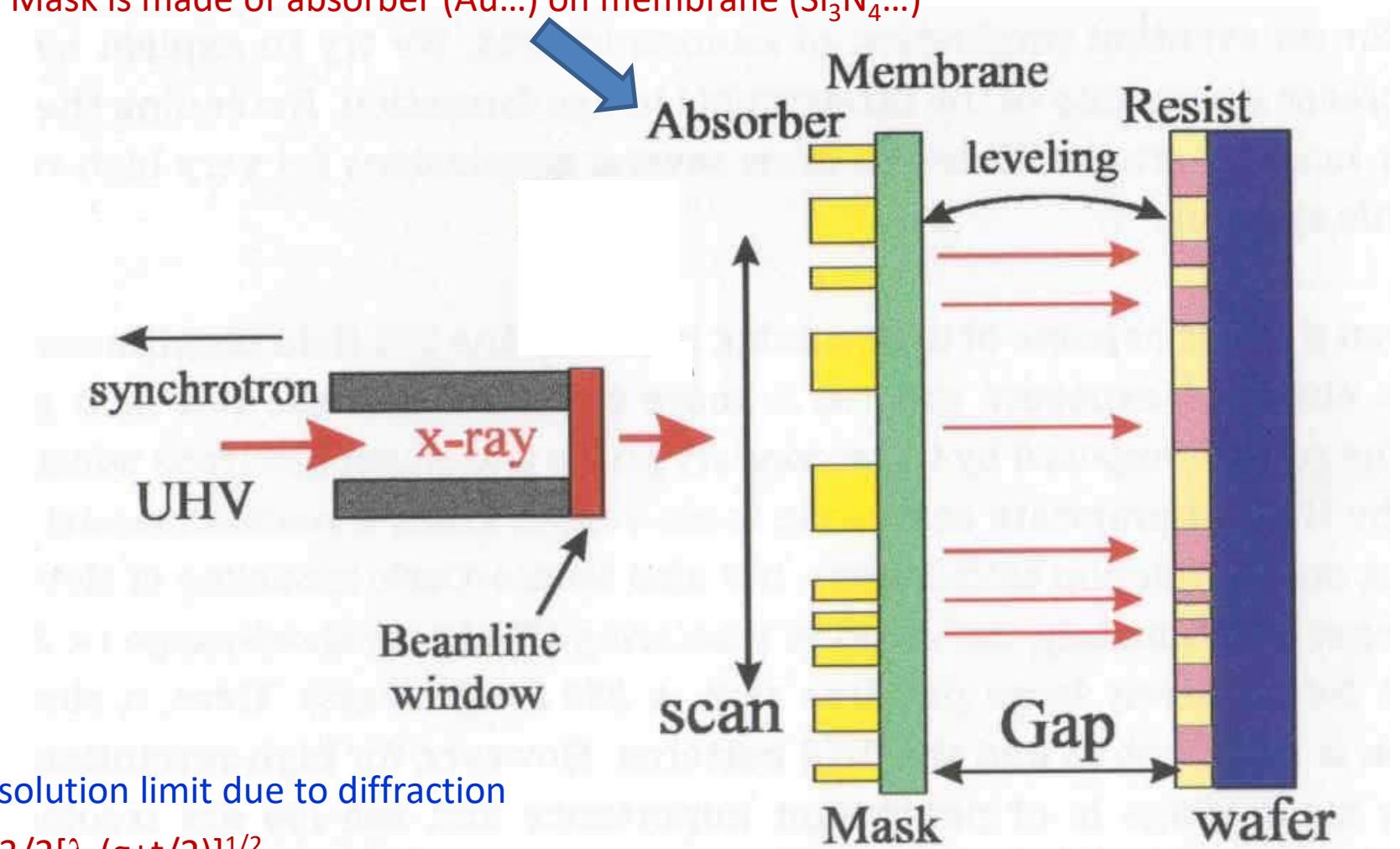


- Roentgen discovered an unknown ray in 1895 (X-ray) that can cause barium platinocyanide-coated screen to glow.
- He won the first Nobel prize in physics in 1901.



Setup of proximity x-ray lithography

Mask is made of absorber (Au...) on membrane (Si_3N_4 ...)



Resolution limit due to diffraction

$$R = \frac{3}{2} [\lambda \cdot (g + t/2)]^{1/2}$$

g: gap; t: resist thickness.

This is the same resolution equation as for photolithography.

X-ray lithography advantages and limits

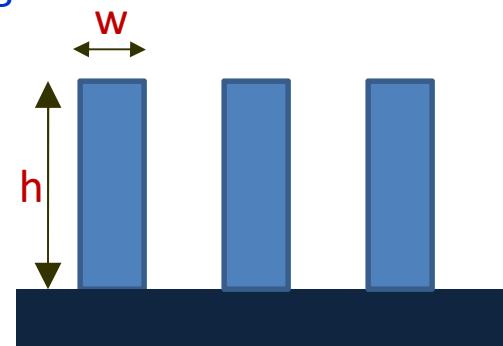
Advantages:

- Wavelength: $\lambda \sim 10's$ nm (soft x-rays) down to $\leq 1\text{\AA}$.
- Little diffraction effects when using such small λ , good for high aspect ratio patterning.
- No backscattering or reflections.
- Very large depth of focus: wafer with non-flat surface is OK.
- Simpler (in principle) than optical or e-beam lithography: no complex optics (don't really have x-ray optics now).
- All that needed is an x-ray source and an x-ray mask.

Limits:

- 1X mask technology because refractive index for all materials is (almost) absolutely 1.0 (no lens for demagnification). (4 \times for DUV lithography, mask easier to make)
- X-ray mask difficult to fabricate with many issues: fragile, defects, bending due to heating.
- Strong, stable, collimated, single frequency x-ray sources are hard to find. X-rays produced in synchrotrons fit this criteria, but with high cost and huge size.
- Resolution is still limited by Fresnel diffraction.
- Typical resist is insensitive, need long time to expose.

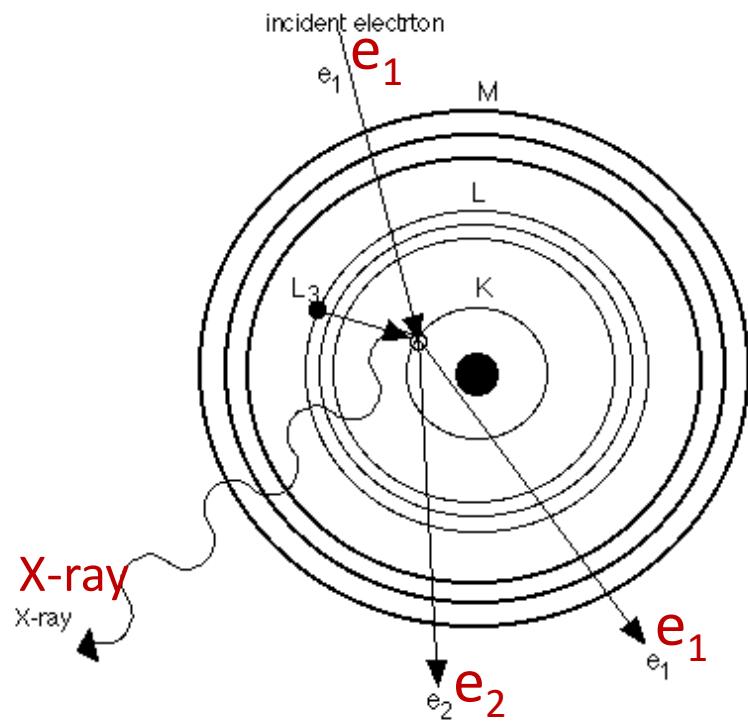
Aspect ratio=pattern height/width=h/w.



X-ray lithography (XRL)

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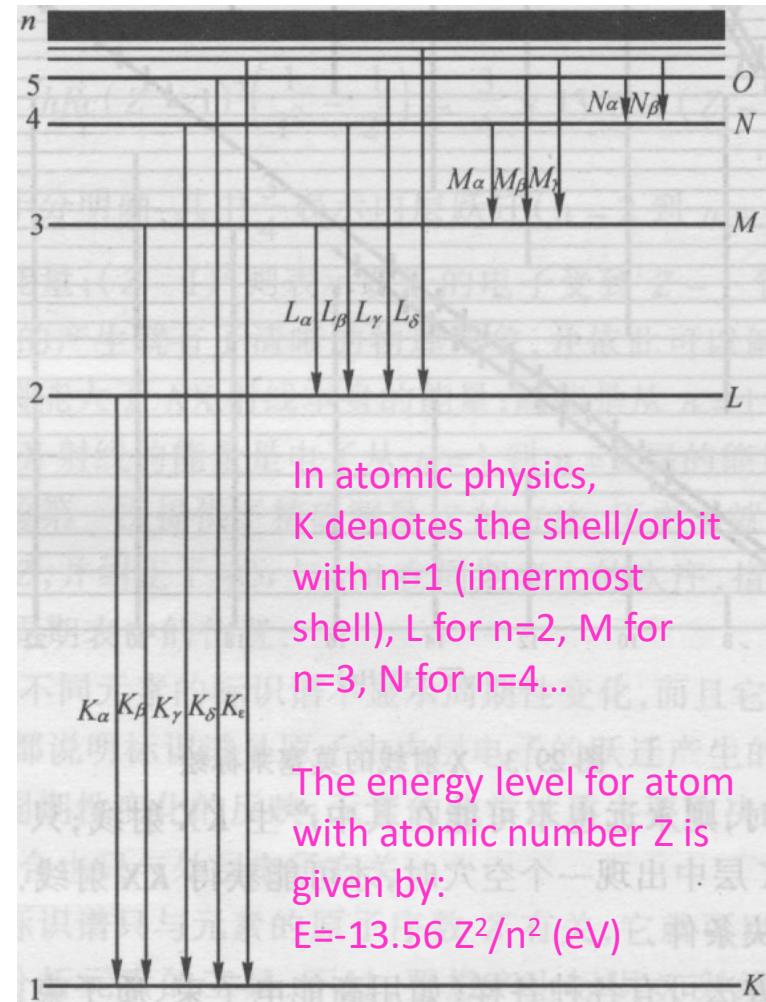
X-ray generation by electron impact (bombardment)



When electron jumps from L to K-shell, it either emits x-ray (as shown in the figure), or gives its energy to an outer-shell electron that escapes subsequently (**Auger electron**, not shown).

$$\text{For } K_{\alpha} \text{ line: } E = E_k - E_L = 13.56(Z-1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \approx 10.17(Z-1)^2 (\text{eV})$$

Here $(Z-1)$ instead of Z due to screening effect of the other electron in $n=1$ level. More generally, $(Z-1)$ should be replaced by $(Z-\sigma)$, with σ accounting for the screening effect.

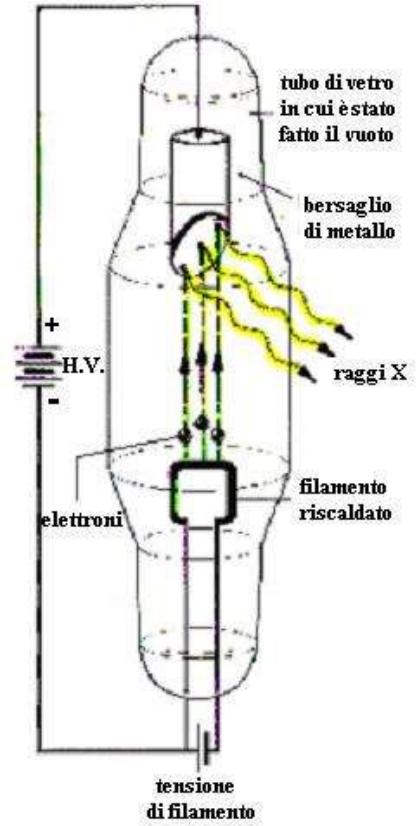
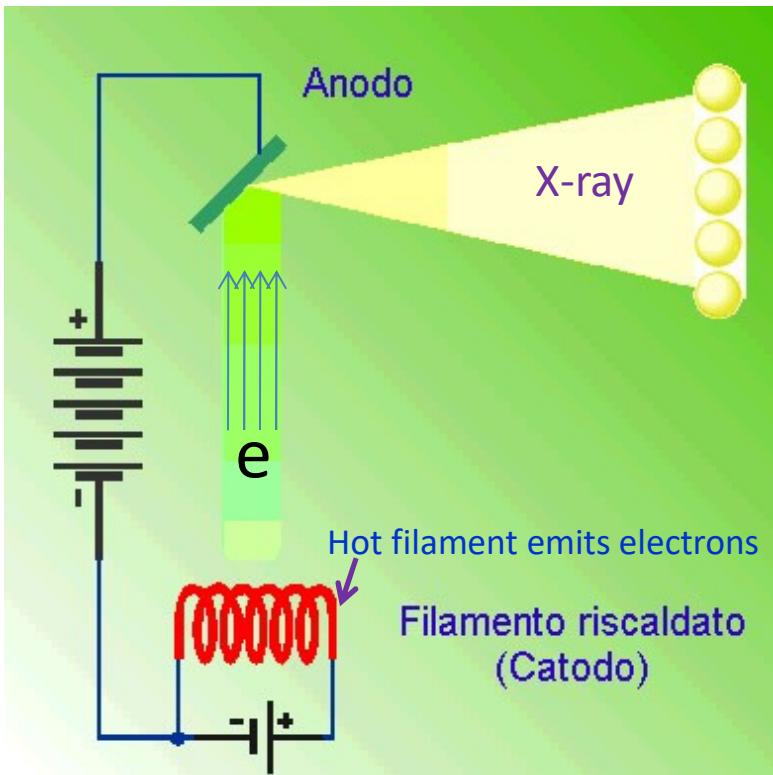


In atomic physics,
K denotes the shell/orbit
with $n=1$ (innermost
shell), L for $n=2$, M for
 $n=3$, N for $n=4$...

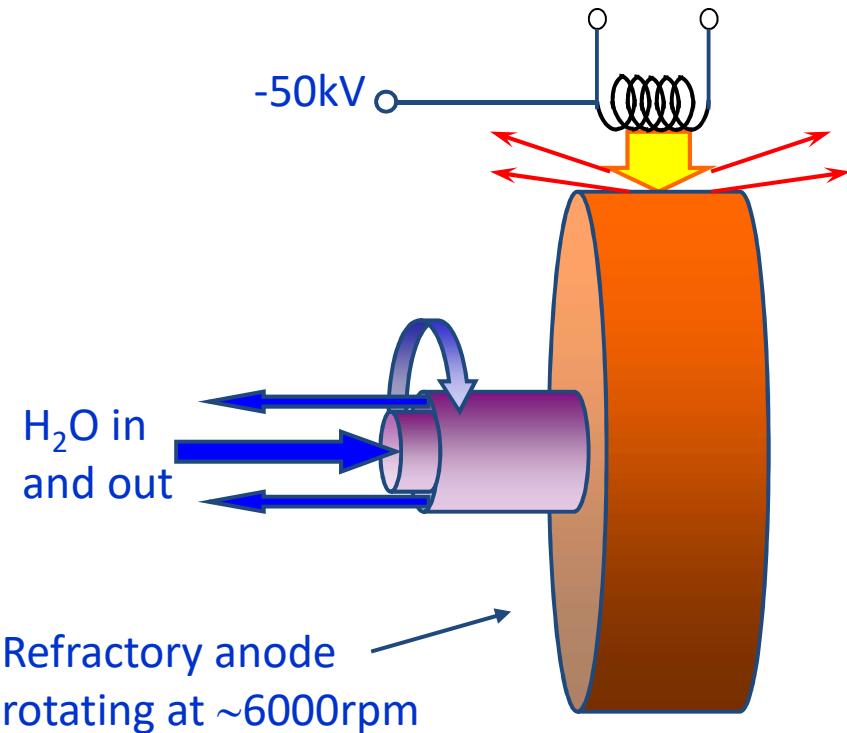
The energy level for atom
with atomic number Z is
given by:
 $E = -13.56 Z^2/n^2$ (eV)

Electron impact: sealed tube x-ray source (point source)

- Developed by Coolidge (at GE) around 1912.
- Electron accelerated at high energy to the anode.
- Low power, tuned to maximize for narrow emission range (for example, Mg or Cu K_α).
- For material characterization by x-ray diffraction and medical imaging

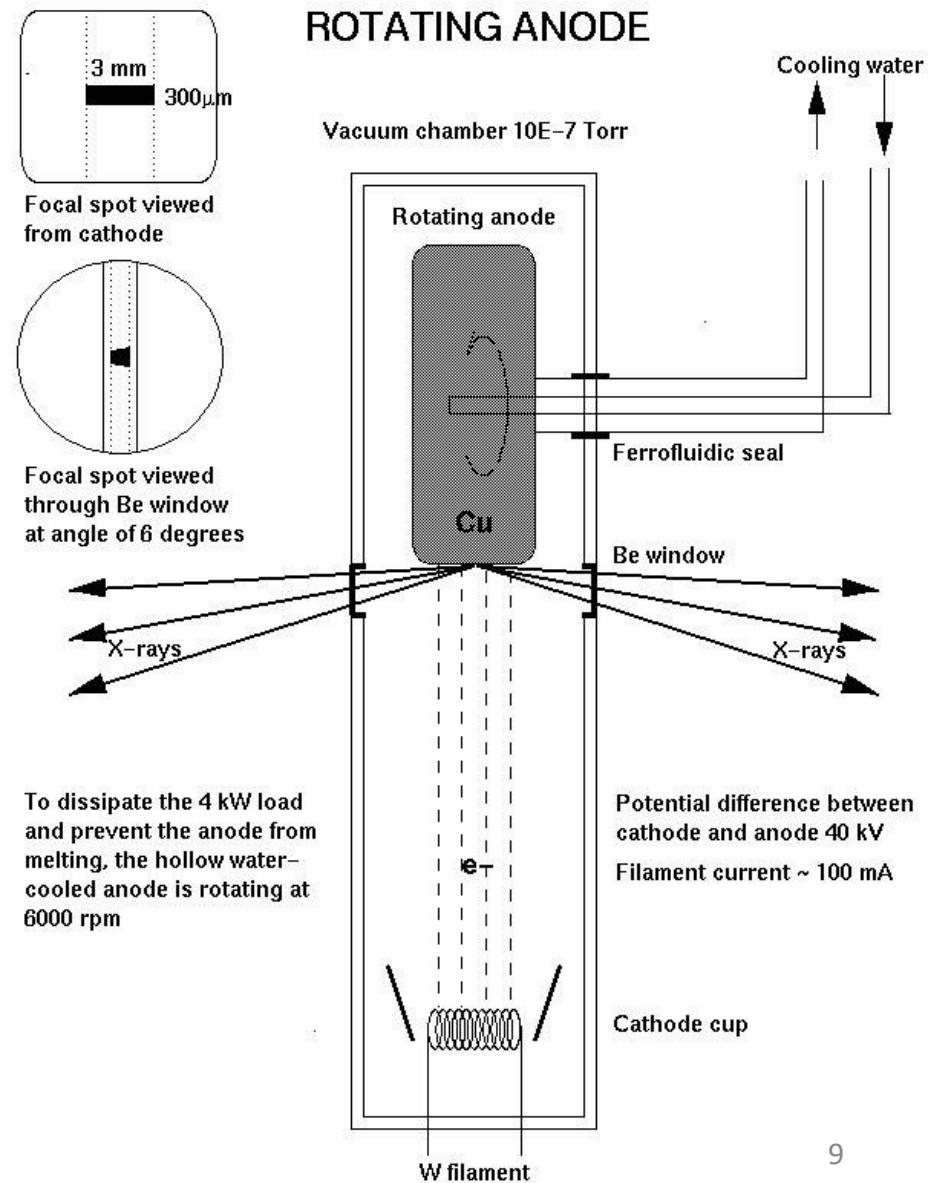


Electron impact: rotating anode source

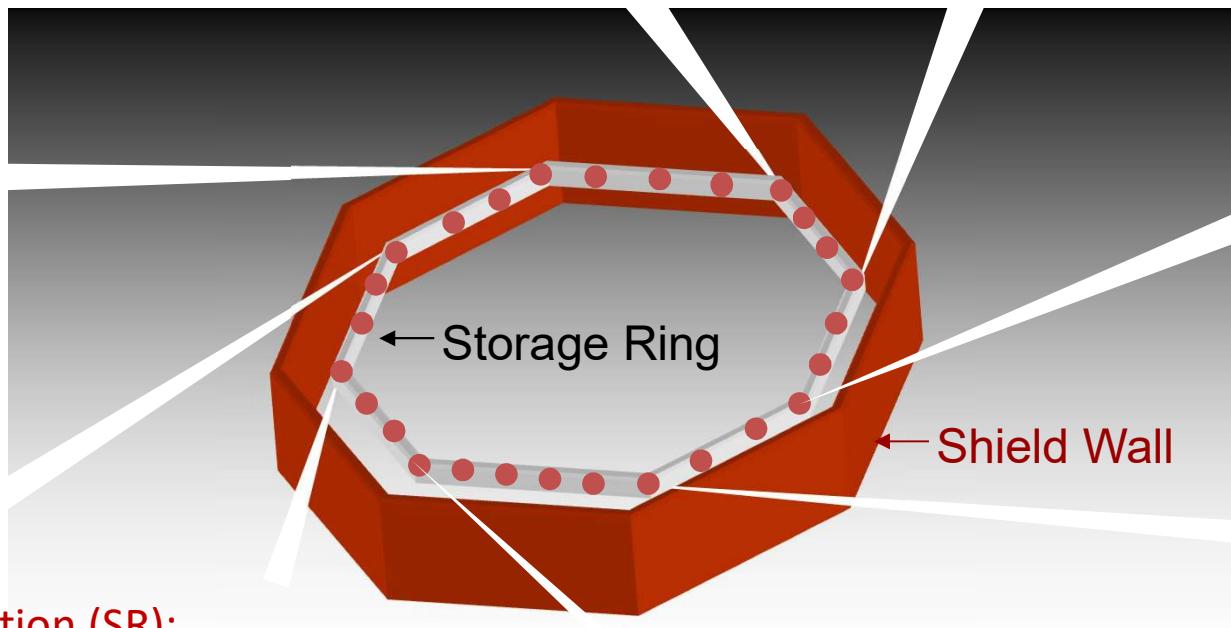


Rotating anode source:

Same principle as sealed tube x-ray source, but with much higher power due to greater thermal capacity – cooling wafer, rotating, refractory metal.



Synchrotron radiation x-ray source: the choice for x-ray lithography



Synchrotron radiation (SR):

- Electromagnetic radiation (light) emitted from electrons moving with relativistic velocities.
- First observed in 1947 from a 70MeV electron accelerator at GE.
- In earlier times, it was just considered as waste product, limiting accelerator performance.
- However, other researchers soon realized that SR was the brightest source of infrared, ultraviolet, and x-rays, very useful for studying matter on the scale of atoms and molecules.
- Radiation is highly polarized and pulsed (e.g. pico-second pulse).
- Observer sees only a small portion of electron trajectory. The pulse length is thus the difference in time it takes an electron and a photon to cover this distance on the circle.¹⁰

How a Synchrotron Works

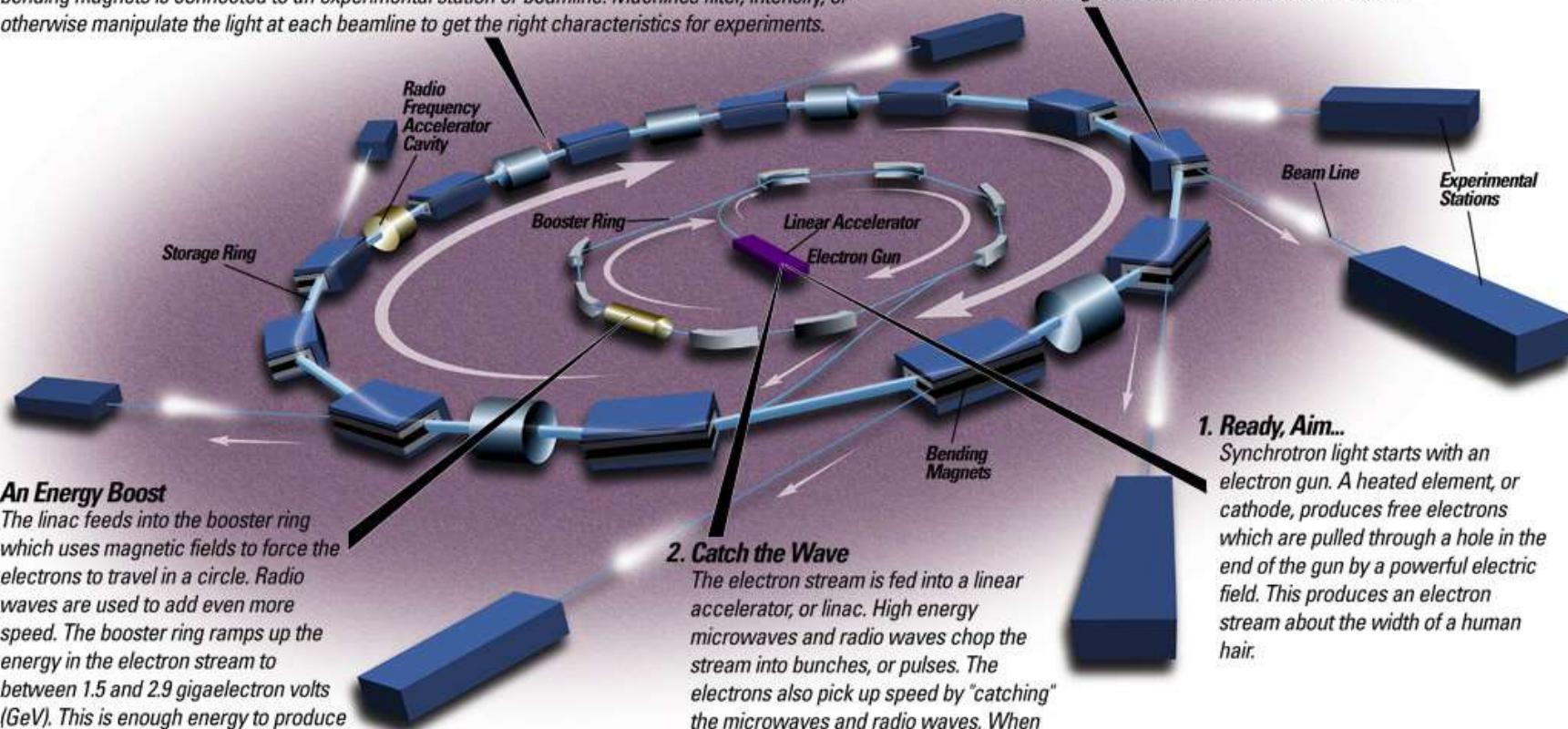
4. Storage Ring

The booster ring feeds electrons into the storage ring, a many-sided donut-shaped tube. The tube is maintained under vacuum, as free as possible of air or other stray atoms that could deflect the electron beam. Computer-controlled magnets keep the beam absolutely true.

Synchrotron light is produced when the bending magnets deflect the electron beam; each set of bending magnets is connected to an experimental station or beamline. Machines filter, intensify, or otherwise manipulate the light at each beamline to get the right characteristics for experiments.

3. An Energy Boost

The linac feeds into the booster ring which uses magnetic fields to force the electrons to travel in a circle. Radio waves are used to add even more speed. The booster ring ramps up the energy in the electron stream to between 1.5 and 2.9 gigaelectron volts (GeV). This is enough energy to produce synchrotron light in the infrared to hard X-ray range.



2. Catch the Wave

The electron stream is fed into a linear accelerator, or linac. High energy microwaves and radio waves chop the stream into bunches, or pulses. The electrons also pick up speed by "catching" the microwaves and radio waves. When they exit the linac, the electrons are travelling at 99.99986 per cent of the speed of light and carry about 300 million electron

5. Focusing the Beam

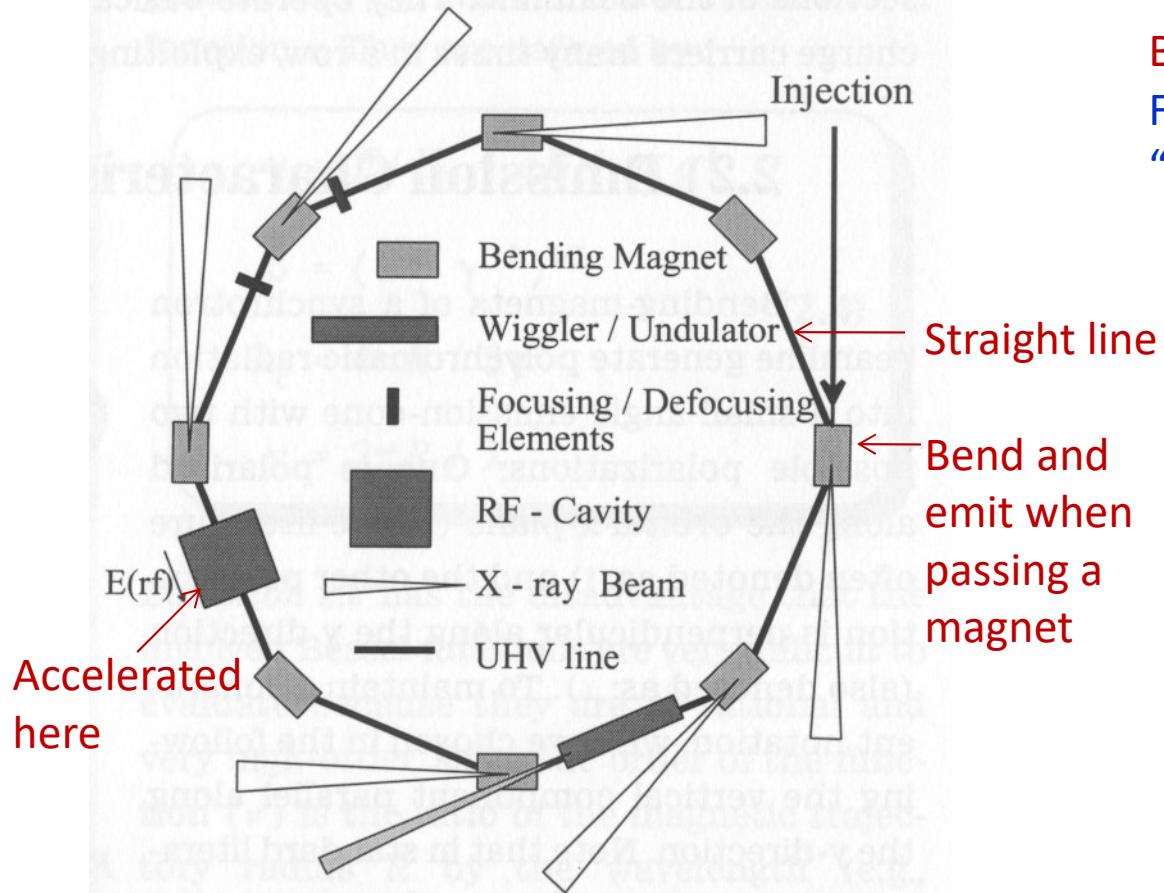
Keeping the electron beam absolutely true is vital when the material you're studying is measured in billionths of a metre. This precise control is accomplished with computer-controlled quadrupole (four pole) and sextupole (six pole) magnets. Small adjustments with these magnets act to focus the electron beam.

1. Ready, Aim...

Synchrotron light starts with an electron gun. A heated element, or cathode, produces free electrons which are pulled through a hole in the end of the gun by a powerful electric field. This produces an electron stream about the width of a human hair.

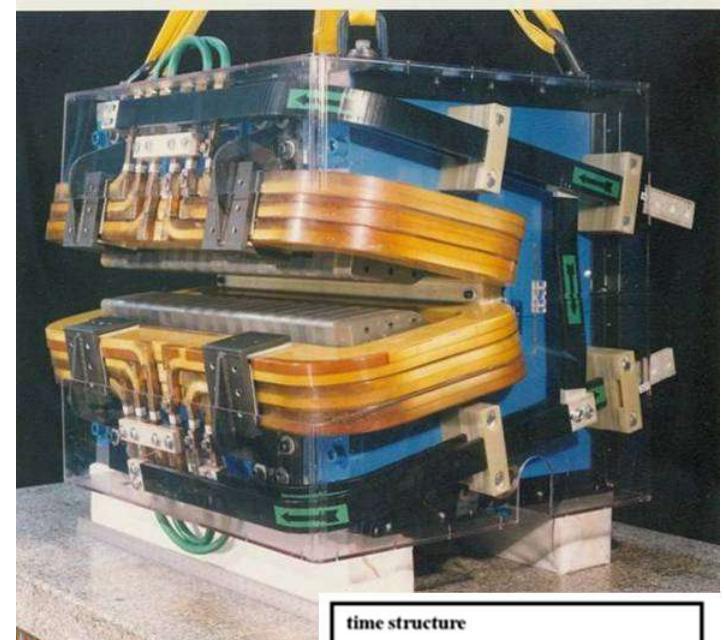
Source: University of Saskatchewan / Paradigm Media Group Inc.

How synchrotron radiation works?

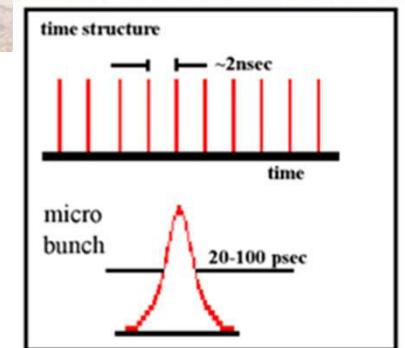


Bending magnet:

For normal-conductive $B \leq \sim 1.5$ Tesla.
“C” shaped allowing radiation to exit



- Typically a low-energy accelerator injects “bunches” of electrons into a storage ring; the charged particle are in pico-second pulses spaced nanoseconds apart.
- Acceleration is produced by an alternating (RF – radio frequency) electric field that is in synchronism with orbital frequency.
- A broad continuum of radiation is emitted by each bunch when it changes direction, with the median (or “critical”) wavelength given by $\lambda_c(\text{nm}) = \frac{0.559 r(\text{m})}{E(\text{GeV})^3}$



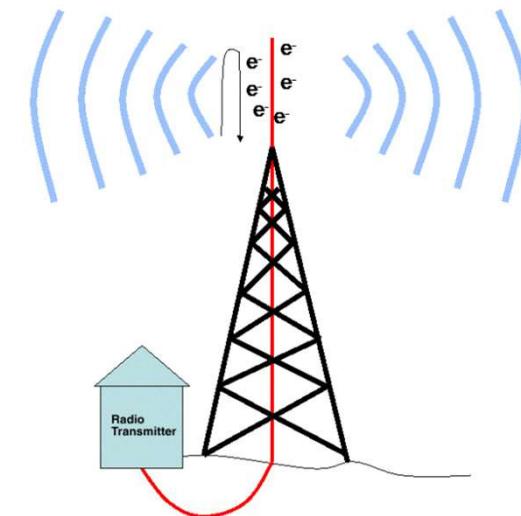
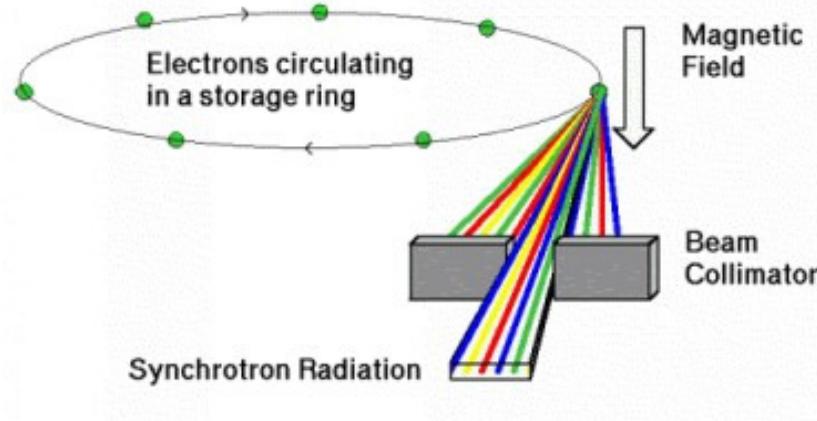
$$\lambda_c(\text{nm}) = \frac{0.559 r(\text{m})}{E(\text{GeV})^3} \quad 12$$

Radiation is due to charge acceleration

Synchrotron radiation:
electromagnetic radiation emitted
when charged particles are *radially*
accelerated (move on a curved path)

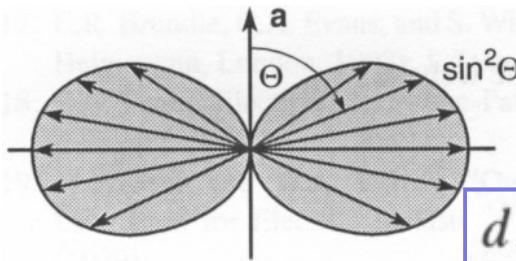
Antenna:
electrons accelerating by running up
and down in a radio antenna emit
radio waves (long wavelength
electromagnetic waves)

Radial acceleration $a=v^2/R$ (v is speed, R is radius)



Both cases are manifestation of the same physical phenomenon:
Charged particles radiate (only) when accelerated.

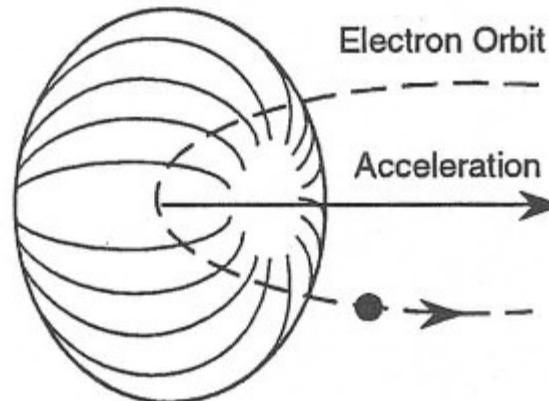
Synchrotron radiation angular distribution



p: power
a: acceleration
 Ω : spherical angle

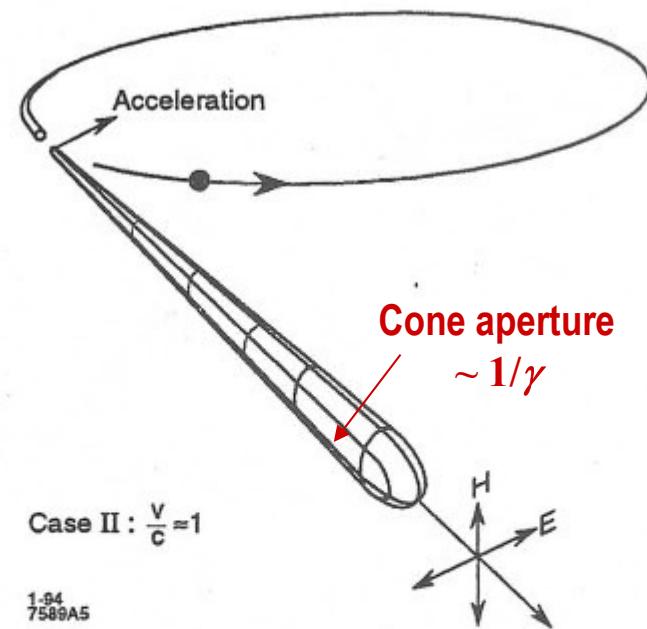
$$\frac{dP}{d\Omega} = \frac{e^2 |a|^2 \sin^2 \Theta}{16\pi^2 \epsilon_0 c^3}$$

No radiation along acceleration direction.
Strongest radiation at perpendicular direction.



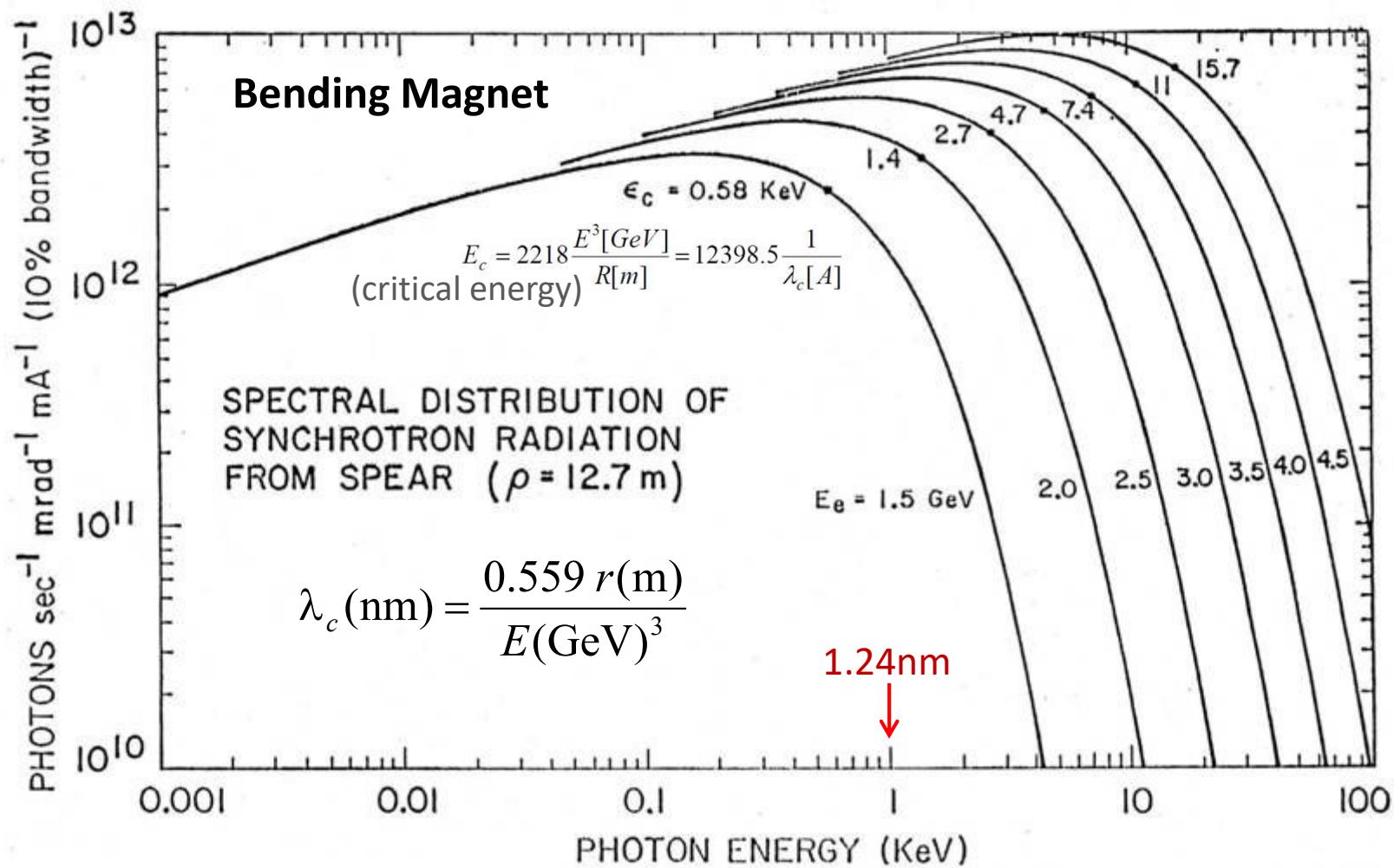
$$\text{Case I : } \frac{v}{c} \ll 1$$

At low electron velocity (non-relativistic case) the radiation is emitted in a non-directional pattern



When the electron velocity approaches the velocity of light, the emission pattern is folded sharply forward.

Spectrum of synchrotron radiation (bending magnet)



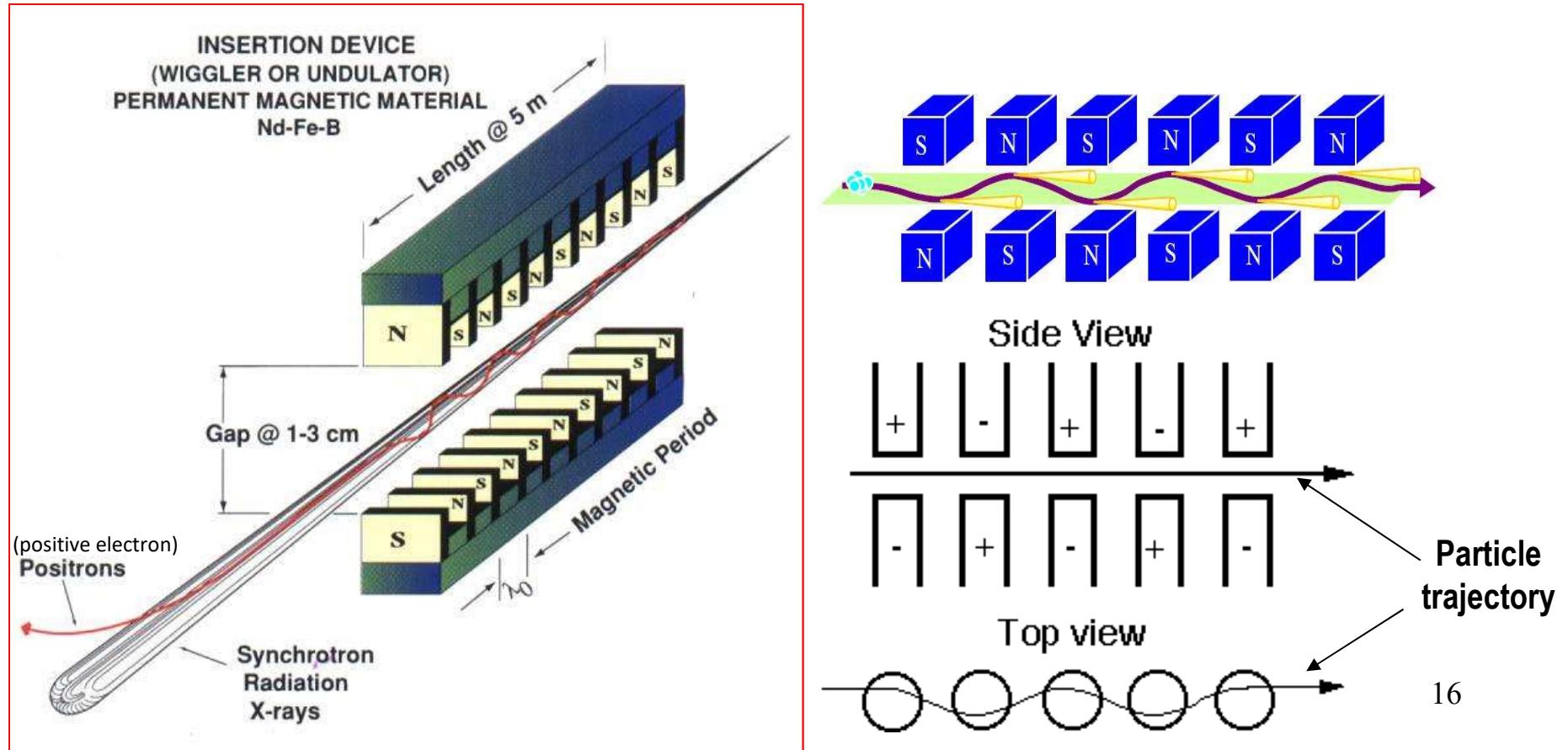
Electron rest energy = $mc^2 = (9.1 \times 10^{-31})(3 \times 10^8)^2 = 8.19 \times 10^{-14} \text{ J} = 0.511 \text{ MeV}$ (very small).

Total electron energy = γmc^2 , with $\gamma = 1/(1-v^2/c^2)^{1/2}$.

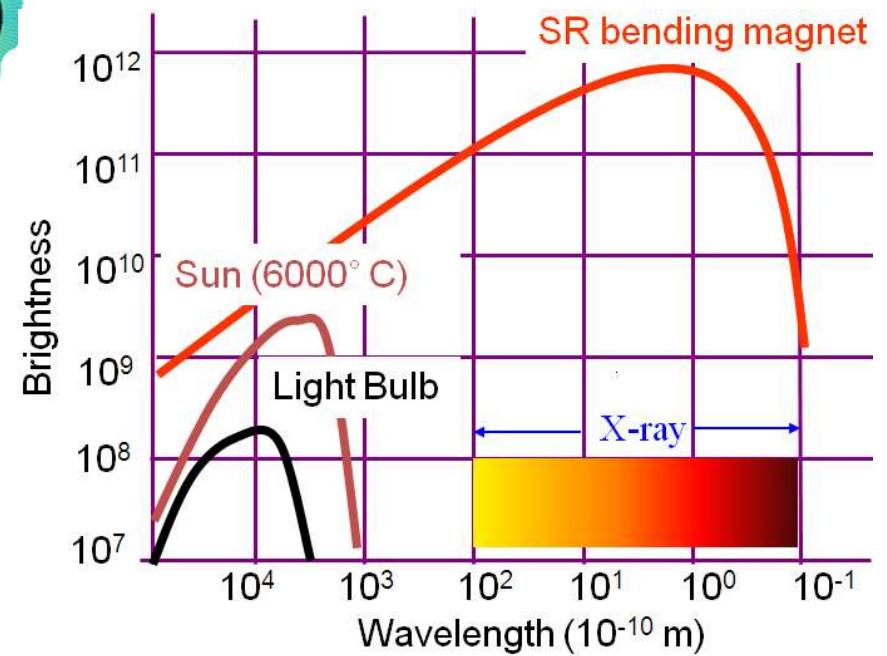
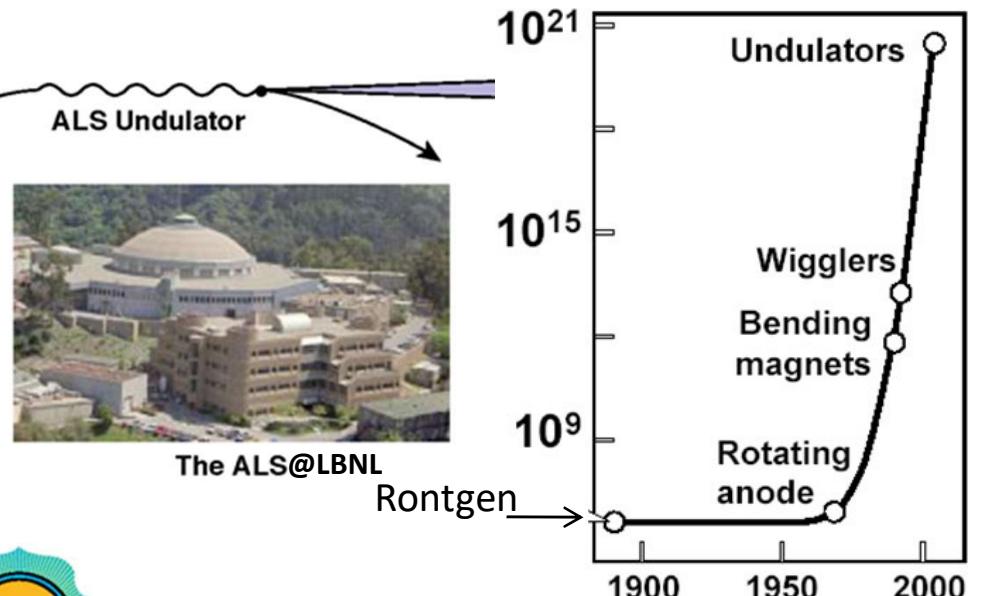
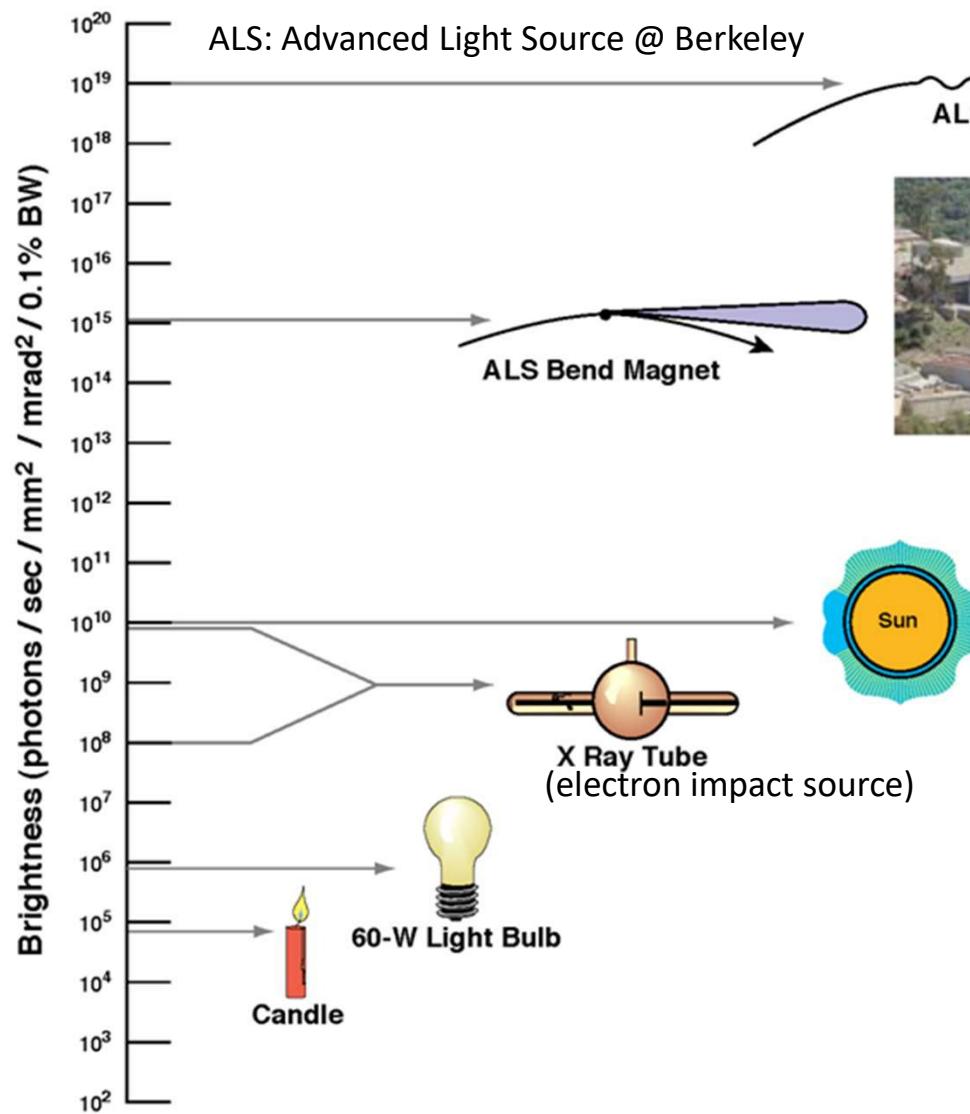
For 1.0 GeV energy, $\gamma = 1000/0.511 = 1957$, so $v/c = 0.99999987$, indeed v is very close to c .

“Wiggler or undulator” radiation

- For bending magnet radiation, electrons are accelerated/bended by uniform magnetic field (B along $+z$ direction, circular electron trajectory).
- By putting an array of permanent magnets like below, magnetic field alternates up ($+z$ direction) and down ($-z$), causing the particles to bend back and forth along the horizontal plane.
- At each bend, the electrons emit synchrotron radiation.



Comparison of brightness ($\frac{\text{# of photons in given } \Delta\lambda/\lambda}{\text{sec, mrad } \theta, \text{ mrad } \varphi, \text{ mm}^2}$)

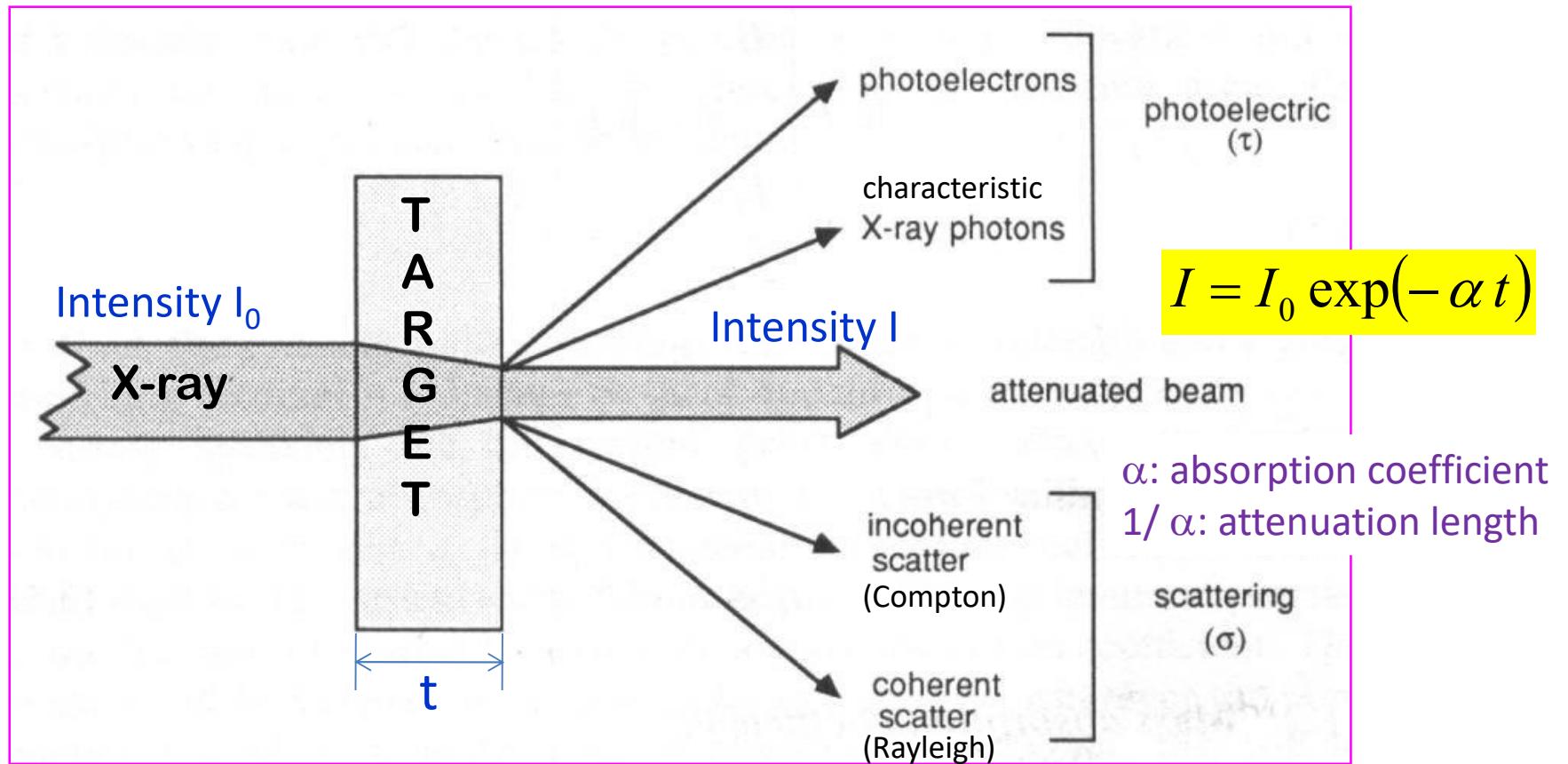


Slides modified from lecture by Fernando Sannibale
 Advanced Light Source Accelerator Physics Group
 Ernest Orlando Lawrence Berkeley National Laboratory

X-ray lithography (XRL)

1. Overview and resolution limit.
2. X-ray source (electron impact and synchrotron radiation).
3. X-ray absorption and scattering.
4. X-ray lithography resist (PMMA and SU-8).
5. X-ray lithography mask (absorber on membrane).
6. LIGA process (for high aspect ratio metal structure).
7. Zone plate for focused x-ray beam array lithography.

X-ray absorption / attenuation



In addition to photoelectric absorption (producing photoelectrons and characteristic x-rays or Auger electrons), the original x-rays may be scattered by electrons.

There are two kinds of scattering: coherent (Rayleigh, no energy loss) and incoherent (Compton).

X-ray scattering

Coherent scattering: happens when x-ray “collides” with an atom and deviates *without* a loss in energy.

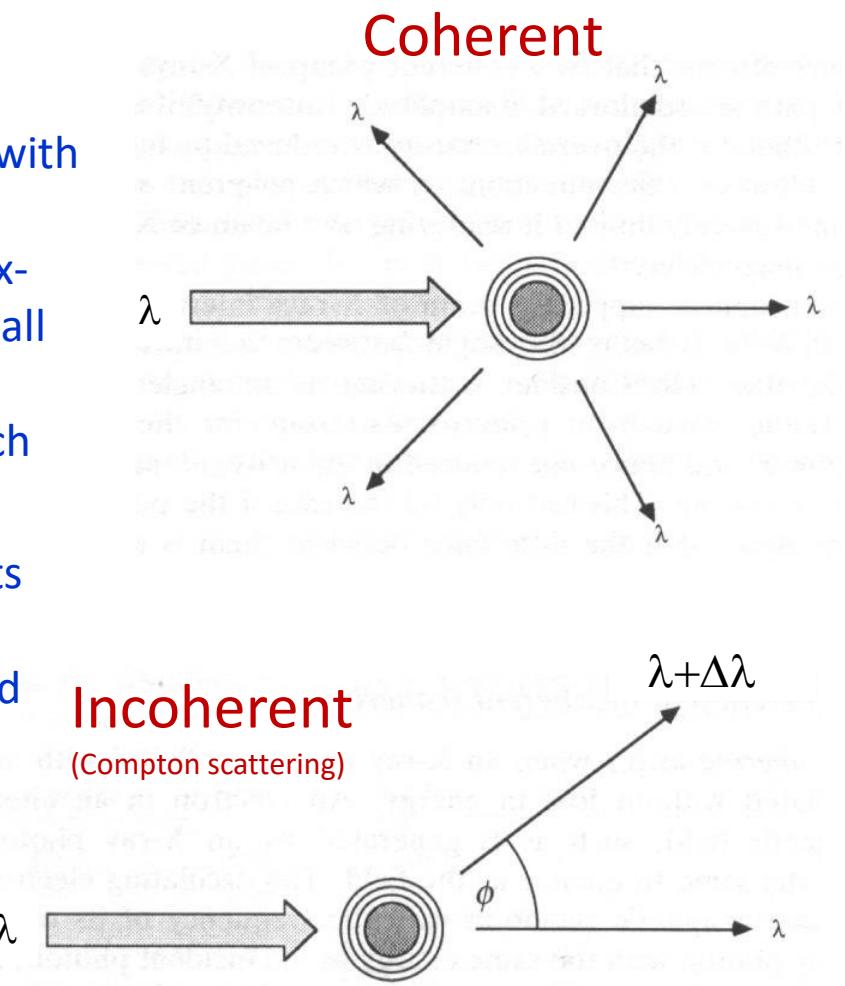
An electron in an alternating electromagnetic field (x-ray) will oscillate at the same frequency and emit in all directions.

This is useful for understanding **x-ray diffraction** (each atom is a new x-ray point source).

Incoherent scattering: incident x-ray loses some of its energy to the scattering electron. As total energy ($=hc/\lambda$) is preserved, the wavelength of the scattered photon increases by:

$$\Delta\lambda = 0.0243(1 - \cos\phi) \text{ (in } \text{\AA})$$

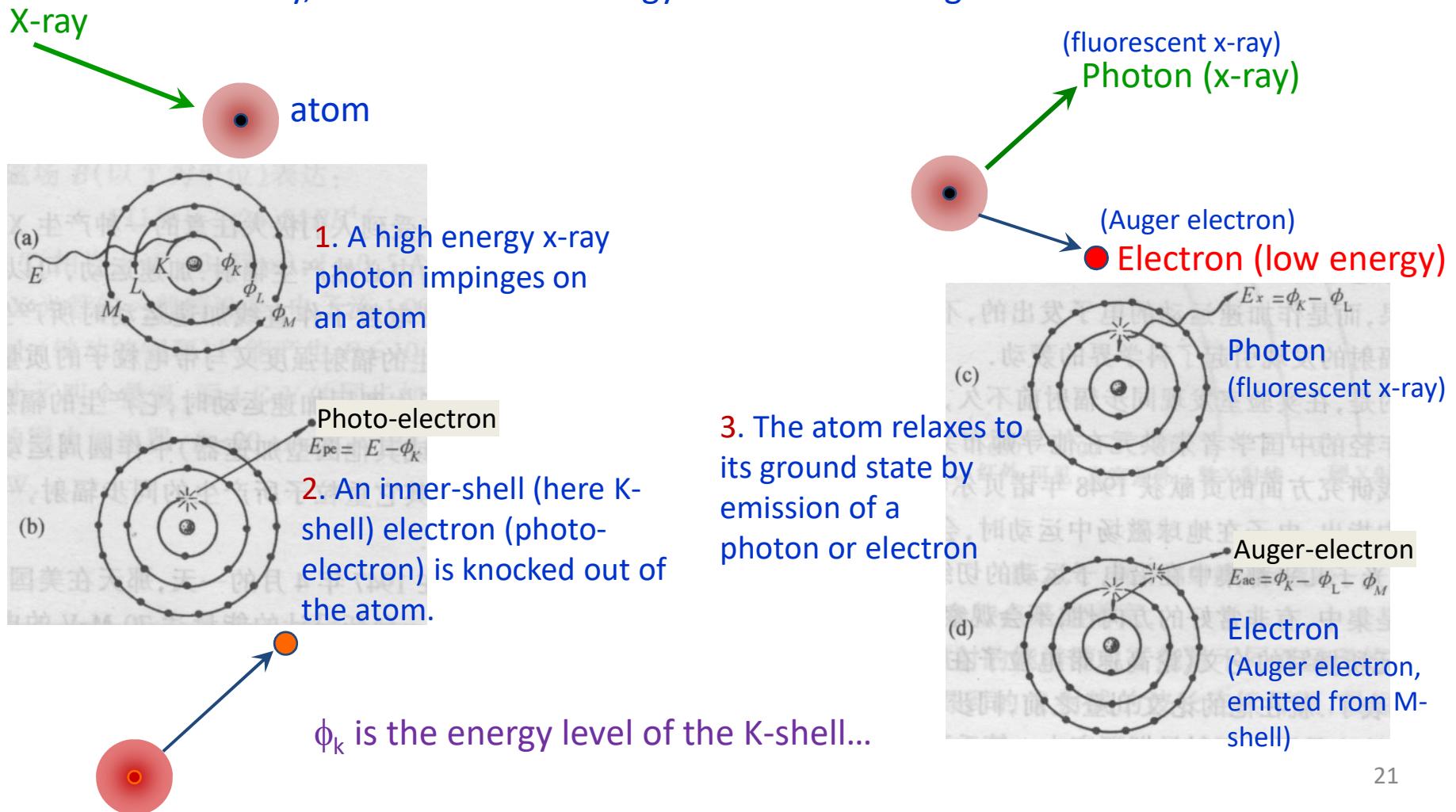
(Here $0.0243 = h/m_e c$, $h = 6.63 \times 10^{-34}$ is Plank's constant, $m_e = 9.1 \times 10^{-31} \text{ kg}$ is electron's mass)



X-ray absorption: photoelectric absorption dominates at <10keV

The picture below is similar to electron bombardment x-ray source, where core electron is kicked off by an incident electron. Here it is kicked off by x-ray (the incident x-ray is absorbed/lost).

In the relaxation process, the lower (than incident x-ray photon) energy photon is a fluorescent x-ray, while the lower energy electron is an Auger electron.



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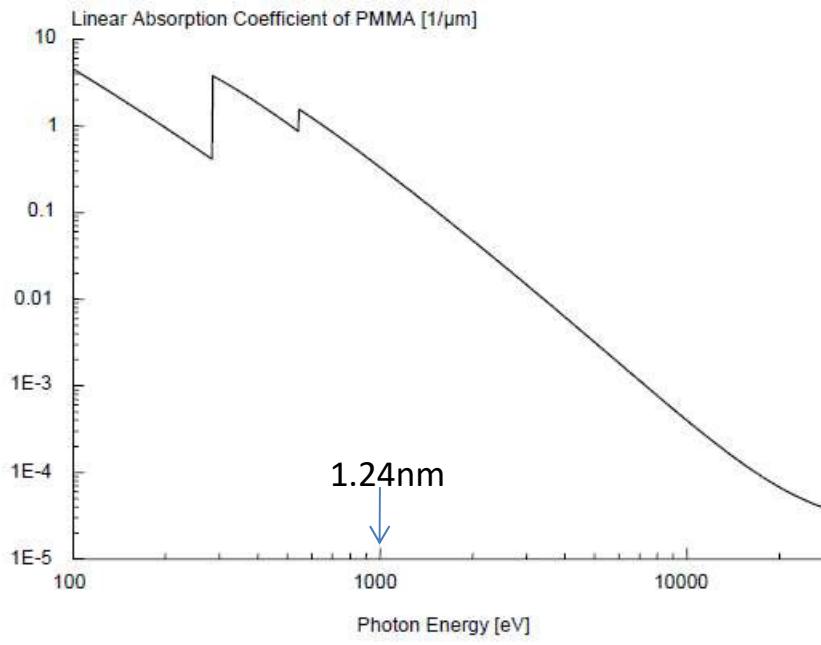
X-ray interaction with resist

- Absorption of x-ray does not lead directly to resist modification.
- Photoelectrons and Auger electrons are responsible for resist modification.
- Therefore, x-ray lithography resist is similar to that for e-beam lithography.
- That is, *any* e-beam lithography resist can also be used as x-ray lithography resist.
- In general, high energy x-rays (e.g. $\lambda=0.3\text{-}5\text{\AA}$) do not interact strongly with materials, so very low absorption.
 - The ***good news***: x-ray resist will be uniformly illuminated (top to bottom) for not-so-thick resist.
 - The ***bad news***: x-ray masks will be hard to make opaque (need many μm Au).
 - The ***worse news***: powerful x-ray sources are needed (most energy just pass through without exposing the resist).
 - To reduce exposure time substantially, one can use chemically amplified resist (SU-8) having high sensitivity.

X-ray absorption by PMMA resist

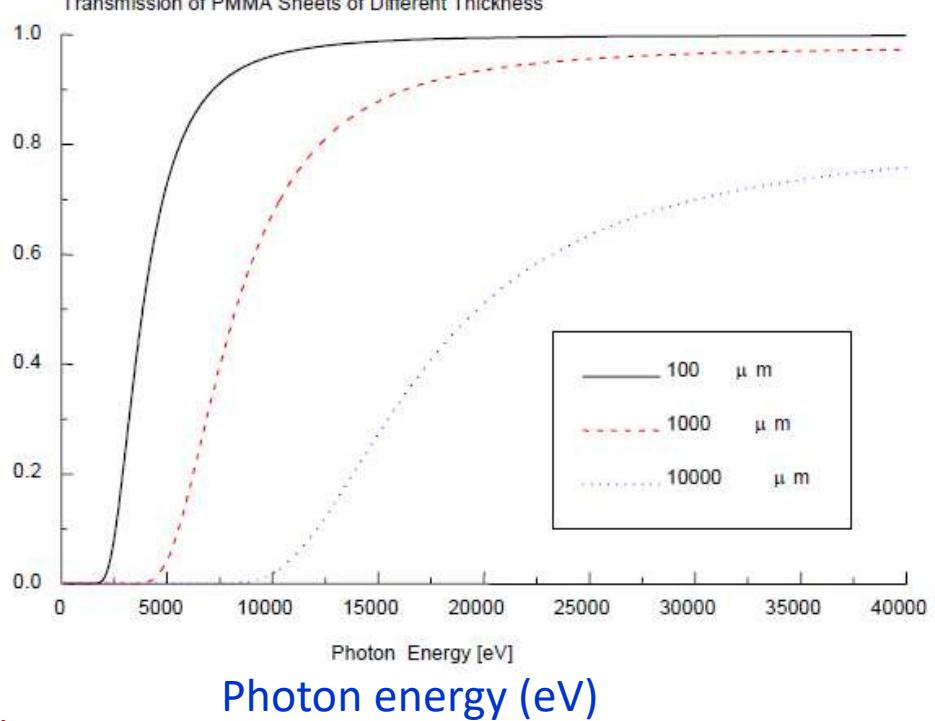
X-ray absorption of PMMA

Linear absorption coefficient α (1/ μm)



Transmission of PMMA

Transmission of PMMA sheets of different thickness



Attenuation length $1/\alpha$ (penetration depth)

100eV (12.4nm, EUV) ~ $0.23 \mu\text{m}$

1keV (1.24nm) ~ $3 \mu\text{m}$

10keV (1.24Å) ~ 3mm

Medical imaging, need many cm, so $\lambda \ll 1\text{\AA}$

For the same resist thickness:

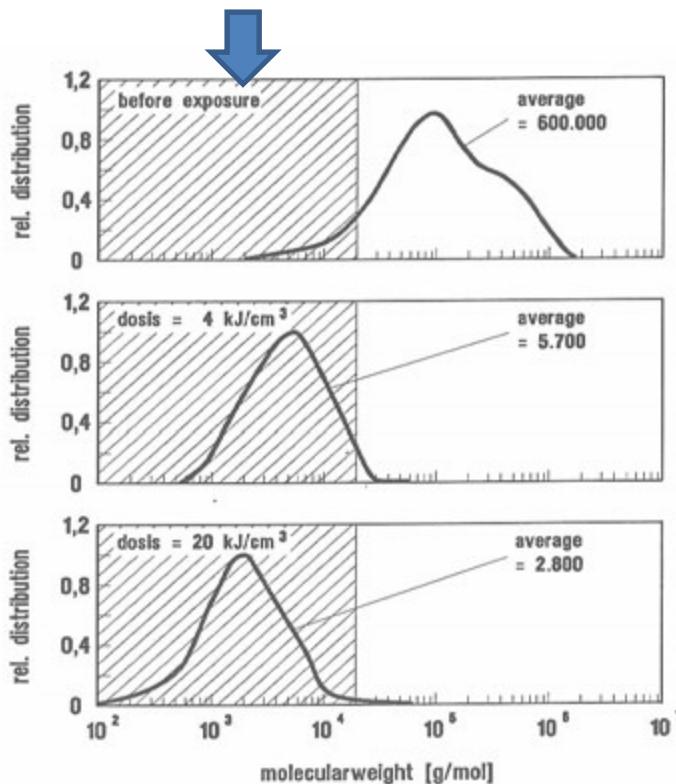
Higher energy → less absorption, more uniform dose profile throughout the thickness, but low resist sensitivity and needs longer exposure time.

Change of mean molecular weight in PMMA

Exposure to x-ray (that generates Auger electrons...) cut the PMMA chains, leading to smaller molecular weight (M_w) that dissolves faster in developers.

PMMA is the most commonly used resist (positive tone) for x-ray lithography with good quality in accuracy and sidewall roughness, but extremely insensitive.

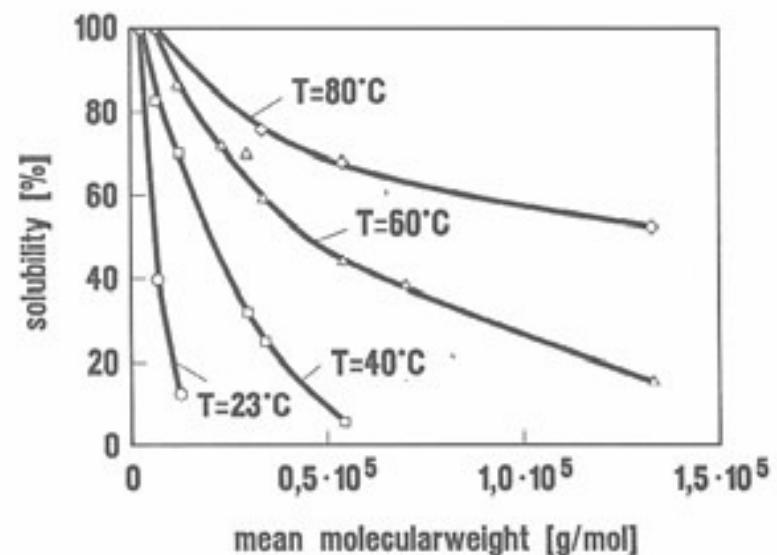
Dissolvable by developer



Initial distribution of high M_w PMMA (500kg/mol)

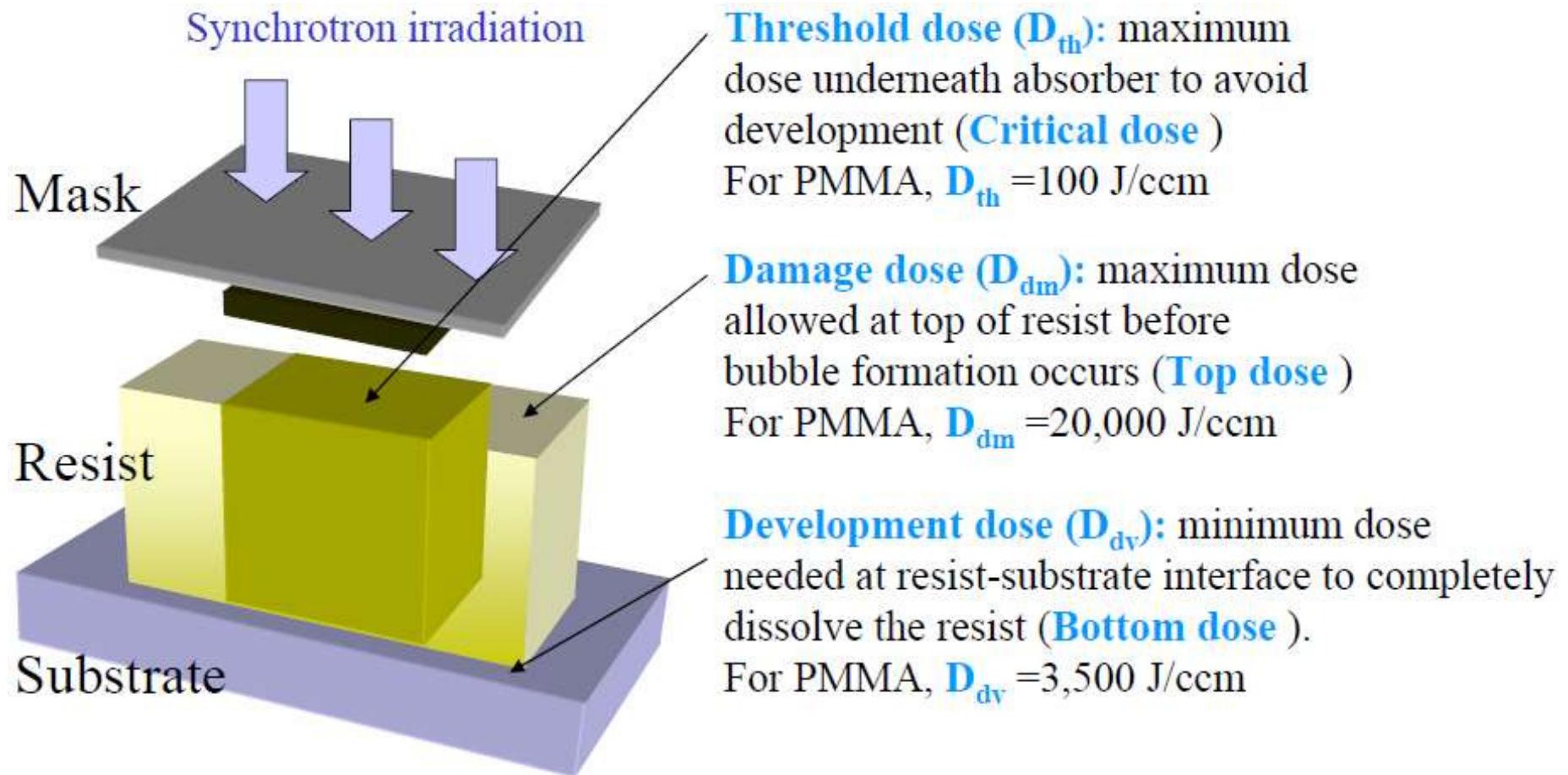
M_w distribution at the substrate (bottom dose). (5.7kg/mol)

M_w distribution at the surface (top dose). (2.8kg/mol)

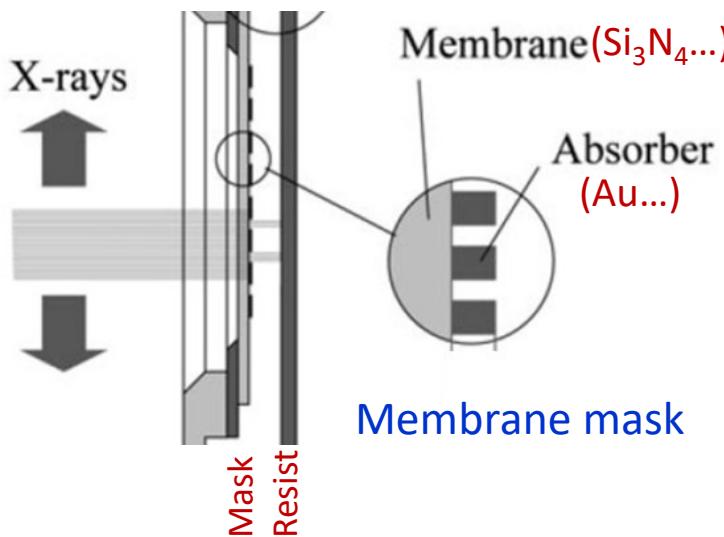
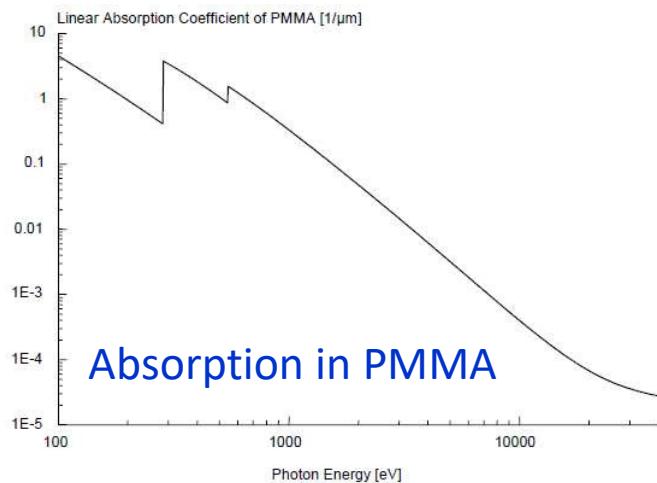


Solubility of PMMA in GG-developer, nearly ideal at room temperature.

Characteristic doses: definition and their values for PMMA



Summary: what wavelengths for what application



- The selection of x-ray wavelength depends on resolution and resist height (aspect ratio).
- Longer wavelength (1-5nm): shorter penetration depth, so thinner resist, thinner Au absorber, thinner membrane (fragile). Long λ means more serious diffraction that limits resolution.
- Shorter wavelength (0.3-5 \AA): thicker resist/absorber/membrane. Low absorption means low resist sensitivity/longer exposure time.
- Therefore:
 - For high resolution applications, longer wavelength will be better, since it allows thinner absorber (easier to pattern with high resolution) and thinner resist.
 - For high aspect ratio application (resist thickness > 100 μm), shorter wavelength must be used. The resolution is then limited by diffraction (since resist is very thick or gap is big), or *non-vertical* sidewall of the *thick* (>10 μm) Au absorber (difficult to make deep vertical sidewall by e-beam/photo-lithography and electroplating).

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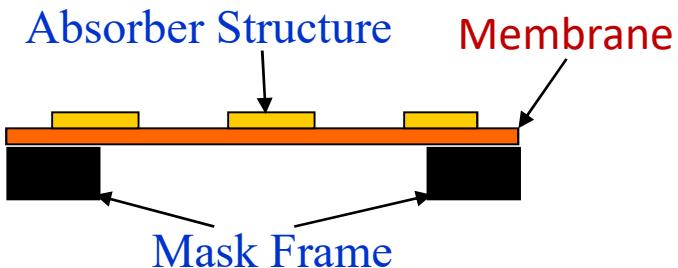
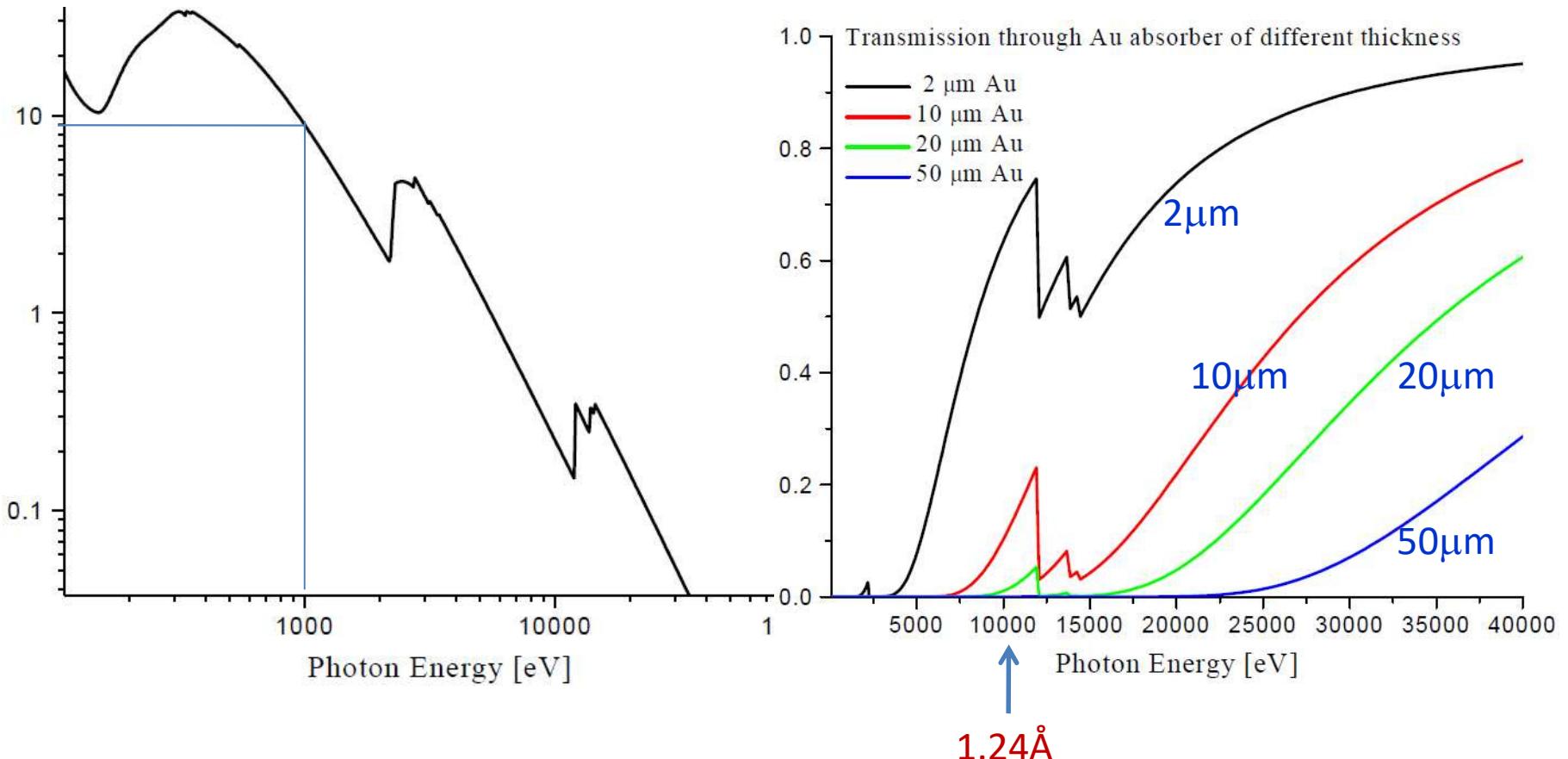
NE 353: Nanoprobing and lithography

Instructor: Bo Cui, ECE, University of Waterloo; <http://ece.uwaterloo.ca/~bcui/>

Textbook: Nanofabrication: principles, capabilities and limits, by Zheng Cui

X-ray mask: absorber (high Z material Au, W, Ta)

Linear absorption coefficient of Au ($1/\mu\text{m}$) Transmission through Au of different thickness

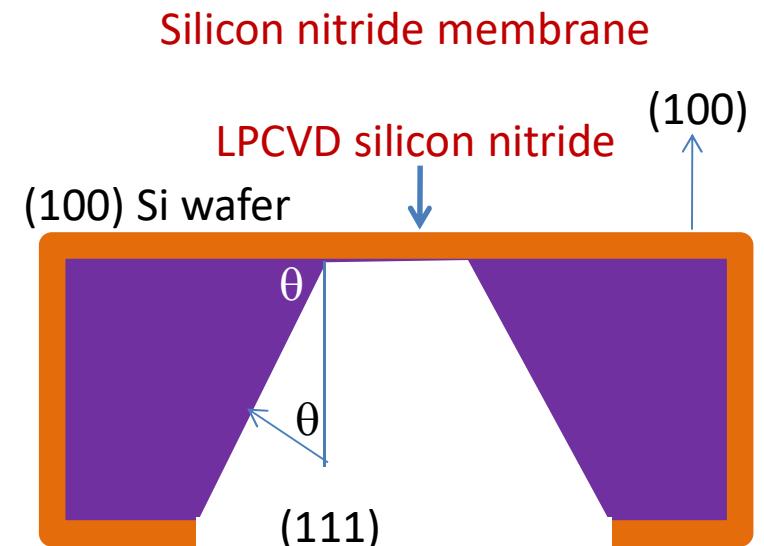
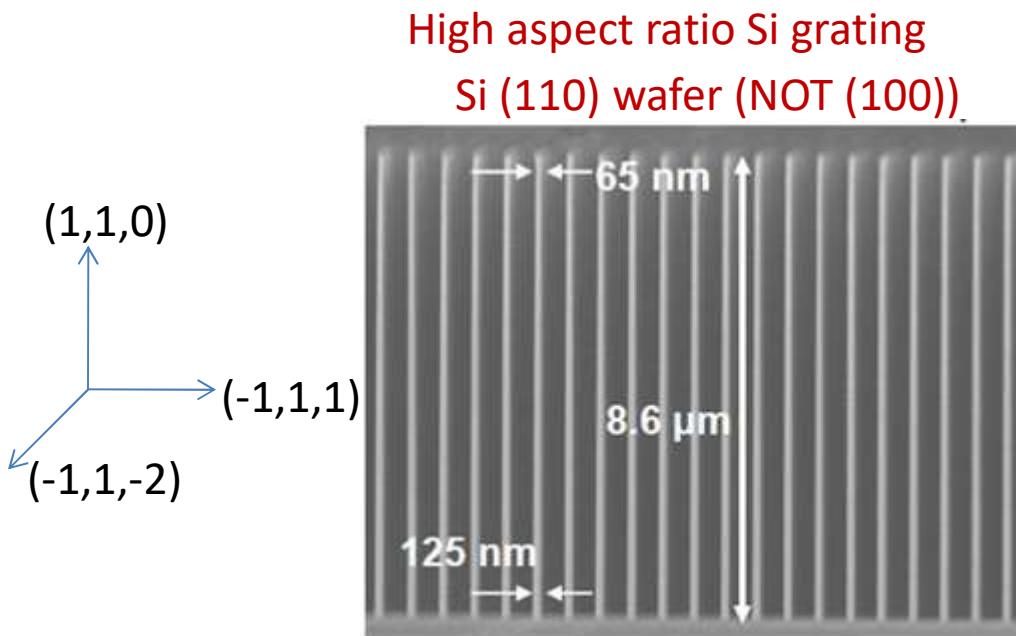


For 10keV, need Au $>10\mu\text{m}$ thick for $<10\%$ transmission, can be done by Au electroplating, yet difficult to have high resolution ($\ll 1\mu\text{m}$).

For 1kV (1.24nm), need $\mu\text{m}/9=110\text{nm}$ in order to have transmission $=1/e=37\%$.

KOH etching of single crystal silicon is anisotropic (for the fabrication of Si₃N₄ membrane support)

- The etching rate R: R(111)<<R(110) and R(100), R(100)/R(111) ~ few 100.
- The etching rate of SiO₂ is about 1/1000 that of R(100), so SiO₂ can be a good etching mask.
- However, for wafer-through etching (etch 0.5mm), better use Si₃N₄ as etching mask, whose etching rate in KOH is negligible.
- Typical etchant contains 20-50% KOH in water at temperature 50-90°C (room temperature is also OK, but etch much slower, need days to etch through 0.5mm-thick wafer).



The angle between (111) and (100) is $\cos\theta=1/\sqrt{3}$, so $\theta=54.74^\circ$.

Various x-ray masks: Ti and Si “membrane”

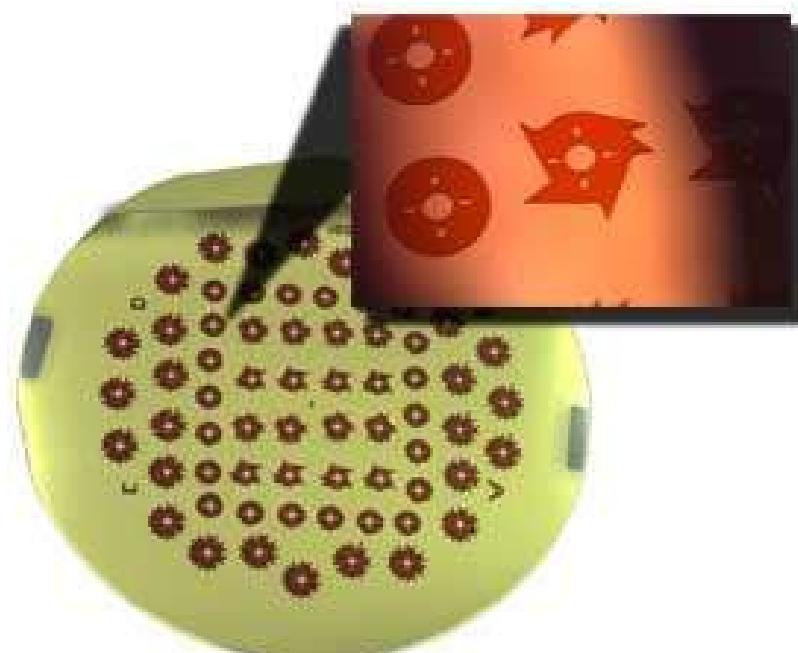
X-ray mask – Ti thin film membrane



Pattern area (6.5 x 2.5 cm²)

Ti mask: FZK IMT

X-ray mask – silicon substrate



100 μ m thick Si wafer, 30 μ m of Au absorber.
Thick Au is needed to prevent exposure in blocked
area when using thick (mm) resist and thus short
wavelength for high aspect ratio resist structure.
Thick resist requires short wavelength (less
absorption in resist and Au) and high dose in order
to fully expose resist bottom.

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LIGA: introduction

- LIGA: Lithographie Galvanik Abformung. (German name)
- It is a fabrication process for high aspect ratio (height/width) microstructures consisting of three major process steps.
 - X-ray lithography (LI=lithographie) to generate primary microstructures. Nowadays similar process but using other lithographies is also called LIGA.
 - Electroplating (G=Galvanik) to produce molds in metals such as Ni.
 - Molding (A=Abformung) using the metal mold to batch produce secondary microstructures in polymers, ceramics...

Naturwissenschaften 69, 520–523 (1982) © Springer-Verlag 1982

Production of Separation-Nozzle Systems for Uranium Enrichment by a Combination of X-Ray Lithography and Galvanoplastics

E.W. Becker, W. Ehrfeld, and D. Münchmeyer

Institut für Kernverfahrenstechnik des Kernforschungszentrums, D-7500 Karlsruhe

H. Betz, A. Heuberger, and S. Pongratz

Fraunhofer-Institut für Festkörpertechnologie, D-8000 München

W. Glashäuser, H.J. Michel, and R. v. Siemens

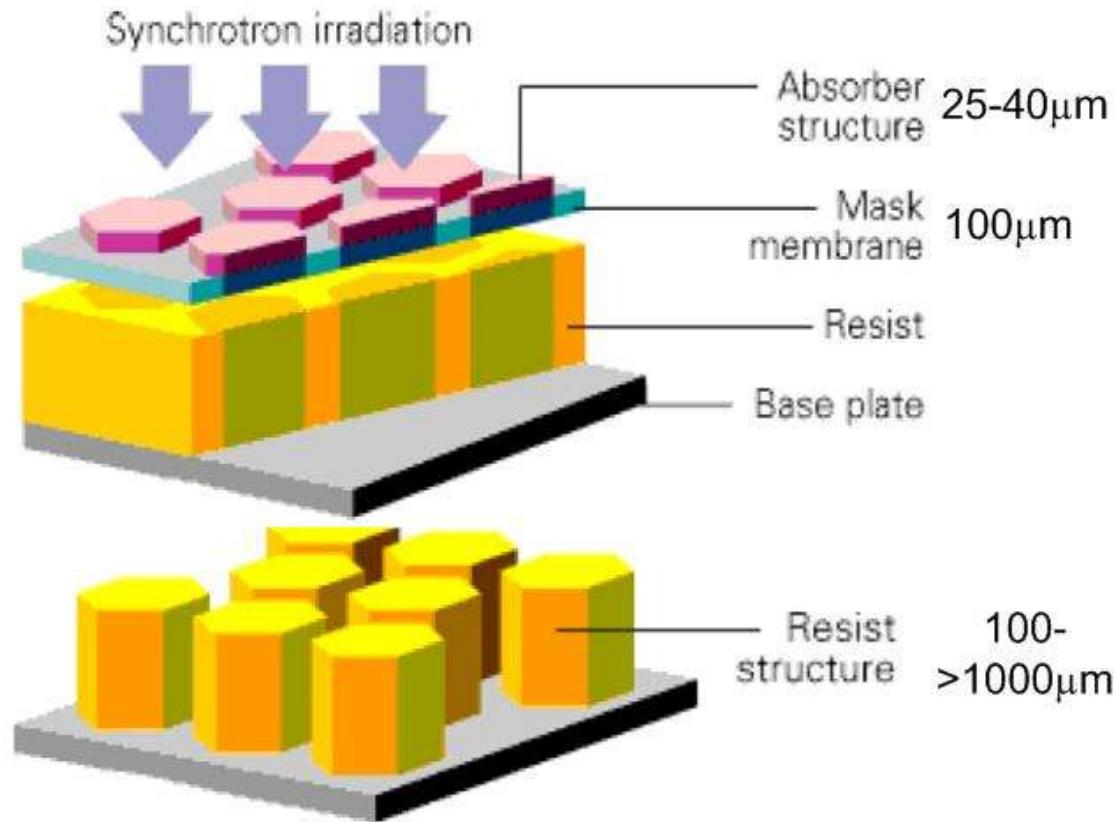
Siemens AG, Zentralbereich Technik, Zentrale Fertigungsaufgaben, D-8000 München

First publication on LIGA
appeared in 1982.

Today, more and more prototypes
are fabricated by LIGA.

Some LIGA companies have been
founded to provide professional
services to users

LIGA process flow



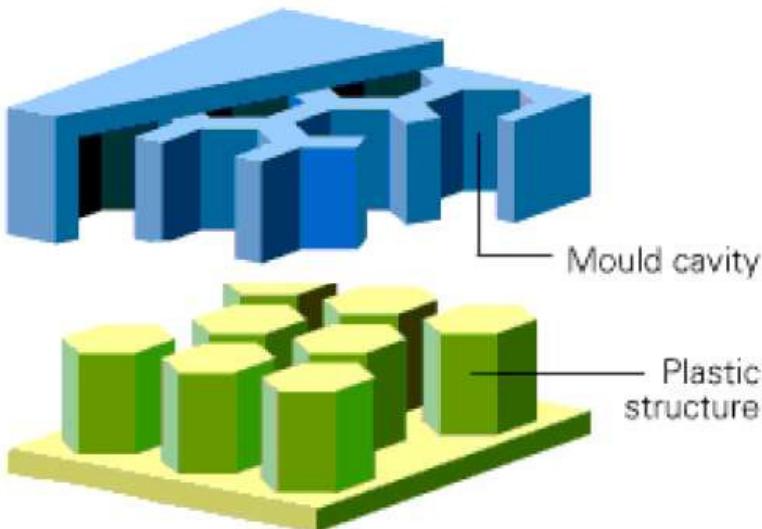
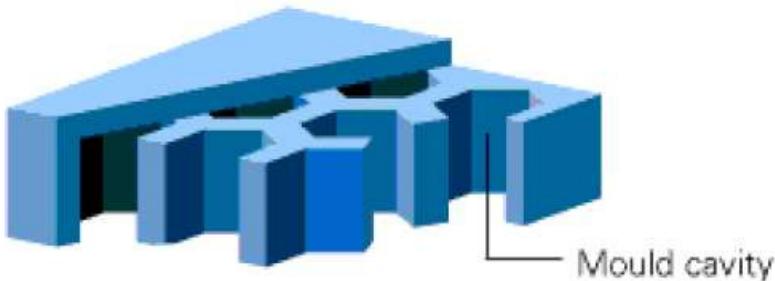
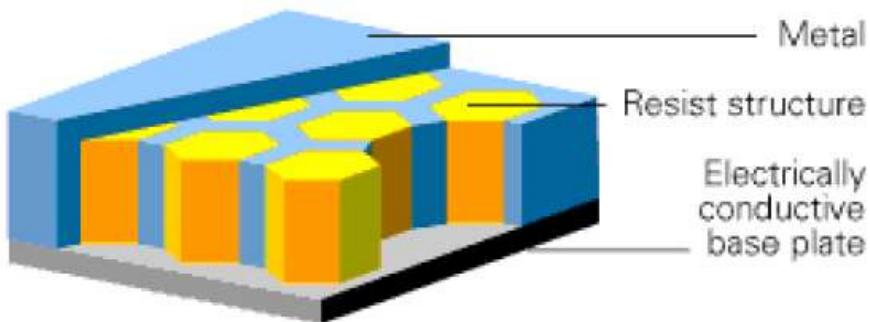
Shadow printing
using x-rays

X-ray mask

Resist
Substrate

Development

Electroplating of metal structures and mold inserts

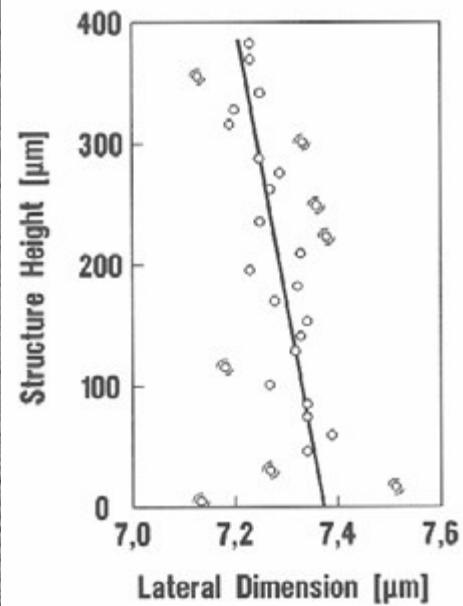
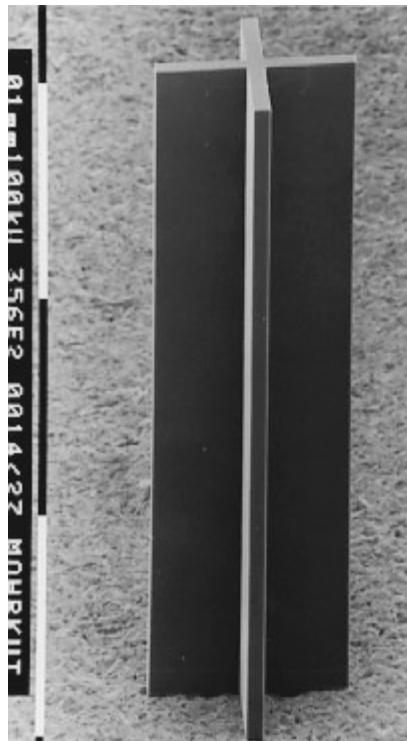


Replication by molding
(hot embossing,
injection molding)

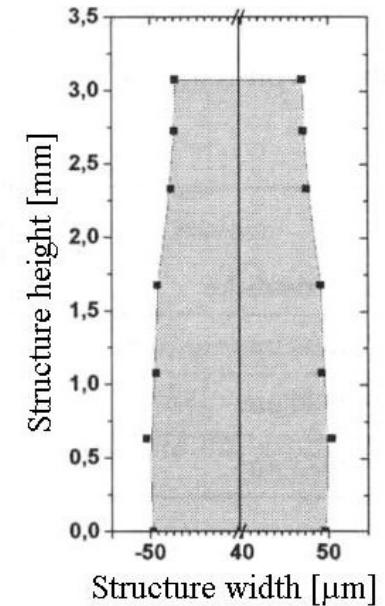
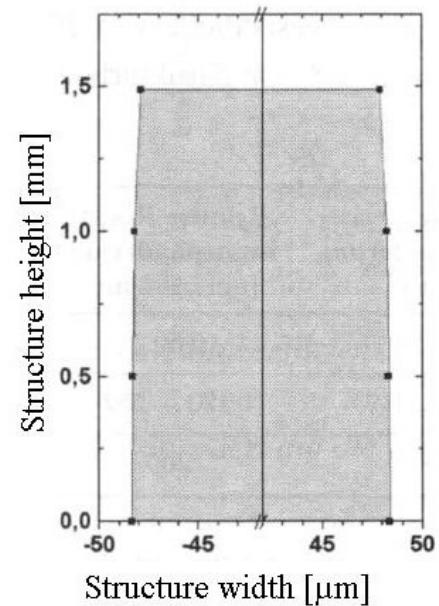
Why is LIGA interesting

- Very high aspect ratio (height : width > 100 : 1) structures can be achieved.
- Vertical and better surface roughness in sidewall
 - Vertical sidewall slope < 1µm/mm
 - Surface roughness <30-50nm (peak to valley)
- It can be applied in both MEMS and traditional precision manufacturing.

Patterning accuracy – DXRL (deep XRL, few Å)

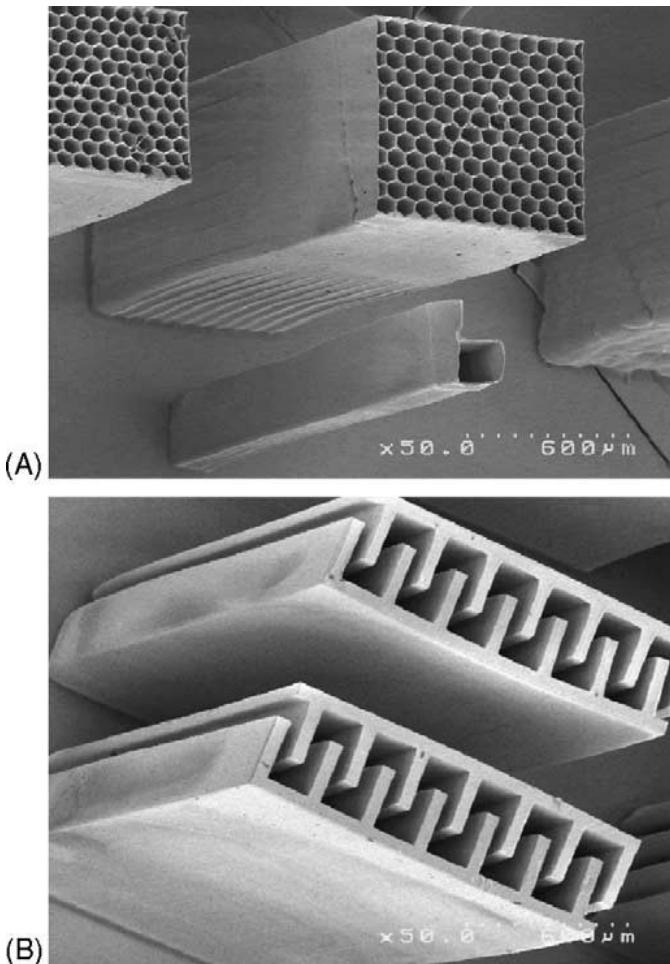


Patterning accuracy – UDXRL
(ultra-deep x-ray lithography, <1Å)



LIGA problems

- X-ray source (synchrotron radiation) very expensive.
- Long time exposure and develop. But SU-8 is $>100\times$ faster than PMMA.
- Other competing technology are rapidly catching up: LIGA-like process using UV lithography with SU-8 resist (see below); deep silicon etching capable of etching through a 0.5mm Si wafer with vertical sidewall.



Structure by photolithography (NOT x-ray lithography) in SU-8, a negative tone photoresist (and x-ray, e-beam resist).

(A) SEM image of honeycomb structures with designed sidewall width of 6 μm and a height of 2000 μm . The micro-feature next to the honeycombs is an Arabic number “6” with designed width of 7 μm and a height of 2000 μm . (aspect ratio 2000:7)

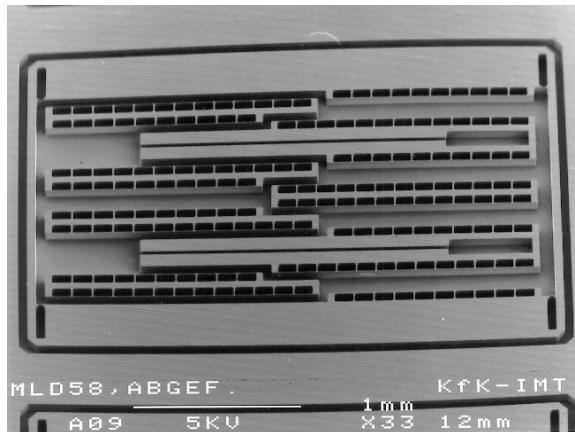
(B) Micro-comb structures with designed thickness of 40 μm and height of 2000 μm .

“A numerical and experimental study on gap compensation and wavelength selection in UV-lithography of ultra-high aspect ratio SU-8 microstructures”, Wang, Sensors and Actuators B, 2005.

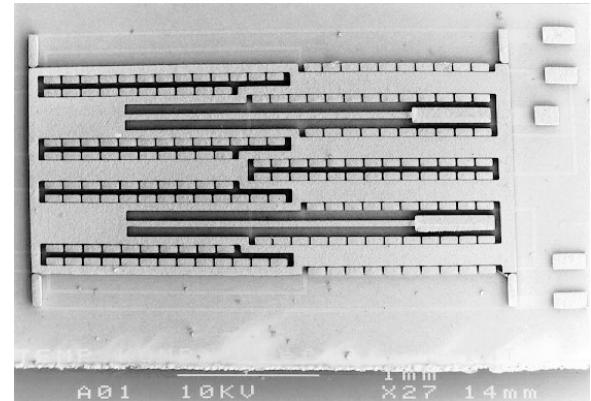
Applications of LIGA: MEMS

LIGA Acceleration Sensor

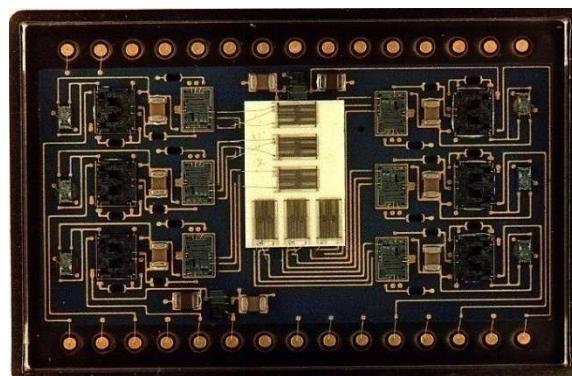
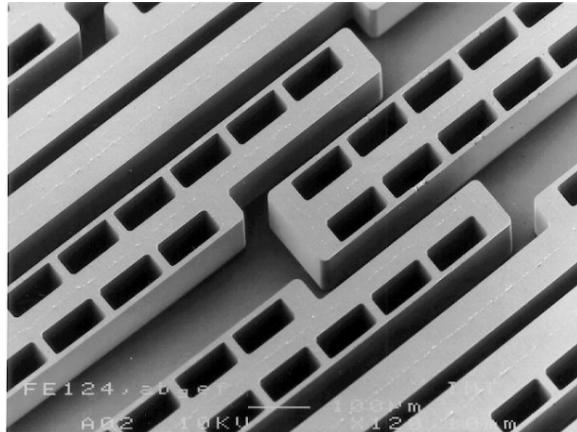
PMMA structure



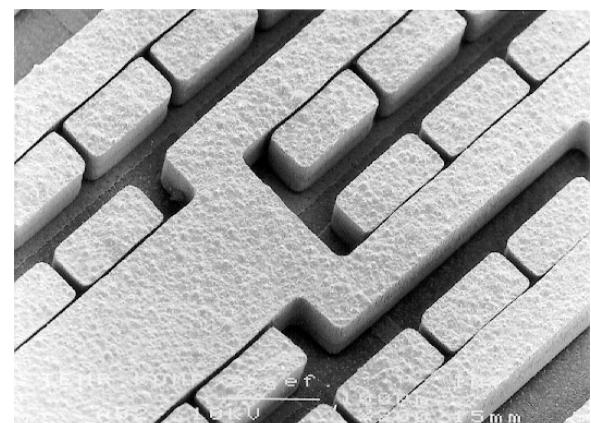
Ni - structures 120 μm high



Detail



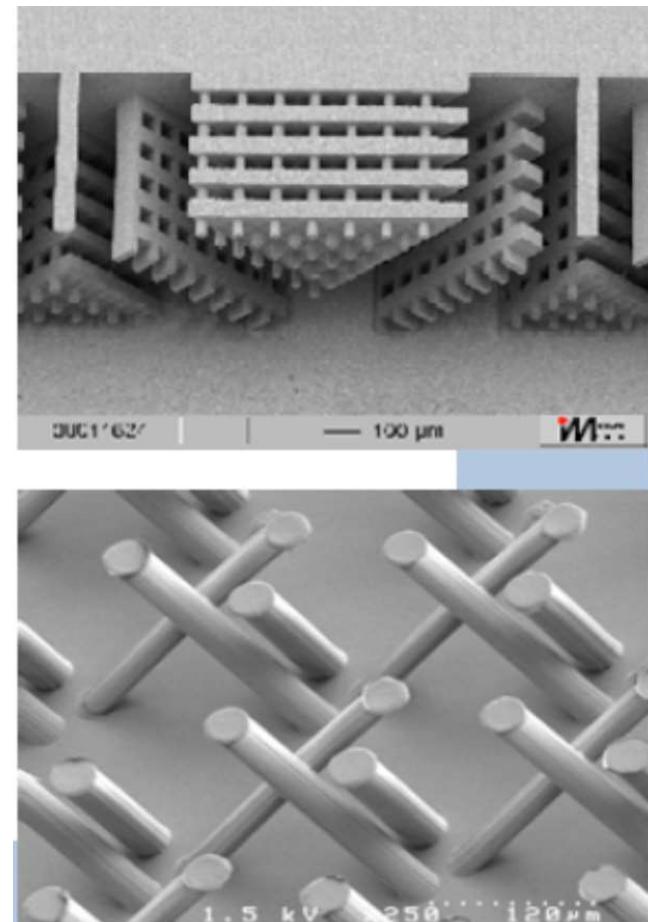
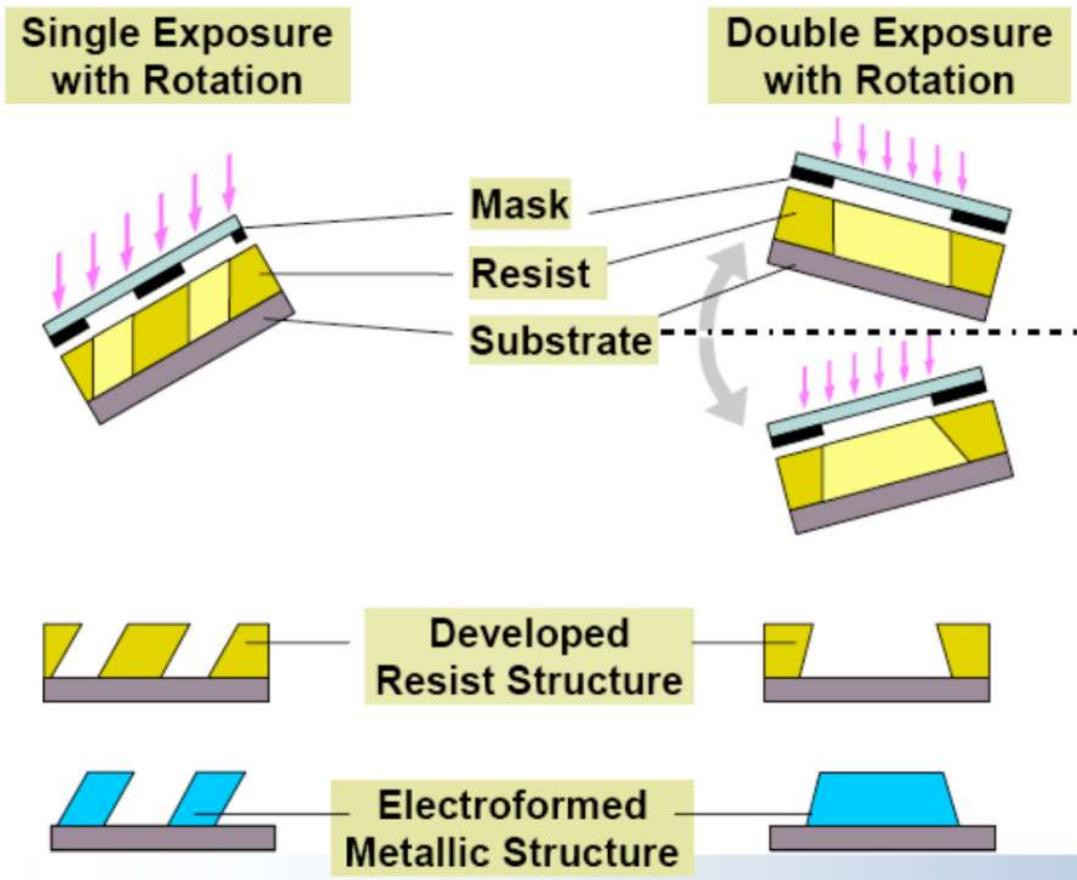
Redundant Sensor System



MEMS: Micro-electro-mechanical systems

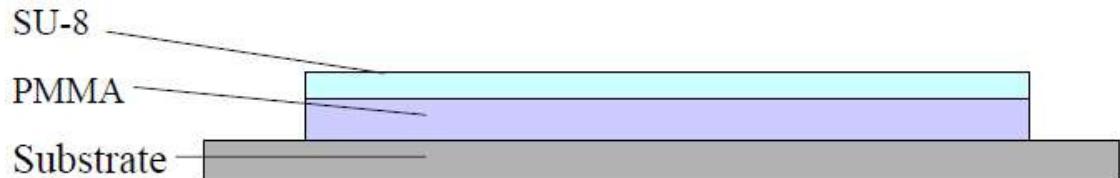
3D structure fabrication by LIGA

(using multiple exposures with rotation)

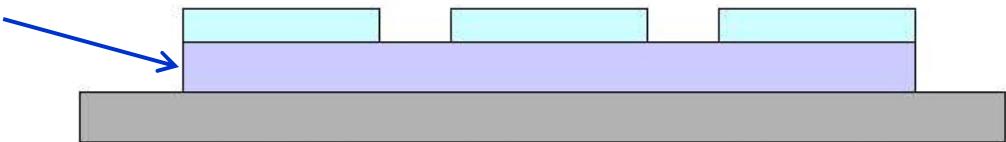


3D structure fabrication by LIGA

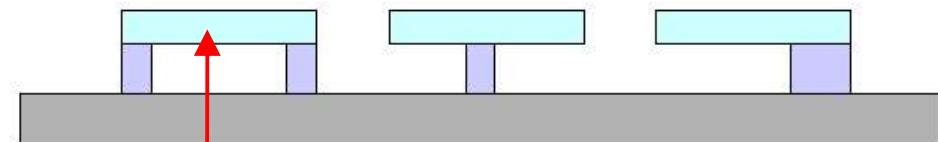
(using PMMA and SU-8 stack)



PMMA won't be exposed at doses sufficient for exposing SU-8

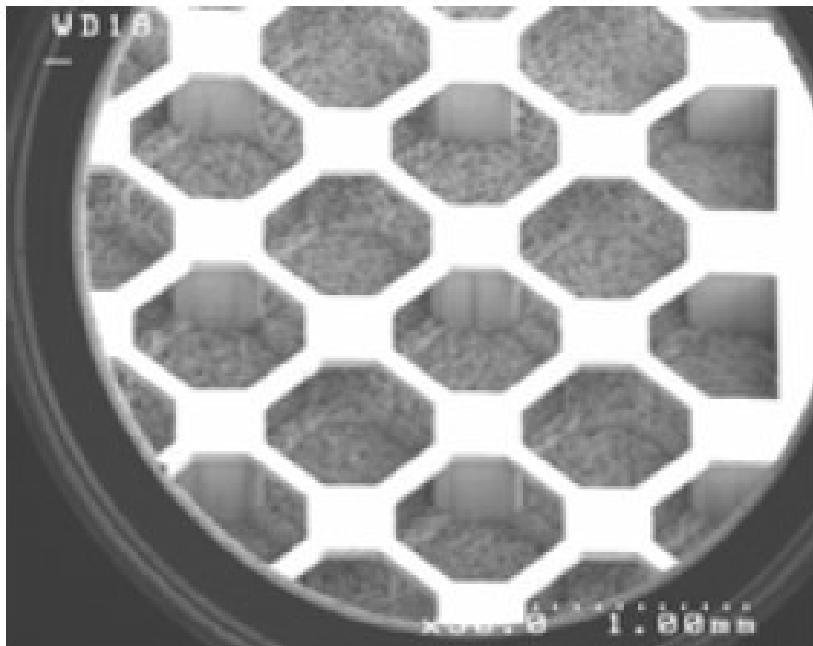


Pattern SU-8 with UV or X-ray lithography



Pattern PMMA with X-ray lithography

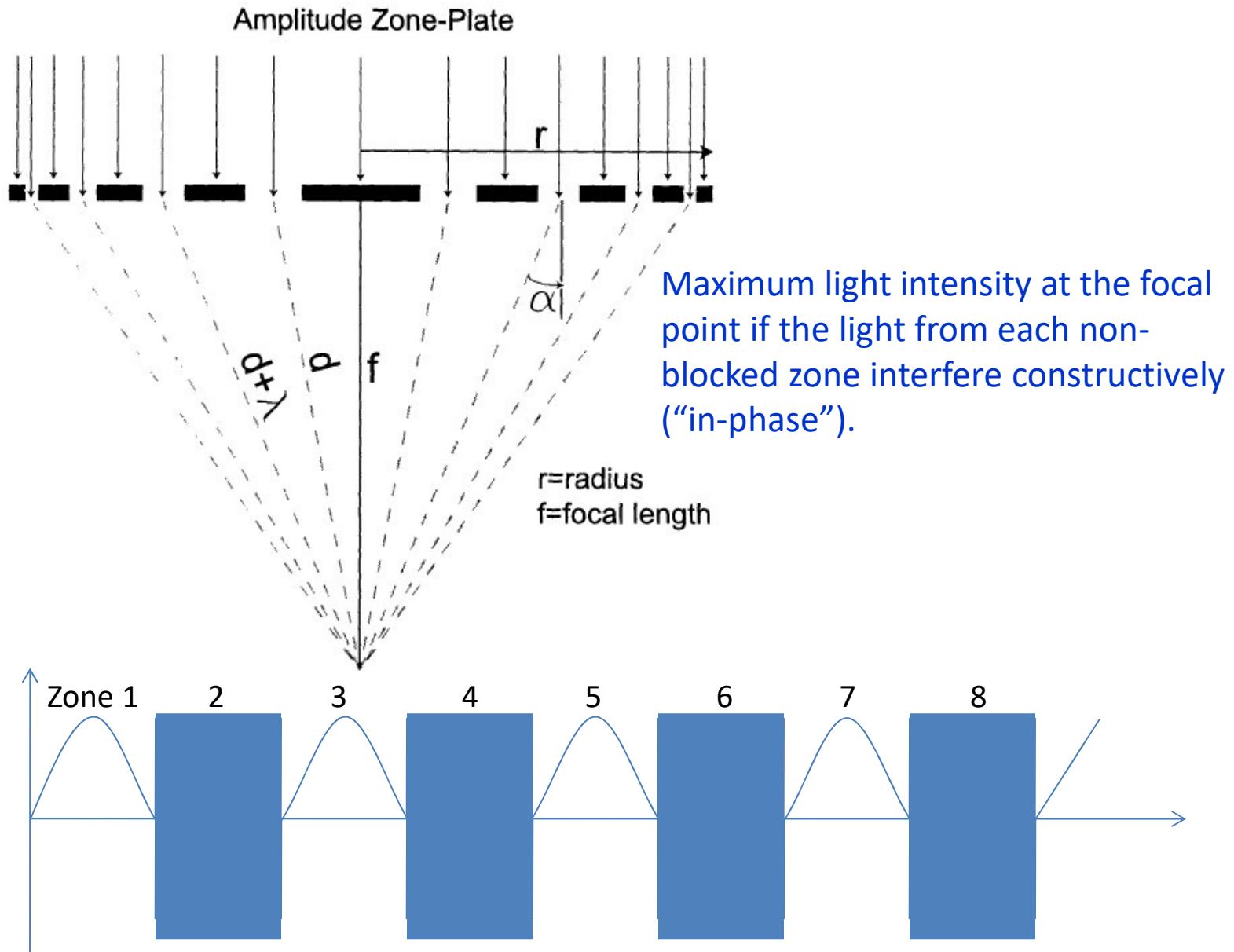
Here SU-8 is already cross-linked,
thus won't be affected by further
exposure to x-ray.



X-ray lithography (XRL)

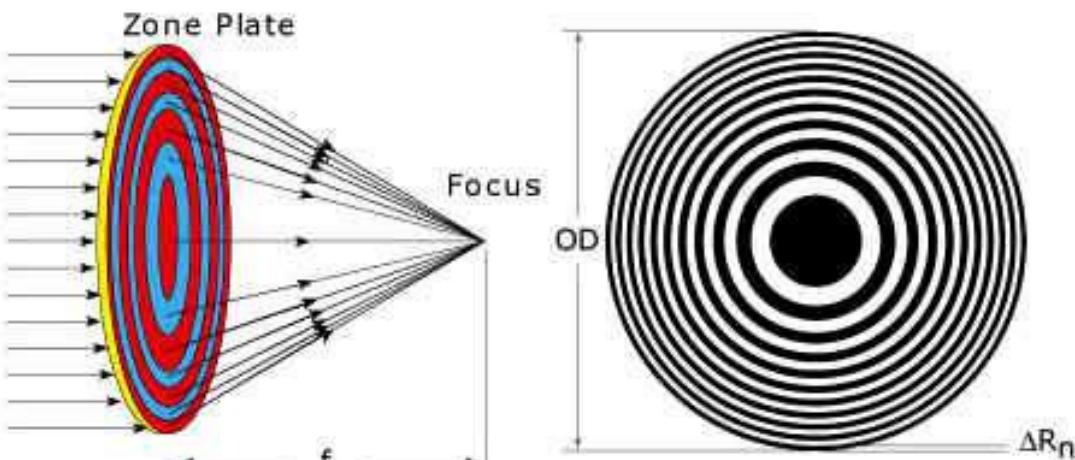
1. Overview and resolution limit.
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How zone-plate works

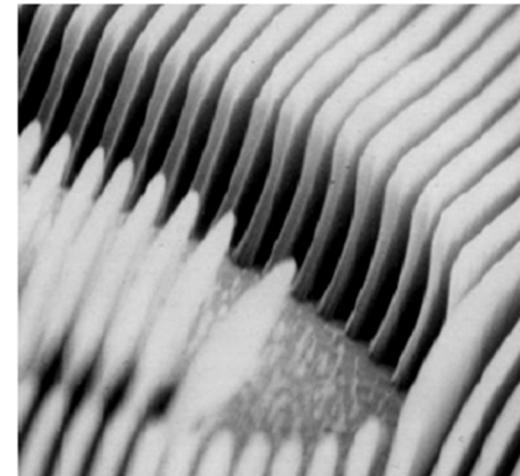


Fresnel lenses (zone plates): overview

- There is only reflection optics for soft x-ray and no optics for hard x-ray.
- Zone plate is the only option for focusing and imaging in this wavelength range.
- Most zone plate is fabricated by e-beam lithography, followed by electroplating of heavy metals into the trenches in resist, with aspect ratio limited to about 1:10.



Zone-plate schematic.



High aspect ratio metal pattern
by EBL and electroplating

Zone-plate equations

The area between r_1 and r_2 is transparent, that between r_2 and r_3 is blocked, that between r_3 and r_4 is transparent...

Here we assume r_1 is such that the distance from r_1 to focal point is $f + \lambda/2$.

$$f^2 + r_n^2 = \left(f + \frac{n\lambda}{2} \right)^2 \quad n=1, 2, 3, \dots, N$$

$$r_n^2 = n\lambda f + \frac{n^2\lambda^2}{4} \approx n\lambda f \quad \text{Assume } N\lambda \ll f$$

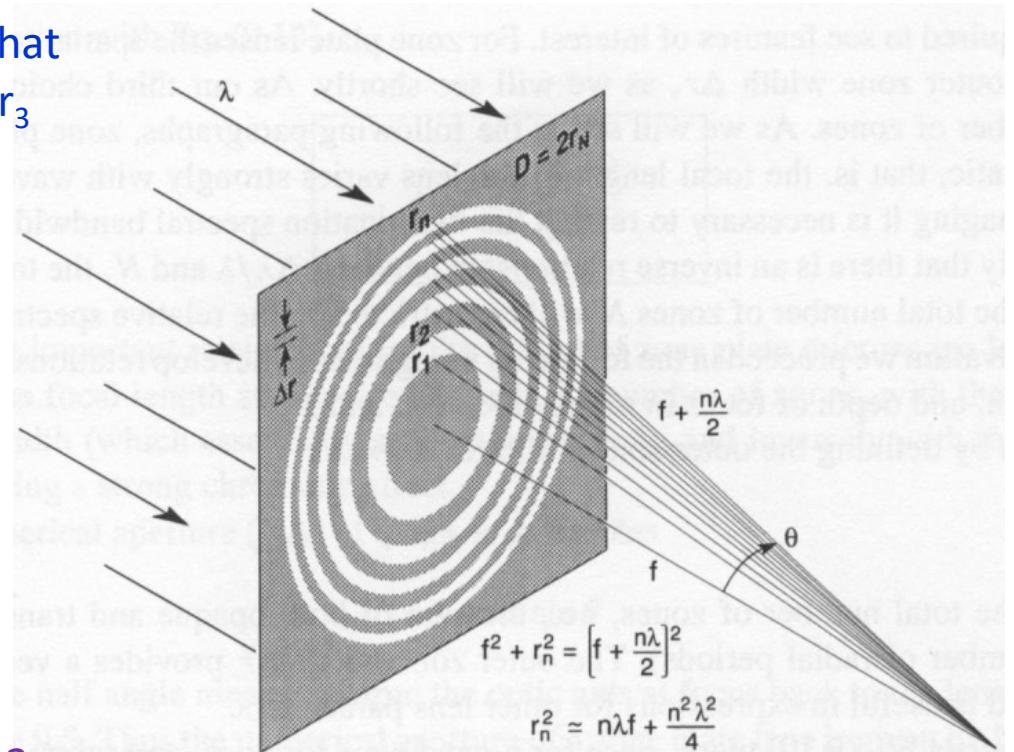
$$r_n \approx \sqrt{n\lambda f}$$

$$\Delta r \equiv r_N - r_{N-1} = \frac{\lambda f}{r_N + r_{N-1}} \approx \frac{\lambda f}{2r_N} = \frac{\lambda f}{D} \quad D \equiv 2r_N$$

$$D\Delta r = \lambda f \approx \frac{r_N^2}{N} = \frac{D^2}{4N}$$

$$D \approx 4N\Delta r$$

$$f \approx \frac{D\Delta r}{\lambda} = \frac{4N(\Delta r)^2}{\lambda}$$



$$NA = \sin \theta = r_N / f = D / 2f \approx \frac{\lambda}{2\Delta r}$$

$$R = \frac{0.61\lambda}{NA} = 1.22\Delta r$$

Δr : outermost zone width
 R : resolution

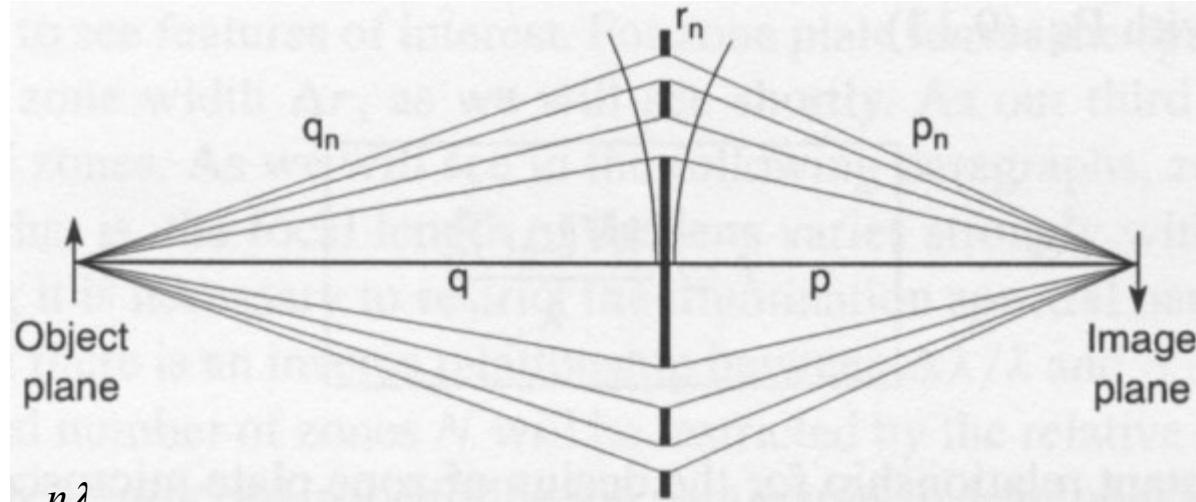
Those equations are good for the case of $N\lambda \ll f$, which is equivalent to small NA.

NA is always small for hard x-ray, but less so for soft x-ray zone plates.

The area of each zone is $\pi(r_n^2 - r_{n-1}^2) = \pi\lambda f = \text{constant}$, so each zone contributes equally to the intensity at focal point.

Zone-plate is indeed a lens

Try your best to understand this slide. It won't be included in exams



$$q_n + p_n = q + p + \frac{n\lambda}{2}$$

$$q_n = \sqrt{q^2 + r_n^2} \approx q + \frac{r_n^2}{2q}$$

$$p_n = \sqrt{p^2 + r_n^2} \approx p + \frac{r_n^2}{2p}$$

$$\frac{r_n^2}{2q} + \frac{r_n^2}{2p} \approx \frac{n\lambda}{2}$$

$$\frac{1}{q} + \frac{1}{p} \approx \frac{1}{f}$$

$$f = r_n^2 / n\lambda \text{ independent of } n \text{ for } r_n = (n\lambda f)^{1/2}, \text{ which is the same as before.}$$

We know that for a regular optical lens, the equation is

$$\frac{1}{q} + \frac{1}{p} \approx \frac{1}{f}$$

Therefore, a zone plate is like a lens, with magnification equal to p/q .

Zone plate fabrication: e-beam lithography + electroplating

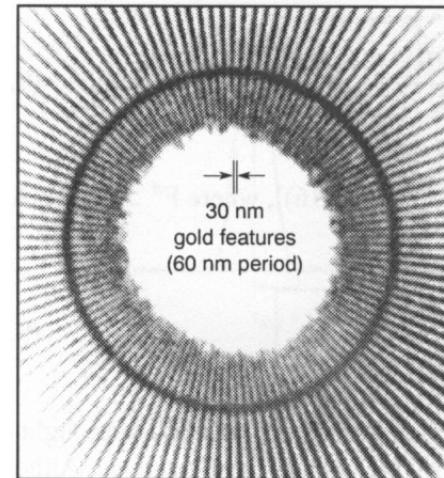
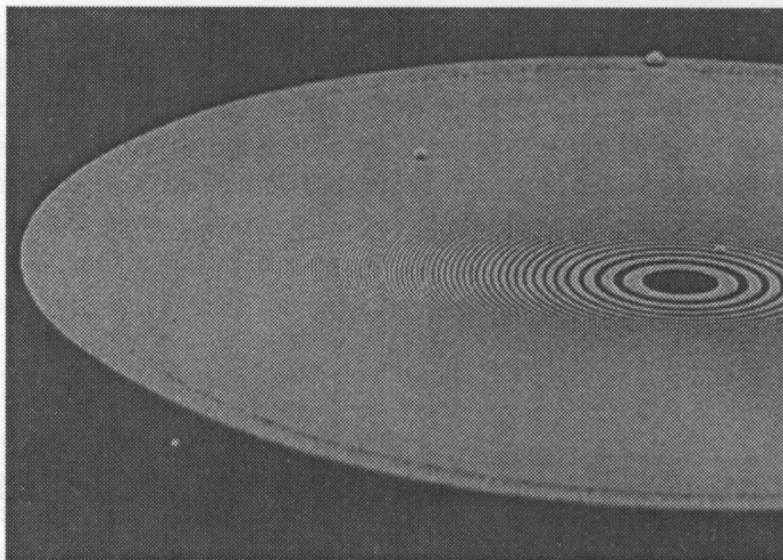
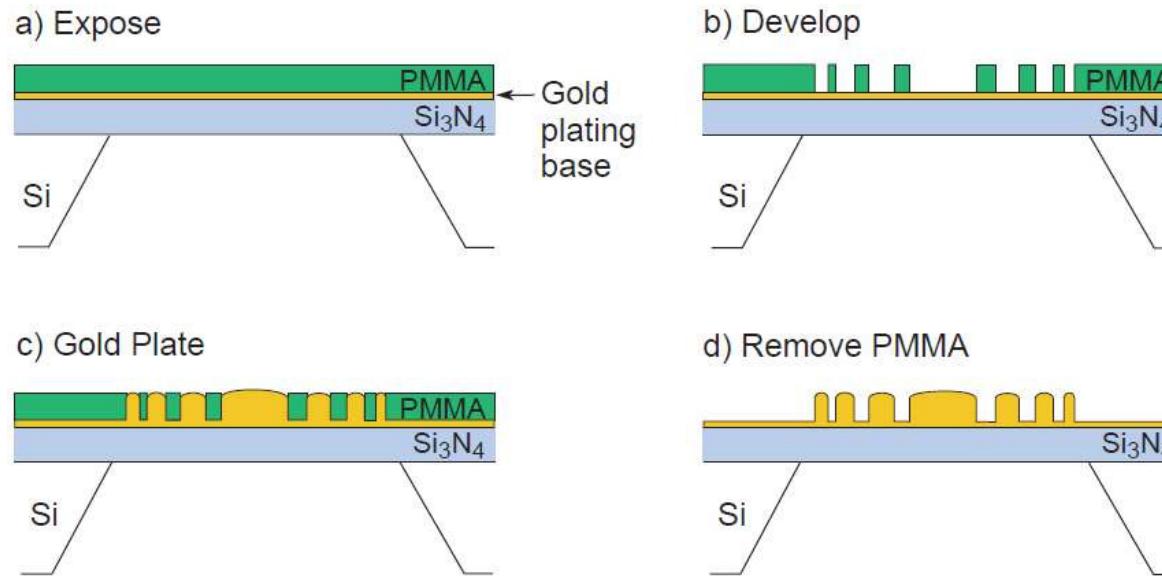
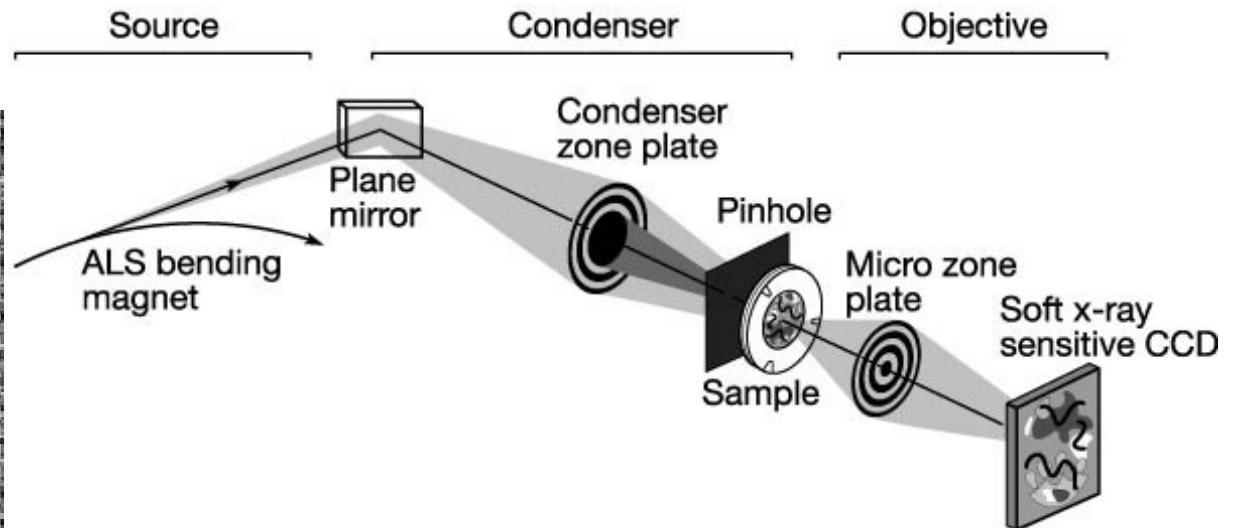
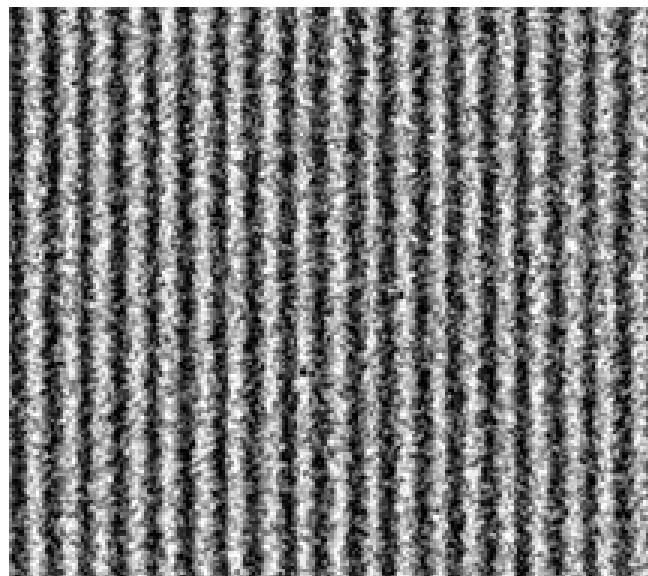


FIGURE 9.15. X-ray image at 2.4 nm wavelength of a radial gold test pattern showing 30 nm gold features (60 nm period). The soft x-ray image was obtained with a CXRO/IBM zone plate lens having a 30 nm outer zone width, and the University of Göttingen soft x-ray microscope at the BESSY synchrotron radiation facility in Berlin (see Refs. 22 and 23).

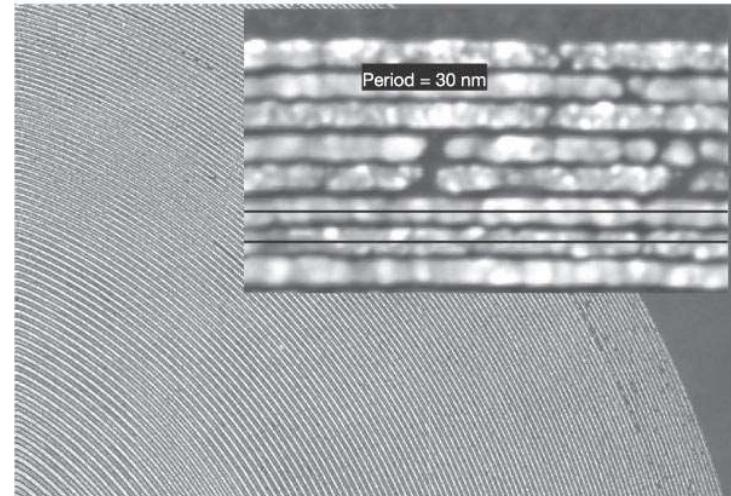
Zone plate with 100nm-thick gold with a 30nm outer zone width and 300 zones. It is used to form the image on the right side with 30nm resolution.

X-ray imaging - highest resolution achieved



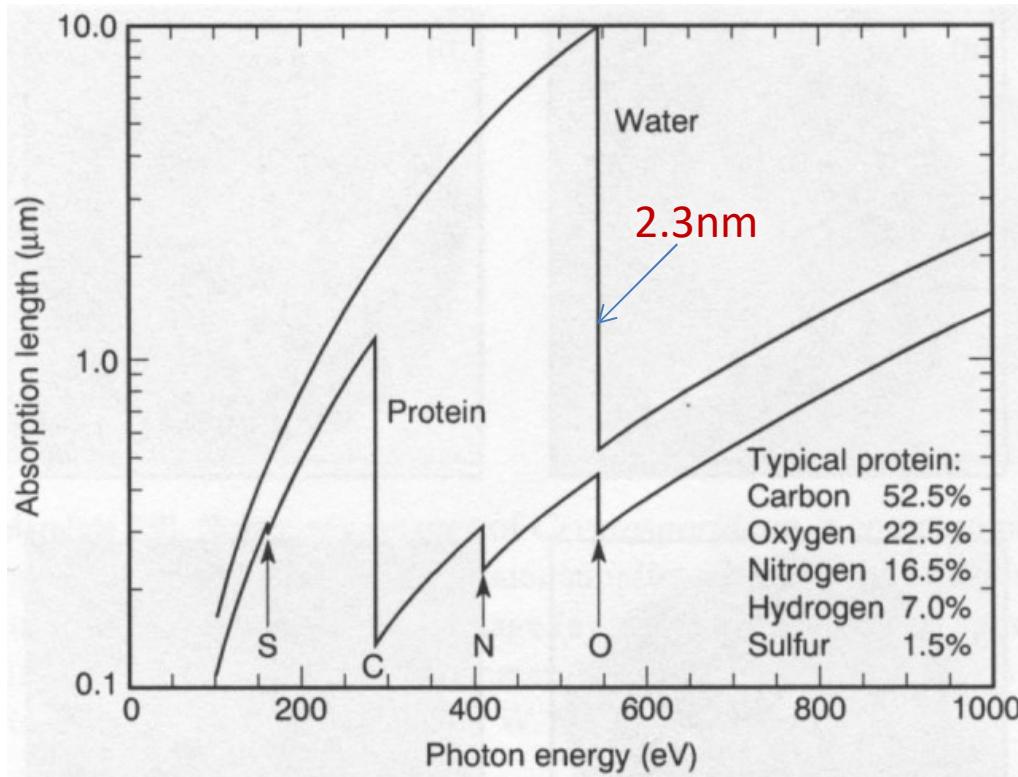
Best spatial resolution achieved:
15nm lines. Sub-10nm is on the way.

Outer zone-width=15nm, Au is 80nm thick.
Zone plate fabrication is the most challenging
task for x-ray microscopy



W. Chao, ... David Attwood, "Soft X-ray microscopy at a spatial resolution better than 15 nm", Nature 435, 1210-1213 (2005).

Application in bio-imaging



Absorption length (penetration depth) for soft x-rays in water and a generic protein as a function of photon energy.

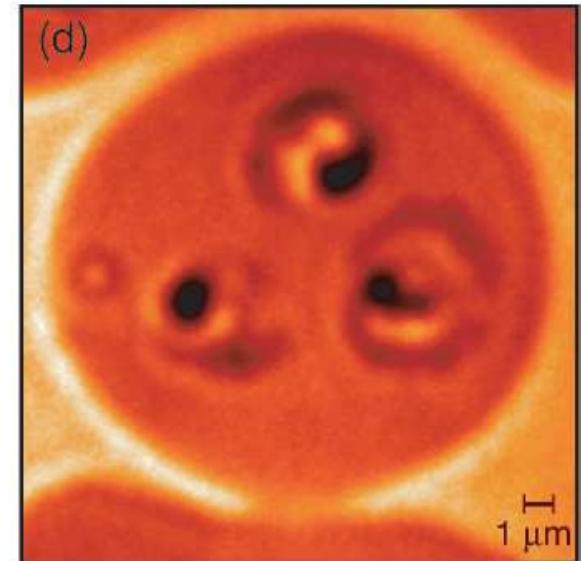
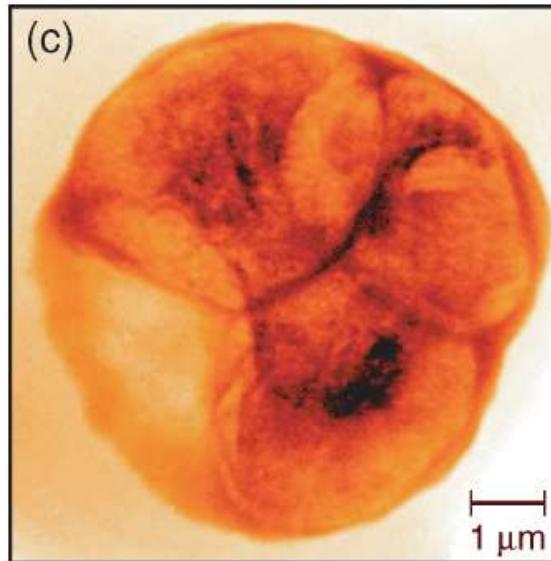
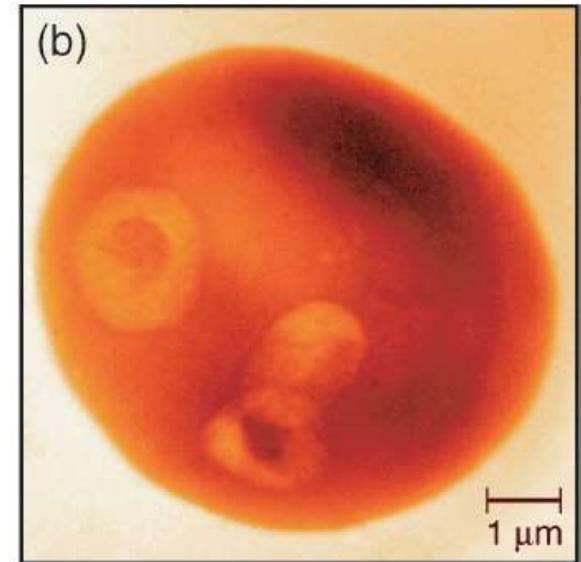
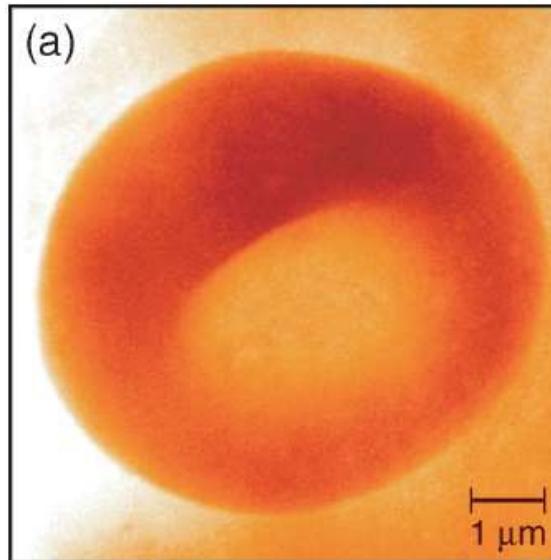
Why S is on the lower energy side?

Natural contrast in the water window, between the carbon and oxygen absorption edges, where the high carbon content protein is absorbing where water is relatively transparent. Imaging of thicker objects ($\sim 10\mu\text{m}$, size of typical mammalian cells) requires operation in the lower λ part of the water-window where the transmission is higher, such as $\lambda=2.4\text{nm}$ from synchrotron radiation or N_2 laser-produced plasma.

Malaria infected red blood cells

$\lambda=2.4\text{nm}$ from bending
magnet synchrotron radiation
at ALS (Berkeley).
Image resolution: $\sim 40\text{nm}$

- a. Uninfected cell
- b. Newly infected cell
- c. 36 hours after infection.
- d. Image with visible light
microscopy, for comparison.



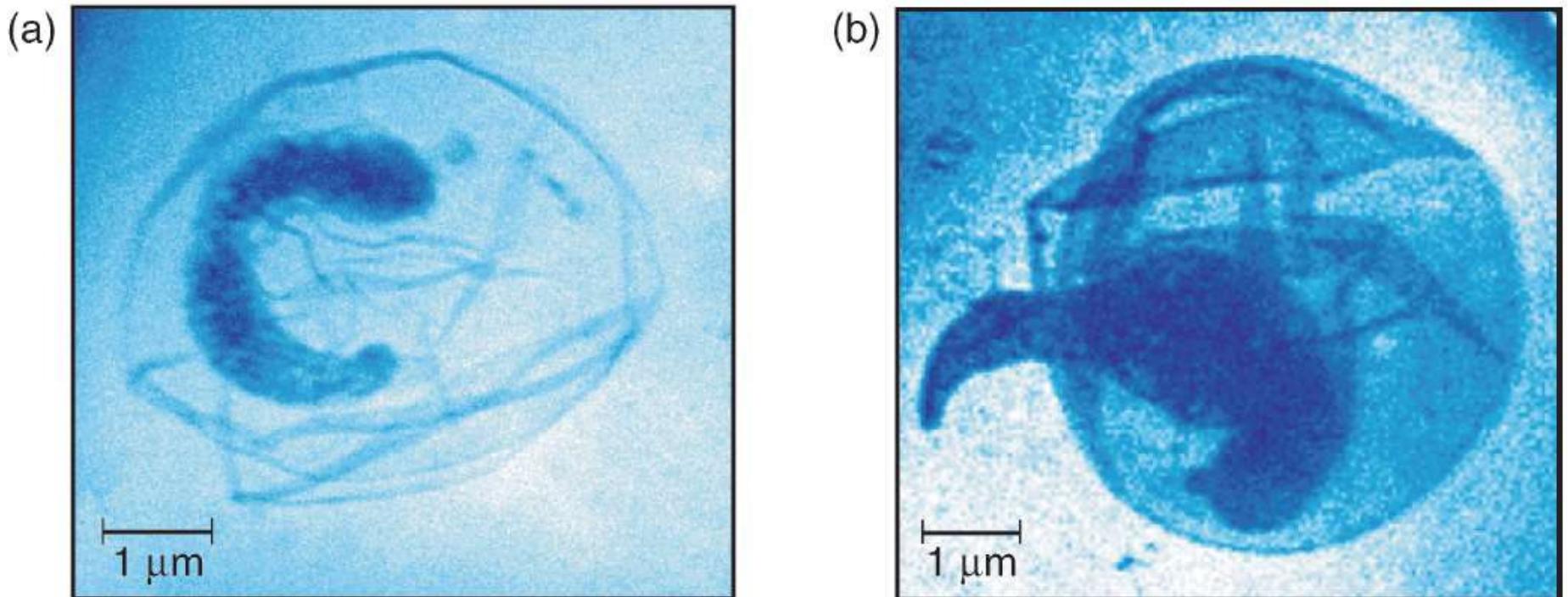
More photos at:
<http://www.cambridge.org/catalogue/catalogue.asp?isbn=9780521029971&ss=res>

Magowan C. et. al, "Intra-cellular structures of normal and aberrant plasmodium falciparum malaria parasites imaged by soft s-ray microscopy", PNAS 94, 6222 (1997)

Soft x-ray images of Cryptosporidium

Cryptosporidium is a common parasite found in lakes and rivers, and occasionally in municipal water supplies that may cause death.

Images taken at 2.4nm wavelength



The last of four sporozoites still in its protective oocyst.

A sporozoite emerging from the oocyst

Electron beam lithography (EBL)

1. Overview and resolution limit.
2. Electron source (thermionic and field emission).
3. Electron optics (electrostatic and magnetic lens).
4. Aberrations (spherical, chromatic, diffraction, astigmatism).
5. EBL systems (raster/vector scan, round/shaped beam)

Note: in the textbook, e-beam lithography and focused ion beam are put within one chapter, because they are both “charged beam”.

Here I will introduce them separately, in order to give you a clearer concept of each.

E-beam lithography (EBL) overview

(direct writing with a focused e-beam)

- Electron beam is focused to spot size <5nm using electron optics.
- Very small wavelength: resolution less limited (yet still limited) by diffraction.
- *Generate* pattern by direct writing: no need of mask or mold.
- Sequential pixel-by-pixel writing: low throughput, unsuitable for mass production.

For electron:
(V is electron kinetic
energy in eV)

$$\lambda = \frac{1.226}{\sqrt{V}} \text{ (nm)}$$

For EBL at 30kV acceleration voltage
 $\lambda=0.007\text{nm}$

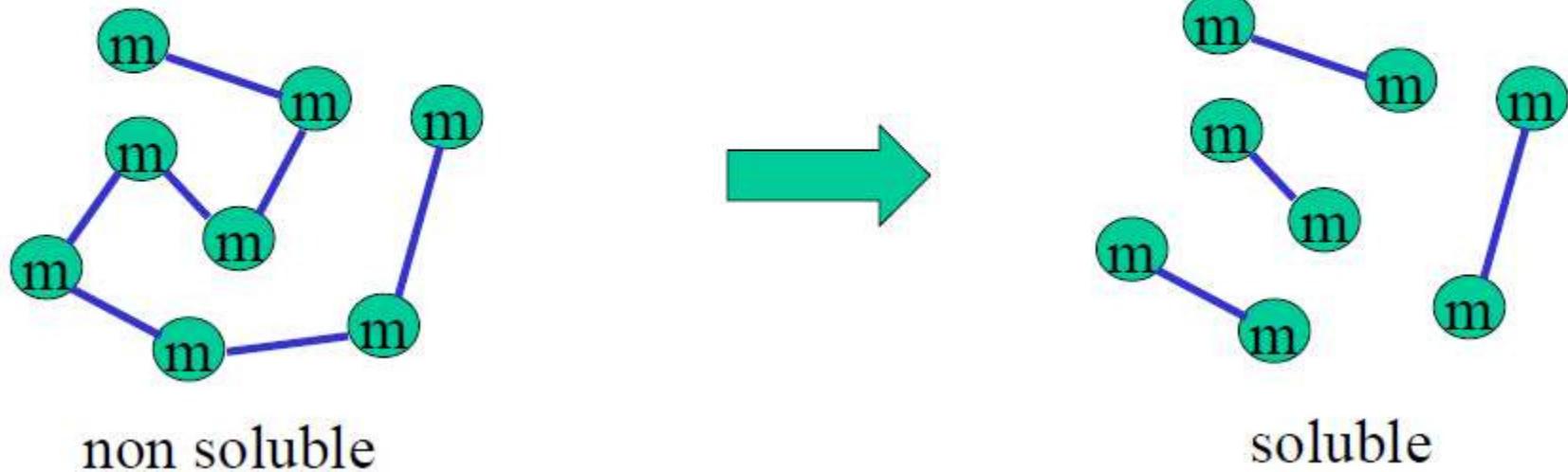
For light:

$$\lambda = \frac{hc}{eV} = \frac{1.24}{V} \text{ (\mu m)}$$

For an electron with kinetic energy of 1eV, the associated DeBroglie wavelength is 1.226nm, about a thousand times smaller than a 1eV photon.
(Note: electron rest mass energy is $mc^2=511\text{keV}$, so relativity is unimportant for <50keV)

Exposure of resist

organic resist (PMMA)



- Typical energy for breaking a bond: 10eV
- But typical energy of the e-beam: 5-100keV
(problems of aberration at low energy that leads to large beam spot size and low resolution, so use high energy for EBL)
- Bond is broken by secondary (including Auger) electrons with low energy.

E-beam lithography facts

- Developed in 1960s along with scanning electron microscope (SEM).
- Breakthrough made in 1968 when a polymer called PMMA (poly methyl meth acrylate) was discovered to have high resolution.
- Fast growth in 1990s when “nano” began to become “hot” and computer became more available for automatic lithography control.
- Since around 2000, focused ion beam (FIB) patterning began to compete with EBL in some applications.
- Today EBL is still the most popular nano-patterning techniques for academic research and prototyping.

EBL systems: most research tools are based on SEM

SEM conversion

- Conventional SEM ($\leq 30\text{kV}$)
- Almost no SEM modification
- Add beam blanker
- Add hardware controller
- Low cost: $<\$100\text{K}$



NPGS system

Dedicated EBL system

- Based on SEM system
- Interferometer stage
- Focus correction (laser sample height control)
- Cost \$1-2M



Raith system

E-beam writer

- High energy column (100kV)
- Dedicated electron optics
- High reproducibility
- Automatic and continuous (over few days) writing
- High cost ($>\$5\text{M}$)



Vistec system

Beam blanker: is a DC bias (~42V between two parallel plate electrodes) *perpendicular* to electron path, so that electrons are deflected away from the axis and thus “turned off”/blocked/blanked by the aperture below.

The beam needs to be blanked so that it won’t expose the resist during its moving to next pattern location.

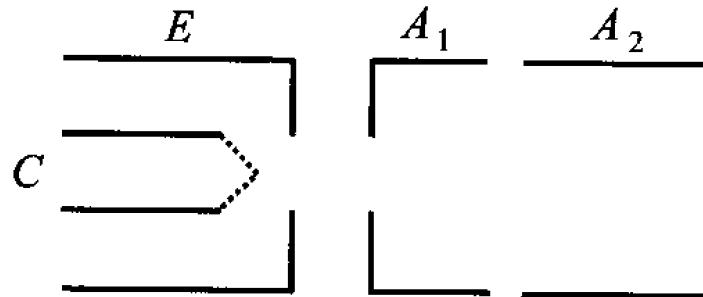
Electron beam lithography (EBL)

1. Overview and resolution limit.
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Electron guns/source

Schematic structure of electron gun

Electrons can be emitted from a filament (emitter or cathode) by gaining additional energy from heat or electric field.



C: cathode for emitting electrons

E: extraction electrode

A₁, A₂: cathode lens electrode to focus the emitted electrons

Three types of electron guns:

- Thermionic emission gun (W, LaB₆, not-sharp tip).
 - Field emission gun (cold, very sharp W tip, tunneling current).
 - Schottky gun (field assisted thermionic emission, sharp tip).
-
- Whether it is field emission or not depends on the electric field near the tip apex, which determines whether tunneling is important or not.
 - Sharper tip leads to higher electric field near tip apex, so field emission (by tunneling) plays a major role, it is thus called field emission gun (FEG).

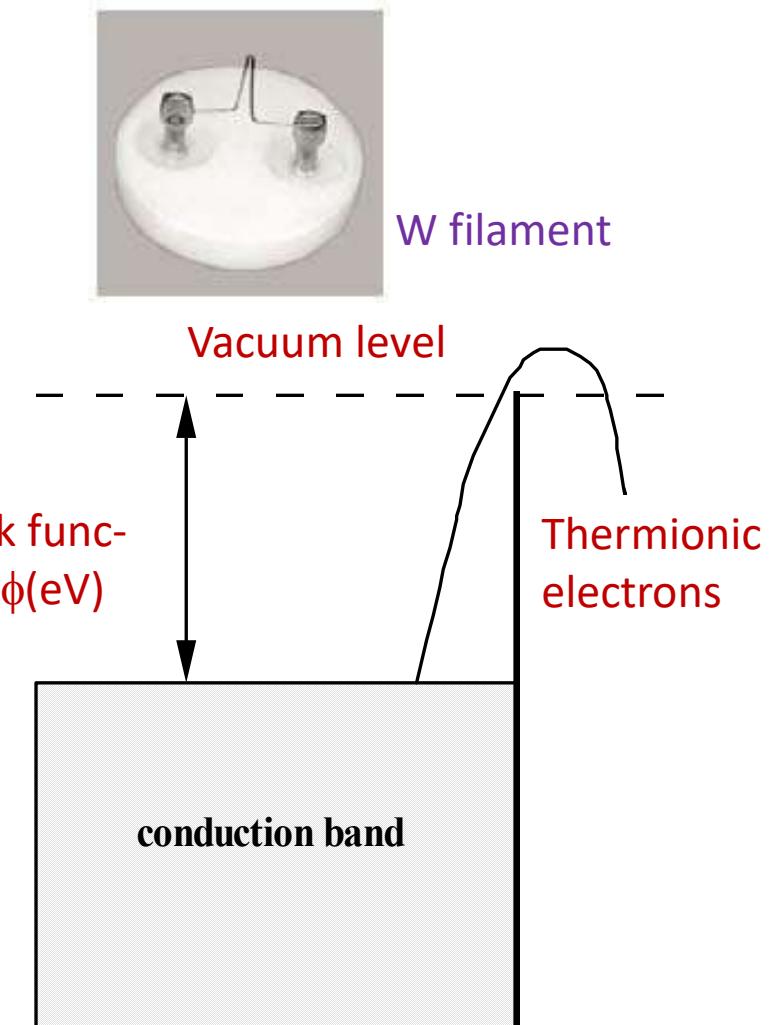
Electron gun: thermionic emission (tungsten hairpin filaments)

- Working at high temperature, some electrons have thermal kinetic energy high enough to overcome the energy barrier (work function)

But kT still \ll work function $\sim 4\text{eV}$. At 2000°C ,
 $kT=1.38\times 10^{-23}\times 2273/1.6\times 10^{-19}=0.20\text{eV}$.

- Escaped electron is then extracted by the electric field generated by the nearby electrode.
- Current density J_c depends on the temperature and cathode work function ϕ .
- Cheap to make and use (\$12.58 ea) and only a modest vacuum is required. Last tens of hours.

For a good introduction, go to:
http://en.wikipedia.org/wiki/Thermionic_emission



Schematic model of
thermionic emission

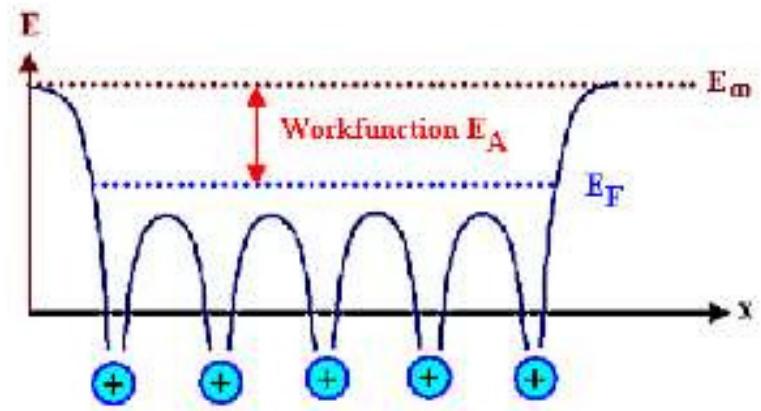
Electron gun: thermionic emission (LaB_6 tip)

Richardson's equation for emission current

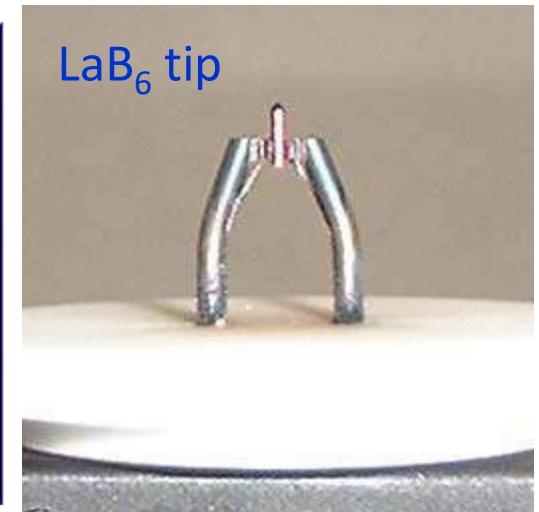
$$j = A \cdot T^2 \cdot \exp\left(-\frac{E_A}{kT}\right)$$

(Here work function is noted as E_A , instead of ϕ)

Low work function, high melting point/T is good.



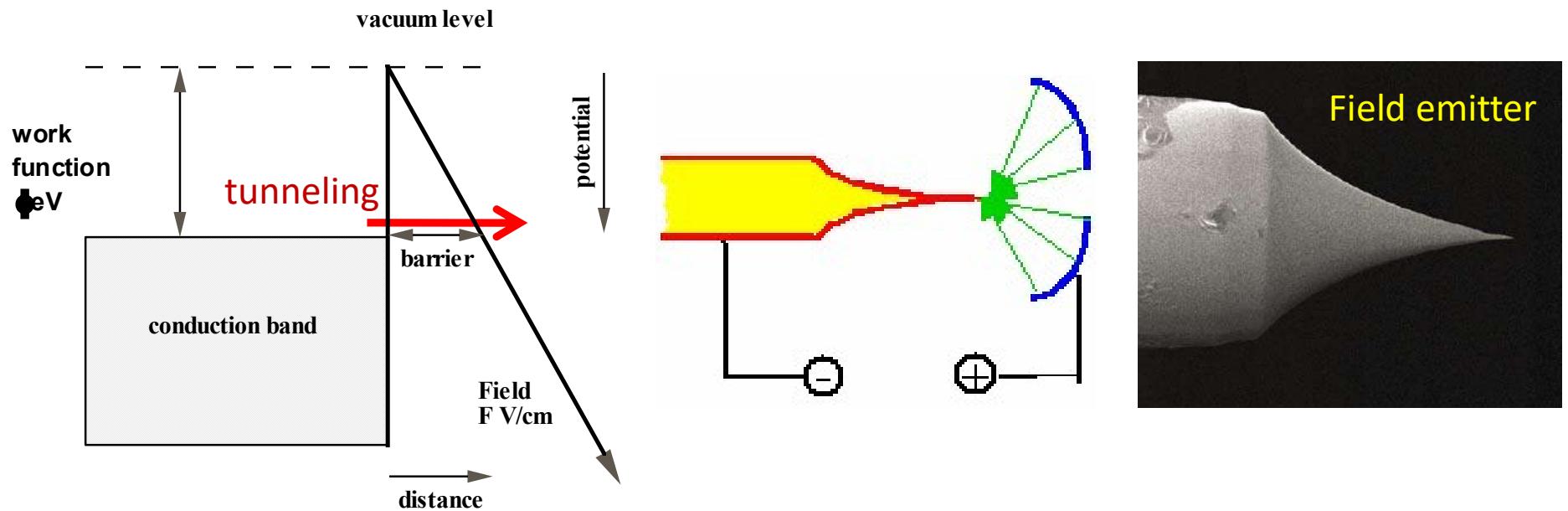
Material	Fe	Ni	Pt	Ta	W	Cs	LaB_6
A [$\text{Acm}^{-2}\text{K}^{-2}$]	26	30	32	55	60	162	25
E_A [eV]	4,5 - 4,8	5,15 - 5,35	5,65	4,15 - 4,8	4,2	1,8 - 2,14	2,6
T_m [$^\circ\text{C}$]	1 535	1 452	1 755	2 850	3 410	28,4	2 210



Besides W, single crystal LaB_6 is another popular tip material for thermionic emission guns.

About 5-10× more expensive than W, but last 5-10× longer and is brighter (higher beam current), but higher vacuum is required (since LaB_6 is very reactive).

Field emission guns (FEGs)



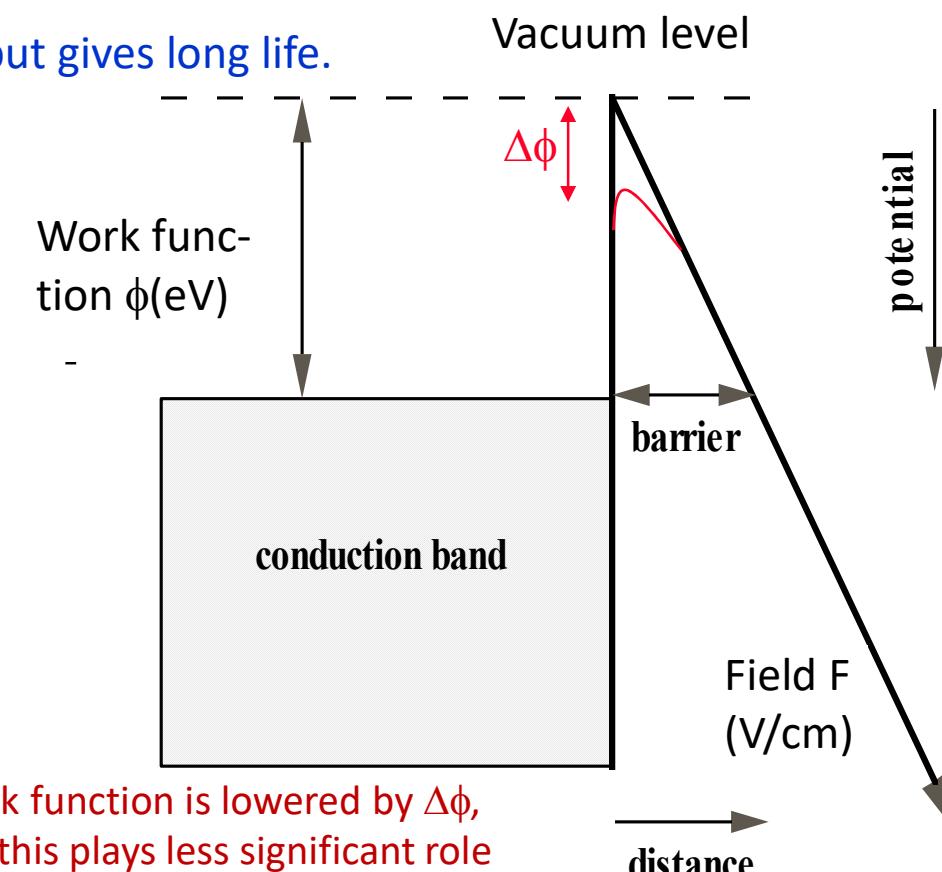
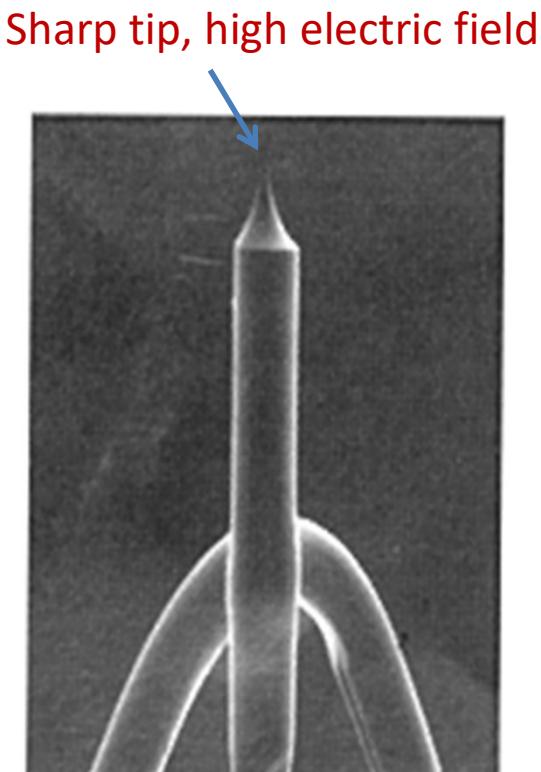
Current density (Fowler-Nordheim equation):

$$J = A \cdot F^2 \cdot \phi^{-1} \exp(-B\phi^{1.5}/F) \quad \text{here } A=1.5 \times 10^{-6}; B=4.5 \times 10^7; F \gg 10^8 \text{ V/m}$$

- Field emission (i.e. tunneling) becomes dominant for electric field $F \gg 10^8 \text{ V/m}$.
- Need very high vacuum to prevent arc-over at tip apex.
- Very short switching time ($t < \text{ns}$), since no need to heat up.
- Small beam spot size, since field is high enough for tunneling only near tip apex.

Cold field emission guns (FEG)

- Electrons “tunnel out” from a tungsten wire because of the high field obtained by using a sharp tip (100nm) and a high voltage (3-4kV).
- The emission current is temperature independent (pure tunneling current, operate at room temperature, so the name “cold”).
- But because it is cold, contaminates (gas molecule) build up quickly, decreasing tunneling current with time (scale: hours) and causing high noise (because gas molecules adsorb and desorb randomly).
- Needs ultra-high vacuum (UHV), but gives long life.



Schottky emitters: field assisted thermionic source

- Work function depends on electric field F by:

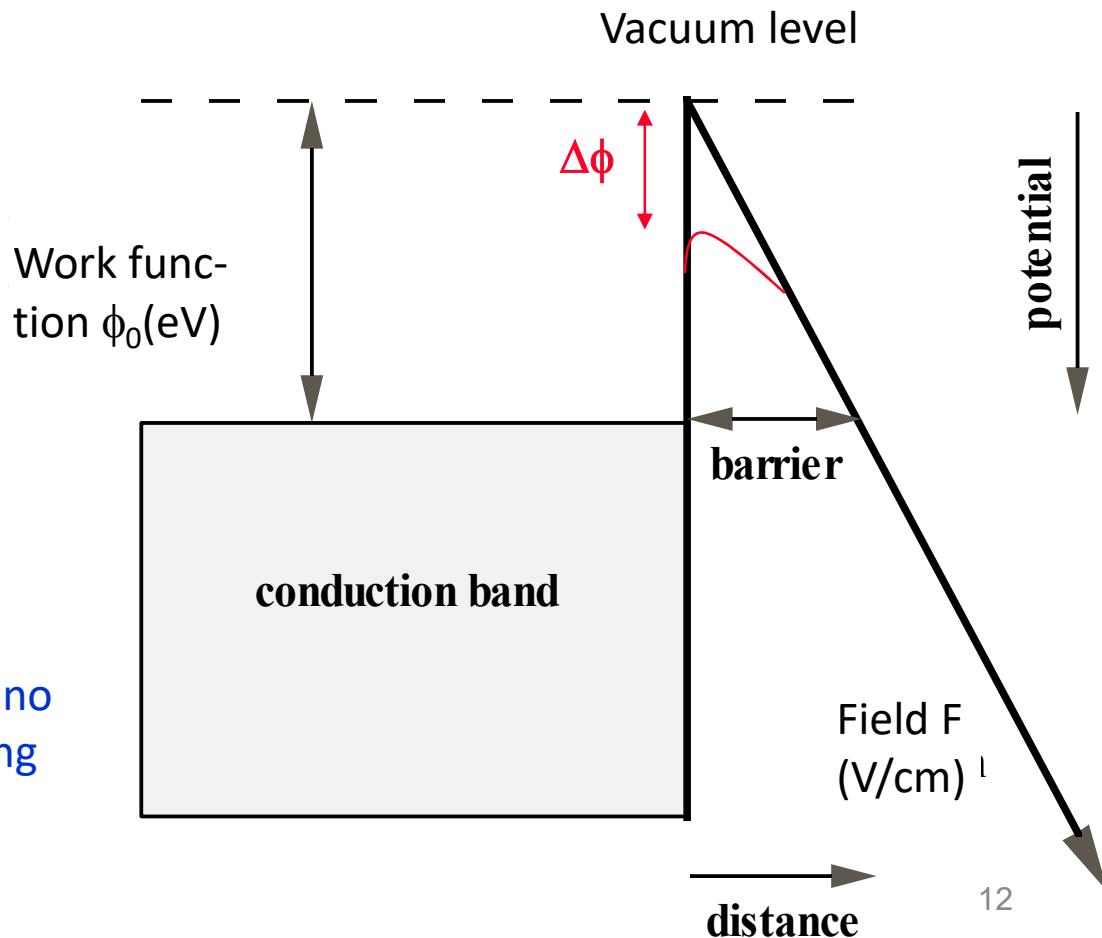
$$\phi = \phi_0 - e \sqrt{\frac{eF}{4\pi\epsilon_0}}; \sqrt{\frac{e}{4\pi\epsilon_0}} = 3.8 \times 10^{-5} (V \cdot m)^{\frac{1}{2}}$$

- Cathode behaves like a thermionic emitter with $E_A = \phi_0 - \Delta\phi$.

$$j = A \cdot T^2 \cdot \exp\left(-\frac{E_A}{kT}\right)$$

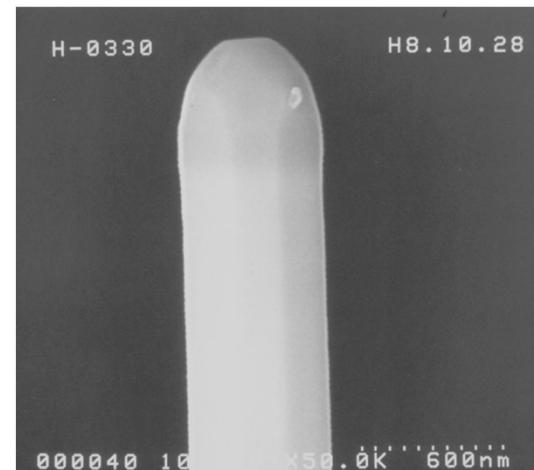
For $F=1 \times 10^8 \text{ V/m}$, $\Delta\phi=0.38 \text{ eV}$.
Take $T=1750 \text{ K}$, then $kT=0.15 \text{ eV}$,
current density is increased by:
 $j/j_0=e^{0.38/0.15}=13$.

For F significantly higher than $1 \times 10^8 \text{ V/m}$, the above equation for j is no longer valid since tunneling is becoming important.

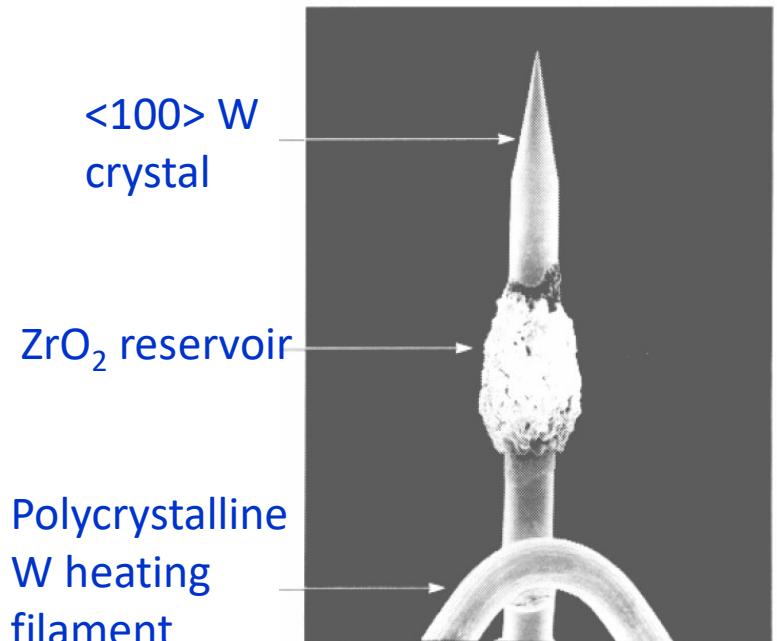


Schottky emitters: field assisted thermionic source

- It is usually misleadingly called thermal or Schottky **field emission gun**.
- But it is not a truly field emission gun, because the tip is blunt and if the heat is turned off there is no emission (tunneling) current.
- A Schottky source is actually a field assisted (to lower ϕ) thermionic source.
- Schottky emitters can produce larger amounts of current compared to cold FEG systems, so **more useful for e-beam lithography**.
- Because they are always on (hot, 1750K), organic contamination is not an issue (burned away immediately), hence **they are very stable** (few % per week change in current)
- They eventually fail when the Zirconia reservoir is depleted, after 1-2 years.
- Zirconia is used to further lower the ϕ (ZrO_2 has a low work function).

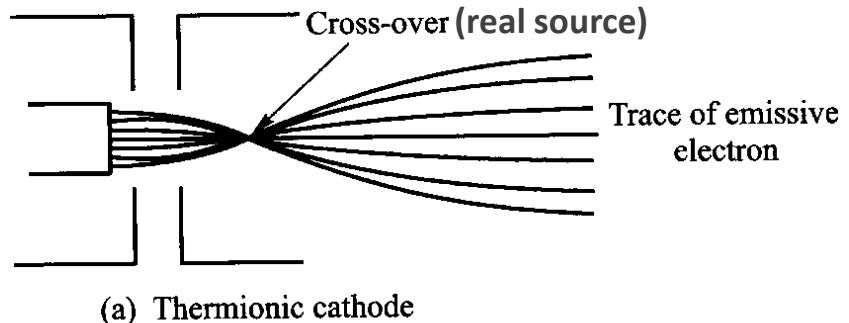


Hitachi Schottky Emitter Tip (not sharp)

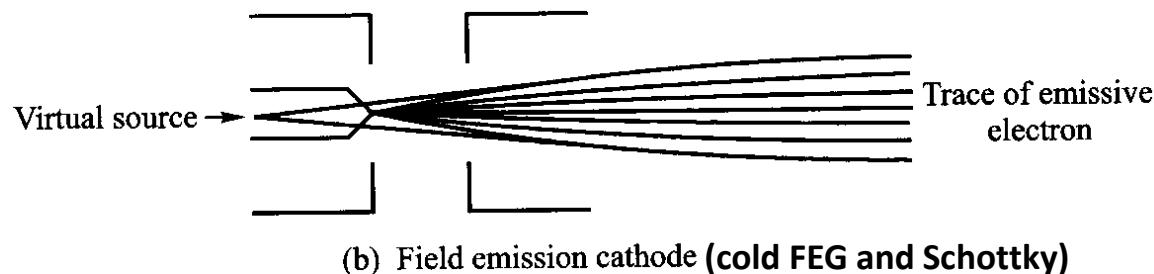


Source size

The cross-over is an *effective real or virtual source* for the downstream electron optical system.

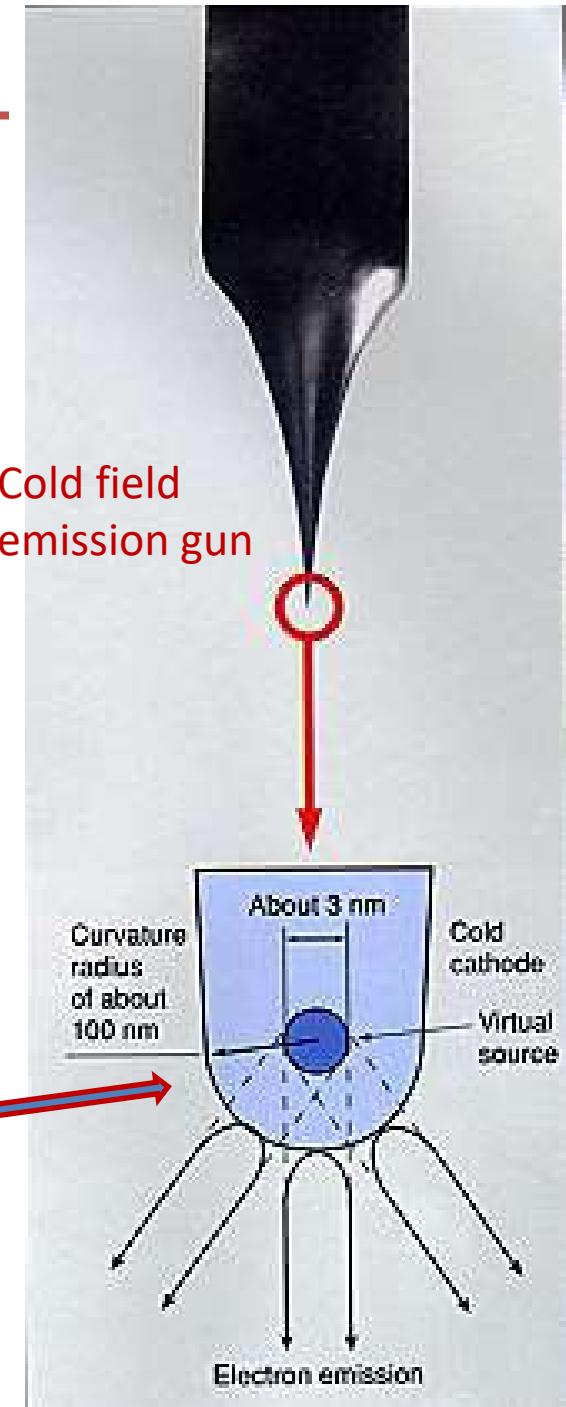


(a) Thermionic cathode



(b) Field emission cathode (cold FEG and Schottky)

- The source size is the *apparent width* of the disc from which the electrons *appear* to come out.
- The tip physical size does NOT determine the source size.
- Small is good for high resolution SEM, because less demagnification is needed to attain a given probe size.



Comparison of electron emission sources

Key parameters of electron sources:
virtual source size, brightness, energy spread of emitted electron

Emitter type	Thermionic	Thermionic	Cold FE	Schottky FE
Cathode materials	W	LaB ₆	W	ZrO/W
Operating temperature (K)	2800	1900	300	1800
Cathode radius (μm)	60	10	<0.1	<1
Virtual source radius (nm)	15,000	5000	2.5	15
Emission current density (A cm ⁻²)	3	30	17,000	5300
Total emission current (μA)	200	80	5	200
Brightness	10 ⁴	10 ⁵	2×10 ⁷	10 ⁷
Maximum probe current (nA)	1000	1000	0.2*	10
Energy spread at cathode (eV)	0.59	0.40	0.26	0.31
Energy spread at gun exit (eV)	1.5–2.5	1.3–2.5	0.3–0.7	0.35–0.7
Beam noise (%)	1	1	5–10	1
Emission current drift (% hr ⁻¹)	0.1	0.2	5	<0.5
Vacuum requirement (Torr)	≤10 ⁻⁵	≤10 ⁻⁶	≤10 ⁻¹⁰	≤10 ⁻⁸
Cathode life (h)	200	1000	2000	2000
Cathode regeneration (flashing)	Not required	Not required	Every 6–8 h	Not required
Sensitivity to external influence	Minimal	Minimal	High	Low

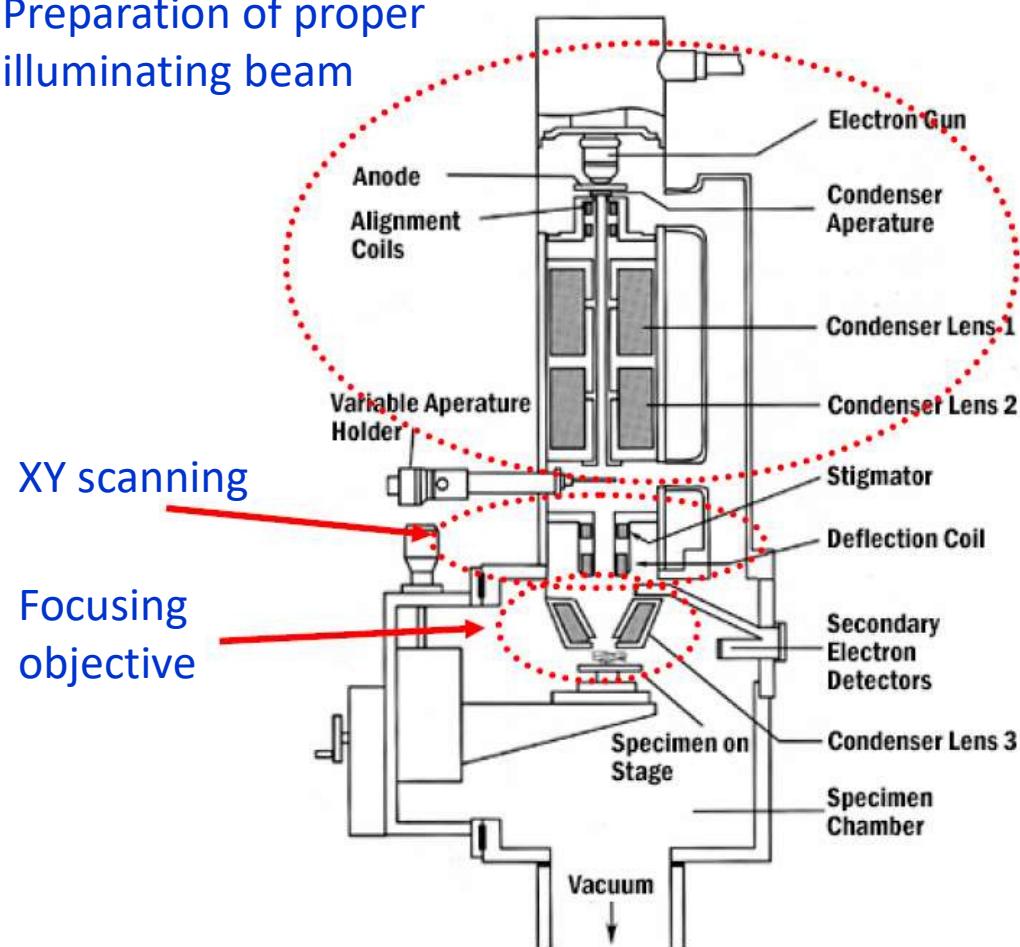
*Hitachi cold FEG SEM can go to 2nA.

Electron beam lithography (EBL)

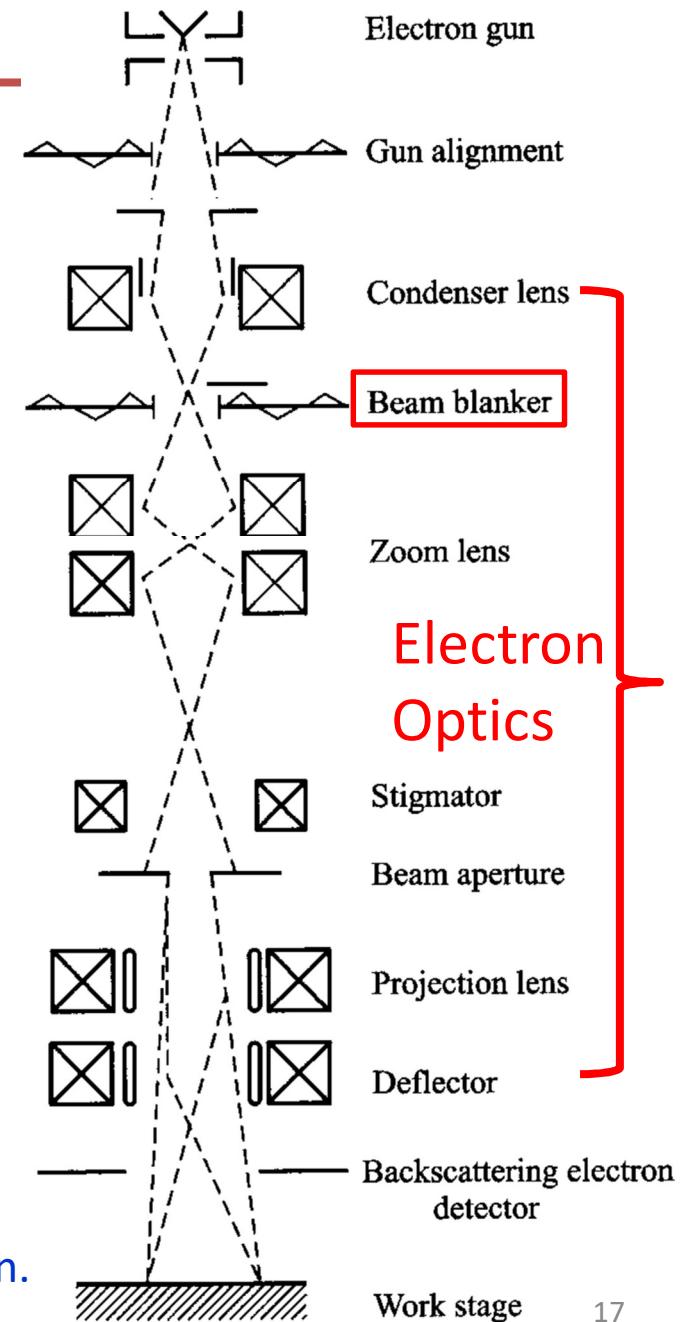
1. Overview and resolution limit.
2. Electron source (thermionic and field emission).
3. Electron optics (electrostatic and magnetic lens).
4. Aberrations (spherical, chromatic, diffraction, astigmatism).
5. EBL systems (raster/vector scan, round/shaped beam)

SEM/EBL electron optics

Preparation of proper illuminating beam

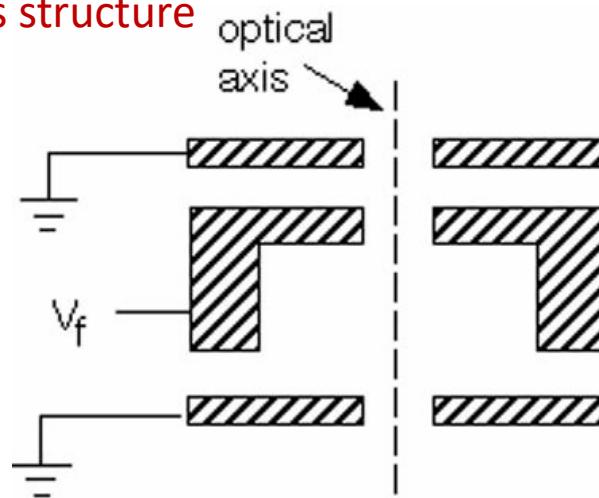


Electron optics is not so obvious – not easy to predict electron trajectory, so one has to do numerical calculation.

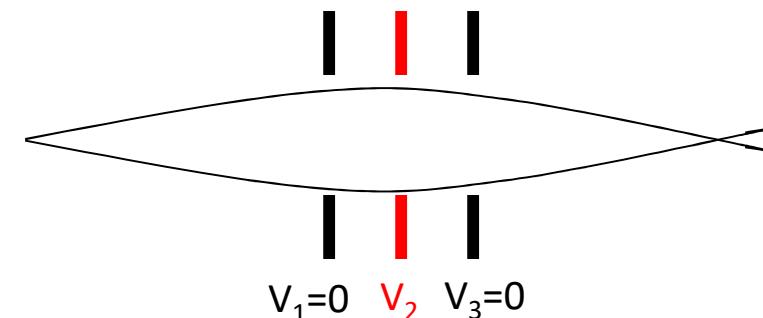


Electrostatic lens

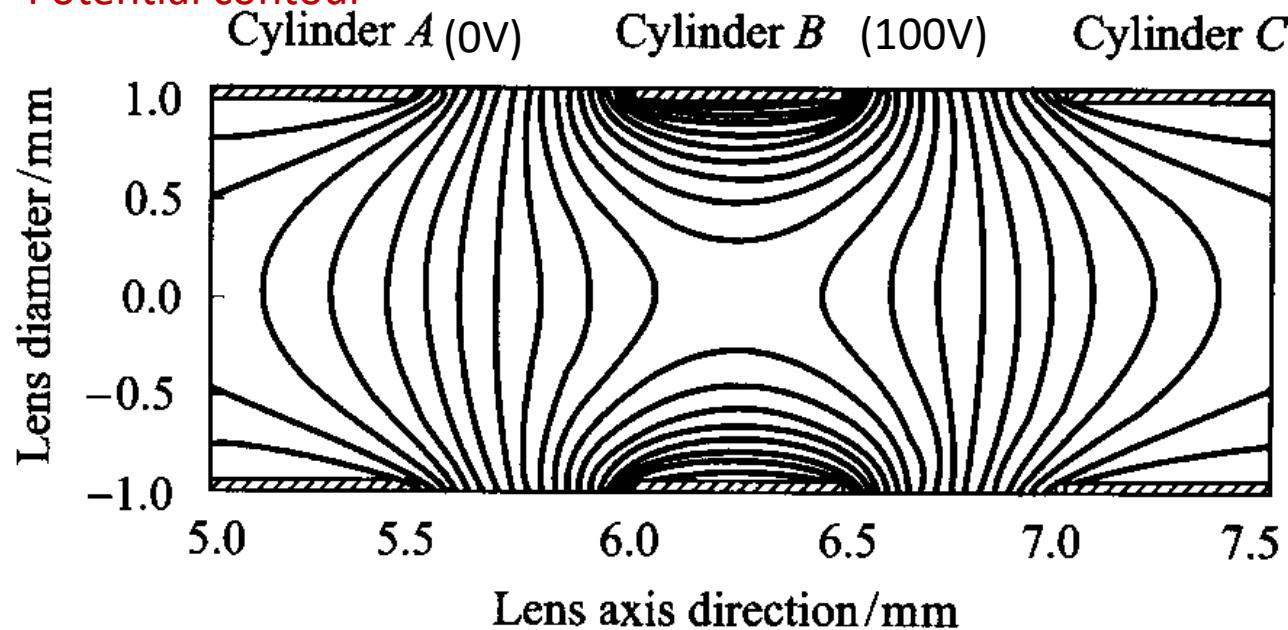
Lens structure



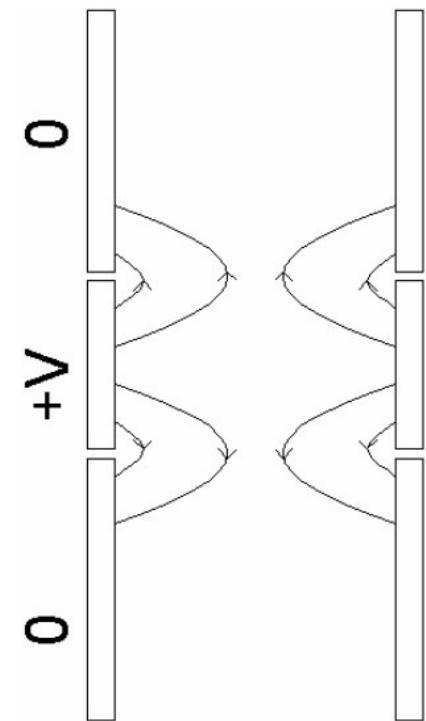
Electron trajectory



Potential contour



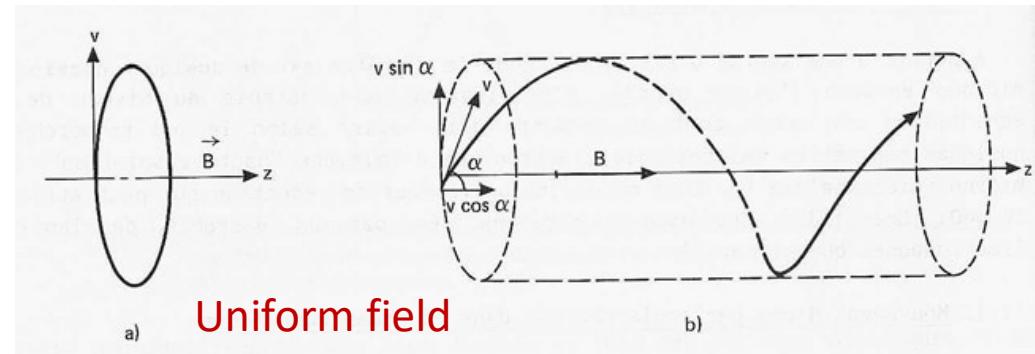
Electric field



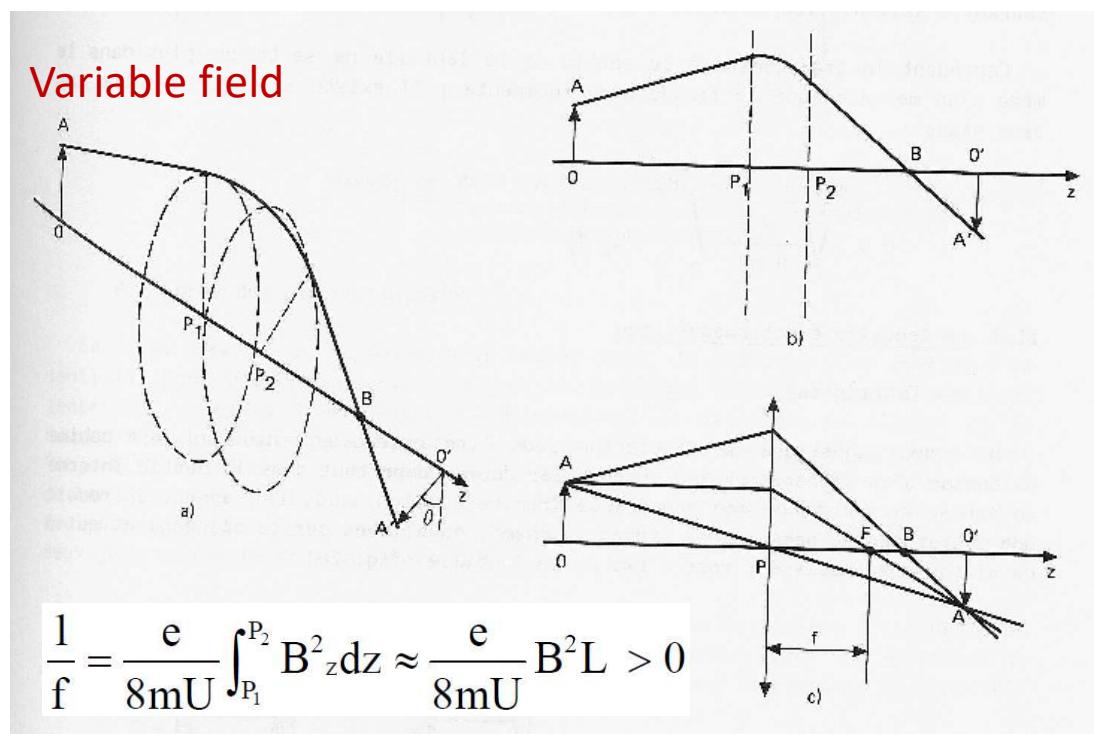
Magnetic lens

For rotationally symmetric magnetic field

$$\mathbf{F} = q \mathbf{v} \times \mathbf{B}$$



- Magnetic lens good for focusing electrons, but not for ions with different charge/mass ratio.
- Modern EBL uses only magnetic lens, since electrostatic lens using high field may lead to electrical breakdown (of residual gas molecules) at the gaps.



$$\frac{1}{f} = \frac{e}{8mU} \int_{P_1}^{P_2} B_z^2 dz \approx \frac{e}{8mU} B^2 L > 0$$

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Aberrations

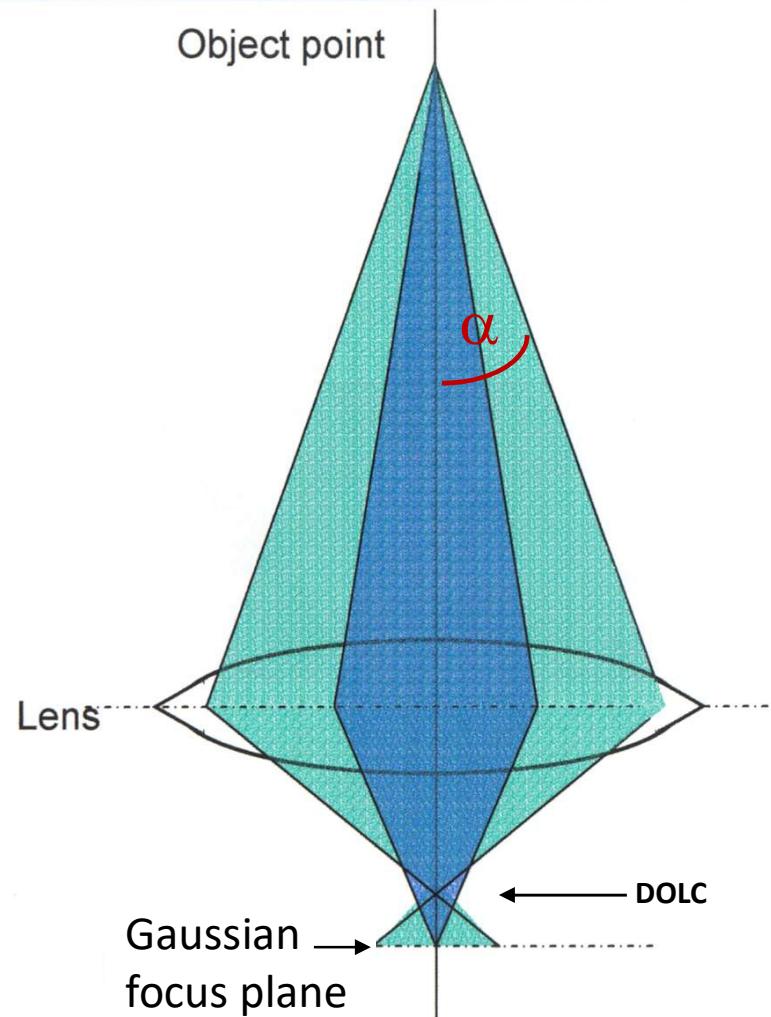
- An ideal lens would produce a de-magnified copy of the electron source at its focus.
- The size of this spot could be made as small as desired.
- But no real lens is ideal. Aberration is defined as deviation from ideal case.
- Geometric aberrations: spherical aberration, coma, field curvature, astigmatism and distortion.
- Non-geometric aberrations: chromatic aberration, diffraction.
- In light optics, the geometric aberration can be eliminated by changing arbitrarily the curvature of refractive surfaces. It may have hundreds of lens.
- But in electron optics the electromagnetic field in space cannot be arbitrary changed. It has just a few lens.

Spherical aberrations

- The focal length of near axis electrons is longer than that of off axis electrons.
- All lenses have spherical aberration, with minimum spot size

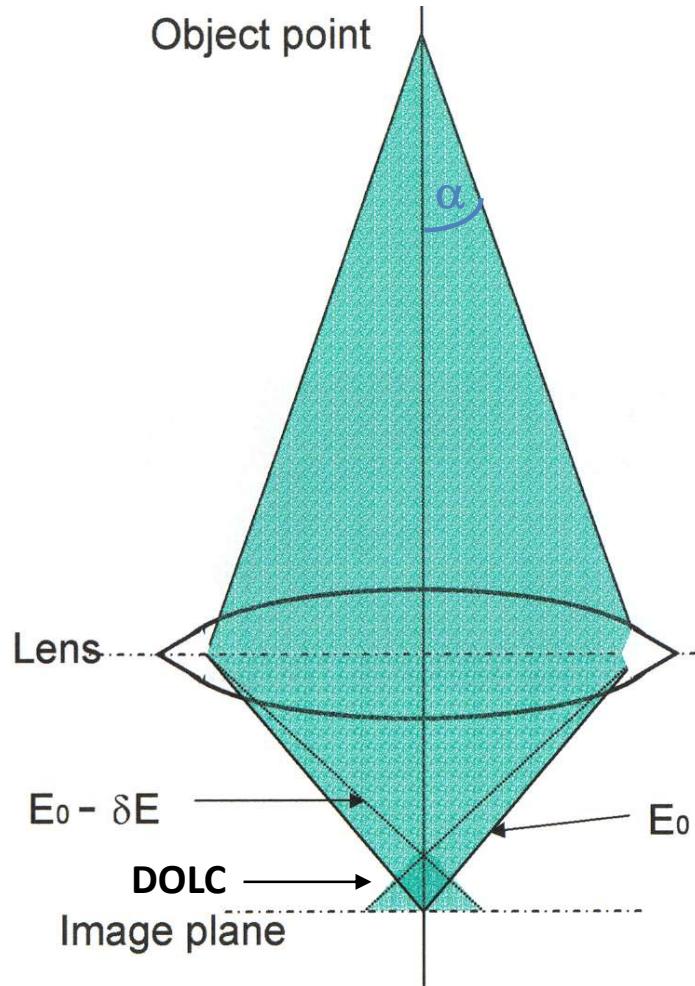
$$d_s = 0.5C_s\alpha^3$$

- C_s is a lens constant related to the working distance of the lens. (minimizing working distance minimizes spherical aberration).
- Spherical aberration makes the probe larger and degrades the beam profile.
- To reduce it, one needs to limit the numerical aperture (α) of the probe lens; but this also reduces the current I_B that varies as α^2 .



DOLC: disk of least confusion

Chromatic aberrations



- The focal length of higher energy electrons is longer than that for lower energy electrons.
- The minimum spot size at DOLC is

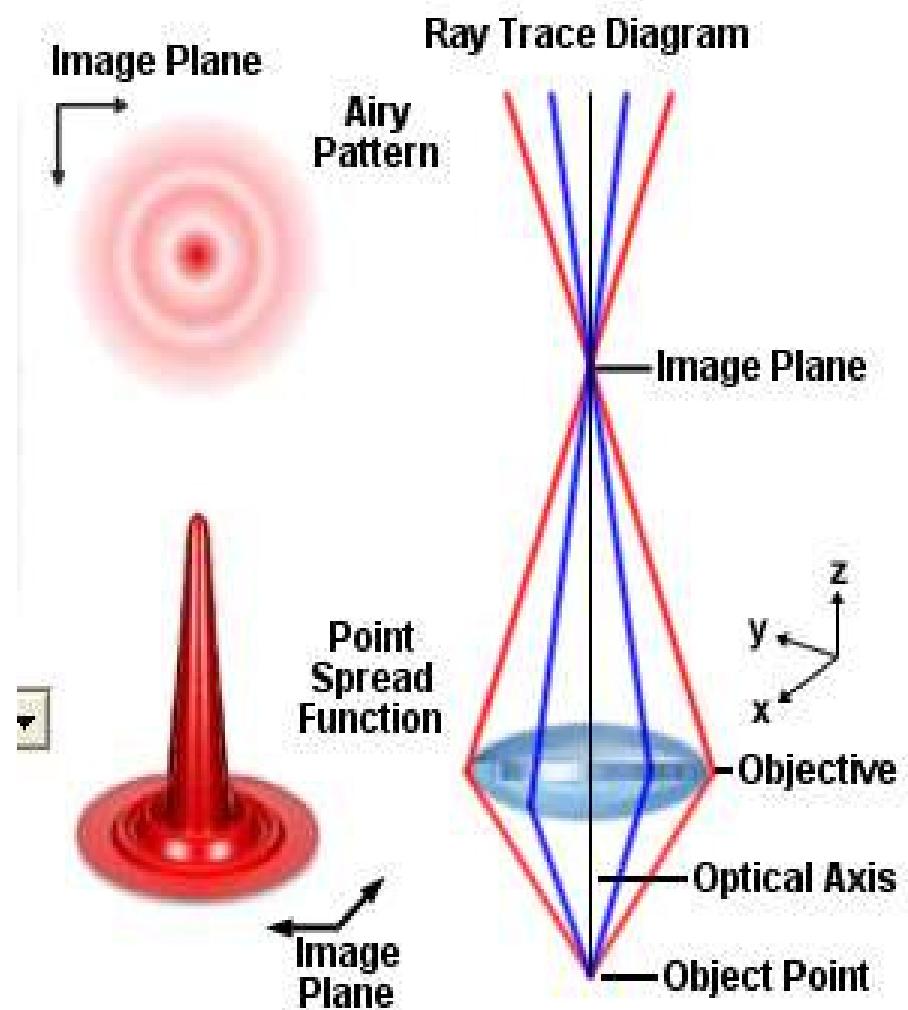
$$d_c = C_c \alpha \cdot \Delta E / E_0 \text{ (or } \Delta V/V\text{)}$$

which is high at low energies E_0 , or when using thermionic emitters with high energy spread ΔE .

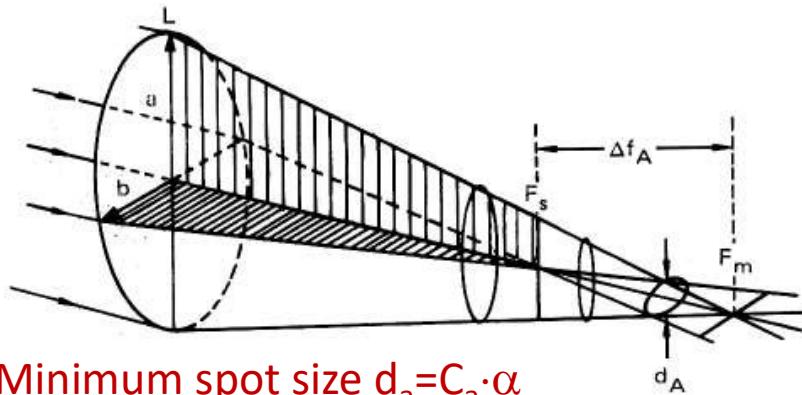
DOLC: disk of least confusion

Diffraction

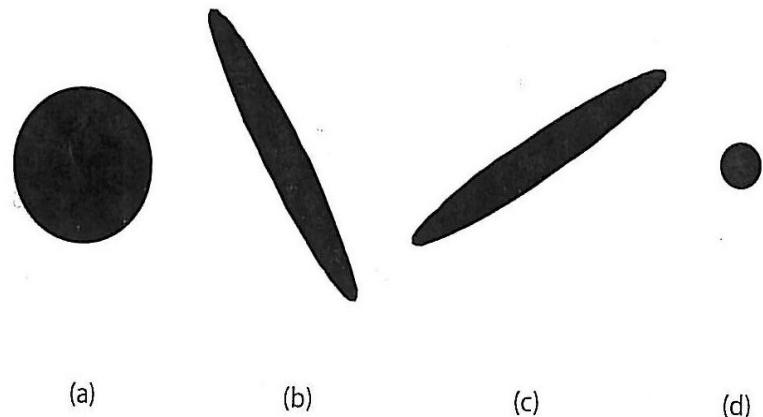
- Electrons are waves so at focus they form a diffraction-limited crossover.
- The minimum diameter
 $d_d = 0.61\lambda/NA = 0.61\lambda/\sin\alpha \approx 0.61\lambda/\alpha$
(Rayleigh criteria, same as optical lens).
- At low energies the wavelength becomes large (0.04 nm at 1keV) so diffraction is a significant factor because α is typically only 10 milli-radians or less in order to control spherical and chromatic aberrations



Astigmatism



$$\text{Minimum spot size } d_a = C_a \cdot \alpha$$



Astigmatism:
focal points for x- and y-directions are different

Beam shape at different planes

- Every time one switch on or adjust an electron lens (magnetic, not electrostatic lens), the magnetization of the metal in the lens changes.
- Because of hysteresis, the lens never quite goes back to where it was.
- The lens will then have non-round features due to different magnetization around the pole-piece, which is the focusing part of the electron lens.
- Apertures tend to charge up if they have dirt on them, leading to another source of asymmetry.
- Stigmators eliminate/compensate astigmatism by adding a small quadrupole distortion to the lens.
- When beam is well optimized, astigmatism causes negligible beam spot broadening.

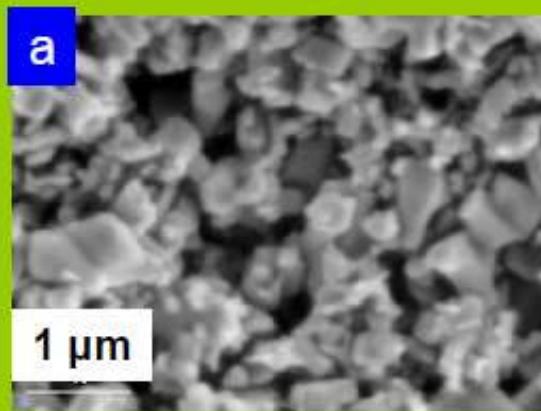
Stigmatism and Resolution

The shape of electron beam affects SEM image

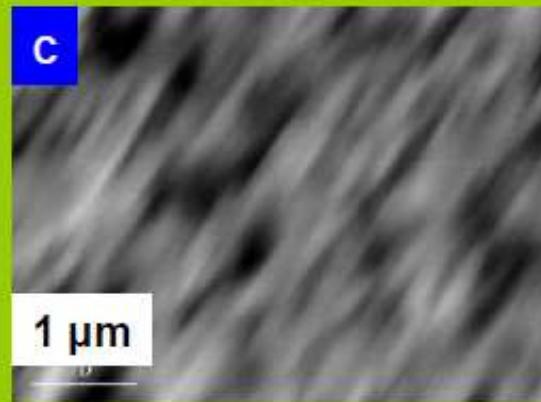
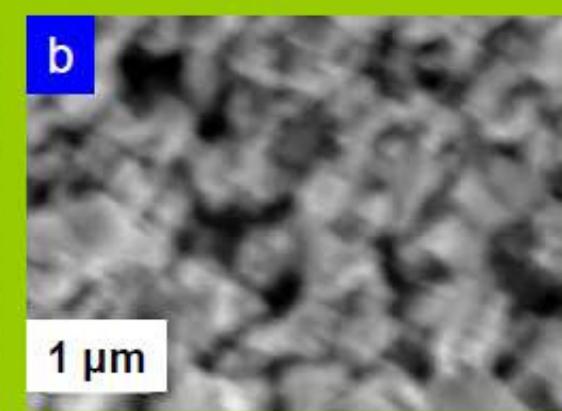
resolution: when the beam is round, or without stigmatism, the image shows small features (high resolution) as seen in Fig. a; when the beam is not round, or with stigmatism, the image details become vague (lower resolution) as seen in Fig. b.

When the image has stigmatism, changing beam focus may result in elongated feature: Figs. c and d were recorded when the beam were under and over focus, respectively.

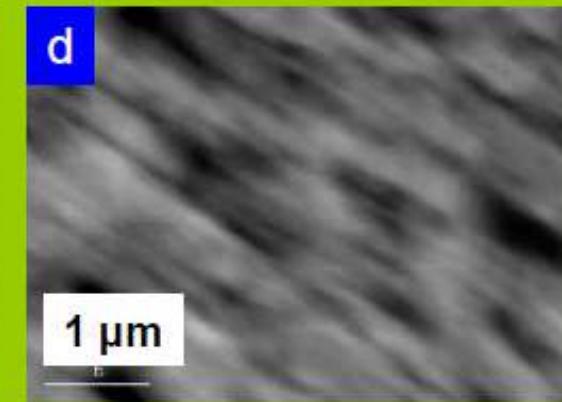
without stigmatism



with stigmatism



Under focus



Over focus

NCLT: June-Aug. 2006

Overall beam spot diameter

$$d = \sqrt{d_g^2 + d_s^2 + d_c^2 + d_d^2} \quad (\text{assume no astigmatism})$$

$$d_g = \frac{d_v}{M}$$

d_v : virtual source diameter
 $M (>1)$: demagnification

$$d_s = \frac{1}{2} C_s \alpha^3$$

Spherical aberration

$$d_c = C_c \alpha \frac{\Delta V}{V}$$

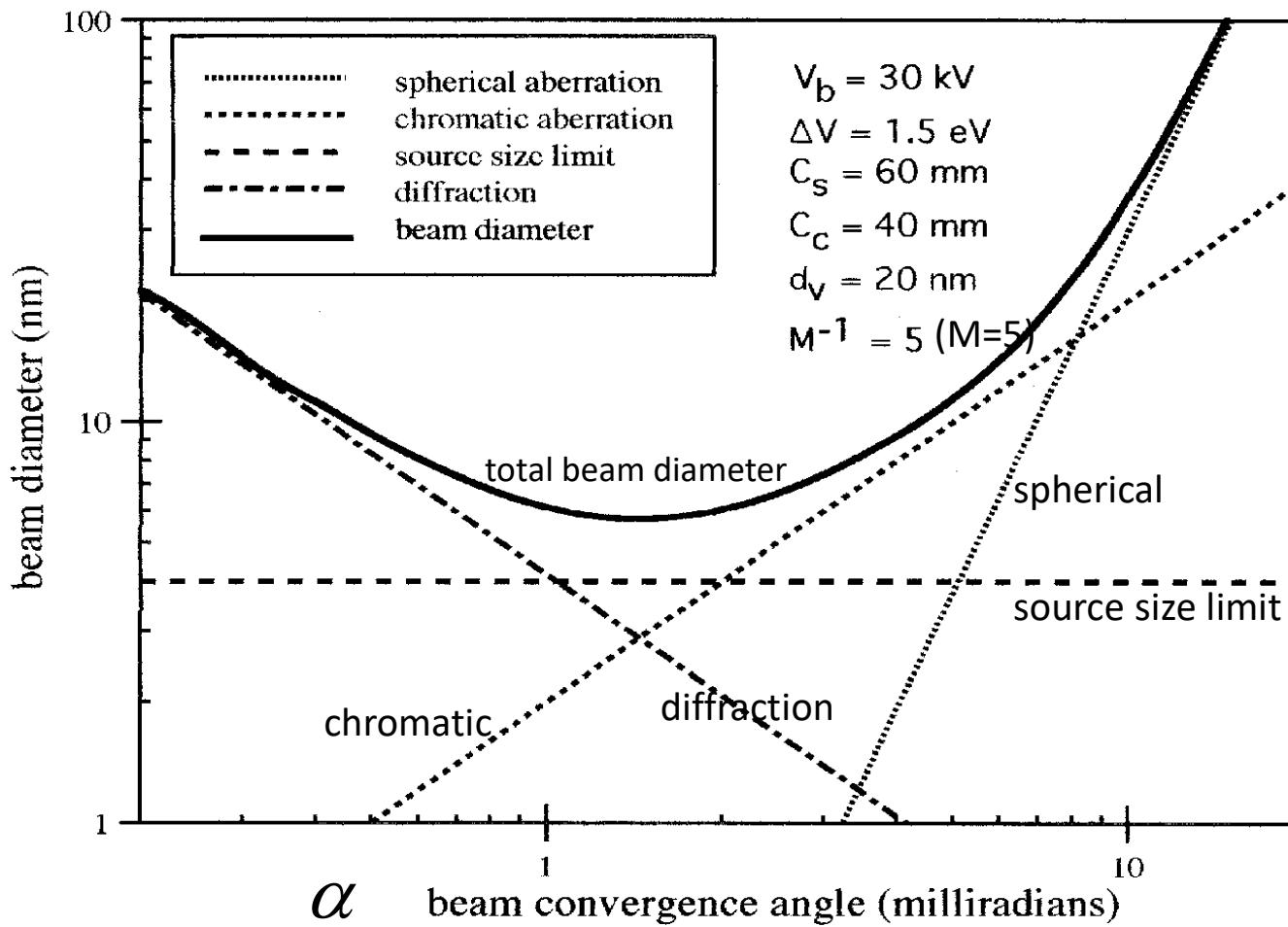
Chromatic aberration

$$d_d = 0.61 \frac{\lambda}{\alpha}, \lambda = \frac{1.2}{\sqrt{V}} \text{ nm}$$

Diffraction

- Beam spot size depends on acceleration voltage, because higher voltage/energy leads to: smaller chromatic aberration, and shorter λ thus smaller diffraction.
- This is particularly true for thermionic emission guns, where high resolution (<5nm) can only be achieved at near 30kV.
- Such resolution can be achieved at <2kV for cold field emission and Schottky guns.

Beam spot diameter: a real example



- α is determined by aperture size ($\sim 10\text{-}100\mu\text{m}$), which should be selected wisely.
- Typically beam diameter is NOT the limiting factor for high resolution, then large α is good for high beam current and thus fast writing.
- But large α also reduces depth of focus ($\propto 1/\alpha^2$), leading to large beam spot size (low resolution) if beam is not well focused due to wafer non-flatness or tilt.

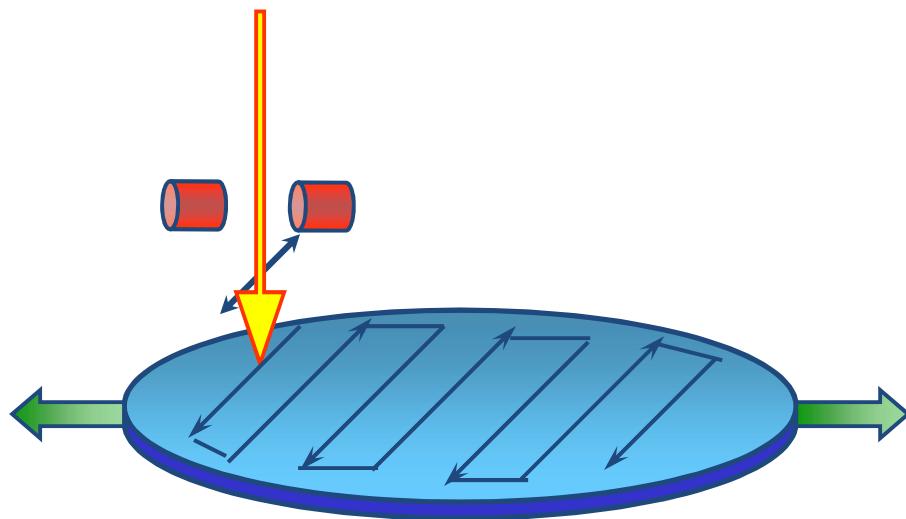
Electron beam lithography (EBL)

1. Overview and resolution limit.
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4. Aberrations (spherical, chromatic, diffraction, astigmatism).
5. EBL systems (raster/vector scan, round/shaped beam)

Raster scan vs. vector scan

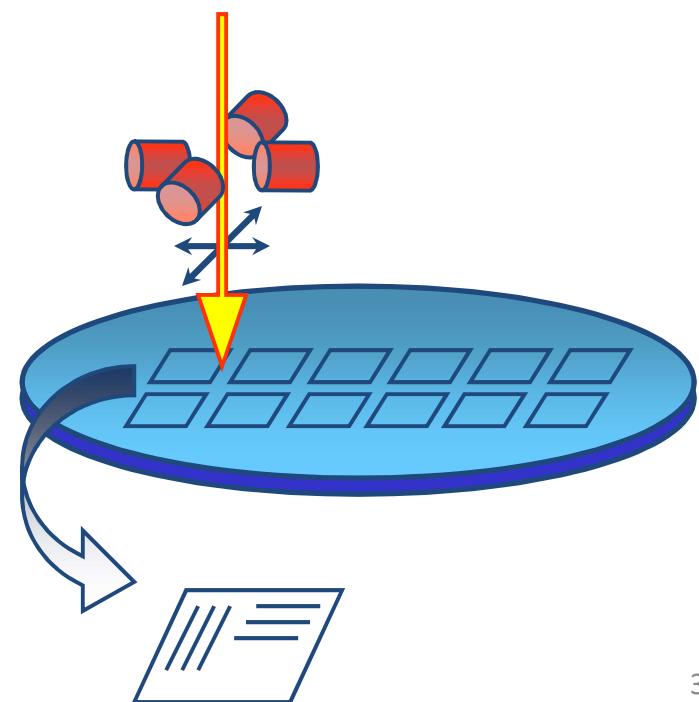
Raster scan:

The e-beam is scanned in only one direction with beam blanking, and the stage is mechanically translated in the perpendicular direction.



Vector scan:

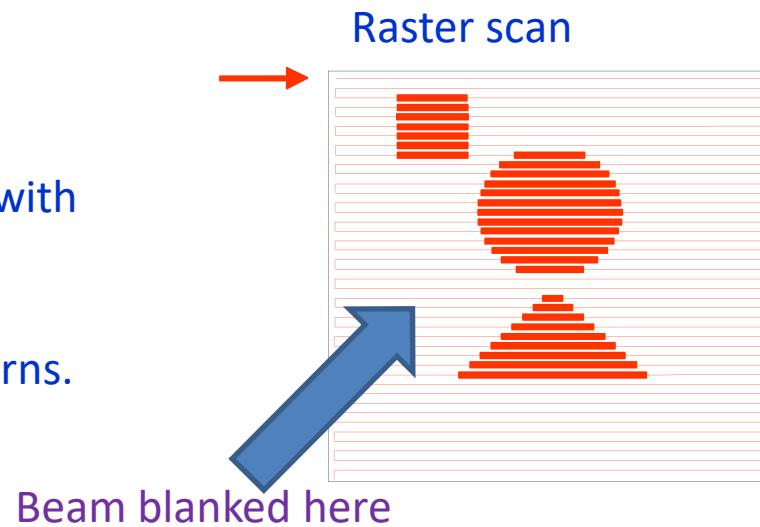
The e-beam is scanned in both x- and y-directions with beam blanking, writing the pattern **pixel-by-pixel**. No stage movement within each writing field. After each writing field, the substrate/stage moves to the next location.



Raster scan versus vector scan

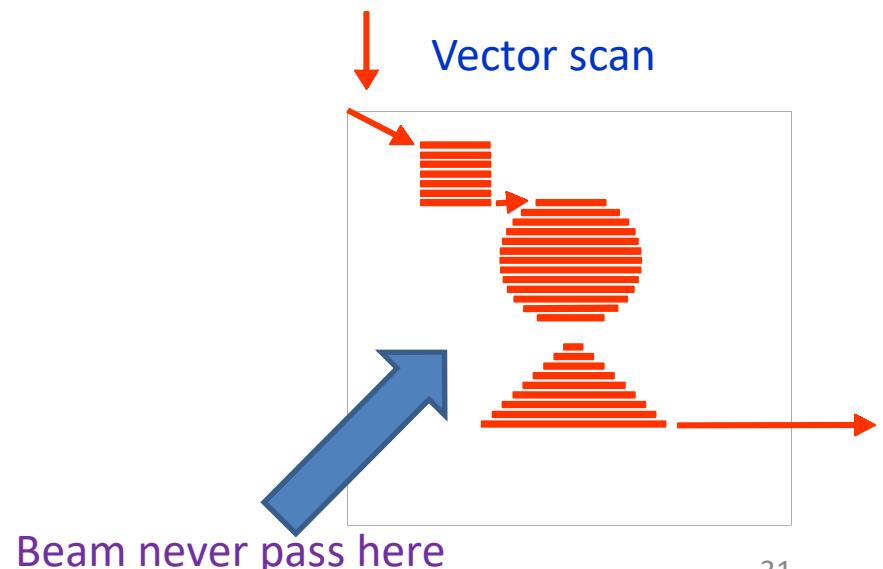
Raster scan:

- Very simple and fast (fast is due to tool design with high cost, raster itself doesn't mean fast).
- Very repeatable.
- But sparse patterns take as long as dense patterns.
- Difficult to adjust dose during writing.
- For photo-mask making.



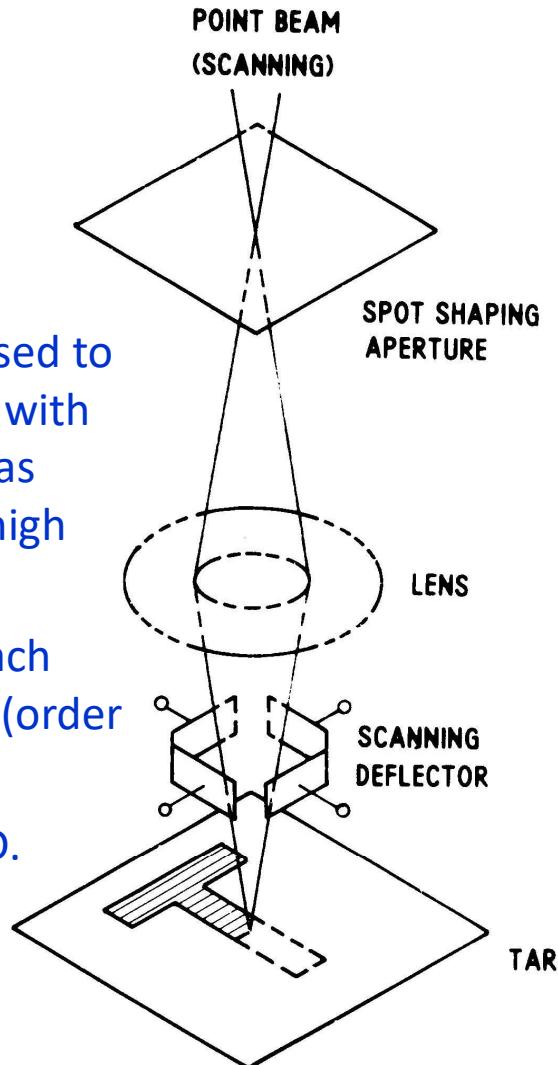
Vector scan:

- Fast writing of sparse patterns (unwritten areas skipped).
- Easy dose variation from shape to shape.
- For nanolithography and R&D.



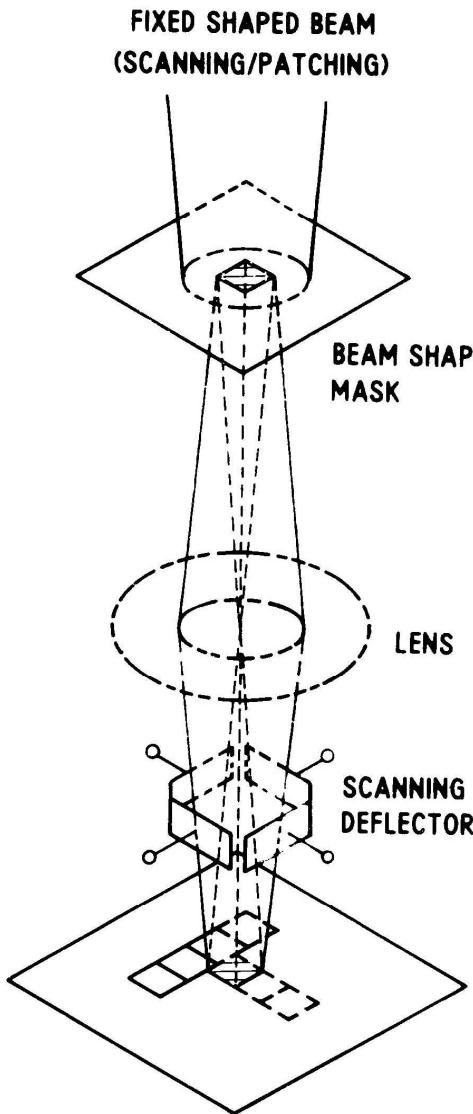
Round (Gaussian beam) vs. shaped beam

- Beam is focused to a round spot with size as small as possible for high resolution.
- Slow since each pixel is small (order 10nm).
- Used for R&D.



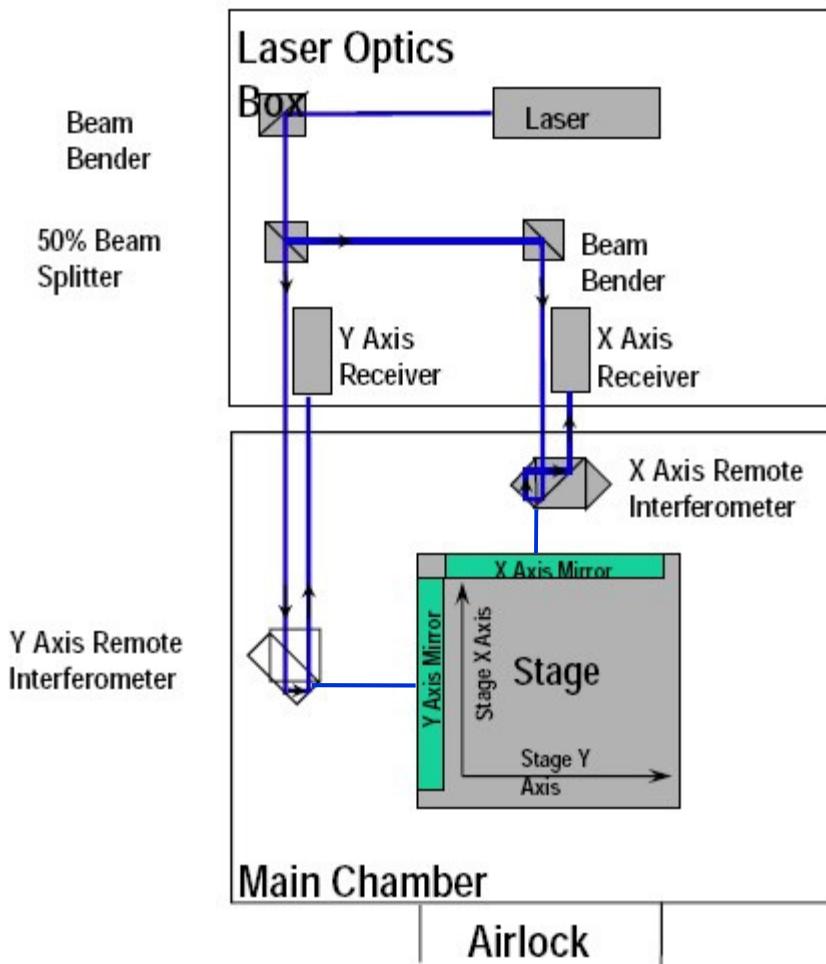
Gaussian beam

- Beam is shaped to a rectangular shape for fast writing.
- Fast since each “pixel” is large.
- Mainly used for photo-mask making, with each square pixel size order of 100nm.



shaped beam

Laser interferometer stage



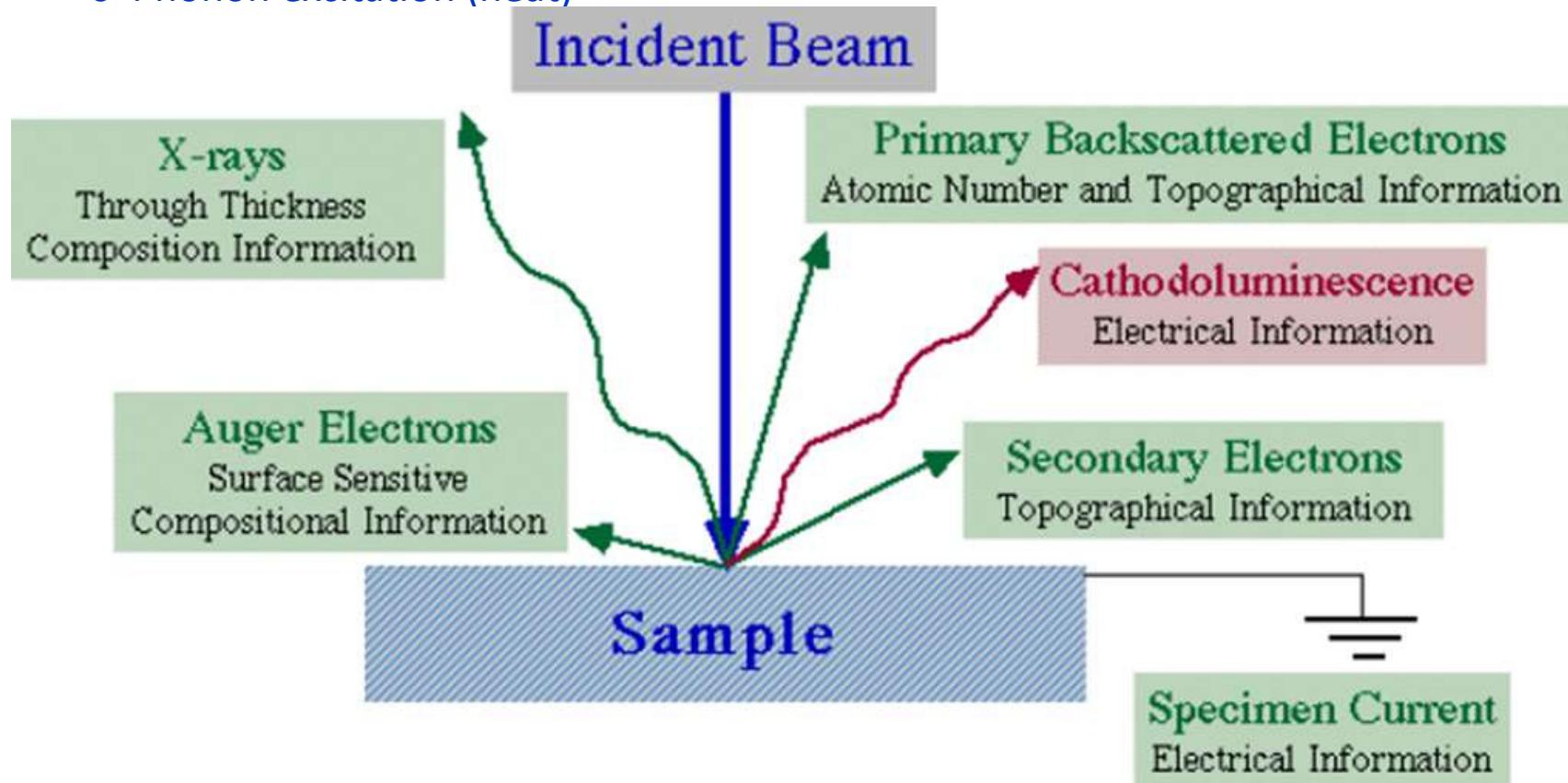
- For conventional SEM, stage accuracy is about $5\mu\text{m}$, so good alignment is not possible.
- Precise alignment of different layers requires local alignment marks (like photolithography).
- For advanced EBL system, use interferometry to precisely position the stage.
- Better than 5nm positioning accuracy, thus different writing fields are nearly perfectly aligned ("stitched").
- Interferometry stage cost $\$0.5\text{-}1\text{M}$, as expensive as a SEM.
- Using laser beam, sample height can also be monitored to maintain focusing/constant sample height.

Electron beam lithography (EBL)

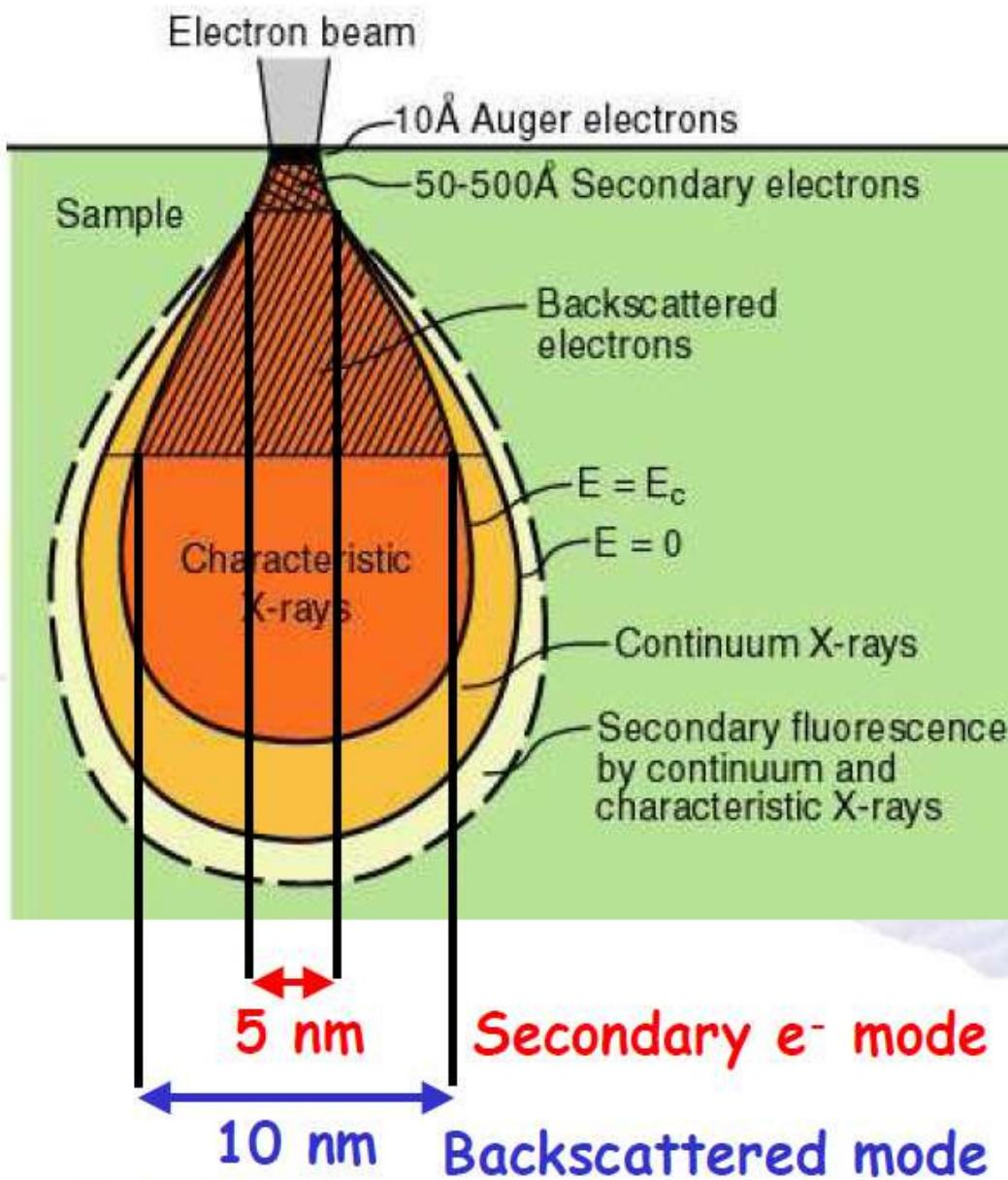
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Interactions of electrons with matter

- Unlike X-rays, electrons interact very strongly with matter
- Elastic scattering (i.e. no loss of energy) of electrons can be treated classically as a form of Rutherford backscattering
- Inelastic scattering arises from numerous interactions:
 - Low energy secondary electrons generation.
 - Inner shell excitations (x-ray fluorescence and Auger electrons)
 - Electron-hole pair creation and recombination
 - Phonon excitation (heat)



Interaction volume



Incident electrons penetrate surface layers to a depth dependent on beam energy and surface composition

Carbon 16 μm @ 40 kV
80 μm @ 100 kV

Gold 3.5 μm @ 40 kV

Multiple elastic and inelastic scattering of electrons in arbitrary directions

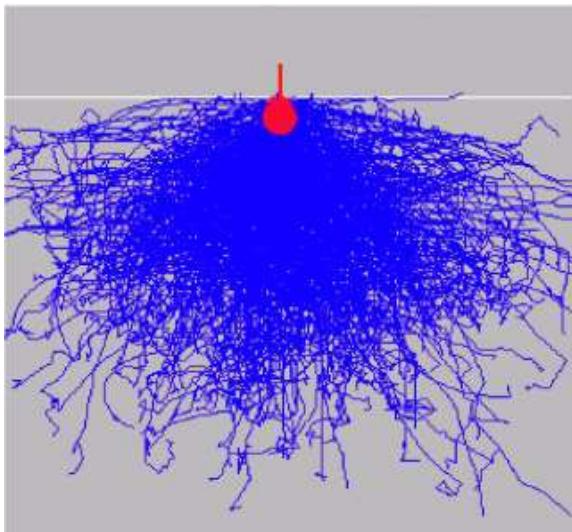
Re-emission from a laterally extended volume surrounding incident beam

Minimise volume by heavy metal sputter coating

Which region is for which application

Secondary electron (SE) region for imaging

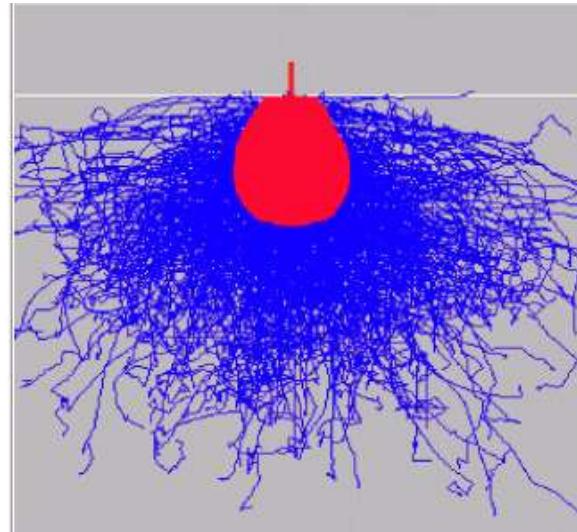
(SE is actually produced wherever primary electron goes, but only those near surface can go out to reach SE detector for imaging)



Best spatial resolution for SEM

Back-scattered electron (BSE) region for imaging

(Again, BSE is actually produced wherever primary electron goes. It has higher energy, so travel longer than SE)



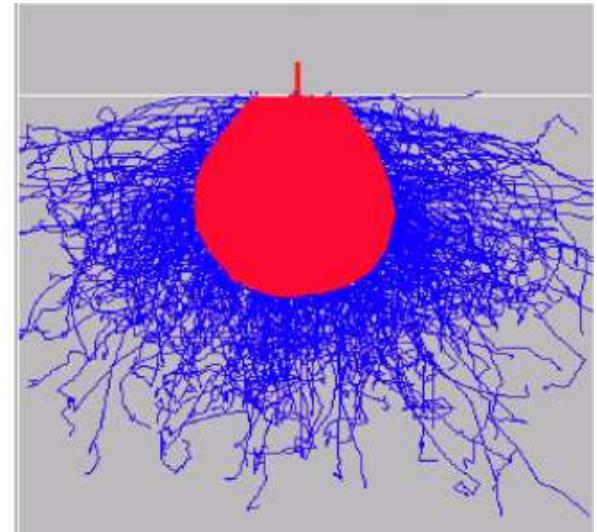
Better Z contrast for SEM
(brighter for higher Z
Z: atomic number)

BSE has lower resolution than SE signal, and is used only when chemical (Z) contrast is wanted.

TEM (transmission EM) gives much higher resolution than SEM because of the much lower interaction volume of the high energy electrons (200keV!) passing the *thin* samples.

X-ray region for EDX

(x-ray is actually produced wherever primary electron goes. It travels/penetrates even farther than BSE)



Best analytical for EDX

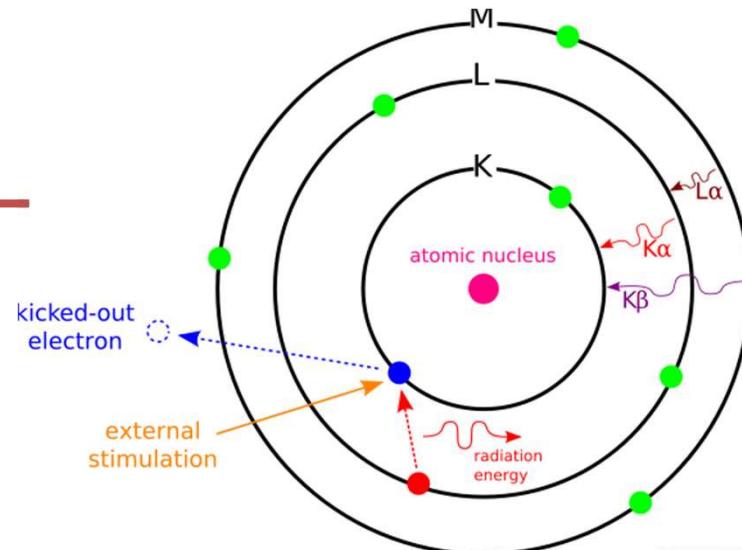
X-ray generation by electron bombardment

$$\text{Energy levels: } E_n = -13.6 \frac{(Z-\sigma)^2}{n^2}$$

$\sigma \approx 1$ for $n=1$, is due to screening ($\sigma=0$ for ideal model).

σ should be much higher than 1 for $n>1$.

$n=1$ (K-shell), 2 (L-shell), 3 (M-shell)....



Emitted x-ray energy $E_{x\text{-ray}}$

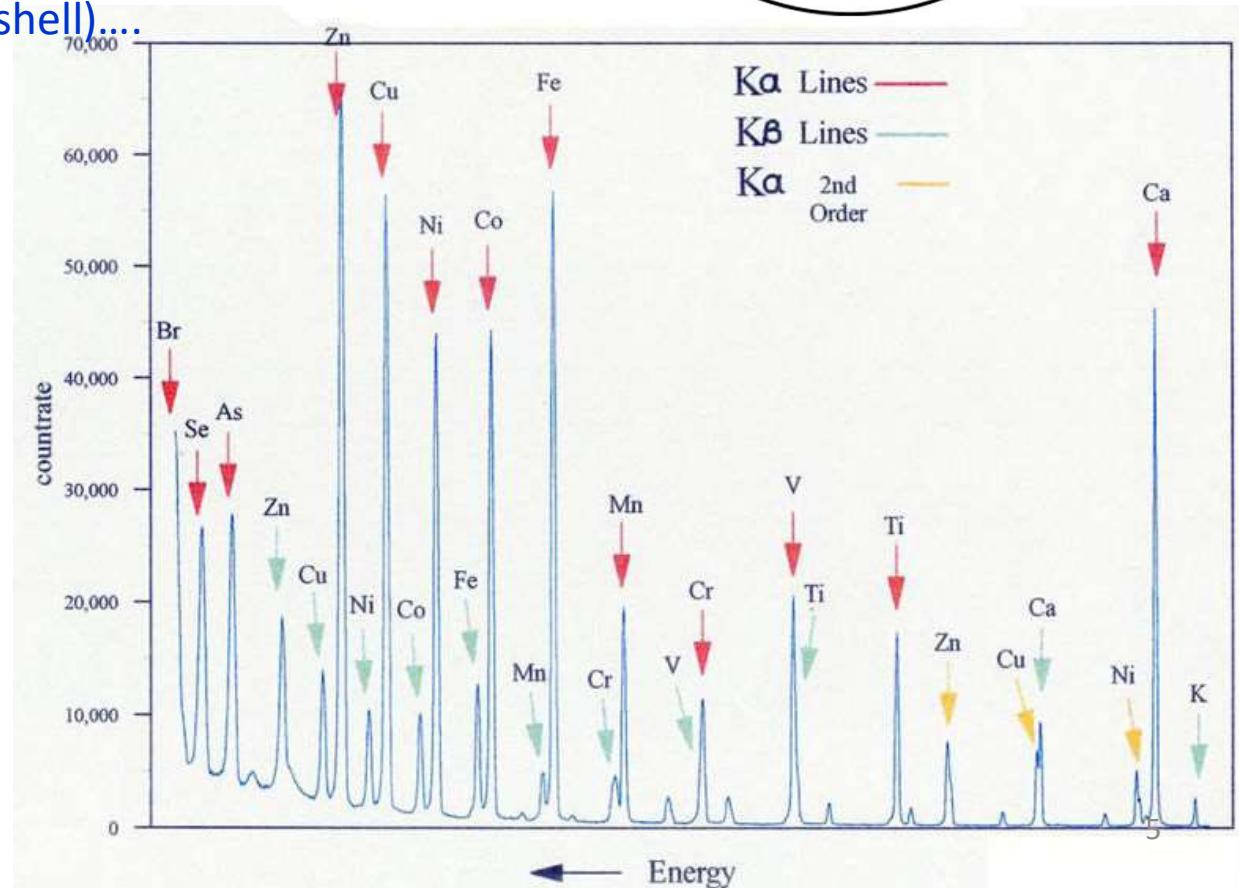
$$K_\alpha: E_{x\text{-ray}} = E_1 - E_2$$

$$K_\beta: E_{x\text{-ray}} = E_1 - E_3$$

$$L_\alpha: E_{x\text{-ray}} = E_2 - E_3$$

....

This is used for energy-dispersive x-ray spectroscopy (EDS, EDX), very popular and equipped to most SEM.

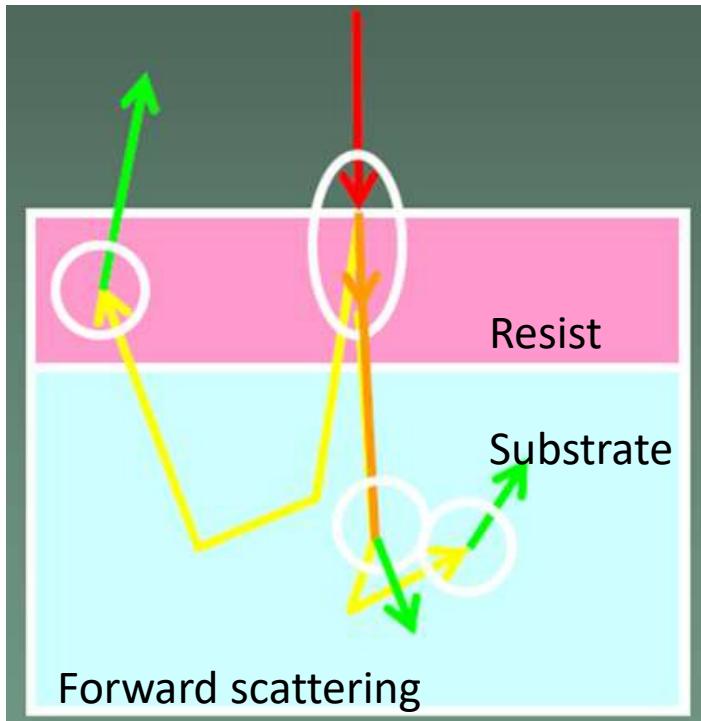


Electron beam lithography (EBL)

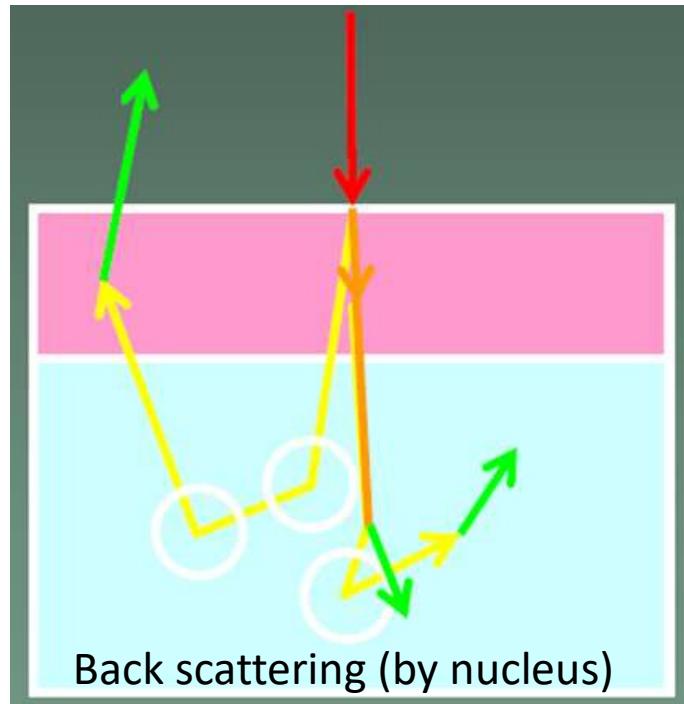
1. Overview and resolution limit.
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Forward/back scattering events

Scattering: spreading of the beam, lost of resolution



Forward scattering



Back scattering (by nucleus)

Properties:

Very often

Small angle

Very inelastic (i.e. lose energy)

Generation of SE (secondary electrons)
with low energy.

Properties:

Occasionally (collision with nucleus)

Large angles, mainly elastic

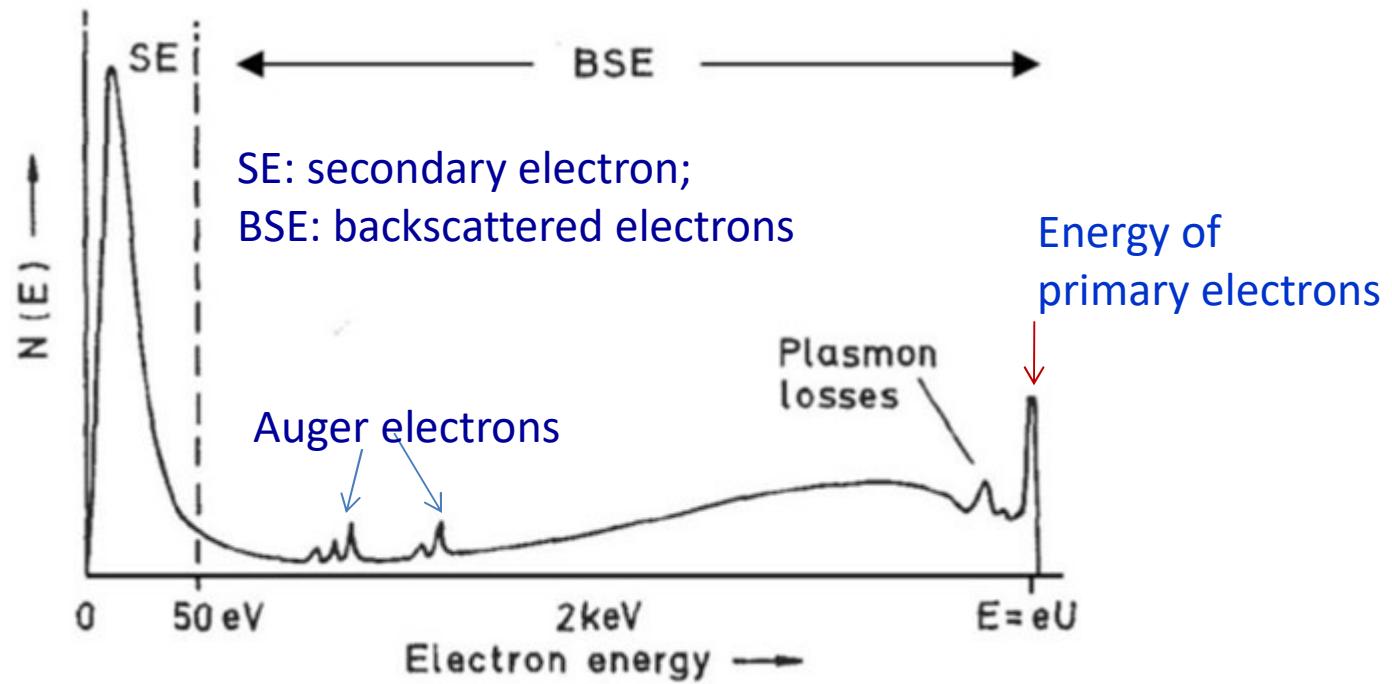
High energy, same range as primary electrons.

Large travel length, cause proximity effect.

Backscattering is responsible for resist exposure far from incidence point (proximity effect), as BSE can generate SE along its path to expose the resist there.

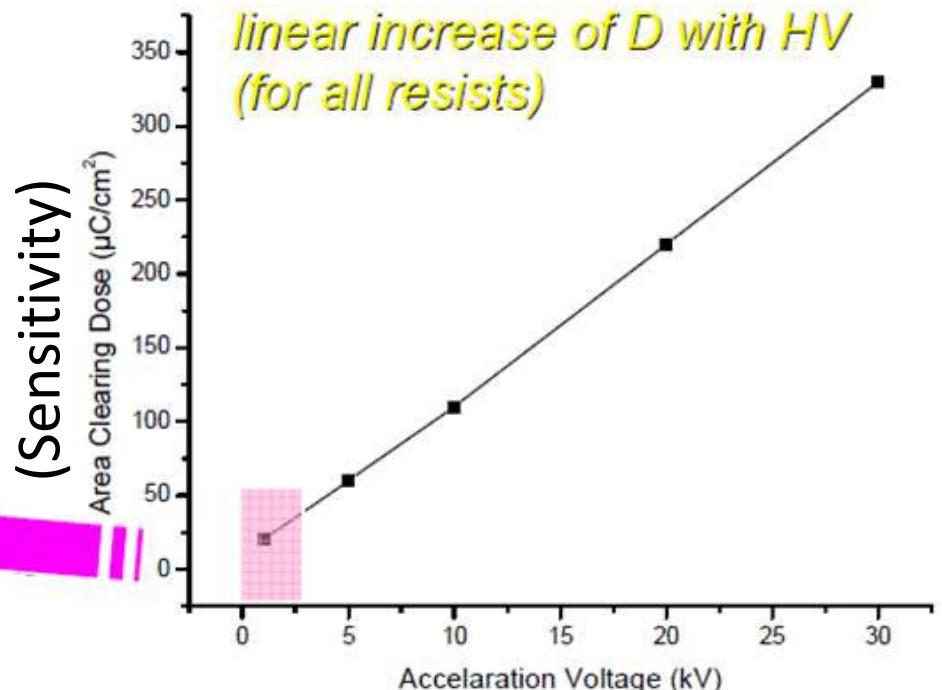
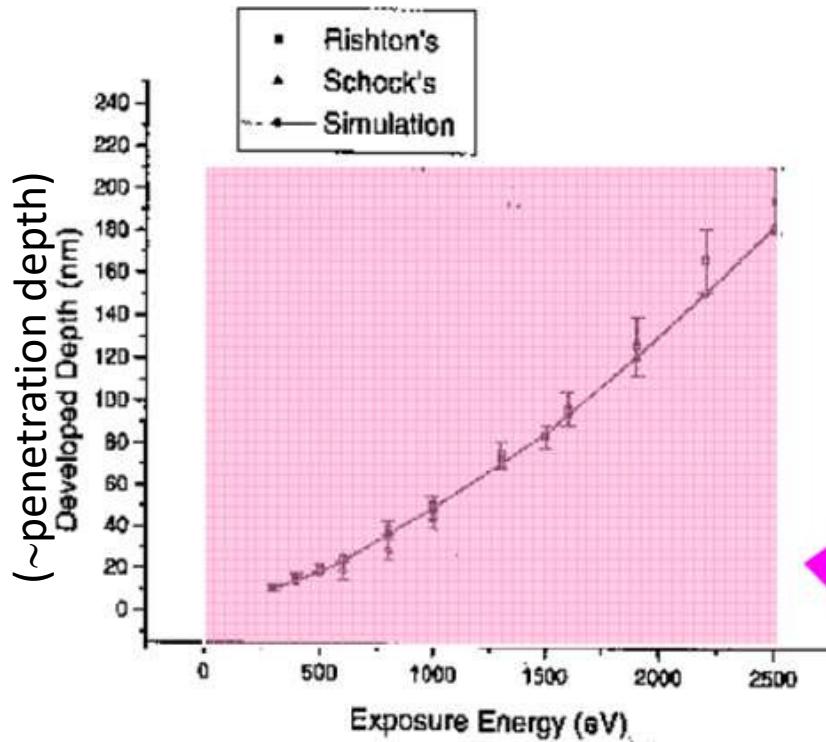
Forward/back scattering events

Energy spectrum of electrons emitted from substrate



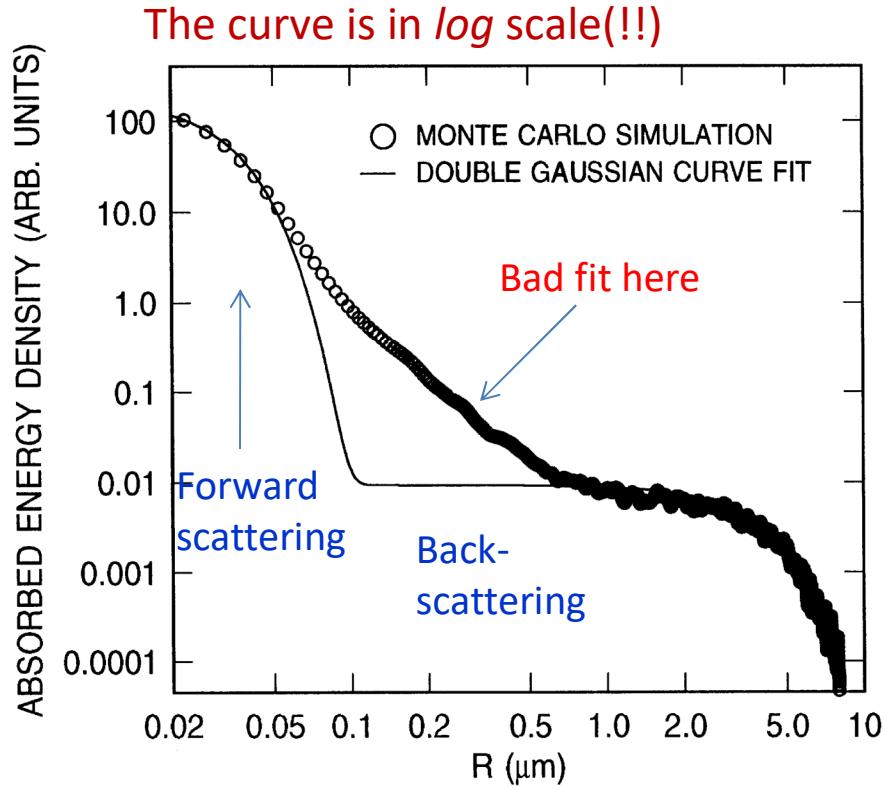
There is no clear-cut distinction of SE and BSE. Typically energy $< \sim 50\text{eV}$ is “called” SE. SE with several eV are responsible for most (not all) resist exposure. Such SE diffuses laterally a few nm, which is one limiting factor for ultra-high resolution EBL.

Effect of voltage on dose



- At small kV, penetration depth is low, so cannot expose thick resist. (e.g. at 0.8kV, penetration depth only ~40nm in PMMA).
- At >2kV, **resist sensitivity is higher for lower kV (!!)**, thus faster writing.
- But lower kV has larger beam spot size due to aberrations, and more serious forward scattering, both of which reduces resolution.
- Therefore, typical EBL is done at >3kV.

Double Gaussian model



$$f(r) = \frac{1}{(1+\eta)\pi} \left\{ \frac{1}{\alpha^2} \exp\left[-\left(\frac{r}{\alpha}\right)^2\right] + \frac{\eta}{\beta^2} \exp\left[-\left(\frac{r}{\beta}\right)^2\right] \right\}$$

α : range of forward scattering (in μm)

β : range of backscattering (in μm)

η : ratio of backscattering to forward scattering

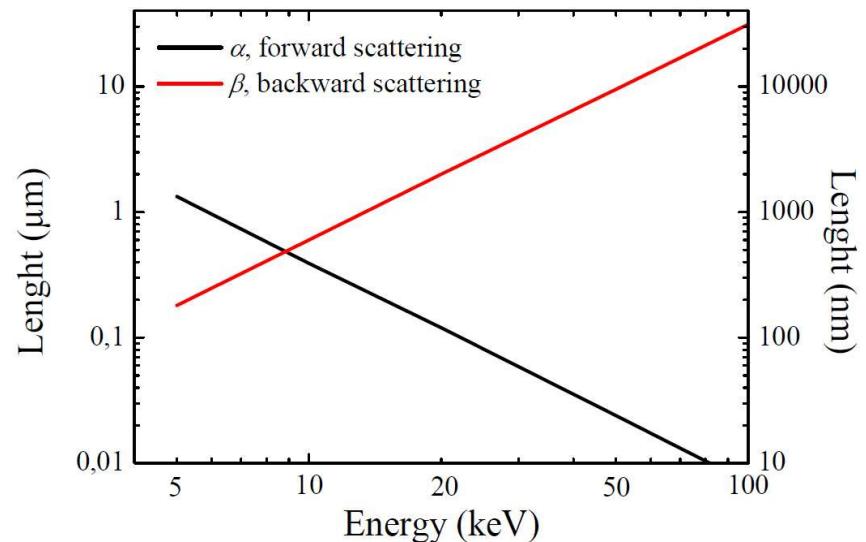
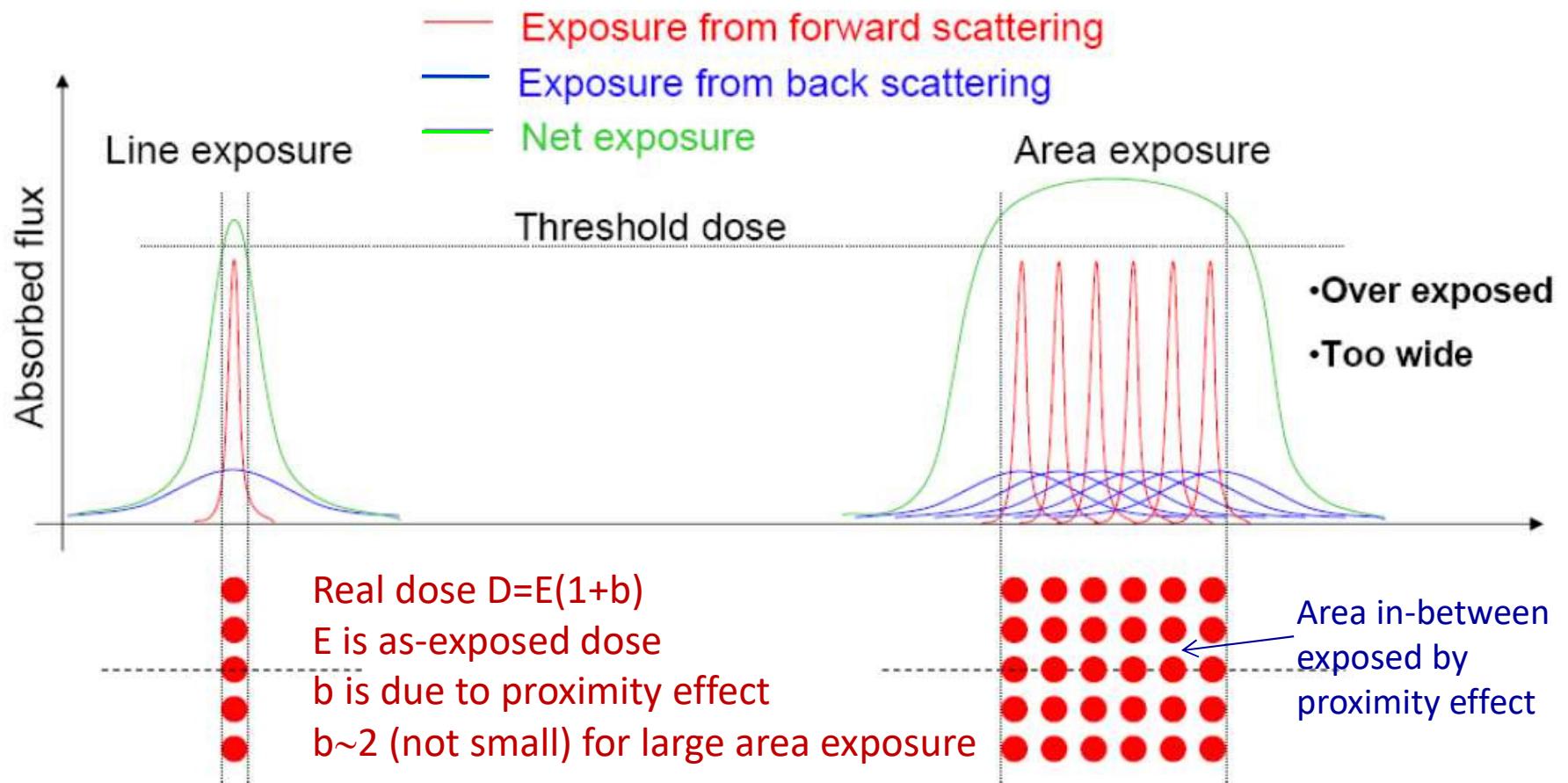


Table-3.12. Double Gaussian fitting parameters at different conditions

energy / keV	substrate	resist thickness/ μm	$\alpha/\mu\text{m}$	$\beta/\mu\text{m}$	η
25	silicon	0.2	0.019,7	2.295,4	0.479,7
50	silicon	0.5	0.016,5	6.689,1	0.314,6
50	silicon	0.5	0.025	5.896,2	0.194,1
50	GaAs	0.5	0.025	3.55	0.674

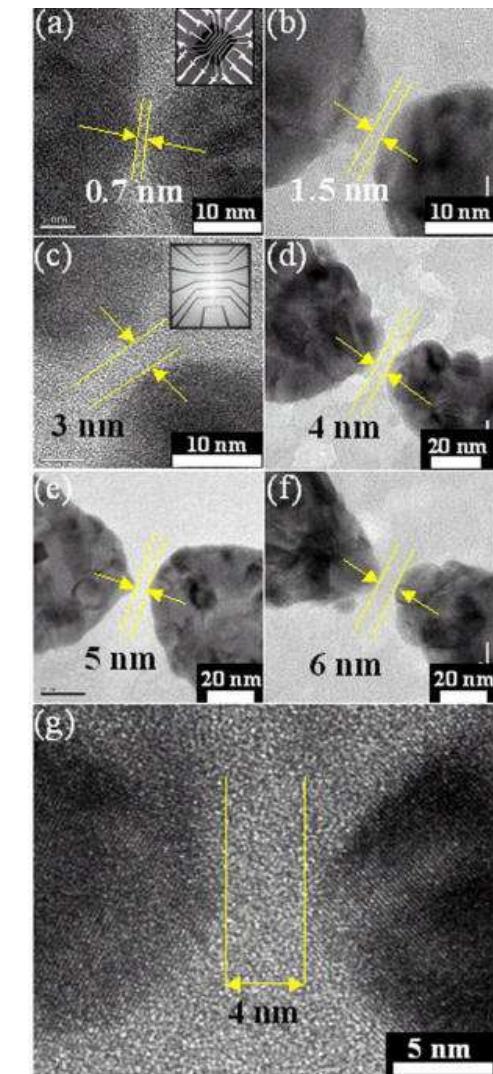
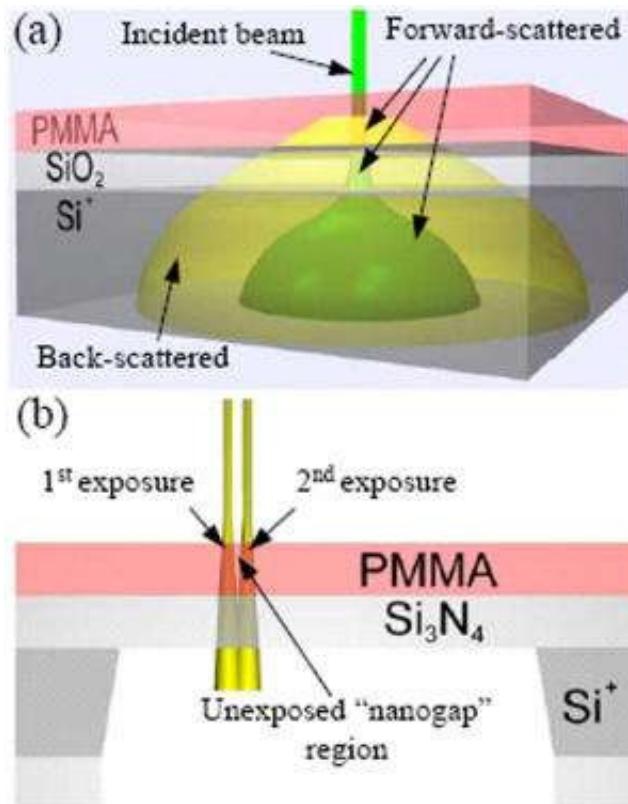
Proximity effect

(similar to that in OPC – optical proximity correction)



- Proximity effect is negligible for isolated/sparse fine features.
- It is good for *areal* exposure (e.g. a big square $>>1\mu\text{m}$), since pixel can be much larger than beam spot size (right figure). E.g., beam step size (pixel) of 50nm is usually enough to give uniform areal exposure, even with a beam spot size only 5nm.
- Proximity effect is worst for dense and fine patterns, such as grating with sub-50nm pitch.

Eliminate proximity effect using resist on membrane



Fischbein, "Nanogaps by direct lithography for high-resolution imaging and electronic characterization of nanostructures", APL 88, 063116 (2006)

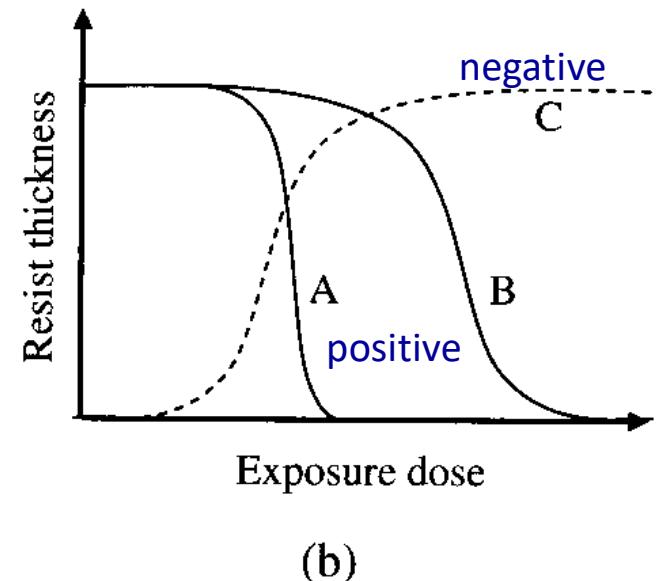
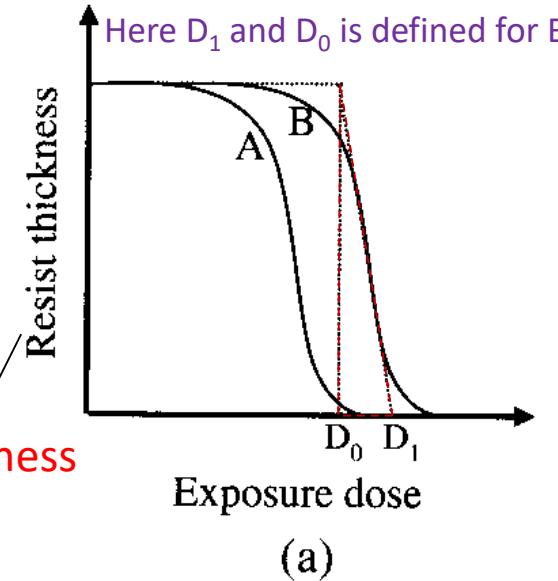
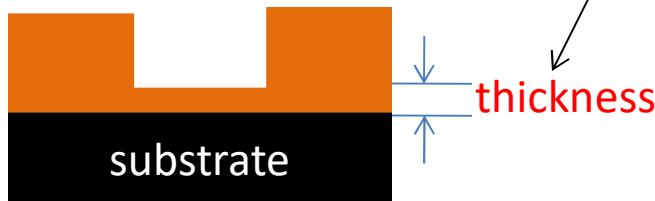
Electron beam lithography (EBL)

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EBL resist: sensitivity and contrast

Resist development curves:

- (a) Resist A is of higher sensitivity than B.
- (b) A is of higher contrast than B; C is negative resist.



Sensitivity:

- For positive resist: D_1 value; or dose required to fully develop the resist to bottom, which is usually close to D_1 value.
- For negative resist: dose that results in half resist thickness remaining after development (this is just a *convenient* definition, not accepted by all EBL researchers).

Contrast γ : defined as slope of the development curve.

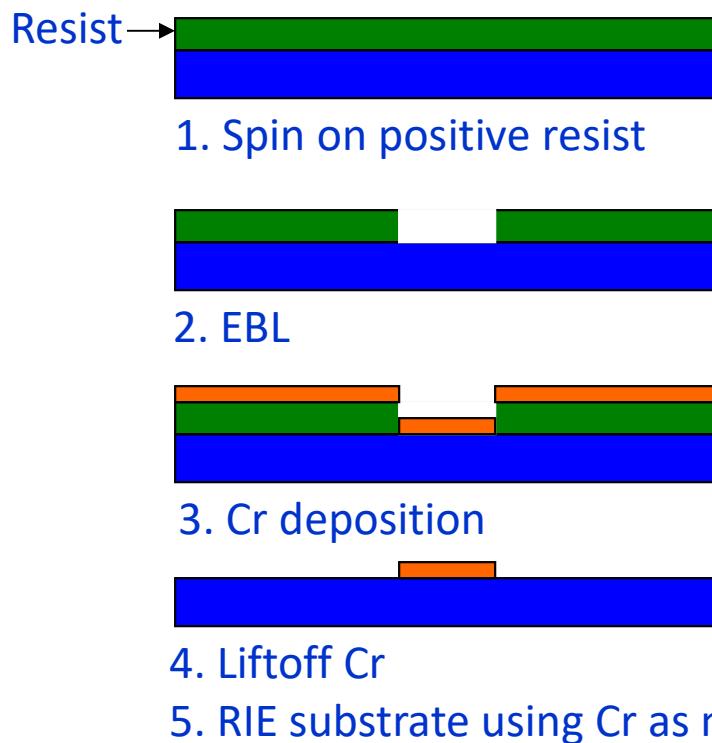
$$\gamma \equiv \frac{1}{\log_{10}(D_1 / D_0)}$$

For “perfect” resist, $D_1=D_0$, so $\gamma=\infty$.
Usually $\gamma>2.0$ is good
For PMMA, $\gamma=5-10$.

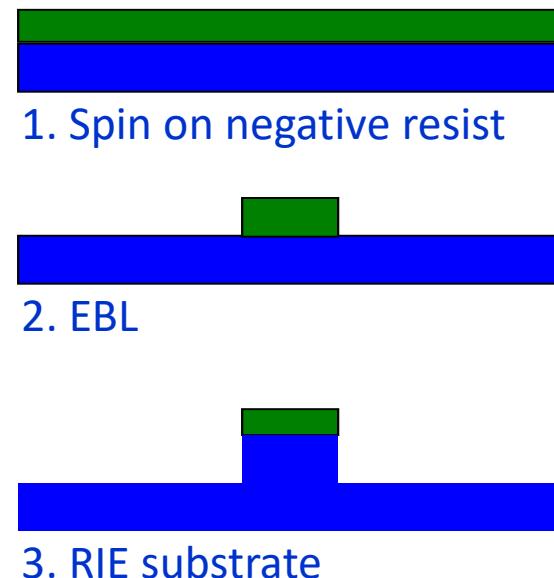
Which (positive or negative) resist to choose

- Which resist to choose depends on which will give the minimum exposure area/time.
- For isolated sparse features, positive resist is suitable for liftoff process, while negative for direct etch process.
- To pattern Si (or SiO₂...), either Cr liftoff then RIE using Cr as mask, or direct etch of Si using resist as mask will work, though Si can be etched deeper with more vertical sidewall using Cr as mask.

Liftoff process using positive resist



Direct etch process using negative resist

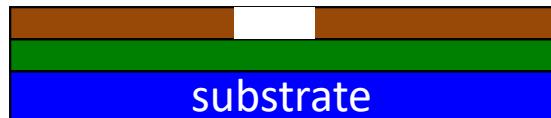


Resist tone reversal process

Very useful if one has only one cheap positive resist: PMMA



Profile
in resist



For positive resist, trench (or
hole) formed after EBL.

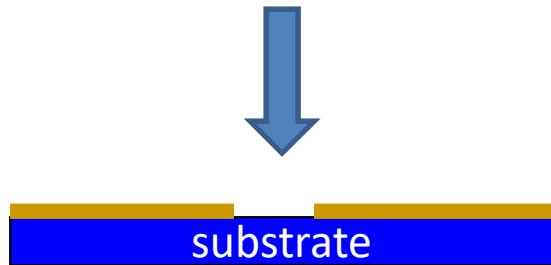


Liftoff a hard material (Cr, SiO₂)

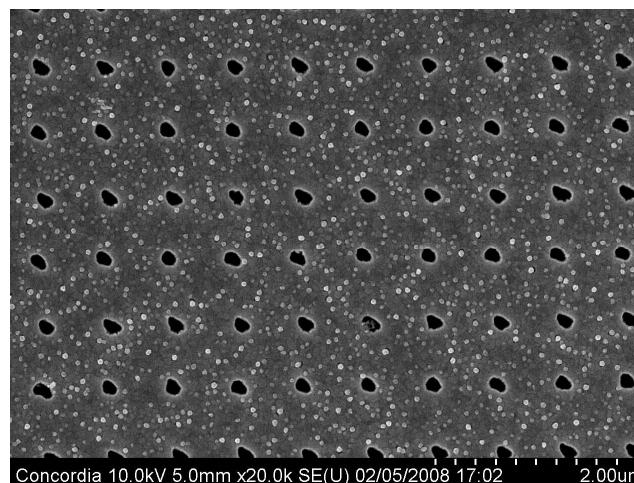
Profile in
under-
layer



RIE under-layer.
The resulted polymer structure is a line
(or pillar), as if negative resist were used.



After metal liftoff



Hole array in
100nm-thick Au
with pitch 600nm.

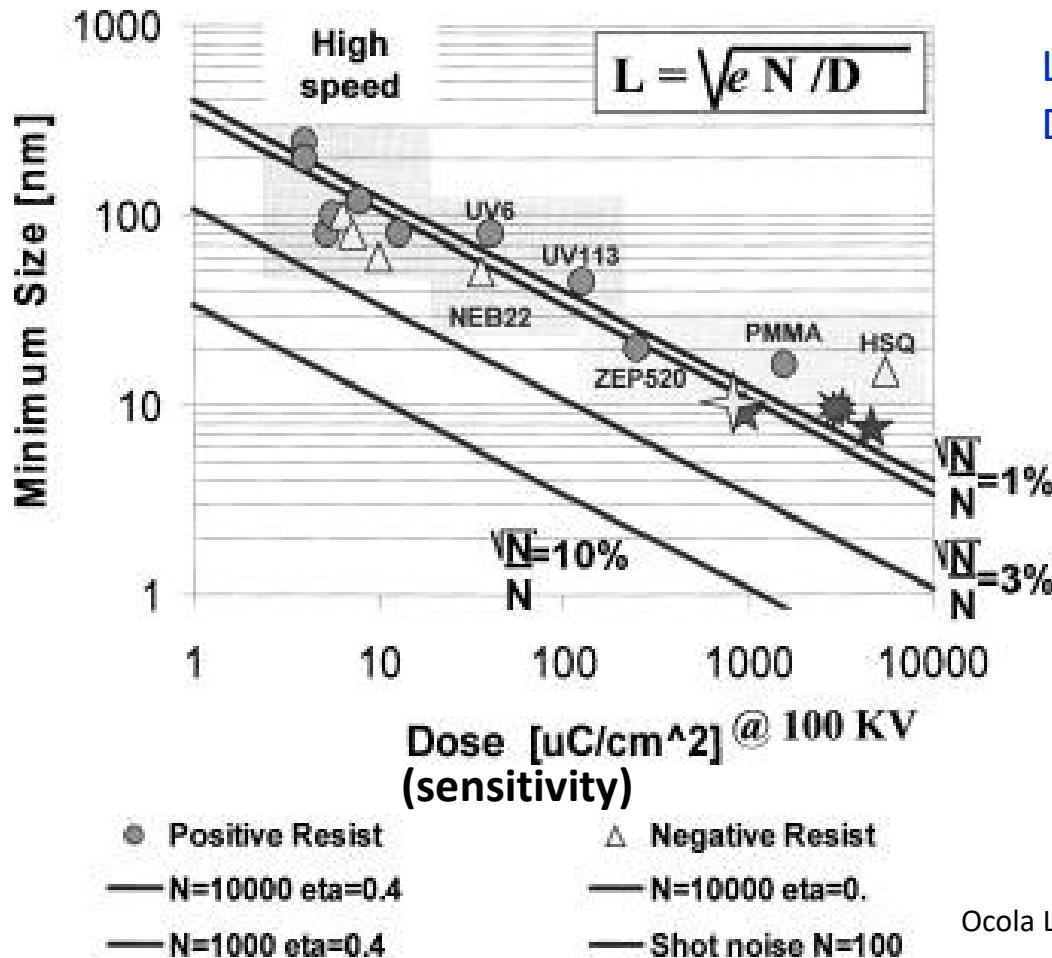
Sensitivity

Sensitivity depends on:

1. Electron energy keV (or acceleration voltage kV). Higher energy requires higher exposure dose, so lower sensitivity.
2. For example, sensitivity for PMMA is $250\mu\text{C}/\text{cm}^2$ with 30kV, but $\sim 600 \mu\text{C}/\text{cm}^2$ with 100kV (high energy electrons pass fast through the resist, generating fewer low energy secondary electron (SE) to expose the resist).
3. Substrate material: high density substrate (high Z) material results in more back-scattering of electrons into resist layers, leading to higher sensitivity (e.g. PMMA on Au sensitivity is $\sim 2\times$ that on Si). But of course more severe proximity effect.
4. Process conditions: post exposure baking conditions for chemically amplified resist; strength of developer, development temperature and time. (sensitivity $\rightarrow 0\mu\text{C}/\text{cm}^2$ (!!)) if developed *infinitely* long time)
5. Developer used. For example, PMGI sensitivity $\sim 50\mu\text{C}/\text{cm}^2$ when using base developer, $\sim 1000\mu\text{C}/\text{cm}^2$ when using solvent developer. (PMGI: Poly(dimethyl glutarimide))

Note: *higher* sensitivity means one needs *lower* dose to fully expose the resist.

Sensitivity vs. contrast: a dilemma



Ocola LE and Stein A, JVST B, 24(6), 3061-3065 (2006).

No resist has both high sensitivity and high contrast/resolution.

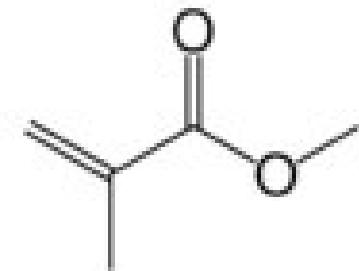
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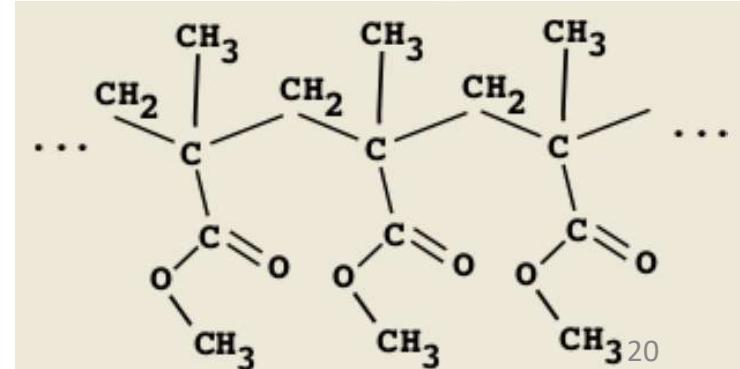
The standard EBL resist: PMMA (positive)

- The most popular e-beam resist, very cheap and last forever, easy handling.
- Very high-resolution and contrast.
- Typical molecular weight is 950kg/mol. Lower M_w (e.g. 15kg/mol) leads to slightly higher sensitivity and slightly lower contrast.
- Usually dissolved in a solvent for film spin-coating: chlorobenzene or anisole (less toxic).
- Developer mixtures can be adjusted to control contrast and sensitivity.
- The downside: low sensitivity, poor dry etch resistance (good for liftoff, not for direct etch pattern transfer).

	10kV	20kV	30kV
Area dose ($\mu\text{C}/\text{cm}^2$)	100	180	250
Line dose (nC/cm)	0.5	0.9	1.3
Dot dose (fC)			1.5



Doses for MIBK:IPA=1:3 developer 60second.
All values are good starting points, need dose test before each writing.



PMMA developer

Table 3.3 Influence of developer concentration on resist resolution

Developer concentration MIBK:IPA)	Sensitivity	Resolution
1:3	Low	Extremely high
1:2 (MIBK: methyl isobutyl ketone)	Medium	Very high
1:1	High	High
Pure MIBK	Very high	Low

The dilemma again: higher sensitivity comes with lower contrast

1. MIBK : IPA (isopropanol)=1:3 for typically 60sec, most popular developer.
2. Cellosolve (2-ethoxyethanol): methanol=3:7 for 7-10sec, claimed by some to have slightly higher contrast than MIBK.
3. MEK (methyl ethyl ketone) : ethanol=26.5:73.5 for 2-5 second also works well.
4. IPA : H₂O=7:3, co-solvent system, i.e. neither IPA nor water alone dissolves exposed PMMA. Claimed by some to have better performance than MIBK.

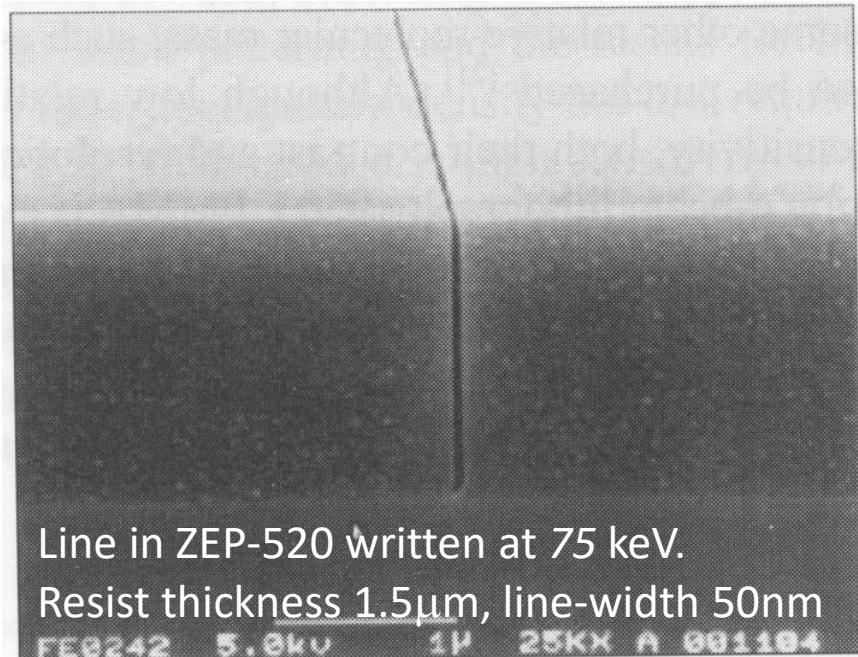
[1] "Enhanced sensitivity in the electron beam resist PMMA using improved solvent developer", Mohsin and Cowie, *Polymer*, 1988, page 2130.

[2] "New high-contrast developers for PMMA", Bernstein and Hill and Liu, *J Appl. Phys.*, 71(8), 1992, page 4066.

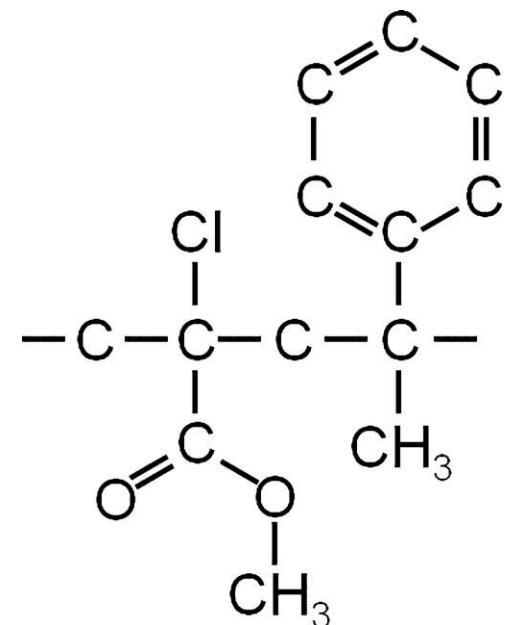
[3] "Comparison of MIBK/IPA and water/IPA as PMMA developers...", Microelectronic Engineering, 61-62, 745-753 (2002).

The most popular *commercial* resist: ZEP-520 (positive)

- Developed by ZEON in Japan to replace PMMA.
- Higher sensitivity (3-5x faster), and higher etch resistance (3x)
- For ultrahigh resolution (sub-10nm), PMMA *might* still be better.
- Expensive: \$2500/100ml including shipping from Japan to Canada.
- One-year shelf time, making it more expensive compared to PMMA.
- Composition: methyl styrene/chloromethyl acrylate copolymer.



Line in ZEP-520 written at 75 keV.
Resist thickness $1.5\mu\text{m}$, line-width 50nm
FE0242 5.0kV 1μ 25KX A 091104



Schematic of the chemical structure of ZEP 520A. Here Cl is for high sensitivity, benzene ring for high etching resistance.

Developer:

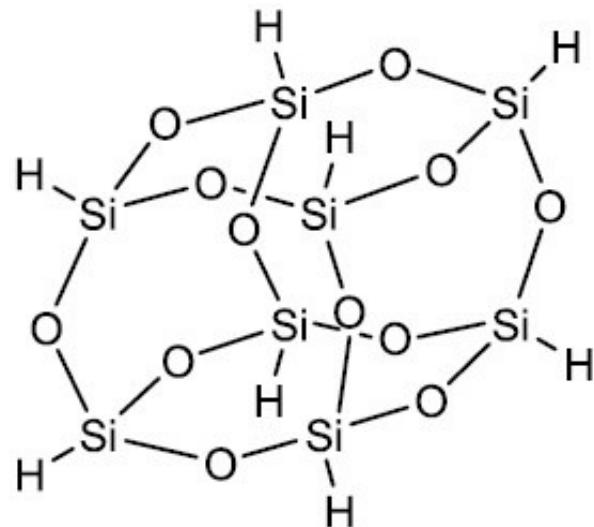
- ZED-N50 (100% n-Amyl Acetate)
- Xylene (o-, m-, p-mixed)

Solvent:

Anisole, for liftoff or diluting the resist for thinner film.

HSQ: hydrogen silsesquioxane (negative)

- Silicon dioxide based inorganic material (not polymer).
- Sensitivity and contrast similar to that of PMMA (depends on developer strength).
- Very high resolution and very dense pattern when using <25nm-thick film.
- Exposed HSQ is in the form of amorphous oxide, good etching mask.
- Salty developer (add NaCl to NaOH solution) increases contrast.



HSQ structure,
Product of Dow Corning under
product code Fox12™

SU-8 (very high sensitivity, but low contrast)

- Chemically amplified negative tone resist
- Extremely high sensitivity – over 100x that of PMMA
- Low contrast (0.9), unsuitable for dense patterning
- High resolution possible for *sparse* patterns at high kV
- Rough edges and “residues” due to random exposure from back scattering electrons and random photo-acid diffusion.
- Ideal for low resolution writing over large area (since it is fast).

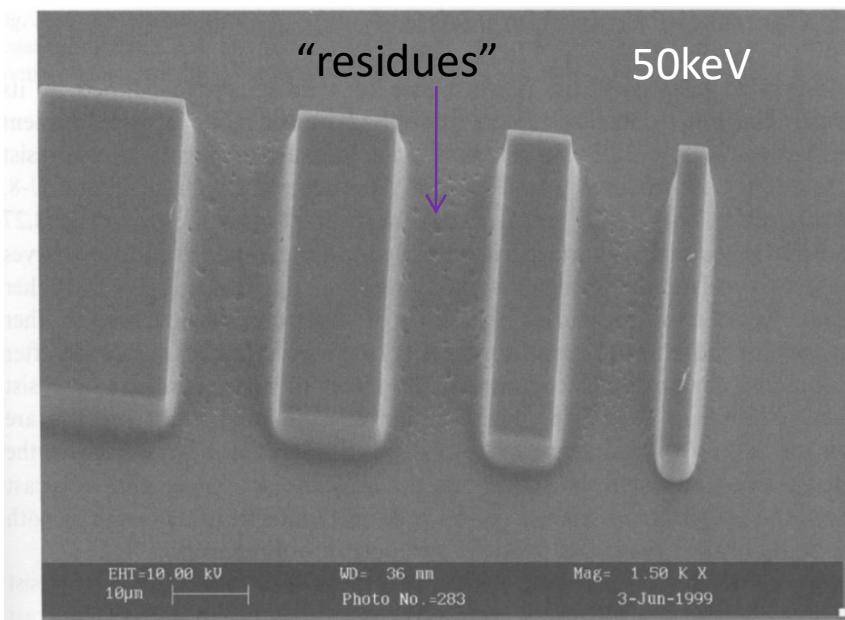
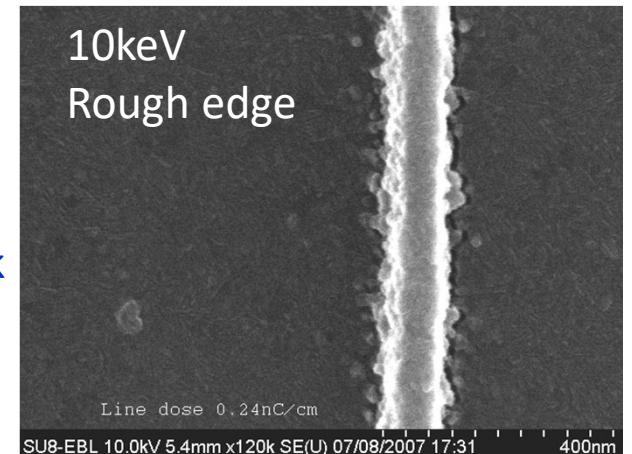
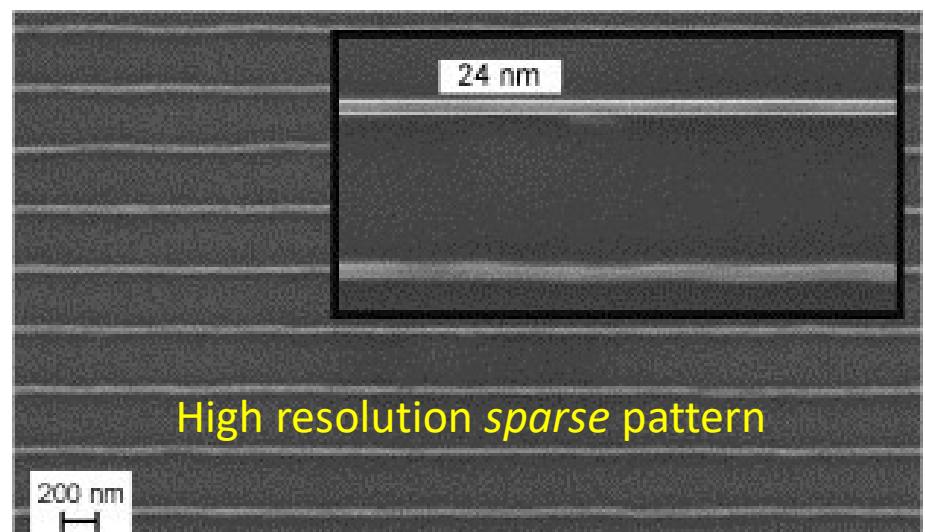


Fig. 3.26 SU-8 resist patterns exposed by e-beam at 50-keV energy



24nm line at pitch 300nm in 100nm thick SU-8

Kristensen A, “High resolution 100 kV electron beam lithography in SU-8”, Microelectronic Engineering, 83, 1609-1612(2006)

Undercut profile for liftoff

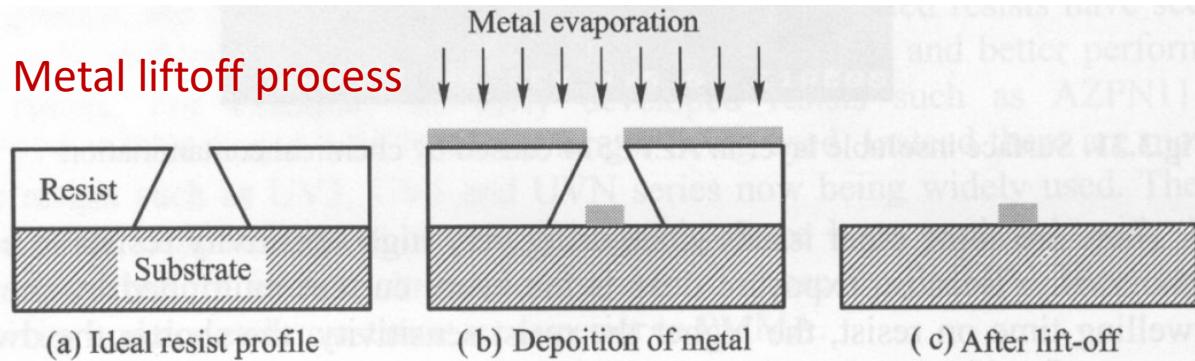
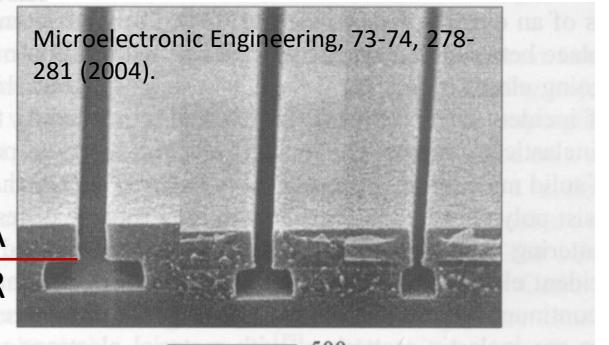


Fig.3.32. Metal lift-off process



Process of double layer stack for easy liftoff

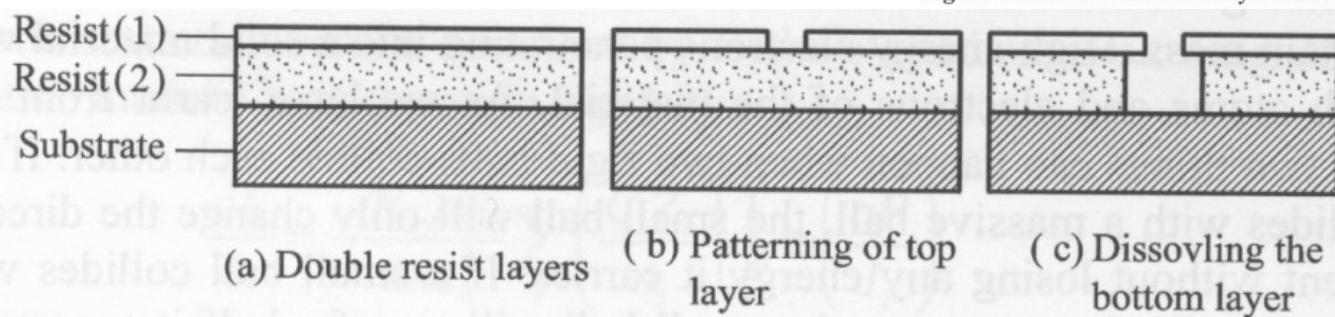


Fig.3.33. Process of double layers resists for lift-off

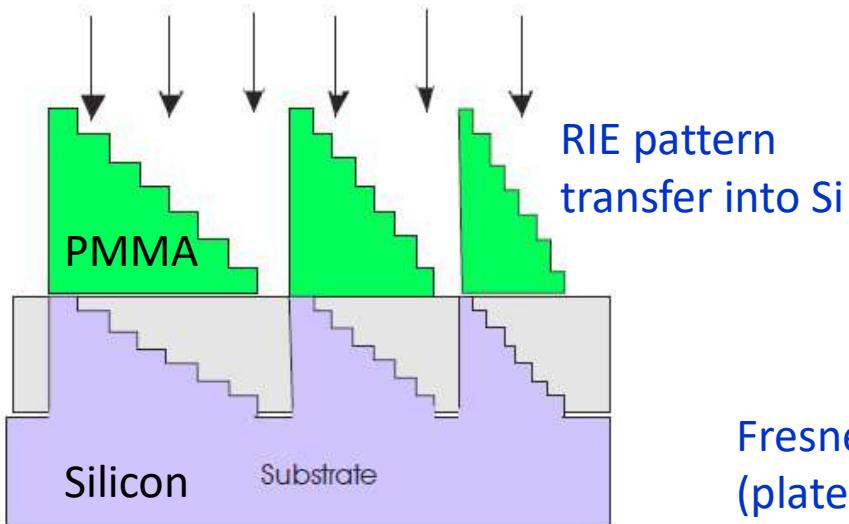
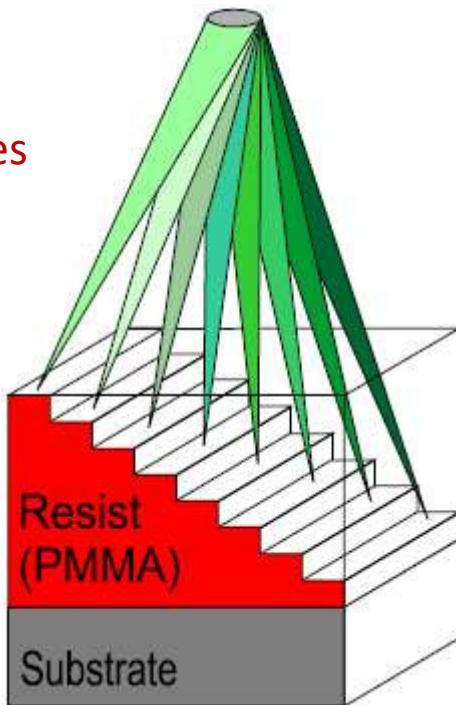
LOR contains PMGI plus additives

Electron beam lithography (EBL)

1. Overview and resolution limit.
2. Electron source (thermionic and field emission).
3. Electron optics (electrostatic and magnetic lens).
4. Aberrations (spherical, chromatic, diffraction, astigmatism).
5. EBL systems (raster/vector scan, round/shaped beam)
6. Interaction of electrons with matter (scattering, x-ray, Auger).
7. Proximity effect and how to reduce it.
8. Resist contrast and sensitivity.
9. Several popular resist materials.
10. High resolution EBL, resolution limit.
11. Grey-scale EBL for 3D structure fabrication.
12. Anti-charging techniques.

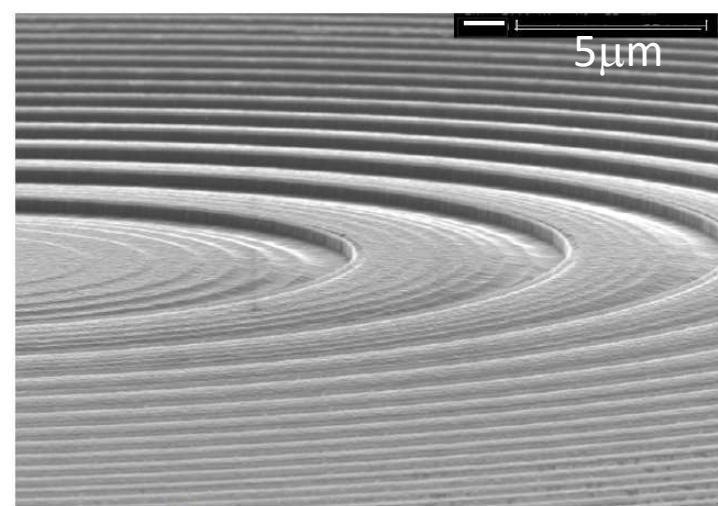
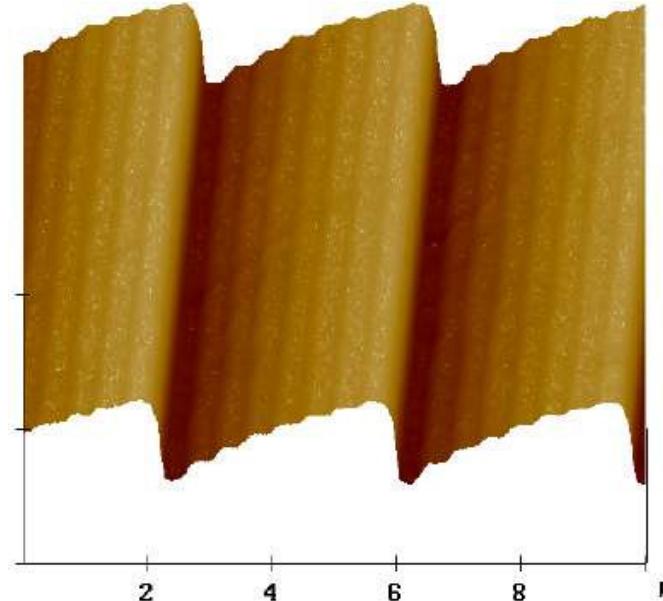
Gray-scale electron beam lithography

E-beam exposure
with variable doses
to create variable
depths after
development.



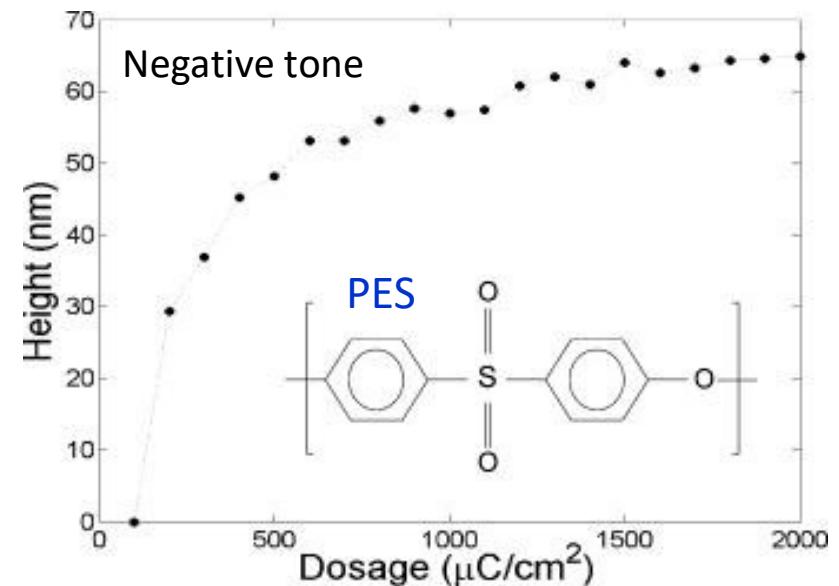
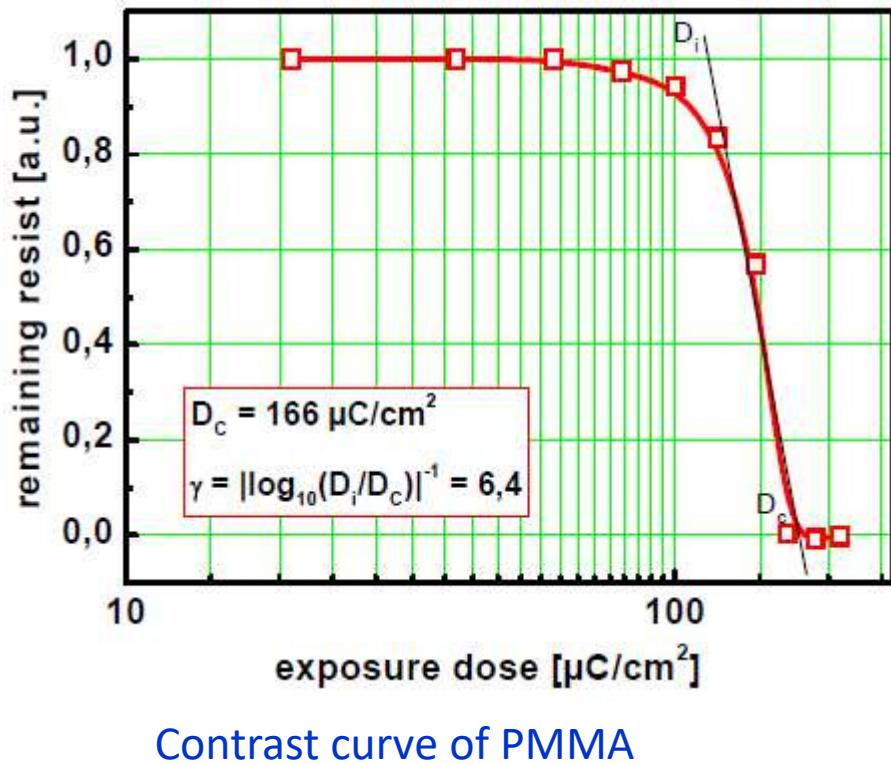
Fresnel zone lens
(plate) in silicon

AFM of a grating in resist



SEM of an 8-level FZL transferred into Si by analog RIE
focal length $f = 62 \mu\text{m}$ @ $1,55 \mu\text{m}$; $d = 610 \text{ nm}$

Which resist is best for gray-scale EBL?



Contrast curve of PES with 10keV electron beam. Sensitivity was found to be $\sim 200 \mu\text{C}/\text{cm}^2$, with contrast only $\gamma \sim 0.8$.

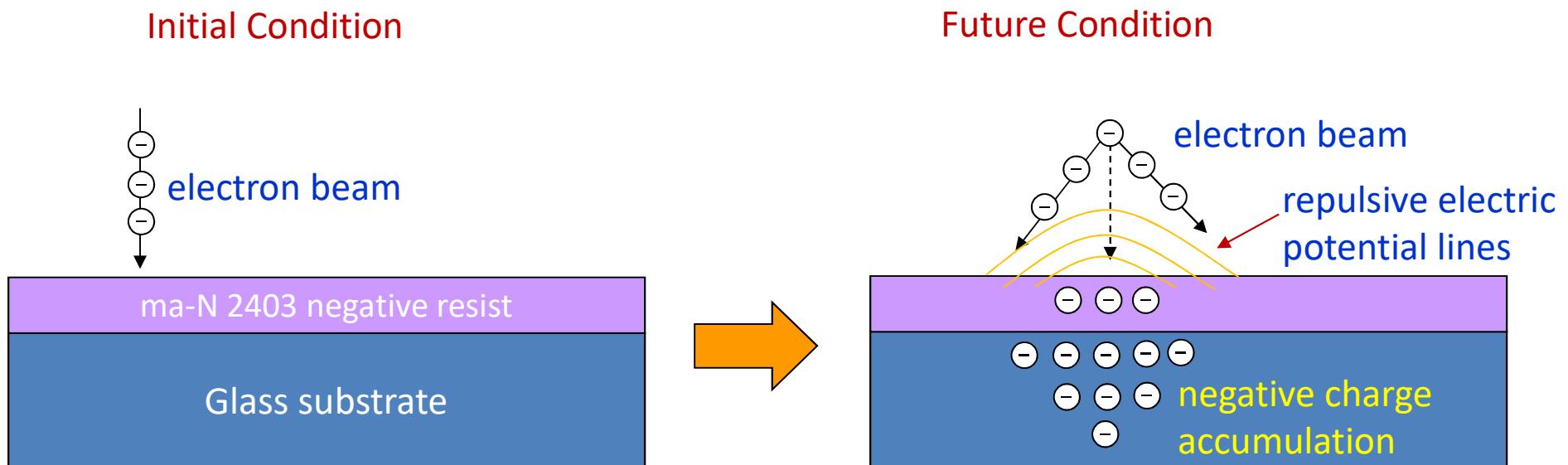
- Ideal resist has very low contrast (ideally $\gamma < 1$) and high sensitivity.
- High contrast leads to very narrow process/dose window (tiny dose change \rightarrow large pattern depth change).

Electron beam lithography (EBL)

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Charging during e-beam writing

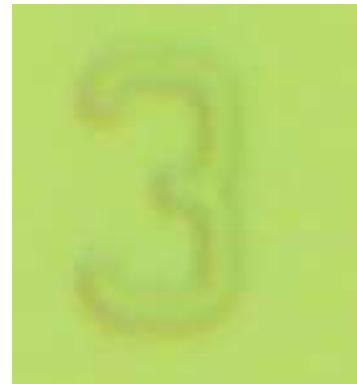
- Even though most resists are insulating, charging is not an issue for typical resist thickness of <500nm, because most electrons penetrate deep into the conducting substrate at 30kV. (more serious charging for lower kV)
- When electron beam lithography must be performed on insulating substrates (quartz, SiO_2/Si ...), negative charge buildup can occur on substrate surface, causing beam deflection, and thus pattern distortion.



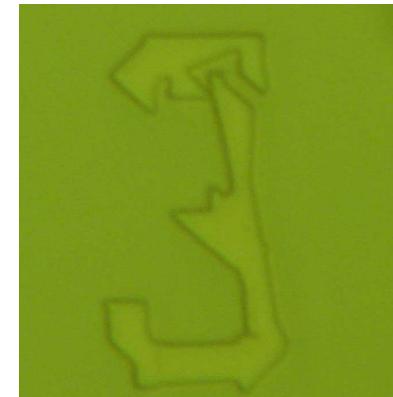
Anti-charging technique: coat conducting layer

- To eliminate charging effect, one can coat a conducting layer on top of or beneath the resist.
- Typically 10nm metal is enough, such as Al, Ti, Cr or Au; conducting polymer may also work.
- Lighter metal (Al) causes less (forward) scattering of electron beam than the heavier one (Au), so is preferred.
- Al and Ti can be removed easily by diluted HF (1:100 diluted).

GOOD
(no charging)
Coat metal



BAD
(severe charging)
no anti-charging layer



Anti-charging technique: variable pressure (VP) EBL

- It is the same idea as VP-SEM, i.e. introducing gas (H_2O , N_2 , Ar, He) into the chamber.
- Gas molecules are ionized by electron impact; these positive gas ions migrate to negatively charged surface and balance surface charge.
- Primary electron beam will be scattered to some slight extent by collision with gas molecules, forming a beam “skirt” around the focused primary beam at sample surface.



VP-SEM images of a pattern on glass substrate with 30keV e-beam writing under

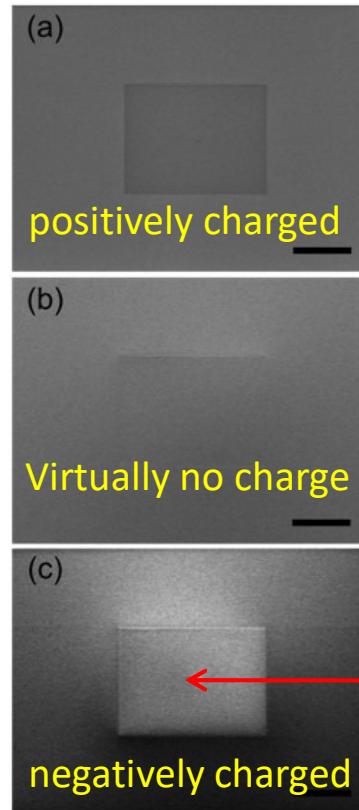
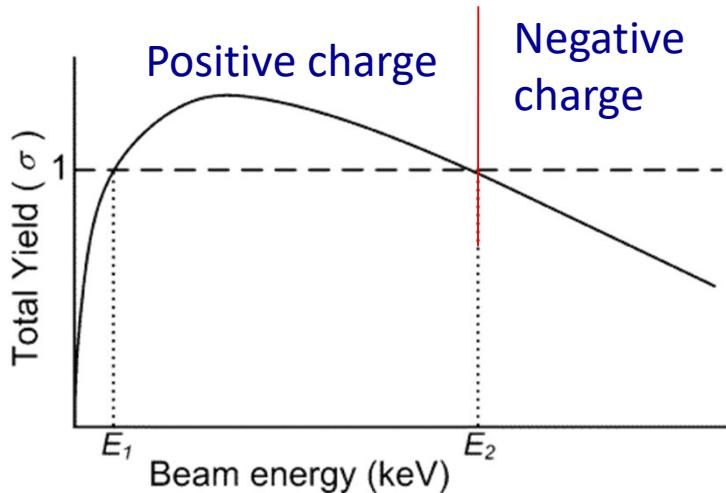
- a) high vacuum
- b) 0.4 Torr (water vapor pressure)
- c) 1 Torr

The dashed red line indicates the pattern dimension as written.

The pattern exposed with 1Torr pressure shows no significant distortion or displacement.

Anti-charging technique: critical energy EBL

Total (ejected) electron yield (σ) vs beam energy for a typical resist.



How to find E_2 ?

Reduce magnification, here from 500 \times to 200 \times at acceleration voltage:

- a) 0.5 keV
- b) 1.3 keV
- c) 2.0 keV

Electron accumulated during imaging at 500 \times . When zoom out to 200 \times , more electrons ejected at the charged region, so is brighter.

- Bulk insulating material is positively charged when $\sigma > 1$ and negatively charged when $\sigma < 1$. Charge buildup is zero at critical energy/crossover voltage (E_1 , E_2), where σ is unity.
- In between, $\sigma > 1$, so >1 electron (including SE and BSE) ejected for each incident electron.
- E_1 is too small, E_2 depends on resist thickness and substrate material.
- For 65nm PMMA on glass, $E_2=1.3\text{keV}$. Such low keV can penetrate such thin resist.

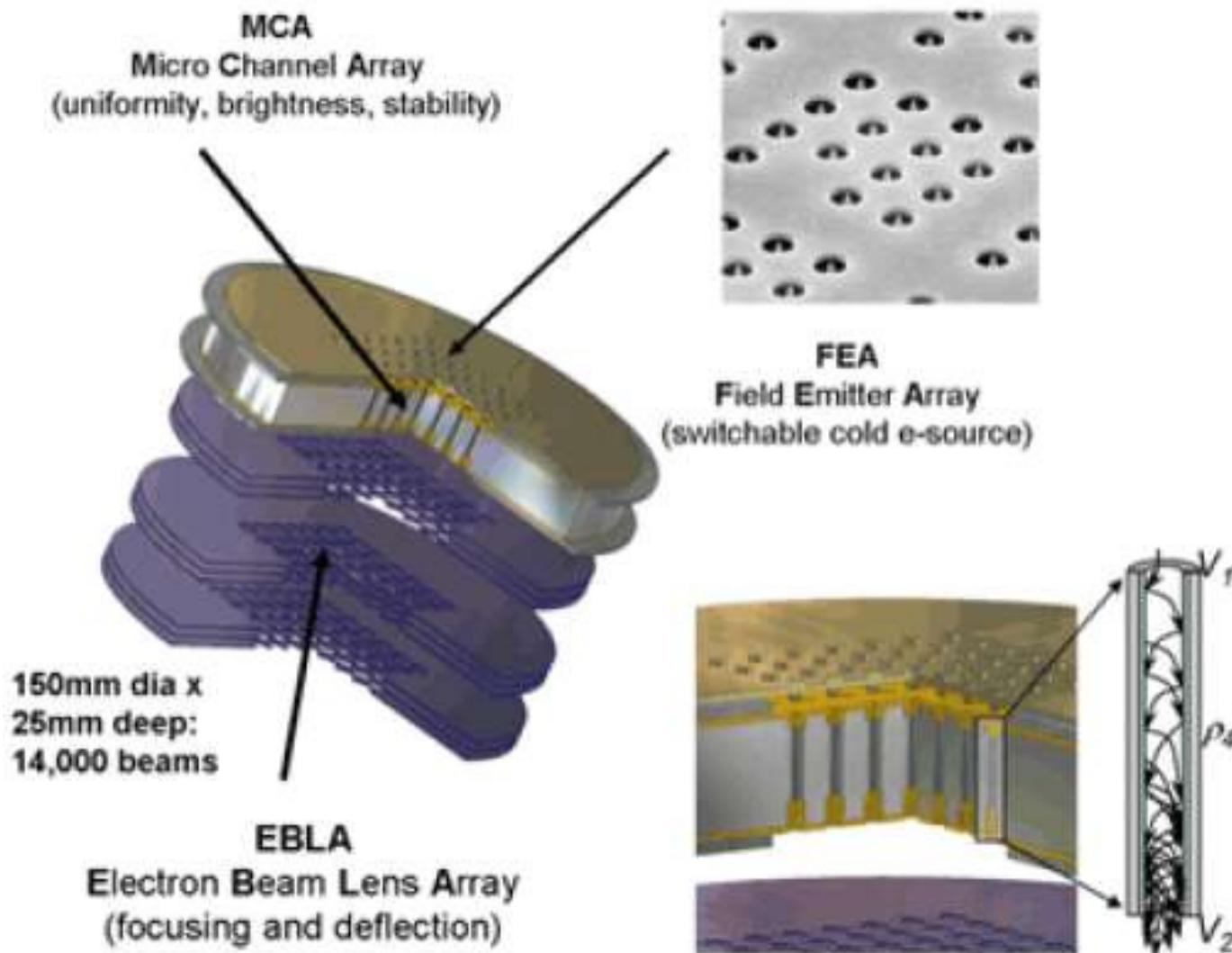
Electron beam lithography (EBL)

1. Overview and resolution limit.
2. Electron source (thermionic and field emission).
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12. Anti-charging techniques.
13. Electron projection and multi-beam lithography

High throughput electron-based lithography: overview

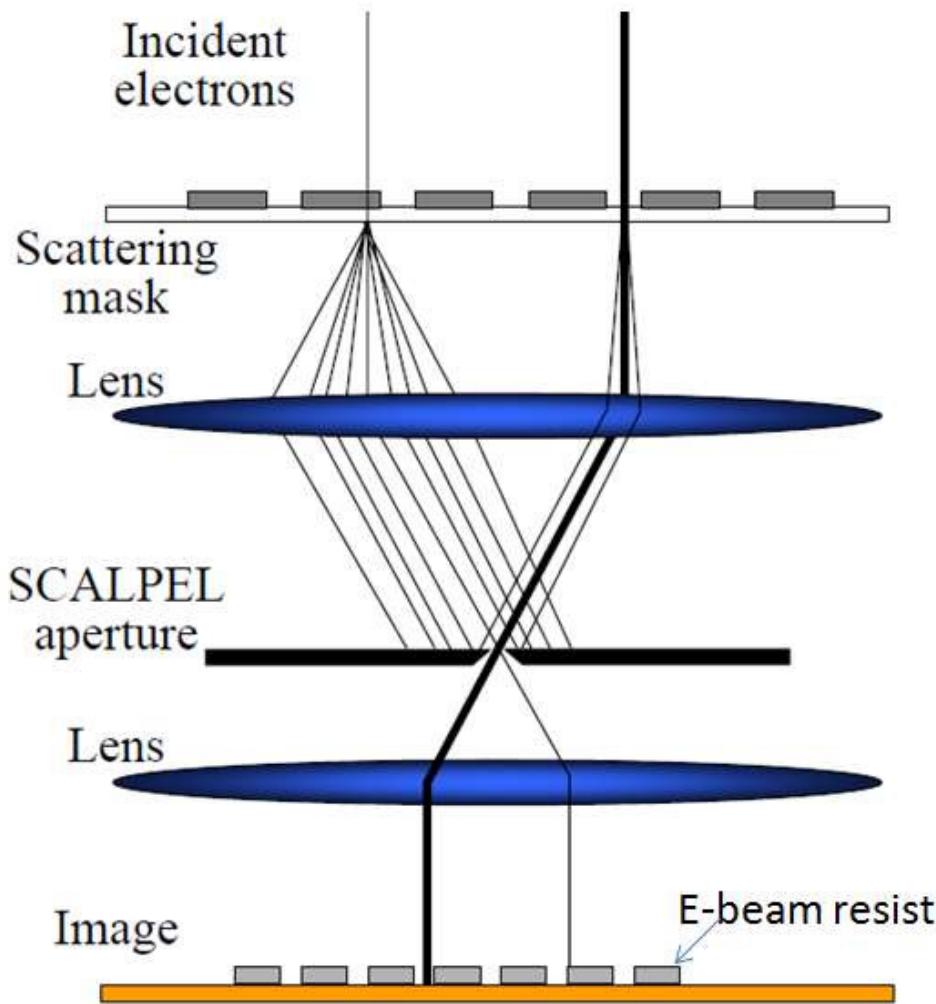
- Electron beam lithography using single beam is too slow for mass production.
- Three directions to increase throughput drastically:
 - Use broad beam and mask, like photolithography. It is called electron projection lithography (EPL), with SCALPEL as best known EPL method.
 - Start from a broad beam, divide into many sub-beams
 - Using an array of mini-electron guns/sources to generate multi-electron beams.
- Those techniques can also be used for ion, will be addressed later.
- Currently, multi-e-beam direct write is competing with EUV lithography for next generation lithography.

MEMS-based electron emitters array



Not mature, far away from mass production tool.
Same principle as field emission display, go to see
http://en.wikipedia.org/wiki/Field_emission_display

SCALPEL: Scattering with angular limitation projection electron beam lithography

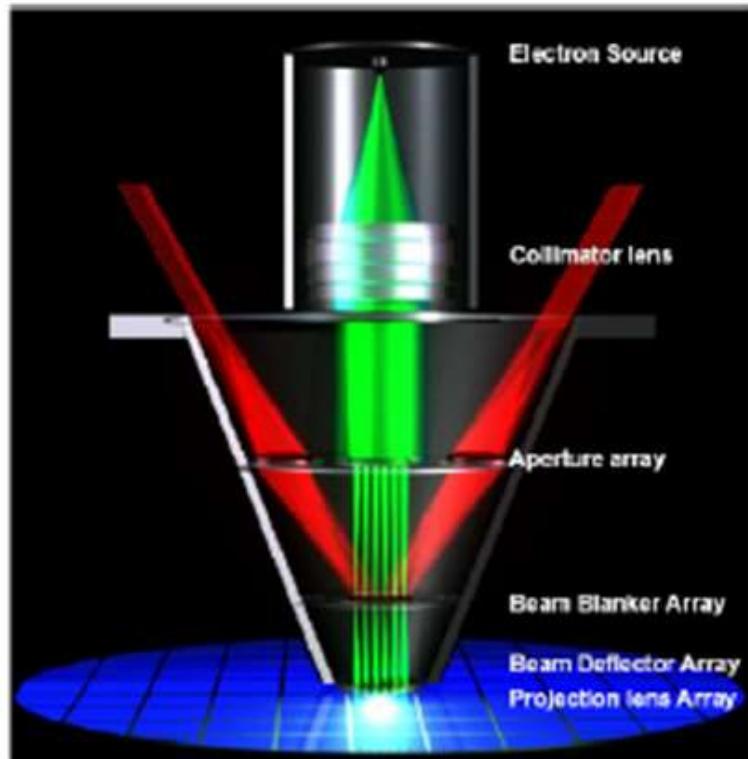


Dark and light regions differentiated by their scattering strength at the SCALPEL aperture.

MAPPER system

At present, MAPPER system seems to be the most promising multi-beam direct write system.

A few demo-tools have been shipped to semiconductor industry.



Schematic of MAPPER system[1]

Raster scan, beam blanker by optical control

Most recent view by Burn Lin:

“Despite the tremendous potential of MEB ML2, it has the least momentum in NGL. Perhaps its conception is way after much investment is made in other NGL such as EUV lithography, even after the ill attempt of e-beam projection printing (i.e. electron projection lithography) which experienced insurmountable mask problems amongst other obstacles. The latter leaves bad taste with e-beam technology while the former consumes development funds too large to abandon.”

Focused ion beam (FIB)

1. Overview.
2. Ion source and optics.
3. Ion-solid interaction, damage.
4. Scanning ion beam imaging.

Comparison of electrons and ions

Electrons

- are very small
inner shell reactions
(ionization)
- High penetration depth
- Low mass -> high speed for given energy
- Electrons are **negative**
- Magnetic lens (Lorentz force)

Ions

- Big
->outer shell reactions (**no x-rays**)
- High interaction probability
less penetration depth
- Ions can remain trapped -> **doping**
- High mass -> slow speed but high momentum
milling !!!
- Ions are **positive**
- Electrostatic lenses

Comparison of electrons and ions

		FIB	SEM	Ratio
Particle	type	Ga+ ion	electron	
	elementary charge	+1	-1	
	particle size	0.2 nm	0.00001 nm	20'000
	mass	1.2 .10-25 kg	9.1.10-31 kg	130'000
	velocity at 30 kV	2.8.105 m/s	1.0 108 m/s	0.0028
	velocity at 2 kV	7.3.104 m/s	2.6.107 m/s	0.0028
	momentum at 30 kV	3.4.10-20 kgm/s	9.1.10-23 kgm/s	370
	momentum at 2 kV	8.8.10-21 kgm/s	2.4.10-23 kgm/s	370
Beam	size	nm range	nm range	
	energy	up to 30 kV	up to 30 kV	
	current	pA to nA range	pA to uA range	
Penetration depth	In polymer at 30 kV	60 nm	12000 nm	
	In polymer at 2 kV	12 nm	100 nm	
	In iron at 30 kV	20 nm	1800 nm	
	In iron at 2 kV	4 nm	25 nm	
For imaging				
Average electrons signal per 100 particles at 20 kV	secondary electrons	100 - 200	50 - 75	
	back scattered electron	0	30 - 50	
	substrate atom	500	0	
	secondary ion	30	0	
	x-ray	0	0.7	

Energy $E=1/2mv^2$ momentum= $mv=(2mE)^{1/2}\propto m^{1/2}$ for same E.

Focused ion beam (FIB)

1. Overview.
2. Ion source and optics.
3. Ion-solid interaction, damage.
4. Scanning ion beam imaging.

Ion sources

Early ion sources were developed for mass spectrometry and nuclear physics research, then for ion implantation for semiconductor manufacturing.

Four types:

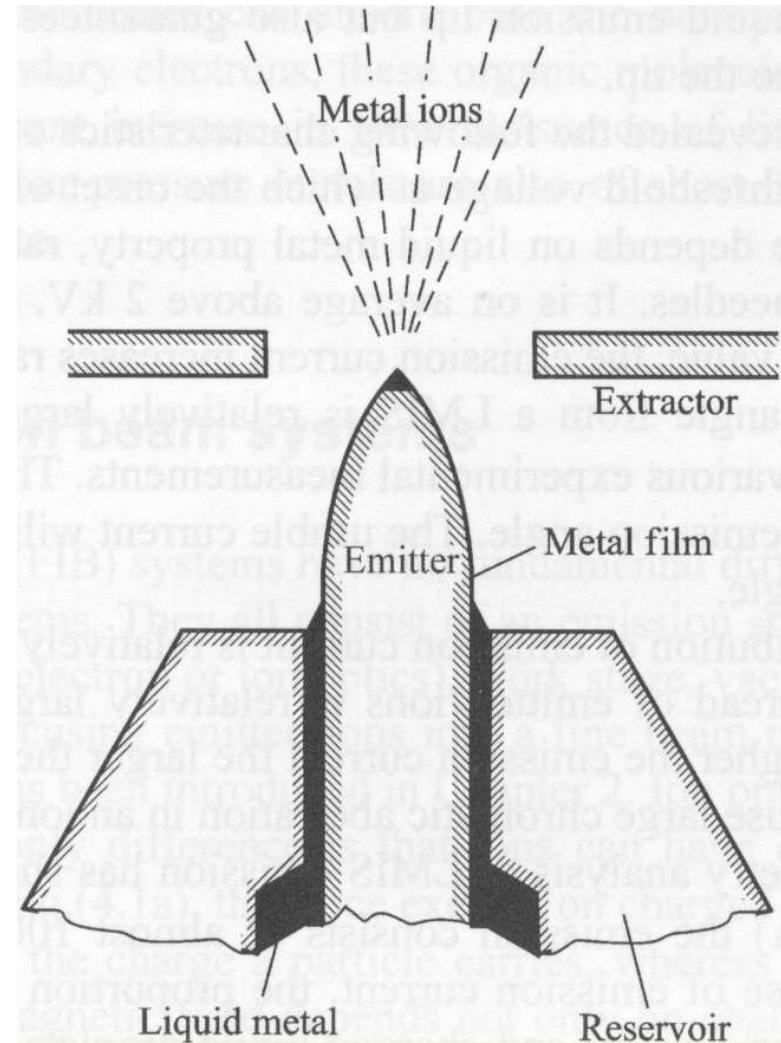
1. Electron bombardment ion sources. Gas molecules bombarded by electrons become ionized, producing a stream of ions. Small ion current and small ion energy spread, used in mass spectrometry.
2. Gas discharge ion source. High current, used in nuclear physics instrumentation such as high energy accelerators and ion implanters.
3. Field ionization source. Gas molecules absorbed on the surface of a fine needle tip can be directly ionized at extremely high electrical field near the tip apex. Used as field ion microscope to study atomic structure of a material.
4. Liquid metal ion source (LMIS). A field emission source from liquid metal under a strong electrical field.

Liquid metal ion source (LIMS)

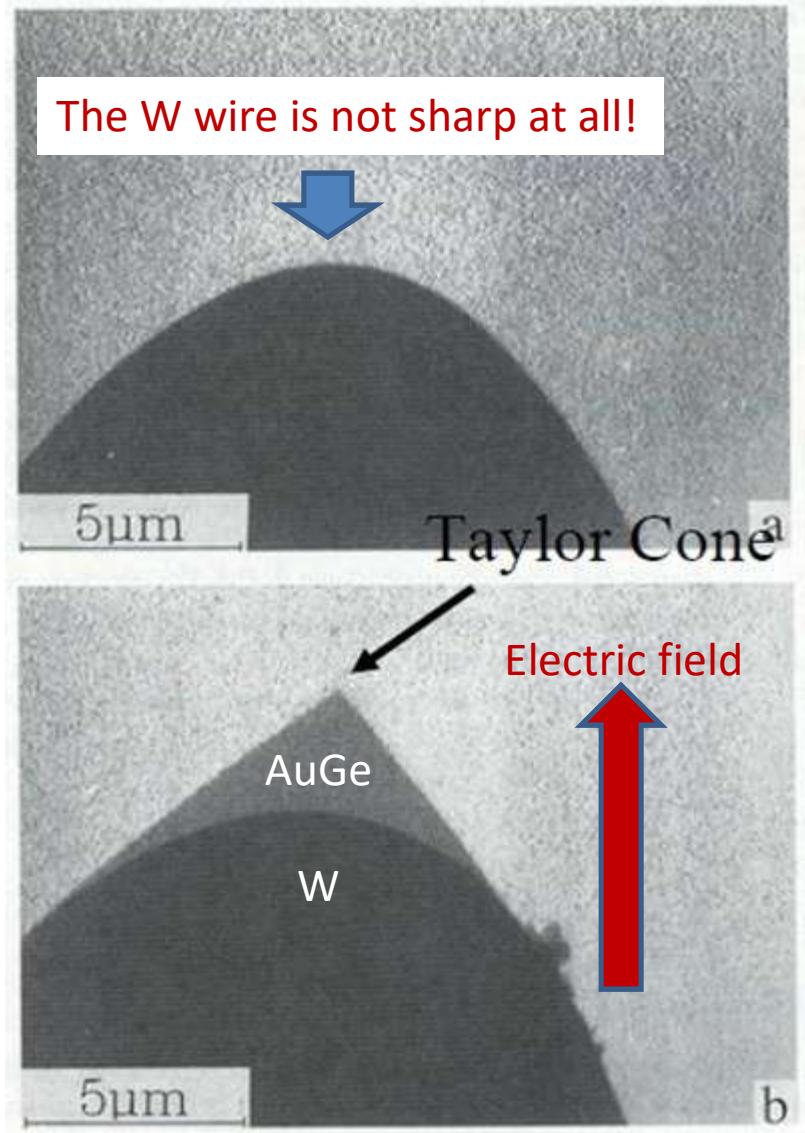
- W wire electrochemically etched into a needle with tip radius $5-10\mu\text{m}$.
- The needle wetted by molten metal.
- The electrical field at the liquid apex can reach 10^8V/cm .
- At this field, metal atoms at the apex become ionized and escape in the form of field evaporation.

Experiment has shown the following.

- There exists a threshold extractor voltage ($\sim 2\text{kV}$) for ion emission.
- The emission angle is large, around 30° .
- The angle distribution of emission current is rather uniform.
- Energy spread of emitted ions is large, $\sim 15\text{V}$, leading to large chromatic aberration in an ion optical system.
- At current $< 10\mu\text{A}$, almost 100% ions are single charged.



TEM image of operating LIMS



LMIS emitter substrate

The W wire is not sharp at all!

But the “Taylor” cone of the liquid metal induced by electric field is very sharp.

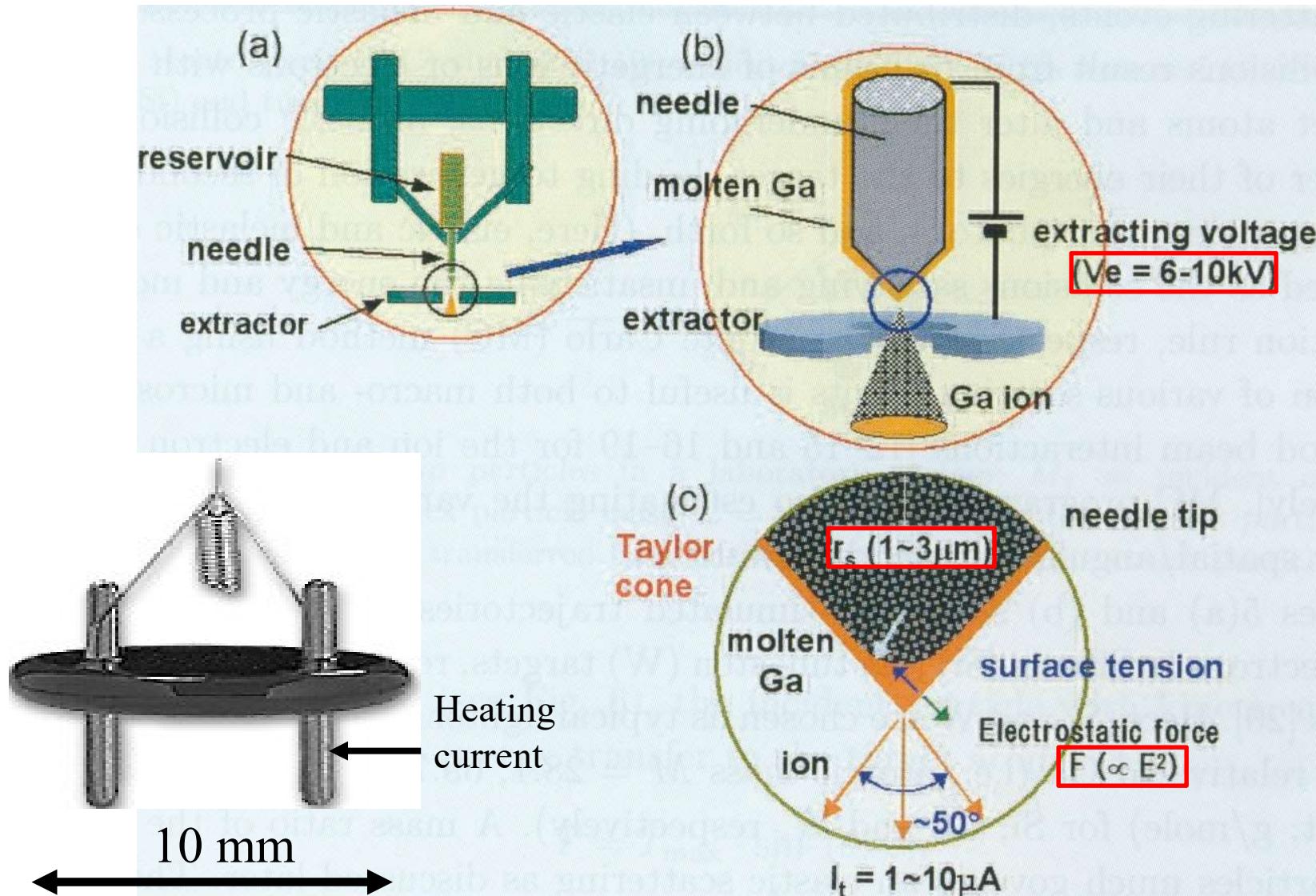
As a result, electric field at cone apex is very high for field emission.

LMIS emitter substrate with AuGe Taylor cone

AuGe has low melting point, so is used.

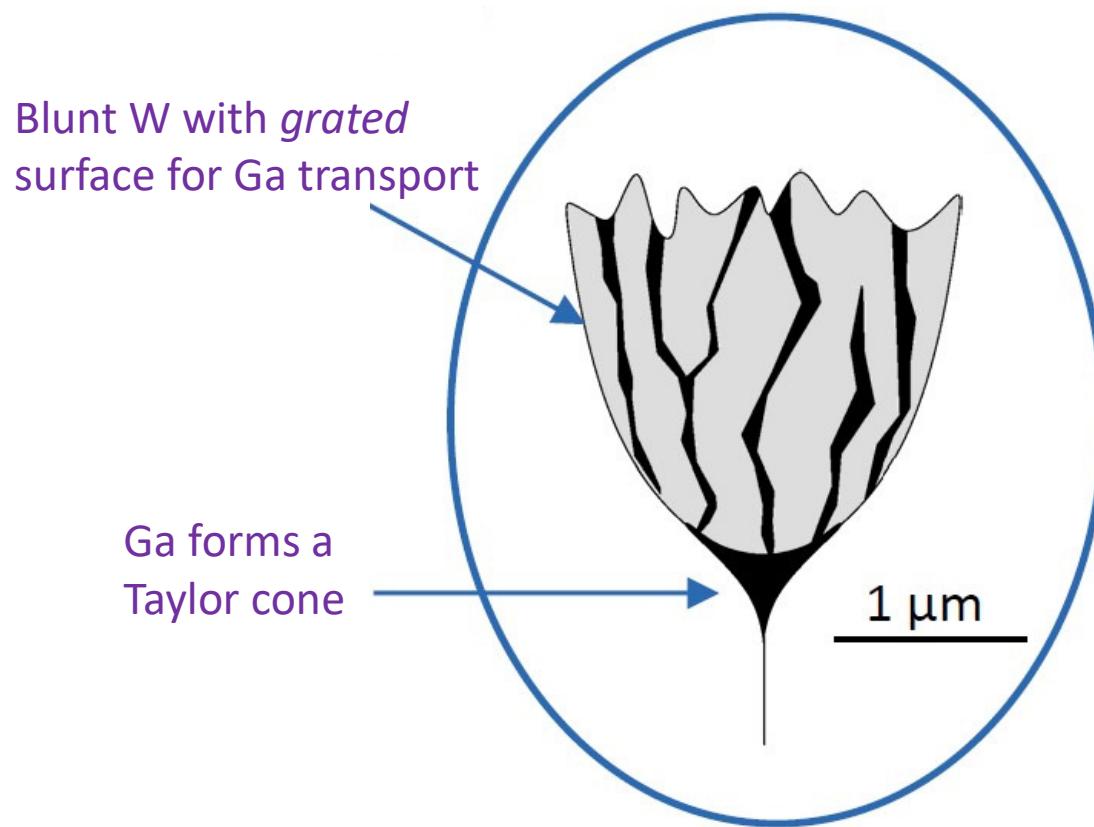
Will Taylor cone form if the field direction is reversed?

Liquid metal ion source



Liquid metal ion source: why Ga

- Melting point at 30°C → liquid around room temperature.
- Low vapor pressure → applicable in high vacuum.
- $[Ga^{2+}]/[Ga^+] \sim 10^{-4}$ at 10µA → narrow energy distribution.
- Long life (up to 1500 hour sources).
- Heavy enough ion for sputtering ($Z=31$).



Ion optics: overview

- Similar to electron optics.
- But use only electrostatic lens and deflectors to focus and deflect ion beam, because for magnetic lens (though they have superior optics):
 - It must be fabricated impractically large to focus 30kV Ga ions.
 - The focusing plane depends on mass/charge ratio.

$$F_e = qE$$

Electrostatic force independent of m, same for electron and ion.

$$F_m = qv \times B$$

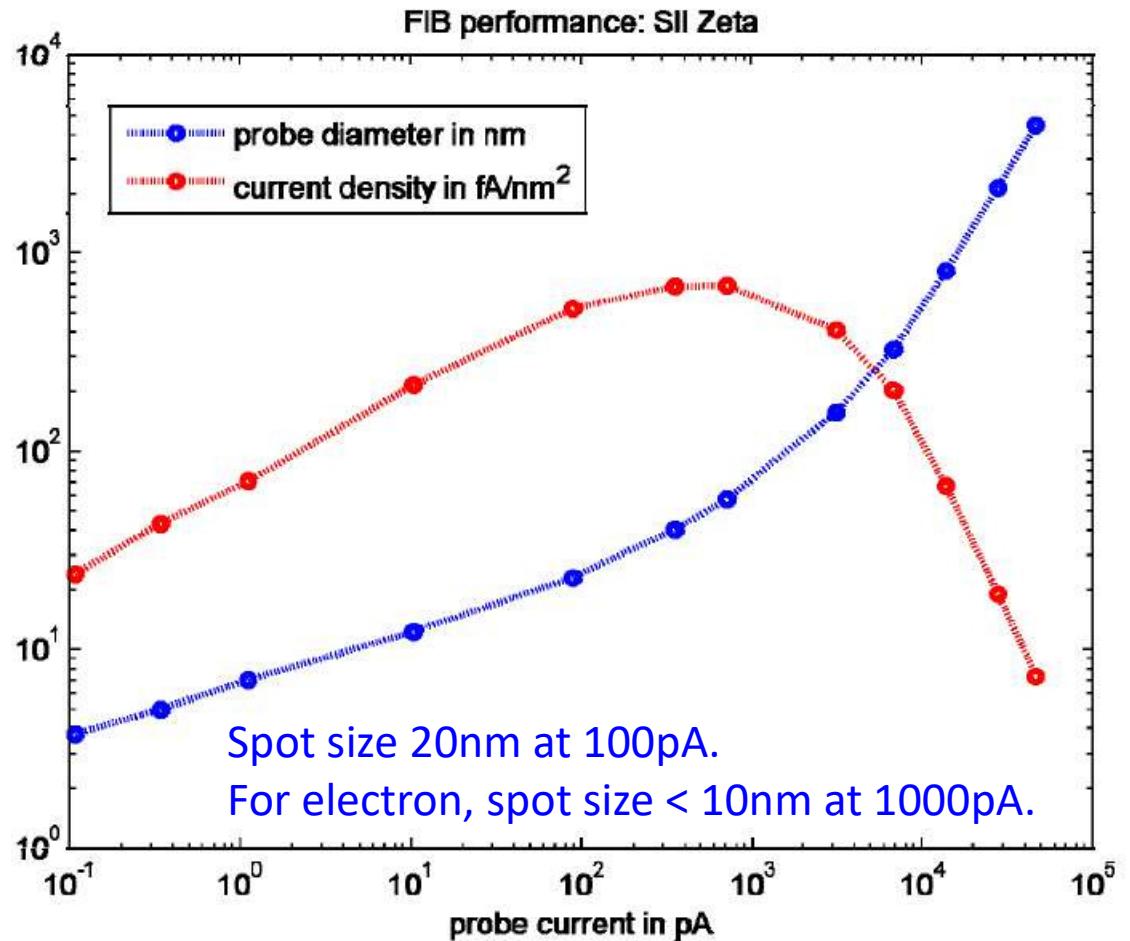
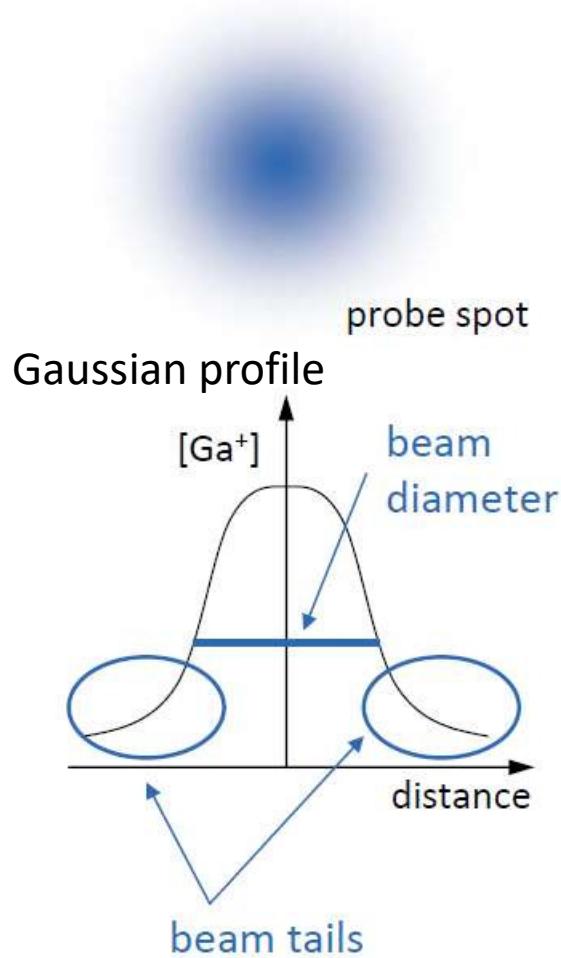
v is speed, much smaller for ions than for electrons; so much smaller force, need impractically large B to focus.

$$v = \sqrt{\frac{2qV}{m}}$$

V is acceleration voltage.

- State-of-the-art FIB has focal spot size below 5nm at current of few pA.
- At medium current (60pA, $\alpha=1\text{mrad}$), chromatic aberration ($=C_c \cdot \alpha \cdot dE/E$) dominates.
- At large current (5nA, 10mrad), spherical aberration ($=0.5Cs \cdot \alpha^3$) dominates.

Beam size vs. current

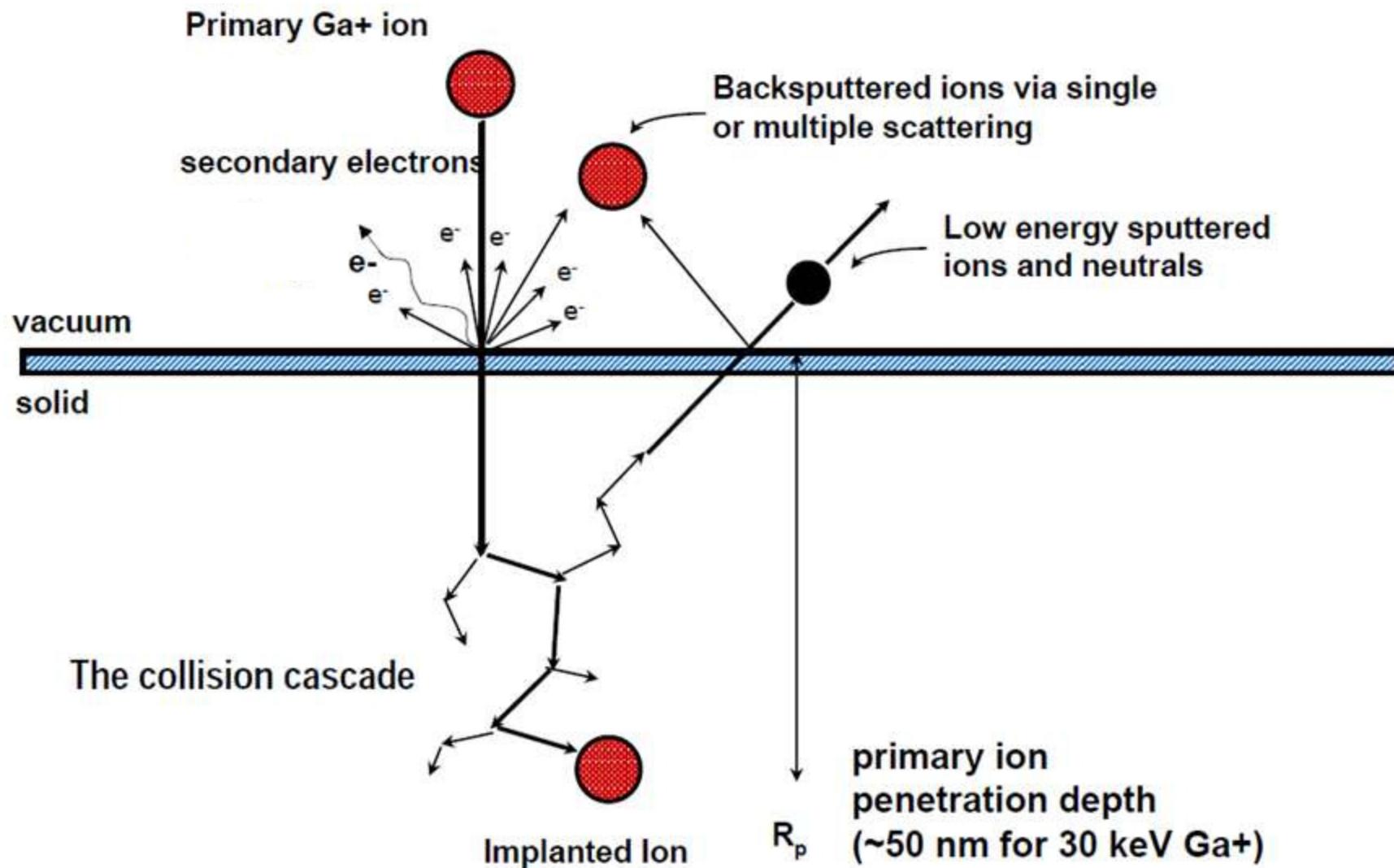


- Small aperture → small beam current (slow) and narrow beam (high resolution). Need a tradeoff.
- Beam tails can extend up to some μm , is one limiting factor when milling deep high aspect ratio trenches/holes (the other factor is re-deposition of sputtered material).

Focused ion beam (FIB)

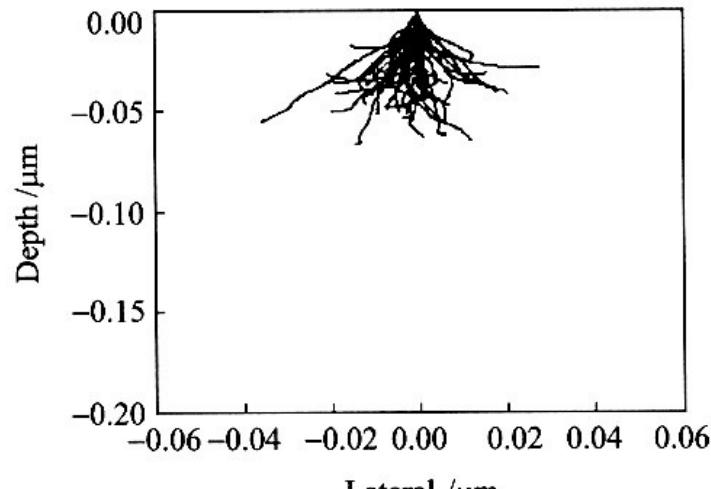
1. Overview.
2. Ion source and optics.
3. Ion-solid interaction, damage.
4. Scanning ion beam imaging.

Ion-solid interactions

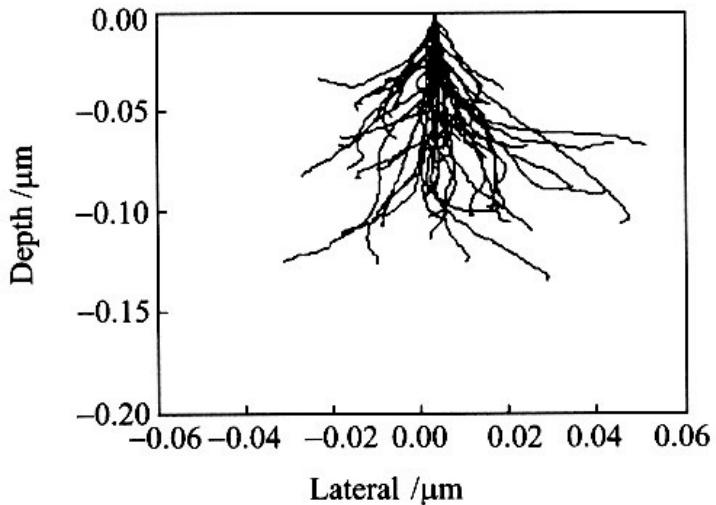


- Imaging (secondary electron image, 1-3 SE per ion), milling and deposition simultaneously.
- Leads to lattice defects (vacancies, interstitials, dislocations).
- Leads to damages, amorphization, re-crystallization.

Trajectories for Ga⁺ bombardment

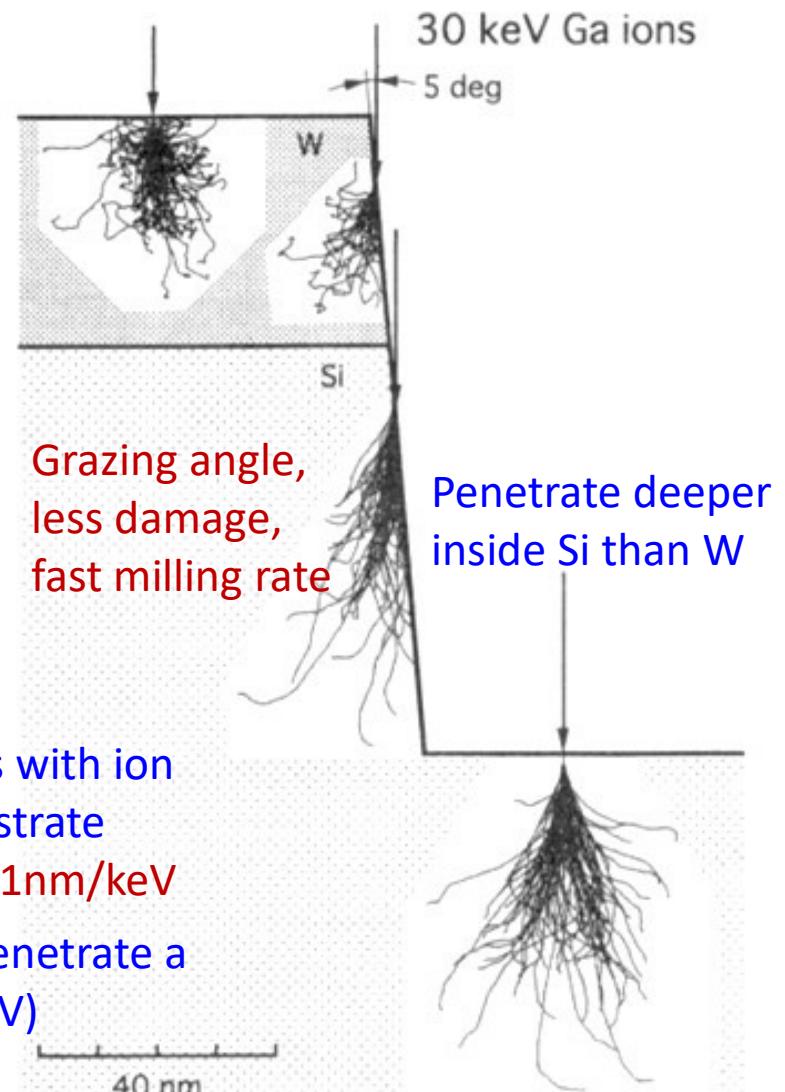


(a) Gallium ion energy = 50 keV



(b) Gallium ion energy = 100 keV

30 keV Ga⁺ on W/Si sample



Grazing angle,
less damage,
fast milling rate

Penetrate deeper
inside Si than W

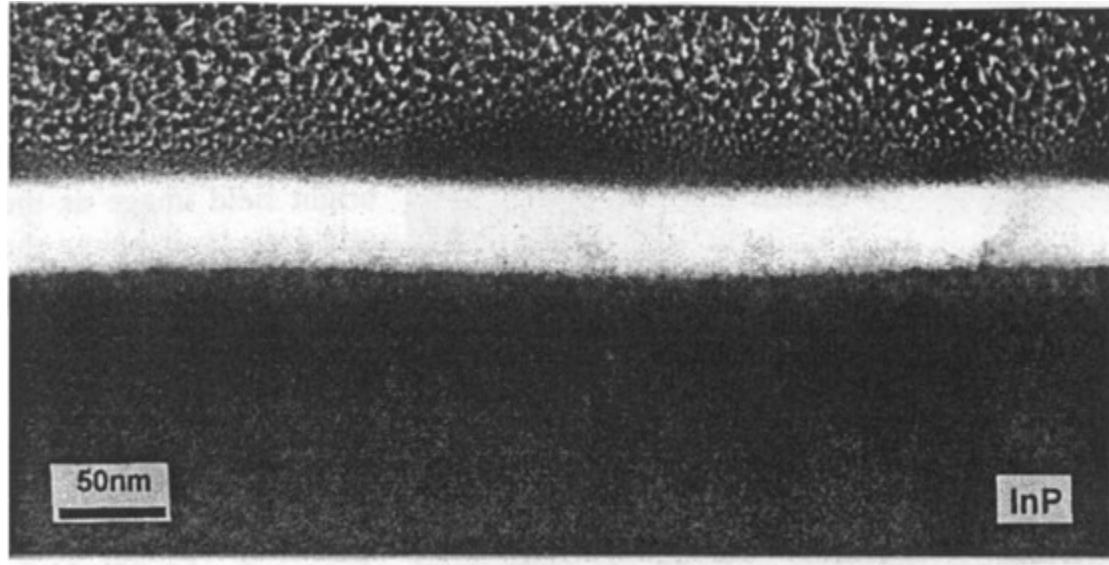
Ion range varies with ion
energy and substrate
material, order 1nm/keV
(for electron, penetrate a
few μm at 30keV)

Damage by Ga⁺ bombardment

- Ion Implantation - Ga atoms remain in the sample target and may reach critical composition for second phase formation.
- Amorphization of surface
- Lattice defects
 - Vacancies – displaced or “missing” atoms from their equilibrium lattice positions
 - Interstitials – atoms which are positioned in between equilibrium lattice positions
 - Dislocations – a missing “half-plane” of atoms
- Local heating within the collision cascade (10’s of nanometers from surface)
- Concentration of primary defects (knock-outs from lattice sites) can be evaluated by Kinchin-Pease formula: $n_D = kE/2E_d$, where $k \approx 0.8$ is a coefficient, E is ion energy, E_d is displacement energy. **Average 1000 defects per ion.**
- Ga in most semiconductors is acceptor, affecting electronic, optical, magnetic and thermal properties.

Damage by Ga^+ bombardment

InP, 40nm damage/amorphization layer thickness

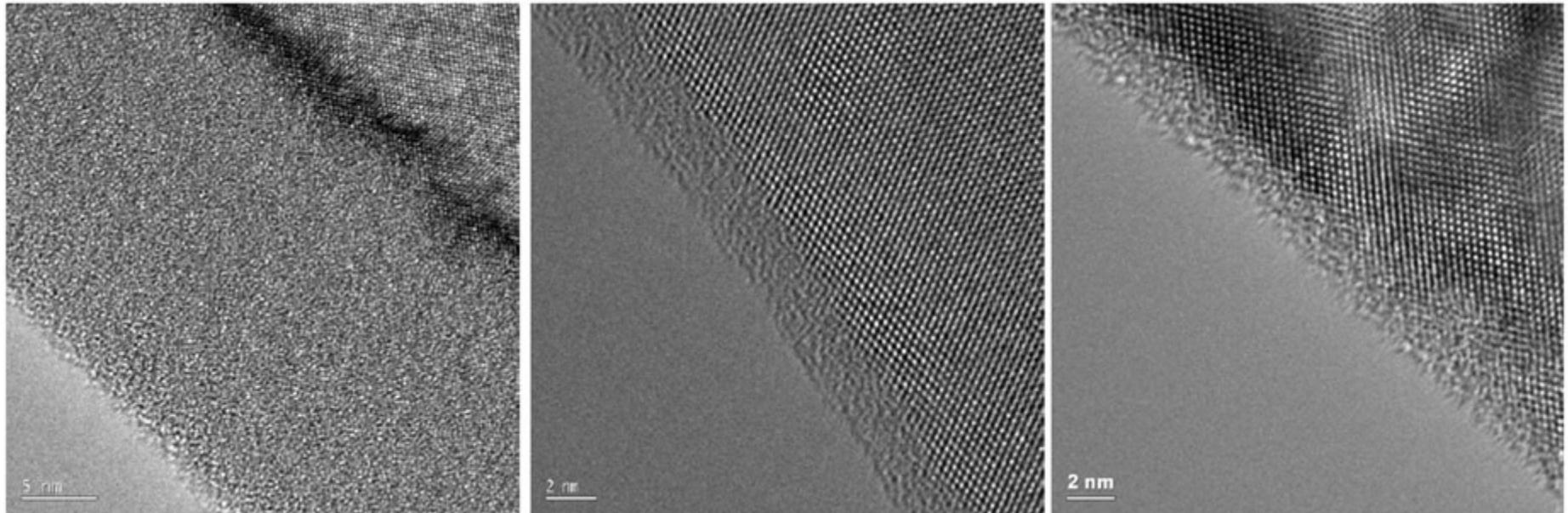


Amorphization depth

	10 keV	30 keV
Si	6 nm	28 nm
GaAs	4 nm	24 nm
InP	15 nm	40 nm

Use low keV FIB milling to reduce ion damage

Reduced amorphous layer with reduced FIB energy



30keV
~21nm

5keV
~2nm

2keV
~0.5-1.5nm

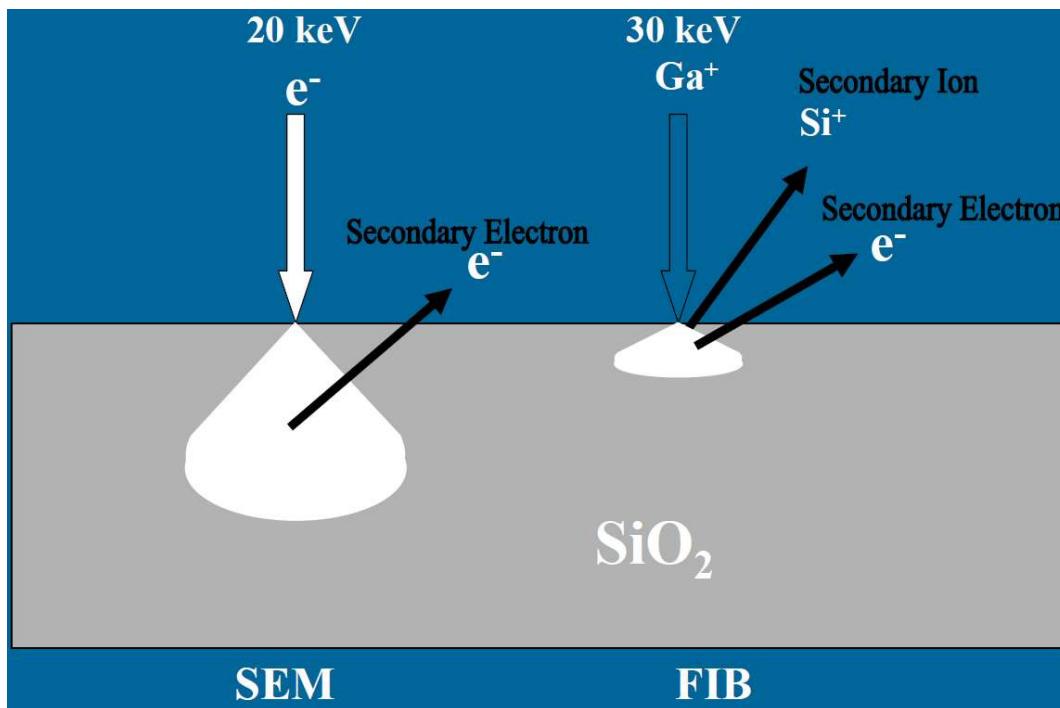
One can start with high energy that mills faster, then reduce energy near the end for thinner damage layer.

Focused ion beam (FIB)

1. Overview.
2. Ion source and optics.
3. Ion-solid interaction, damage.
4. Scanning ion beam **imaging**.

Ion beam imaging

- FIB imaging is destructive, yet may be used to remove (insulating) oxide layer.
- Secondary electron and secondary ion images.
- Ion channeling contrast for grain size measurements.
- Material contrast - local compositional differences.
- Voltage contrast - electrical state differences - passive and active voltage contrast.



Scanning ion microscope (SIM)

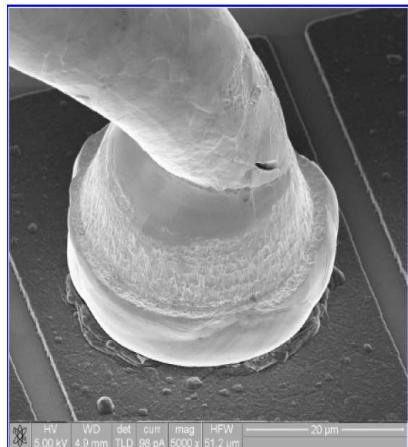
Secondary electron mode

- Detector biased positive
- Emitted from top 5-10nm
- Typically 30kV 40pA for optimal resolution and signal
- Grounded metals very bright, oxides dark

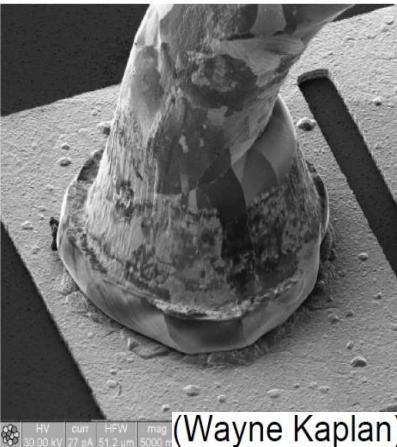
Secondary ion mode

- Detector biased negative
- Emitted from top 0.5-1nm (very surface sensitive)
- Oxides brighter
- Lower secondary ion yield, so images noisier.

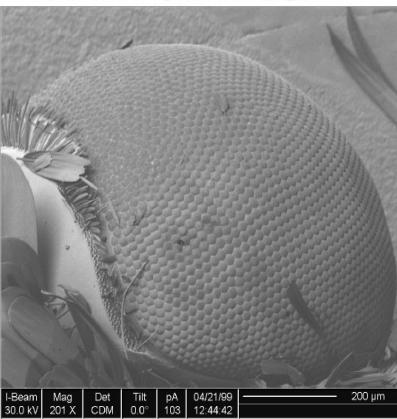
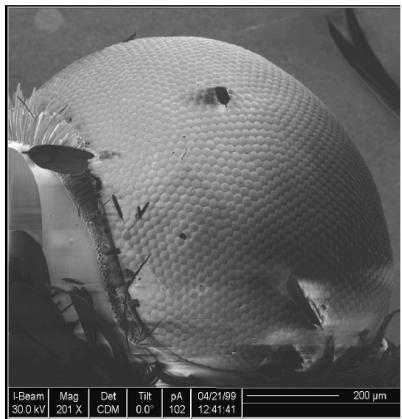
Ion beam imaging



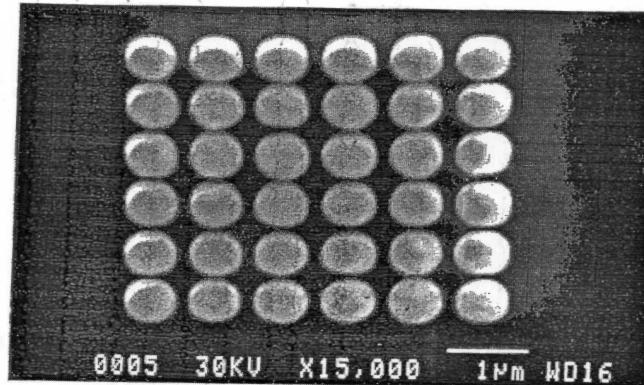
secondary electron image



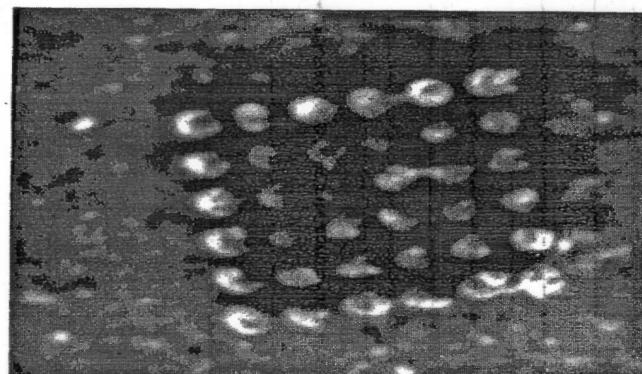
secondary ion image



Before imaging

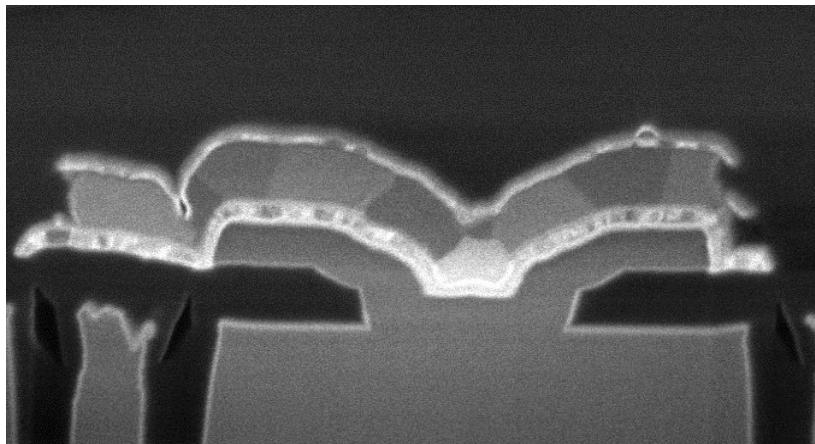


After 1min imaging

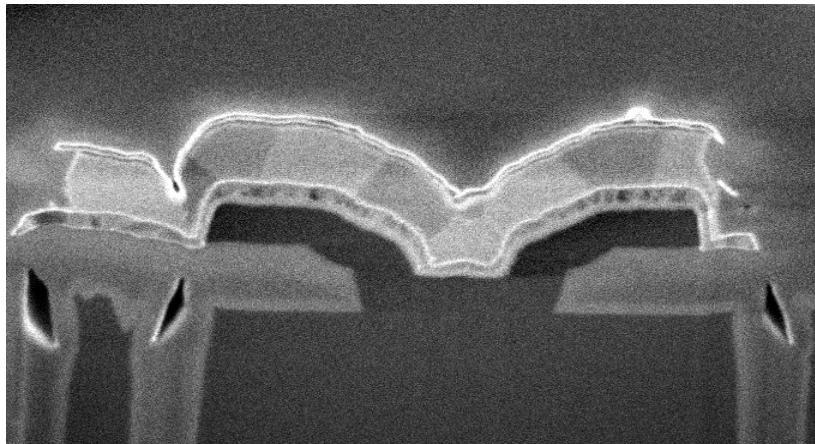


Problem with FIB imaging resolution: if an object is small enough, it will be sputtered away before sufficient signal (secondary electrons) can be collected to resolve it.

Materials contrast



SEM (secondary electron (SE) image)



Scanning ion microscopy (SIM)
Secondary electron (not ion) image

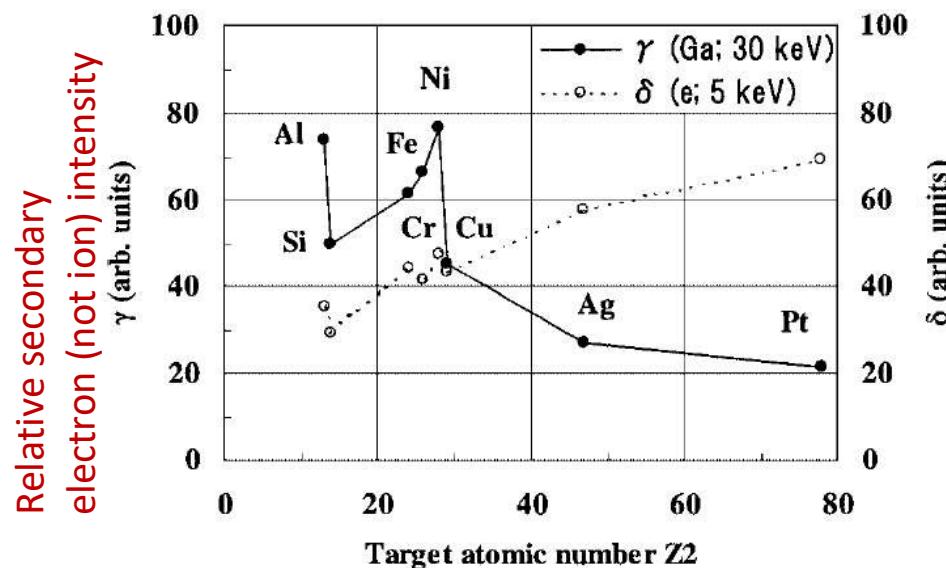
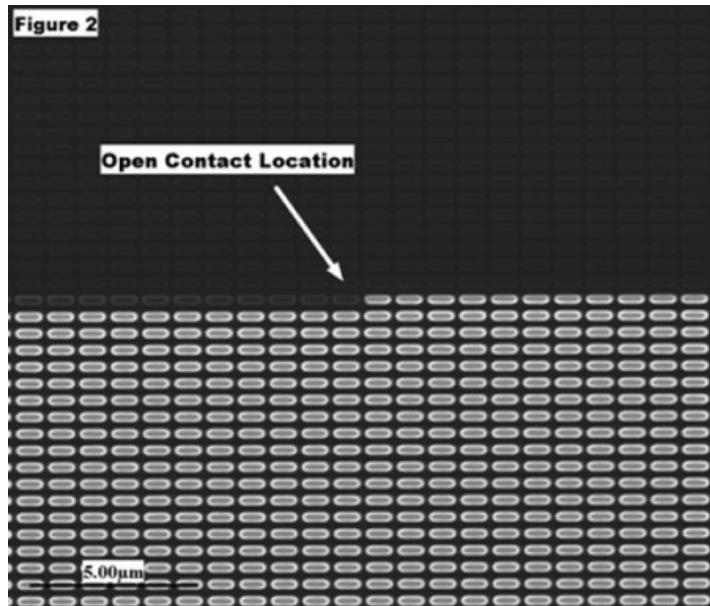
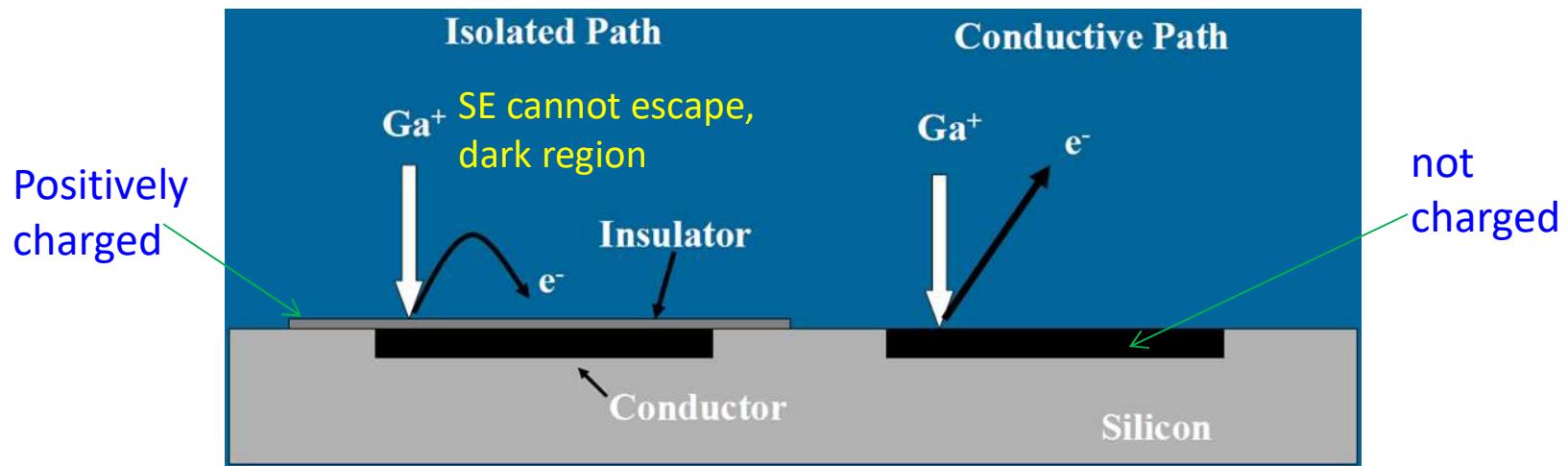


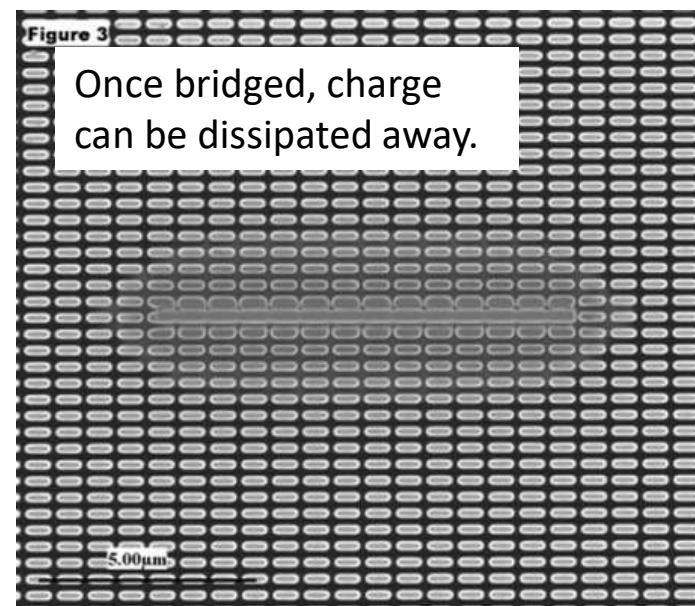
Fig. 1 Relative SE intensities as a function of Z_2 for the Ga-SIM and SEM images.

- SIM image has higher material contrast than SEM image, and with fine structure (peaks and valleys in the curve).
- Unlike SEM, the signal brightness is lower for heavier materials (larger Z).
- For SEM, heavier materials have higher SE yield since there are more electrons for high Z materials.

Passive voltage contrast



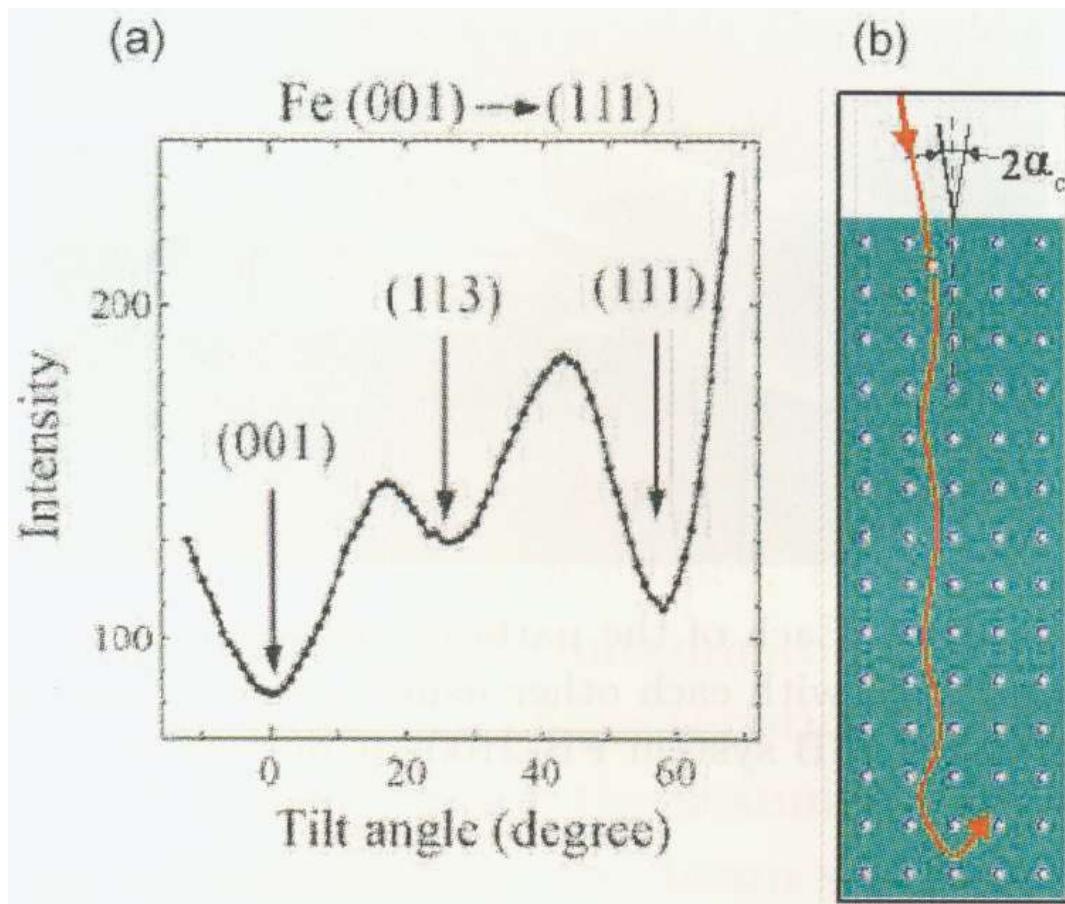
Open contact shown by charging. (top half has same pattern as bottom, but charged, so is dark)



Bridging open contact with metal deposition indicates pattern at top half is also good.

Ion channeling contrast

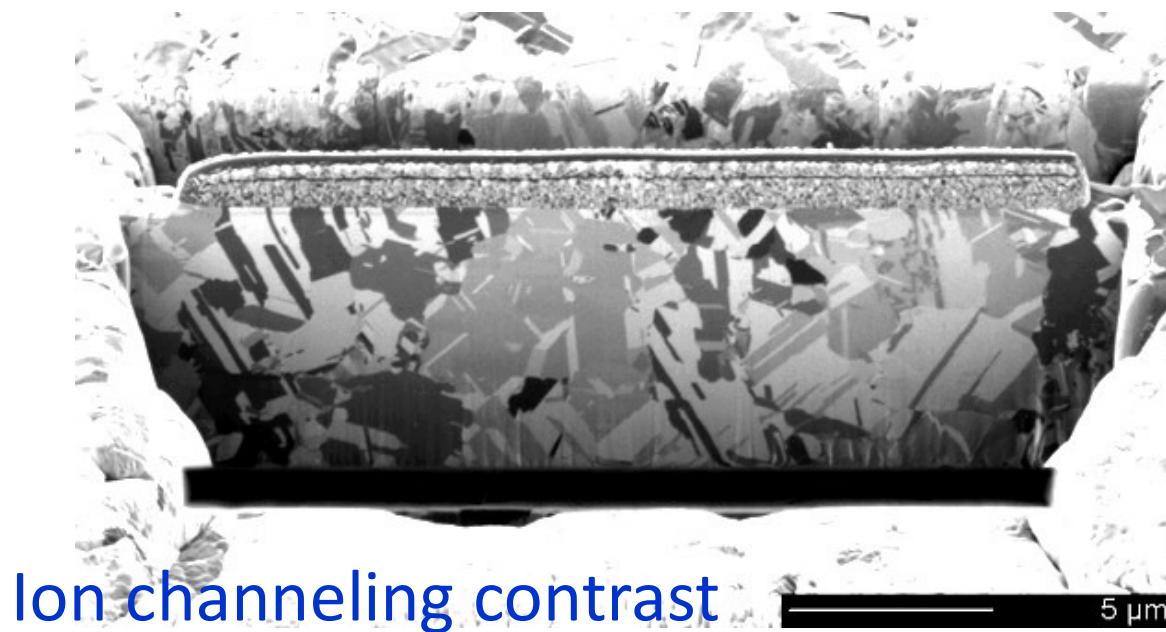
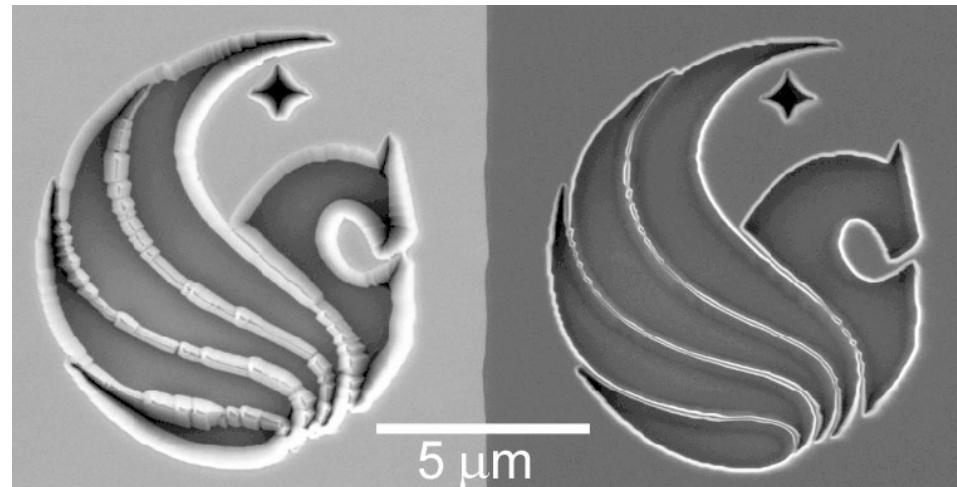
- Ions penetrate deeper in crystalline material for certain grain orientations.
- Those channeled ions have lower sputtering yield (slower milling rate).
- Secondary electron (SE) yields are also lower for areas that channel better.
- Polycrystalline materials have grains with different orientations.
- Grain size can be determined by images at different incidence angles.



Typical SE intensity with respect to tilt angle for Fe single crystal sample under 30keV Ga-FIB bombardment.

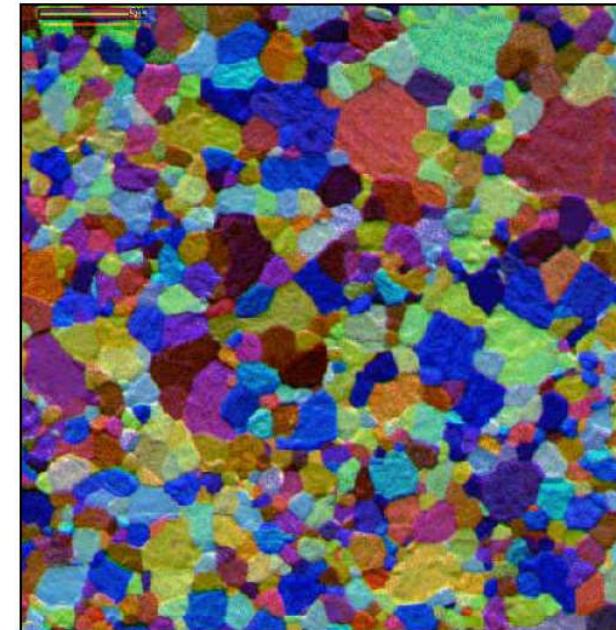
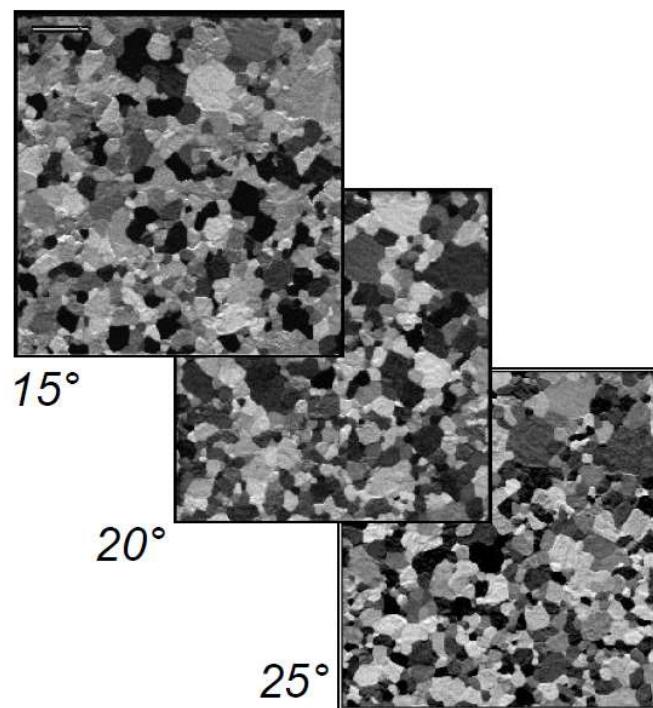
Ion channeling contrast

Left: not aligned with crystal direction
Right: channeled (aligned, darker)

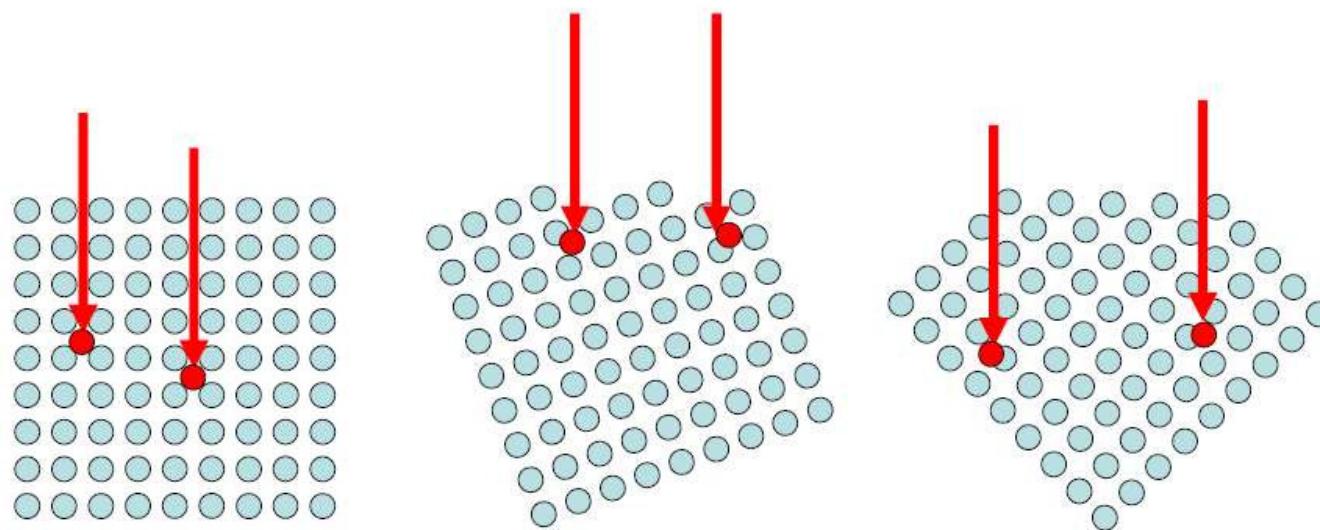


Ion channeling contrast

Channeling contrast for grain size analysis



Color Composite



Focused ion beam (FIB)

1. Overview.
2. Ion source and optics.
3. Ion-solid interaction, damage.
4. Scanning ion beam imaging.
5. FIB lithography using resist.
6. FIB milling, sputtering yield.
7. Redeposition.
8. Single line milling.
9. Other types of FIB lithographies (implantation, intermixing...).
10. Gas-assisted FIB patterning.

Focused ion beam (FIB) lithography overview

FIB lithography resembles e-beam lithography (EBL), but with more capabilities:

- Write pattern in a resist (exposure followed by resist development), like EBL.
- Etch atoms away locally by sputtering, with sub-10nm resolution (subtractive), most popular application of FIB.
- Deposit a material locally, with sub-10nm resolution (additive).
- Ion implantation to create an etching mask for subsequent pattern transfer.

Like EBL, ion-matter interaction can also generate low-energy secondary electrons, which can expose the resist for lithography.

Naturally, in principle all EBL resists can also be used as FIB lithography resist.

Comparison: EBL and FIB lithography (with resist)

- Proximity effect of FIB lithography is negligible, no electron backscattering.
- This means writing pixel size \approx beam spot size, thus short dwell time on each pixel that beam blanker may not follow. (For EBL, pixel size $>>$ beam spot size, exposure between pixels by proximity effect)
- For the same beam spot size, higher resolution than EBL, due to shorter ion range, weaker forward scattering, lower energy of secondary electrons with smaller lateral diffusion.
- Higher resist sensitivity than EBL that increases throughput.

(I think this is because for electron, most energy deposited in substrate since it penetrates so deep; for ion, all energy deposited within the thin penetration depth inside the resist)

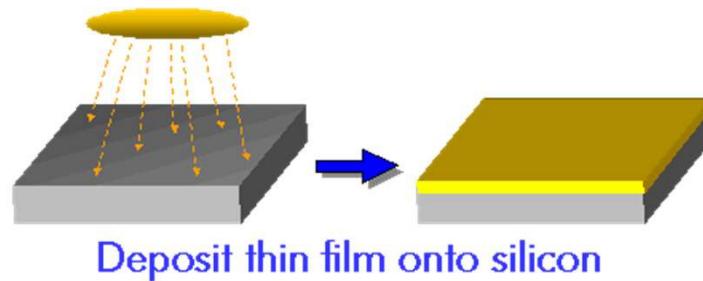
- However, it is more difficult to focus ion beam (chromatic aberration...).
- So one must use low beam current (sub-50pA) for high resolution, which offset its high sensitivity and reduces writing speed. (for electron beam, sub-10nm beam size even for nA current)
- Impurity of source ions within resist is an issue.
- The biggest disadvantage of FIB lithography: limited exposure depth in resist (<100nm for 100keV); thin resist makes following liftoff or etching process difficult.

Focused ion beam (FIB)

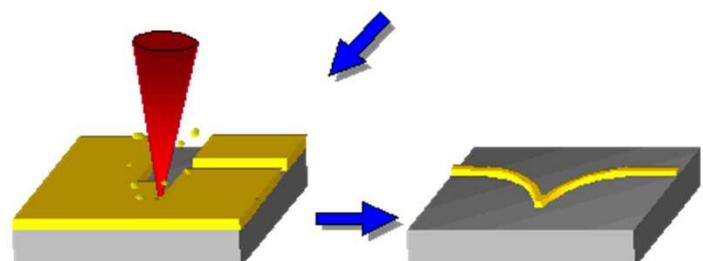
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Sputtering by ion beam

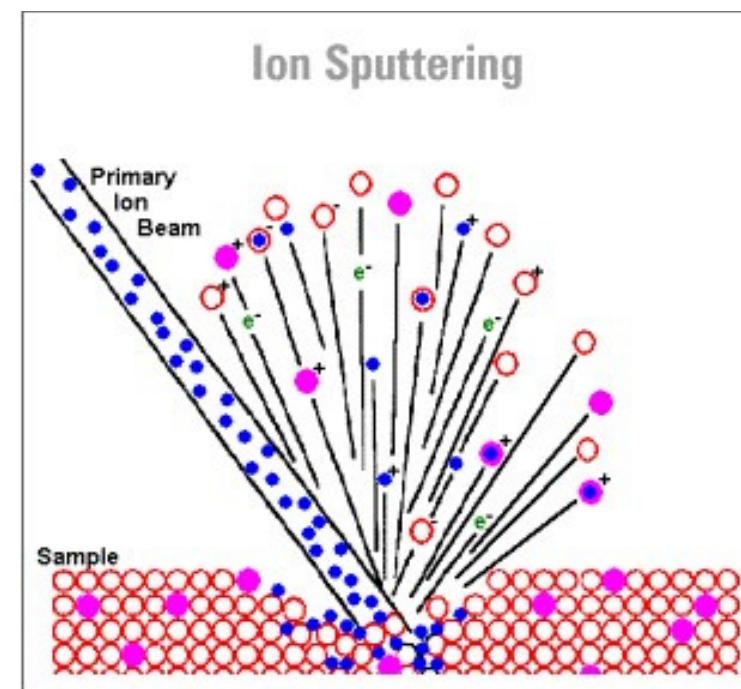
- Sputtering rate depends on ion energy, mass, crystal orientation, substrate nature.
- One Ga ion of energy 30keV sputters a few atoms from Si surface.
- With a 1nA ion beam current, sputtering order of $0.1\mu\text{m}^3/\text{sec}$.
- Optimal ion energy 10-100keV.
- Higher energy leads to more implantation.
- For energy $>1\text{MeV}$, backscattering and nuclear reaction become dominant.



Deposit thin film onto silicon

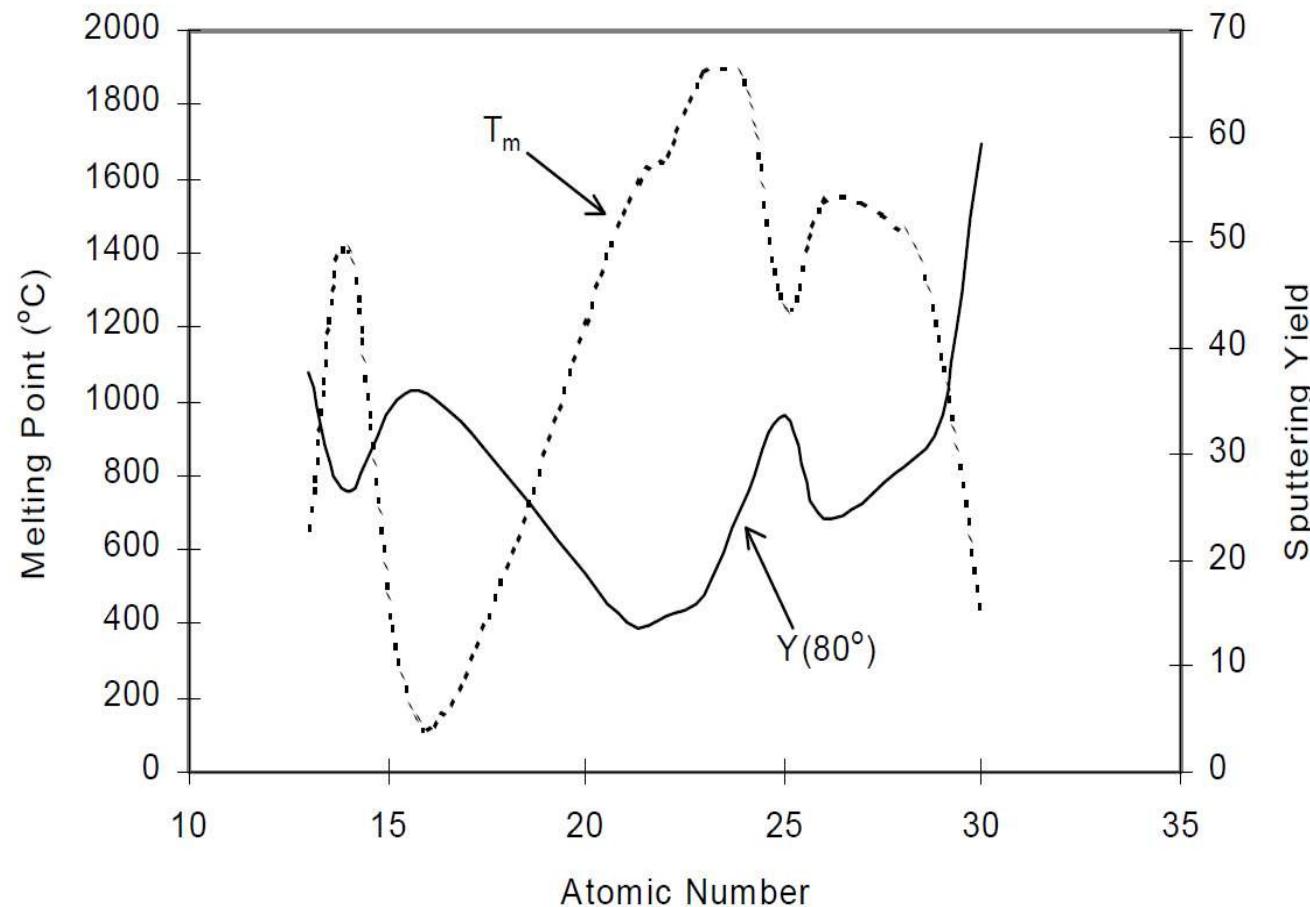


Remove unwanted material using FIB
to leave desired structure



Sputtering yield Y

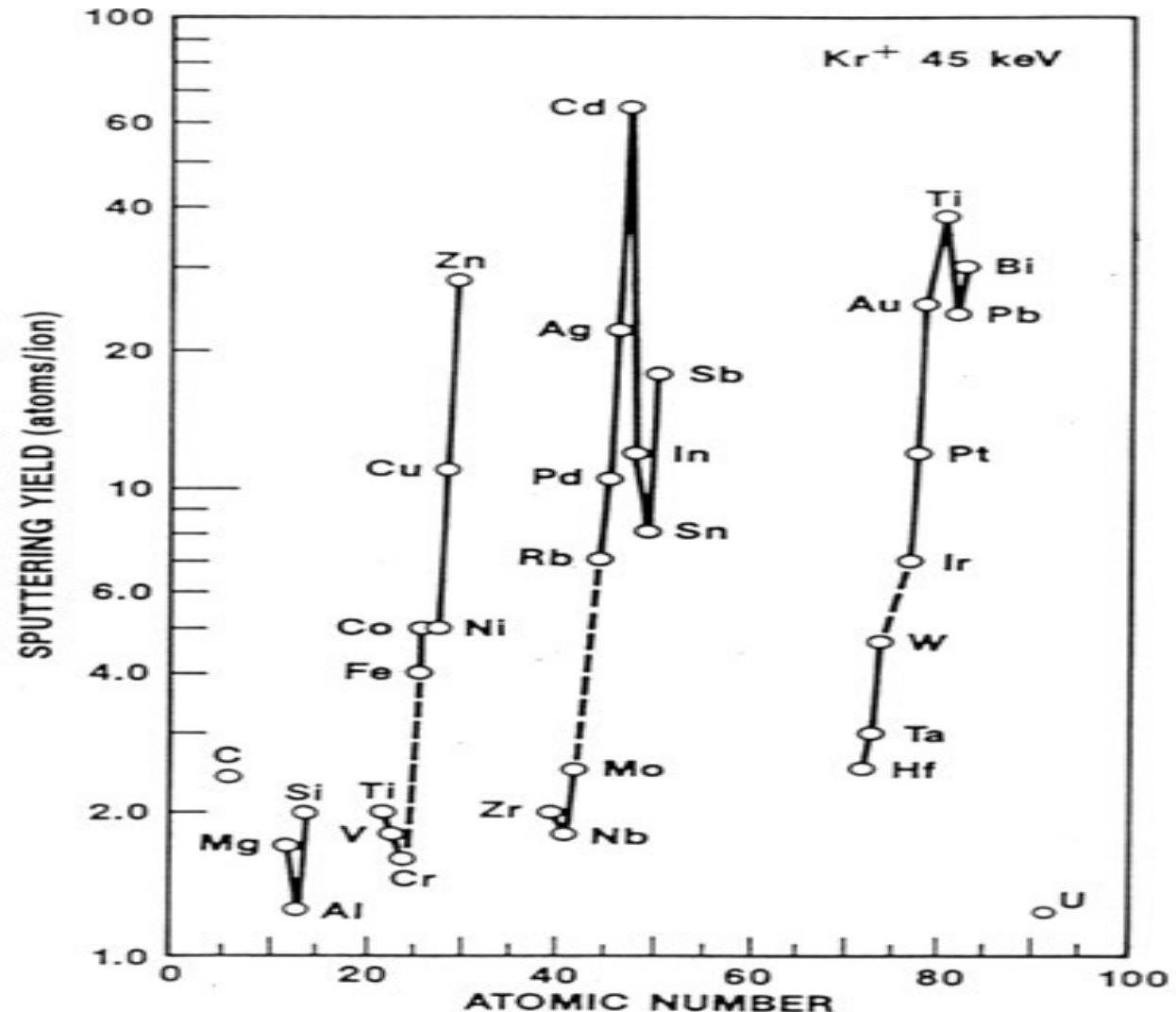
$Y = \text{number of recoiling atoms out of the target surface per incident ion} = 1-50$



Sputtering yield is correlated with melting point.

Sputtering yield of different material

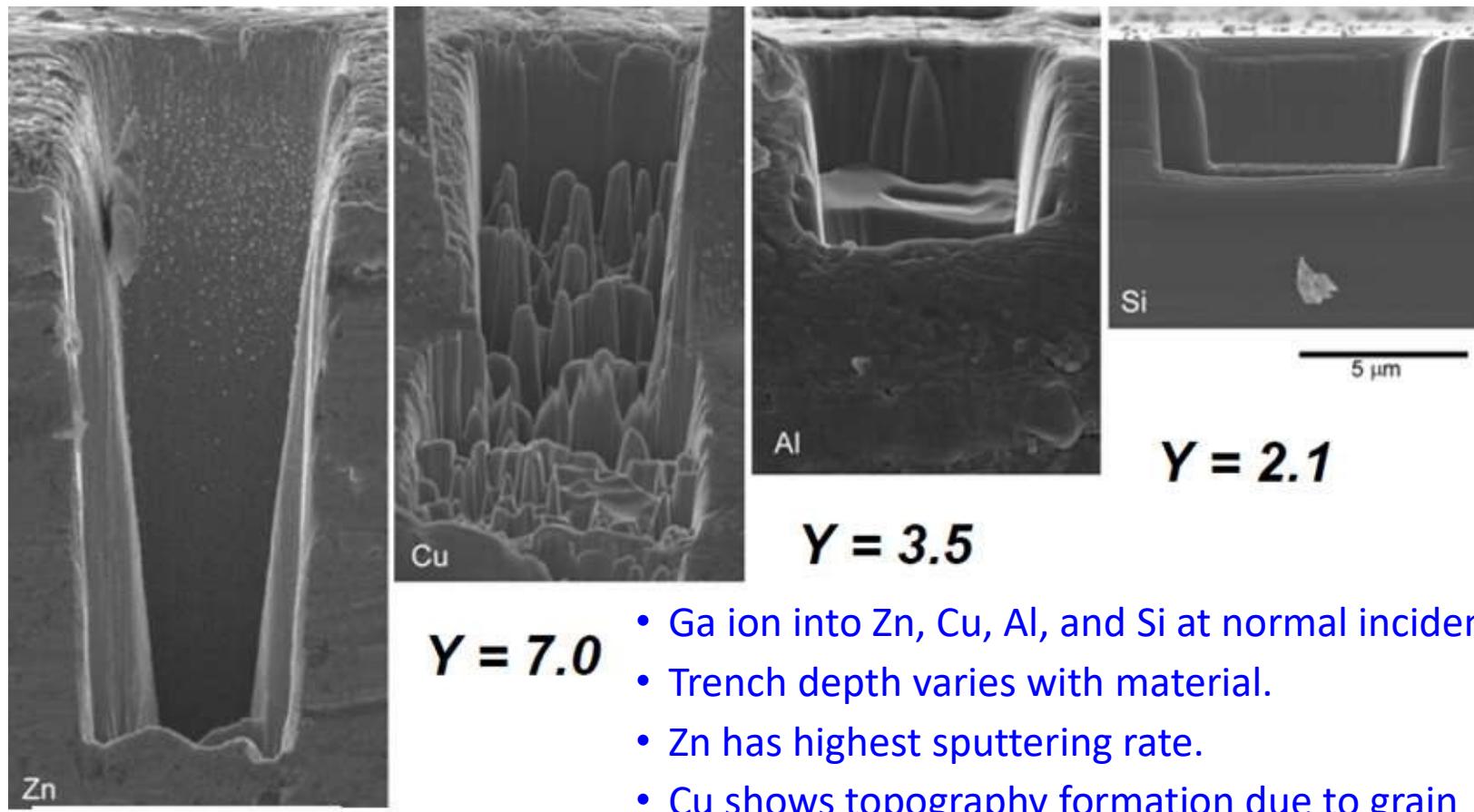
Material	Sputterrate [$\mu\text{m}^3/\text{nC}$]
Si	0.27
Thermal Oxide	0.24
TEOS	0.24
Al	0.3
Al ₂ O ₃	0.08
GaAs	0.61
InP	1.2
Au	1.5
TiN	0.15
Si ₃ N ₄	0.2
C	0.18
Ti	0.37
Cr	0.1
Fe	0.29
Ni	0.14
Cu	0.25
Mo	0.12
Ta	0.32
W	0.12
MgO	0.15
TiO	0.15
Fe ₂ O ₃	0.25
Pt	0.23
PMMA	0.4



- Sputter rate ($\mu\text{m}^3/\text{sec}$) = yield(atoms/ion) \times flux(# of ions/sec)/number density(atoms/ μm^3).
- Actual rate much lower due to re-deposition of sputtered material.

Rate of material removal: constant dose different materials

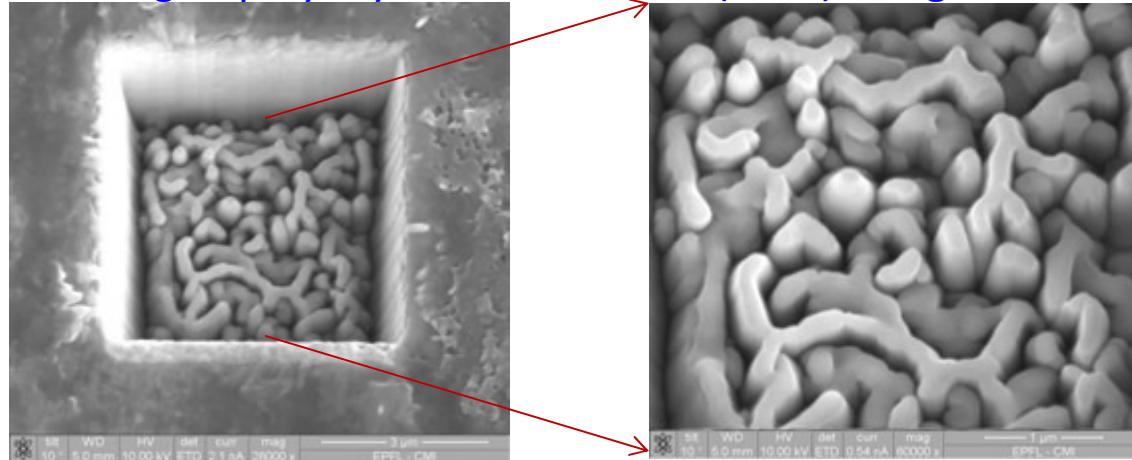
Constant dose of $\sim 7.5 \times 10^{12}$ Ga⁺, delivered with 1nA beam current.



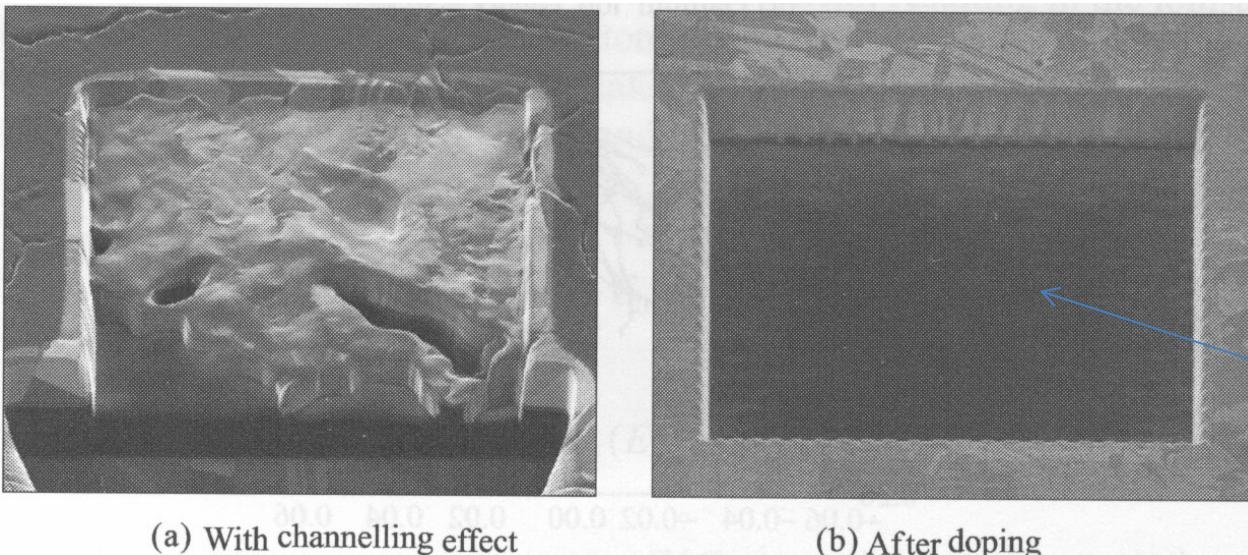
- Ga ion into Zn, Cu, Al, and Si at normal incidence.
- Trench depth varies with material.
- Zn has highest sputtering rate.
- Cu shows topography formation due to grain structure/textured and channeling effect... (topographic effects will grow and exacerbate as FIB milling continues)
- Si has smoothest crater bottom.

Channeling effect when milling crystalline material

Box milling of poly crystalline material (steel), rough surface.

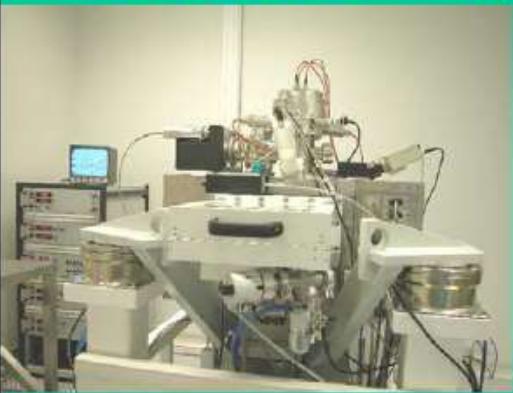


Box milling of poly crystalline Cu.

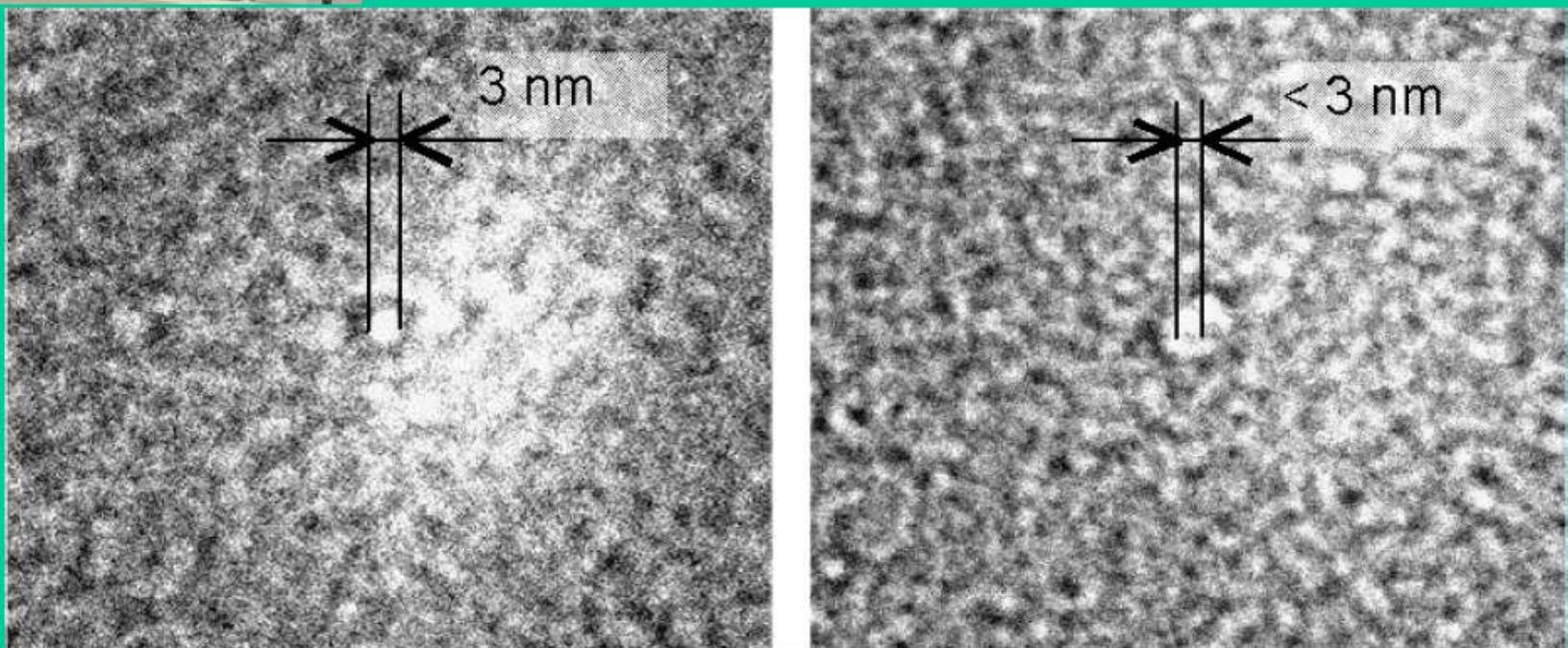
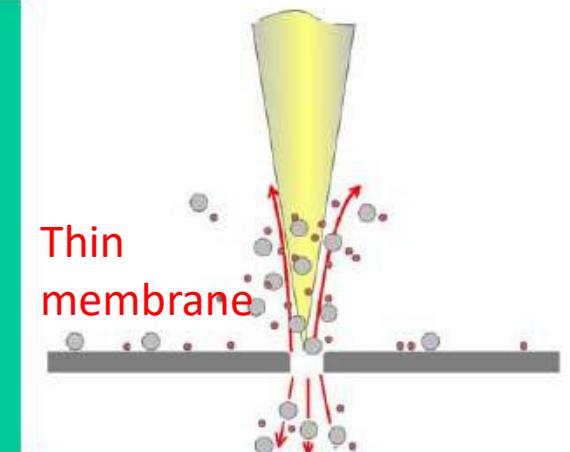


Channeling effect suppressed by doping with impurity atoms that block the ion channels.

State-of-the-art: 3nm!



NanoFIB

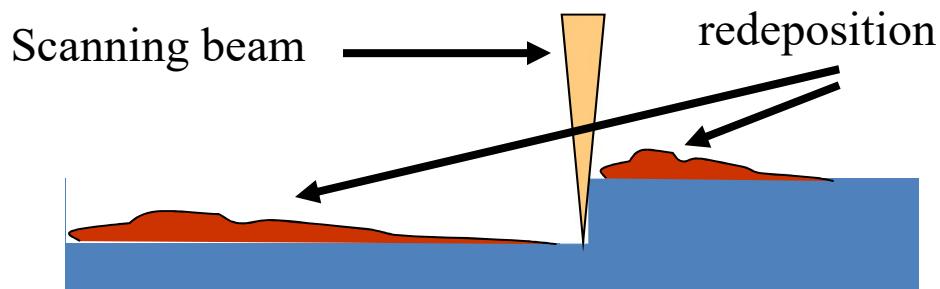


20 nm thick membrane (dose: one spot of 106 ions, Image sizes 50 x 50 nm)

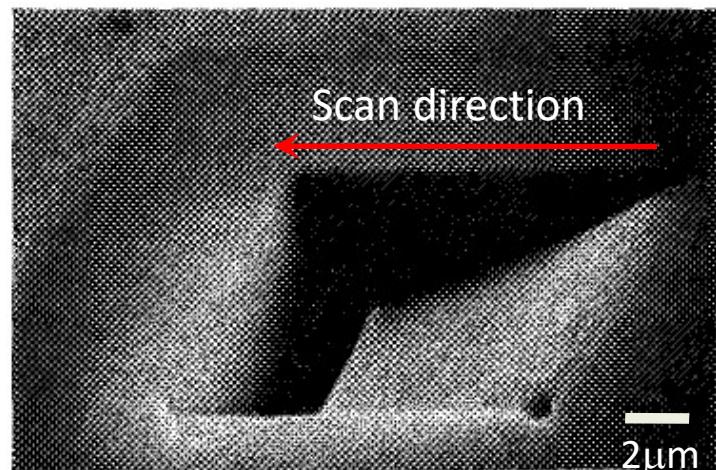
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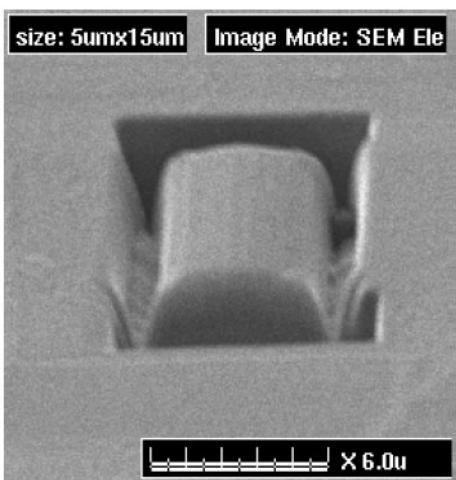
Re-deposition



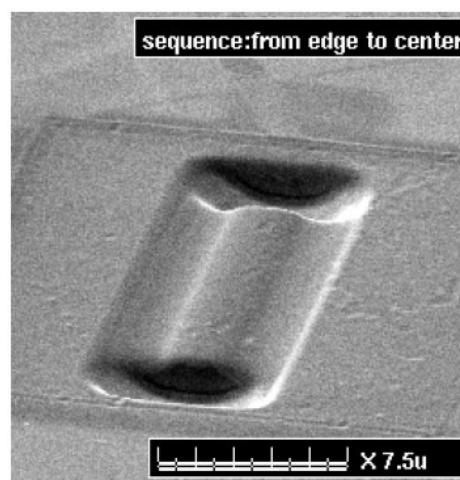
The above figure is wrong!! There will be no re-deposition on the top surface. Re-deposition only happens when the two points can see each other. There is no force to bring the sputtered atoms back (gravity too small, no electrostatic force for neutral atoms).



Si milled by 30keV Ga⁺, slow *single* pass at 2sec per line with 300 scan lines.



Milled from center to edge

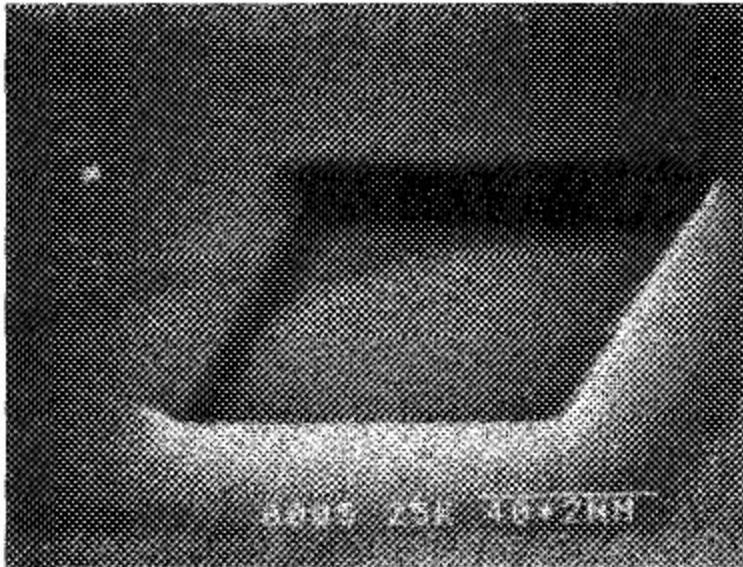


Milled from edge to center

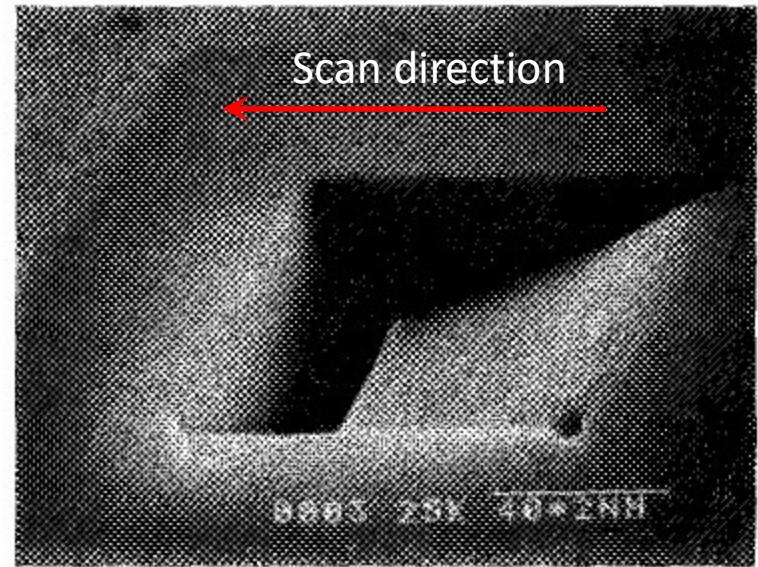
The earlier the region is milled, the more re-deposited material is accumulated there.

How to deal with re-deposition

Si milled by 30keV Ga⁺, total dose 1.9×10^{18} ions/cm².



Fast 200 repetitive passes at 10ms per line with 300 scan lines.



Slow *single* pass at 2sec per line with 300 scan lines.

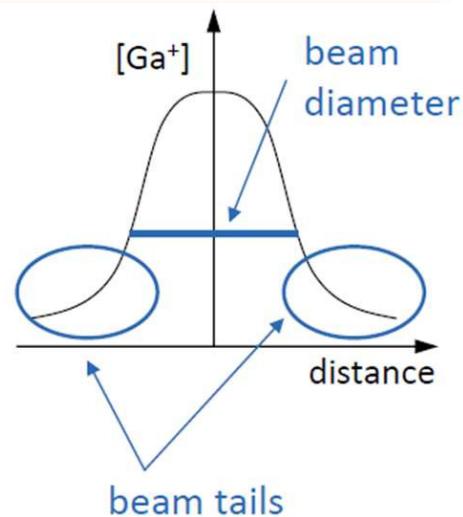
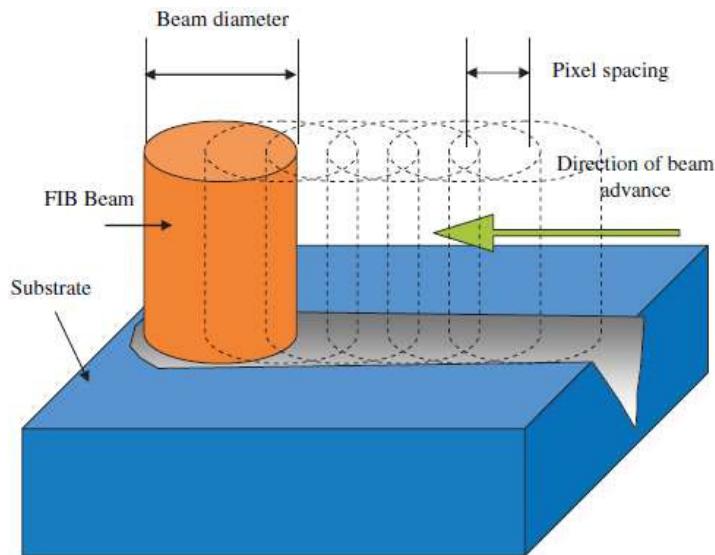
Summary for minimizing re-deposition effect:

- Mill large and less critical pattern first, using high beam current.
- Use multiple passes, not single pass.
- Mill fine and critical pattern last, using low beam current and multiple passes.

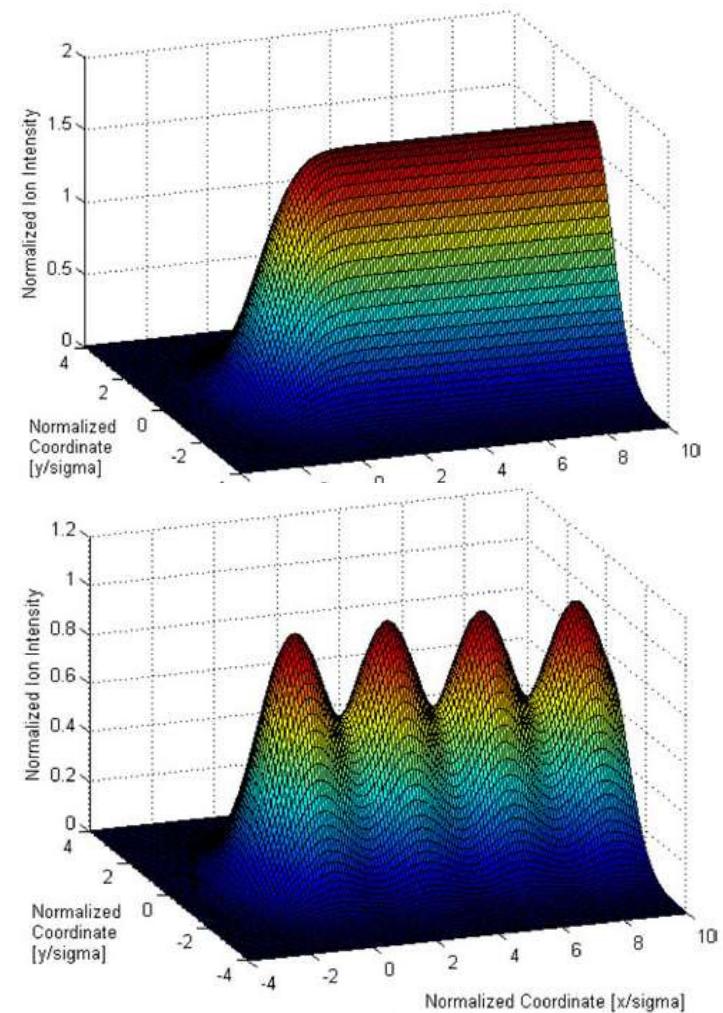
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Pixel size vs. beam size



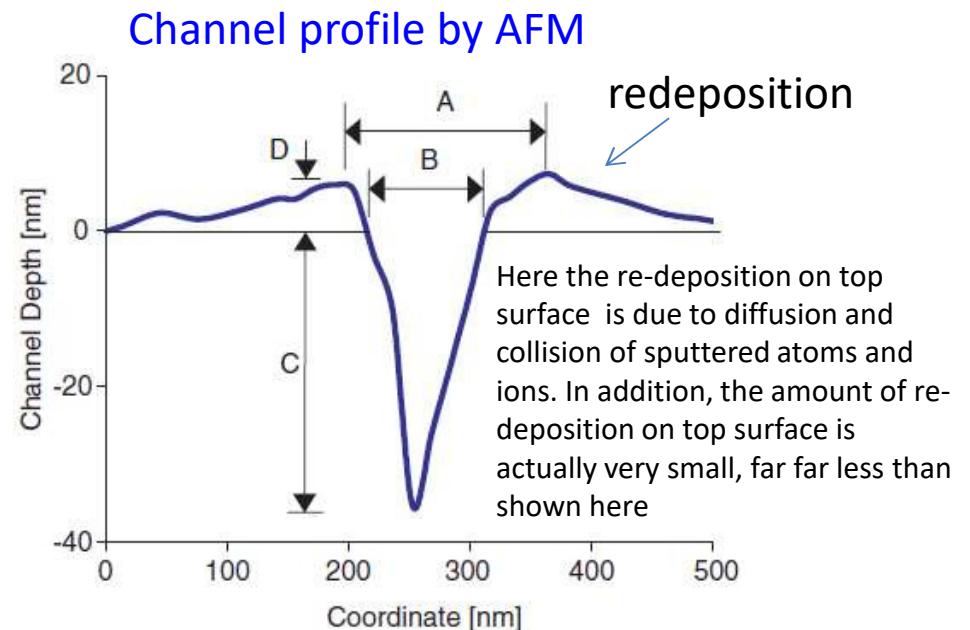
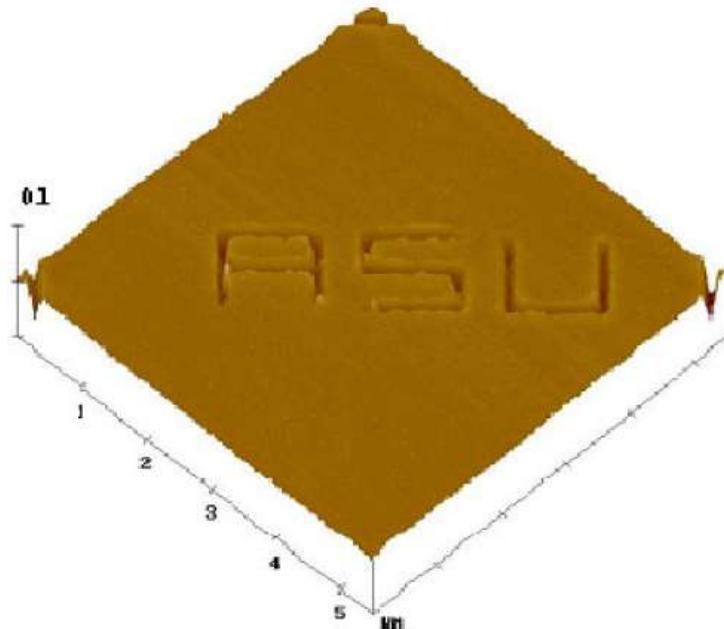
As a rule, for continuous non-wavy milling,
pixel spacing/beam diameter ≤ 1.5



Ion flux distribution along a scan line with
pixel/diameter=1.5 (top), 3.0(bottom)

40

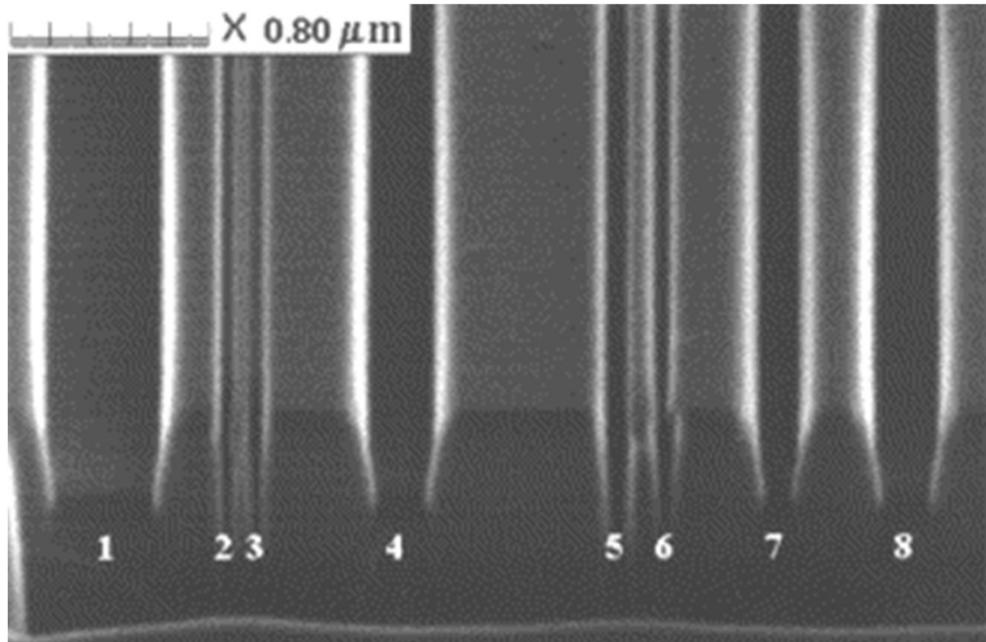
Channel milling using single pass



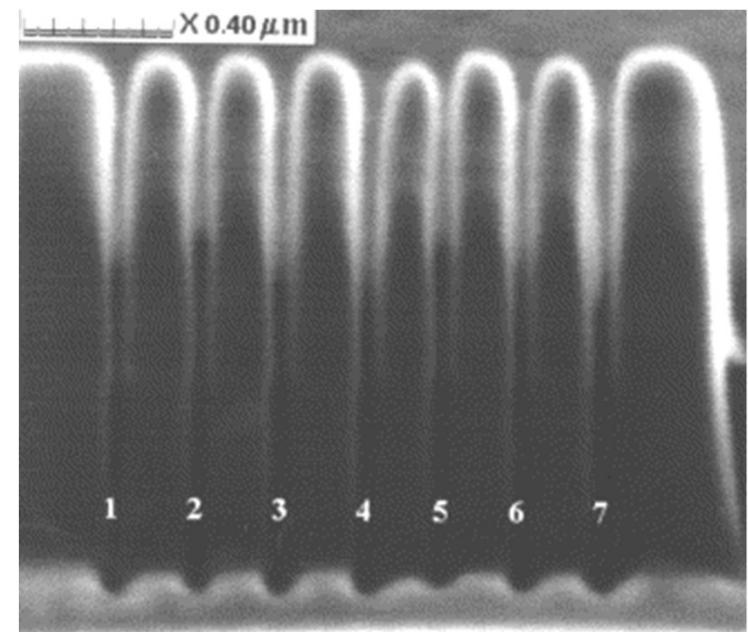
Milled into Au by 90keV As²⁺ FIB with 5ms dwell time. I=5pA, pixel spacing 14.5nm, beam diameter 50nm. Single pass, aspect ratio ~1/3 and is insensitive to dwell time.

- Due to re-deposition, channel depth cannot be calculated simply by sputter yield.
- V-shaped channel profile is the inherent shape obtained by single-pass FIB milling.
- At long dwell time, the mouth width of the channel (B) can be one order larger than beam size, because the “tail” of the beam can mill sizable amount material.

How to mill high aspect ratio narrow trench



FIB milled trenches in Ta-C film using beam current (from left to right) of 32, 3, 3, 32, 7, 7, 32 and 32 pA, respectively.



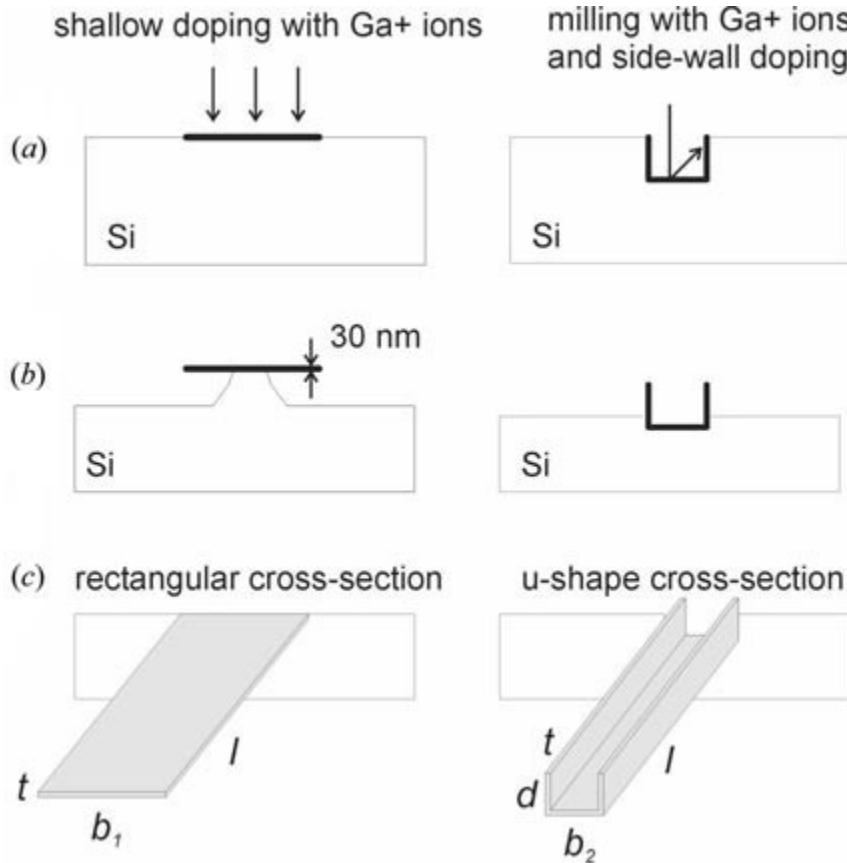
Trenches with width 30–40 nm, aspect ratio up to 25, beam current 1.8-3pA (very low)

For high aspect ratio, use small beam current and large number of repetitive passes.

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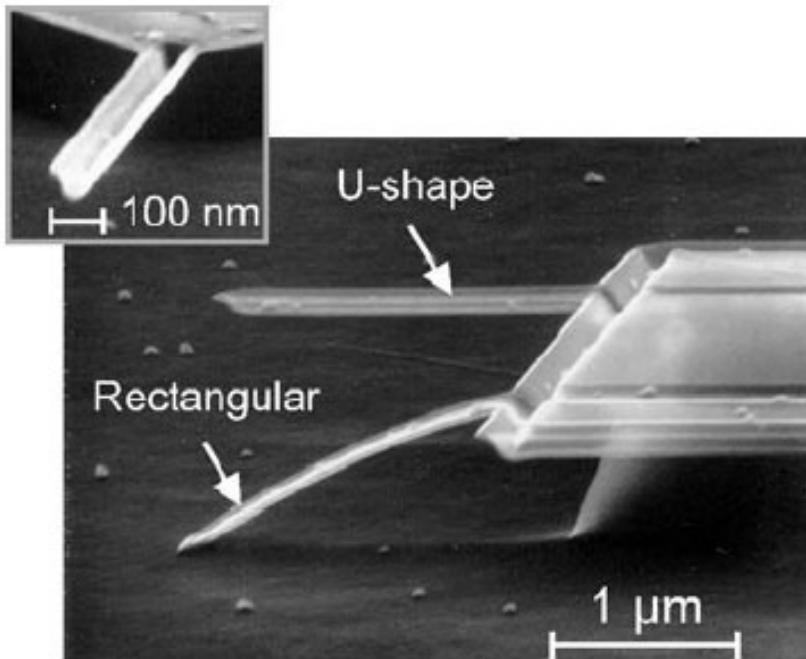
Patterning etching mask by ion implantation



Fabrication of cantilevers by shallow doping (left-hand side) and milling and sidewall doping (right-hand side): (a) FIB exposure (milling and/or implantation), (b) during KOH etching and (c) after etching is completed.

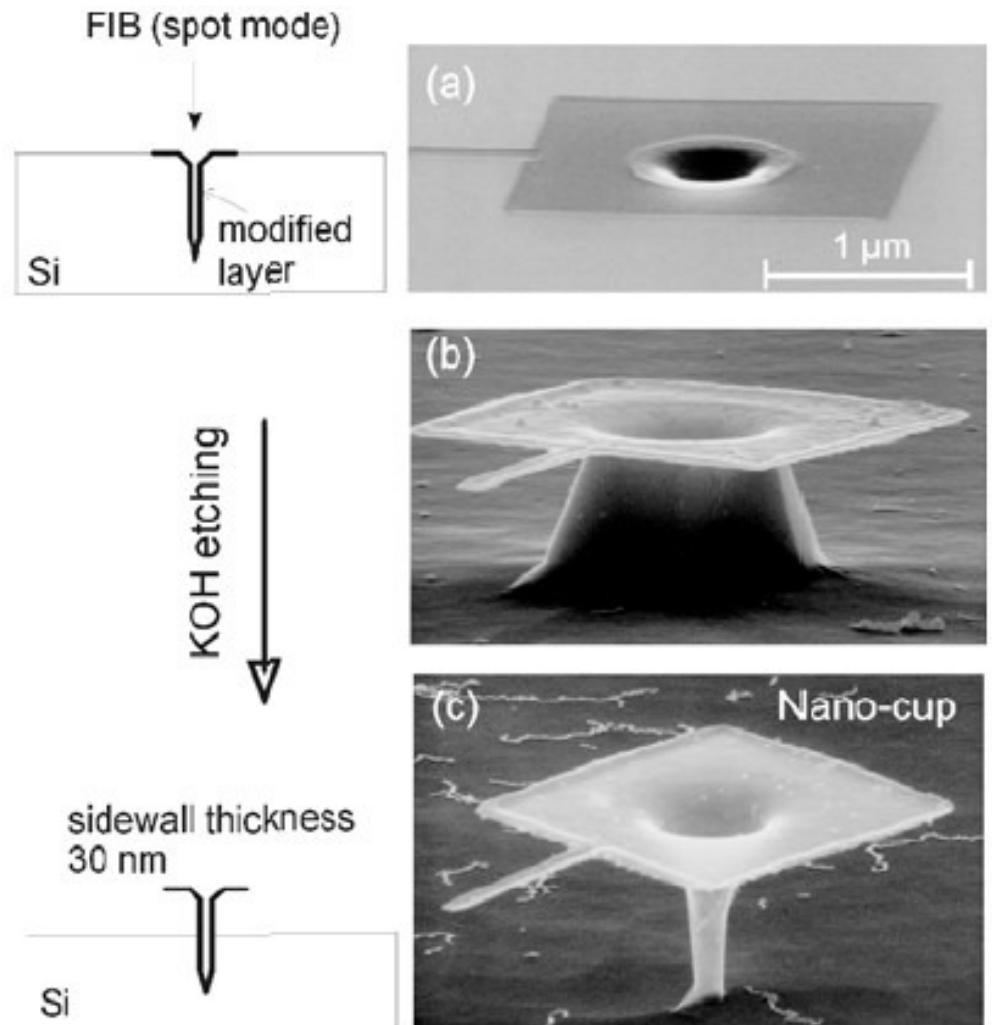
- High concentration p^+ doping in Si drastically reduces the etch rate by KOH.
- The implantation depth is roughly 1nm/keV (e.g. 30nm for 30keV Ga^+ ion).
- The critical dose for the etch mask to be effective is $\sim 1 \times 10^{15} \text{ ions/cm}^2$ ($= 160 \mu\text{C/cm}^2 = 10 \text{ ions/nm}^2$).
- The implanted region is completely amorphous (amorphization dose is $1 \times 10^{14} \text{ ions/cm}^2$).
- At higher doses such as $1 \times 10^{16} \text{ ions/cm}^2$, sputtering (milling) of sample surface becomes significant.

FIB implantation and pattern transfer: results



SEM photomicrographs of cantilevers
(2 μm long, 100 nm wide and 30 nm thick).

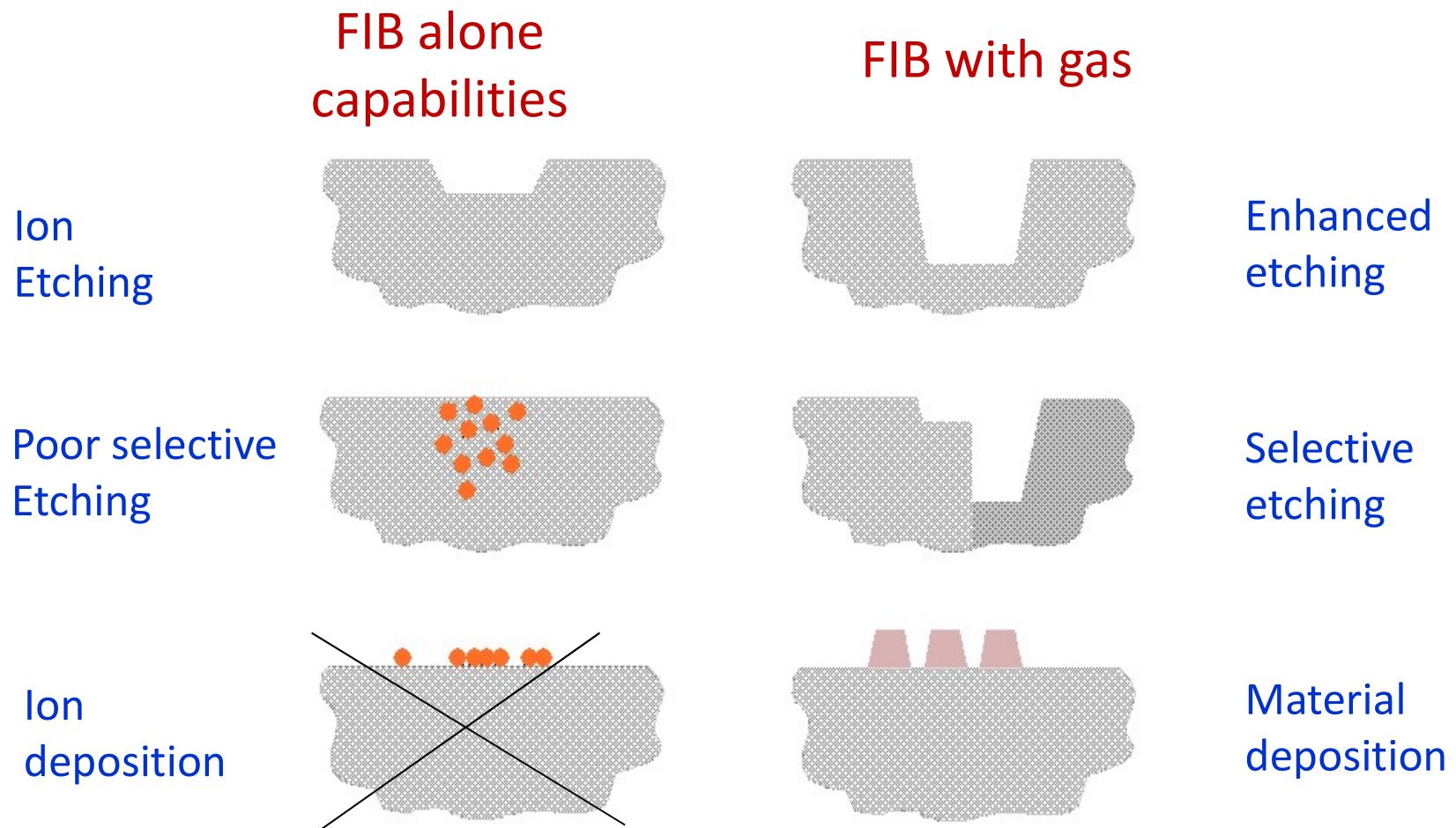
Nano-cup by extending vertical FIB milling to several μm .



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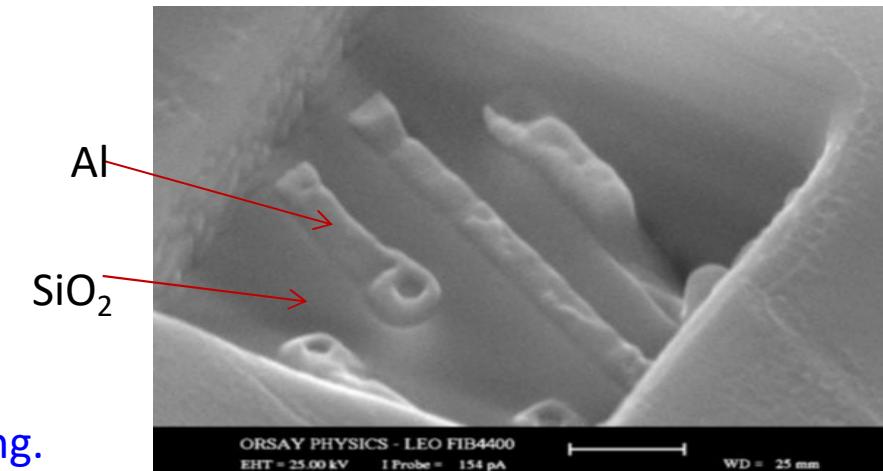
Gas-assisted FIB lithography



Gas-enhanced FIB milling (etching)

- Redeposition is prevented by chemical reaction with the adsorbed gas - formation of volatile species.
- Etching gases that react only with certain species - selective milling
- Examples of etching gases
 - XeF₂ enhances Si and SiO₂ milling.
 - Cl₂, Br₂, I₂ enhances metal milling.
 - H₂O enhances carbon (polymers, ...) milling.

Selective etching



Sputtering yield enhancement factors

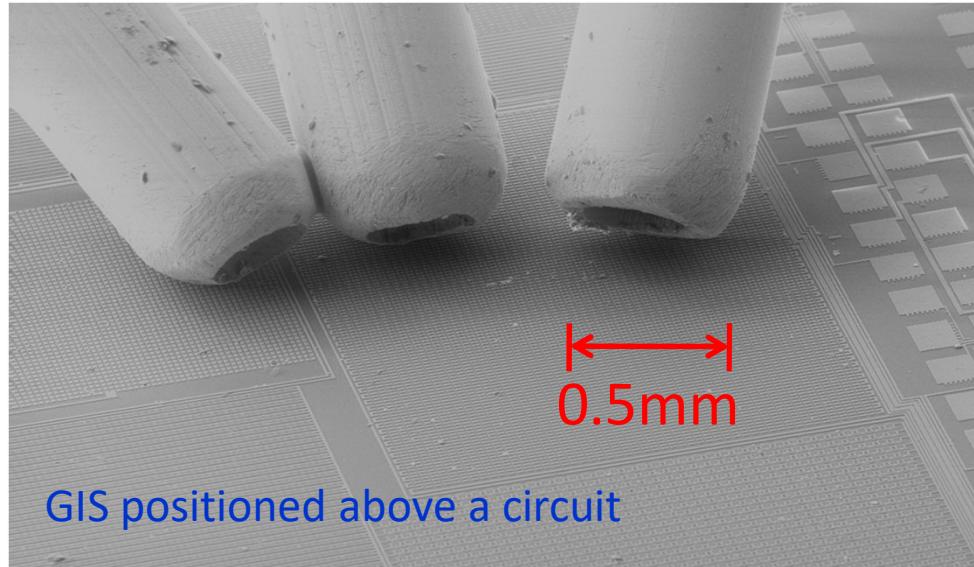
gases	Al	Si	SiO ₂	W
Br ₂	8 ~ 16	5 ~ 6	0	0
Cl ₂	7 ~ 10	0	0	0
XeF ₂	0	7 ~ 12	7 ~ 10	7 ~ 10

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11. Focused ion beam induced deposition.
12. Focused electron beam induced deposition.
13. Deposition rate (electron and gas flux-limited regimes)
14. Deposit composition (carbon/metal)

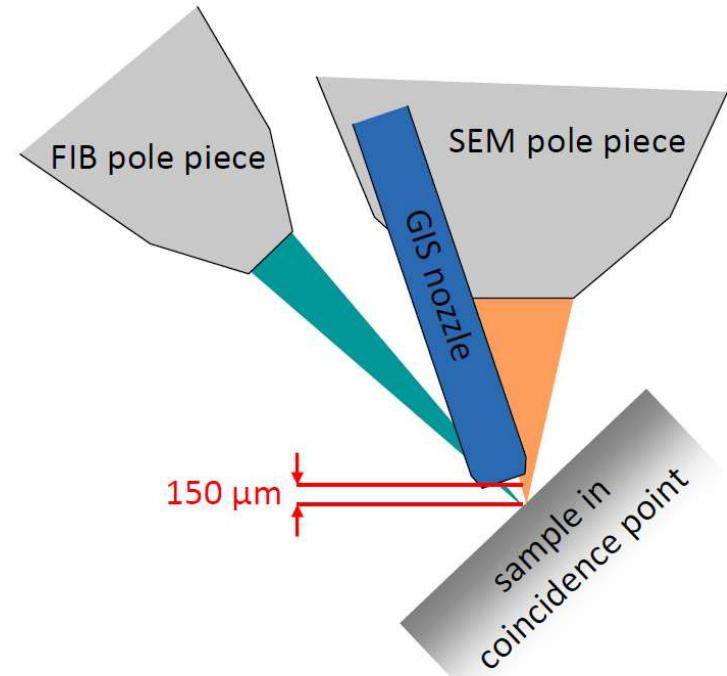
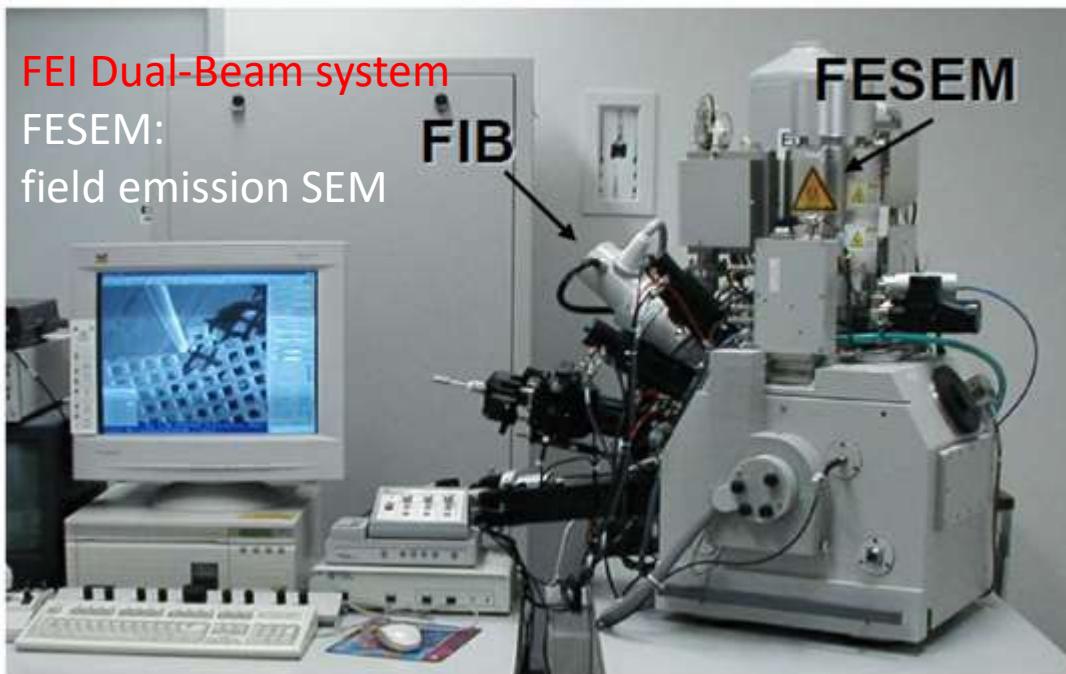
FIB deposition or etching using precursor or reactive gas

GIS: Gas Injection Systems



- Gases are delivered to the sample surface via a needle in close proximity to the surface ($\sim 50\text{-}150\mu\text{m}$).
- Gas pressure is of order 10^{-5} mbar.
- Interaction of ion beam with gas causes either enhanced removal of sample material, or deposition of one of the elements within the gases.
- A metal-organic gas is used to deposit metals via ion/electron beam assisted chemical vapor deposition.
- An insulator can also be deposited, e.g. SiO_2 from tetra ethyl orthosilicate (TEOS).
- Reactive gases are used to enhance sample etching.

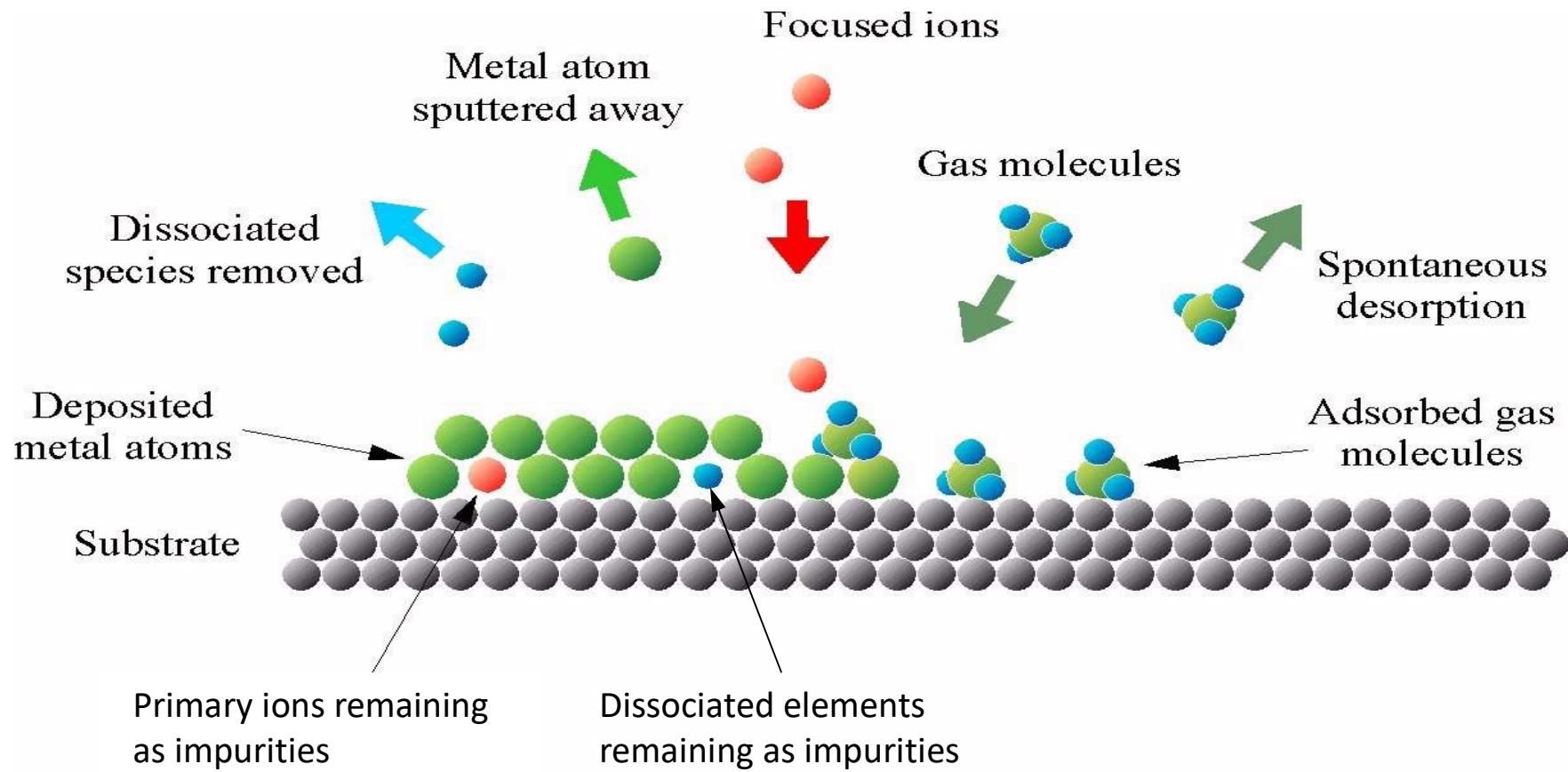
DualBeam FIB/SEM plus GIS



GIS: Gas Injection Systems



FIB assisted (chemical vapor) deposition process



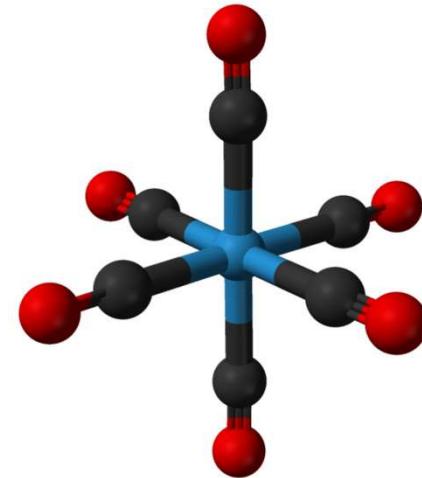
1. Adsorption of gas molecules on substrate
2. Dissociation/decomposition of gas molecules by the ion beam
3. Deposition of the material atoms and removal of the organic ligands

Gases used for metal, oxide and C deposition

Gas	Yield (atoms/ion)	Composition (M : C : Ga)	Resistivity ($\mu\Omega\text{cm}$)
$\text{W}(\text{CO})_6$	2	75:10:10	150-225
$\text{Mo}(\text{CO})_6$	2-3	67:19:12	200
$(\text{CH}_3)_3\text{NAlH}_3$	≈ 5		900
$\text{C}_9\text{H}_{17}\text{Pt}$	2.5 -35	45:24:28	70-700
$\text{Au}(\text{hfac})(\text{CH}_3)_2$	3-8	50:35:15	500
$\text{Cu}(\text{hfac}) \text{ TMVS}$	10-30		100 (*5)

hfac – hexafluoro acetyl acetanoate

TMVS – trimethyl vinyl silane



More deposition materials:

- Al: Trimethylamine alane (TMAA, $(\text{CH}_3)_3\text{N}\cdot\text{AlH}_3$), 1Torr vapor pressure at 25°C)
- SiO_2 : O_2 and tetra meth oxysilane (TMOS) $\text{Si}(\text{OCH}_3)_4$. (TEOS is also fine, here E=ethyl)
- C: phenanthrene, and many other hydrocarbon gases.



The precursor gas are usually quite expensive, but we need them as otherwise the elemental metal is not volatile.

Ion beam assisted deposition

Properties:

- Resistivity much higher than bulk value ($10\text{-}5000\times$)
- Carbon contamination
- Gallium contamination
- Chemistry not well understood

Collision cascade model – Au deposition

- In principle, decomposition of precursor gas may take place either in the gas phase or on the surface; but actually deposition rate insensitive to gas pressure, so **gas phase decomposition is unimportant**.
- Deposition goes beyond beam spot size with yield higher than would be by only direct ion-molecule collision.
- Yield better correlated with energy loss to the nuclei than with energy loss to the electrons.
- Therefore, collision cascade has to play an important role in the decomposition.
- In the case of gold, for energy $E > 0.95\text{eV}$ (dissociation energy of the adsorbate), deposition will occur. Sputtering (of excited surface atoms) will occur for $E > 3.8\text{eV}$.

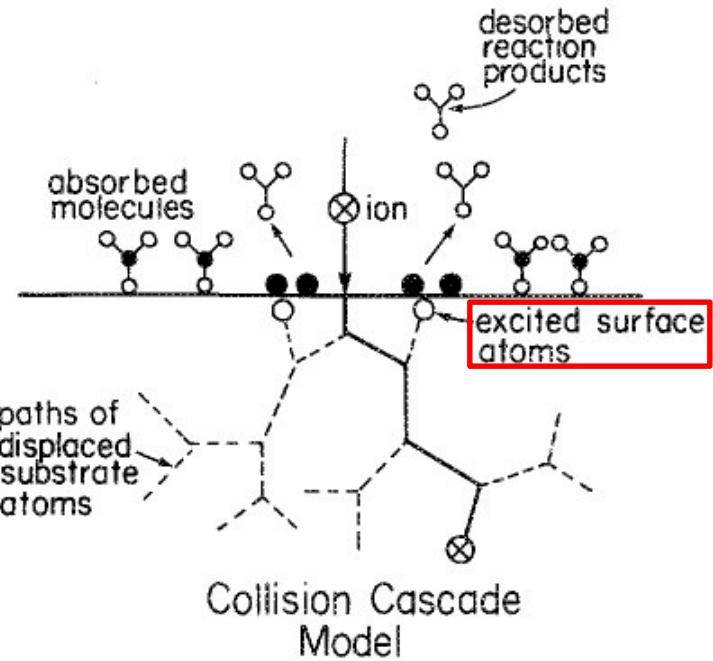


FIG. 4. Schematic of the collision cascade process of surface adsorbate decomposition.

The nuclei of the substrate material gains energy from incident ions and becomes “excited”, which causes the gas molecule near it to decompose.

Effect of ion species and energy on yield and purity

TABLE I. Effect of ion species and energies on the decomposition yield and film purity. Decomposition yield was calculated by summing a measured net deposition yield and a measured sputtering yield. Films were deposited at 1.0 mTorr and room temperature. For comparison the measured sputter yield of pure gold is also included in parentheses.

Ion	Energy (keV)	J current density ($\mu\text{A}/\text{cm}^2$)	Purity (%Au)	Y_N (Au atoms per ion)	Y_S (Au atoms per ion)	Measured yield	
						of pure Au) Y_S (Pure Au)	Y_D (au atoms per ion)
Ne	50	2.6	40%	2.3	1.7	(4)	4.0
	100	4.2		2.2	1.2	(3.5)	3.4
Ar	50	3.4	45%	5.5	3.1	(8.8)	8.6
	100	5.0		4.7	4.2	(9.2)	8.9
Kr	50	3.0	80%	6.2	18.0	(29)	24.2
	100	5.5		7.0	18.7	(35)	25.7
Xe	50	3.6	80%	7.7	19.6	(45)	27.3
	100	5.4		10.6	21.3	(52)	31.9

$$Y_N = Y_D - Y_S$$

Y_N =net deposition, Y_D =deposition, Y_S =sputtering

Heavier ion, higher yield.
Lighter ion, poorer purity, would be
worse for e-beam induced deposition.

Deposition parameters

Dwell time: residence time at one point, desire one monolayer deposition per dwell time. About $0.4\mu\text{s}$ for C; $0.2\mu\text{s}$ for Pt, depends on beam current.

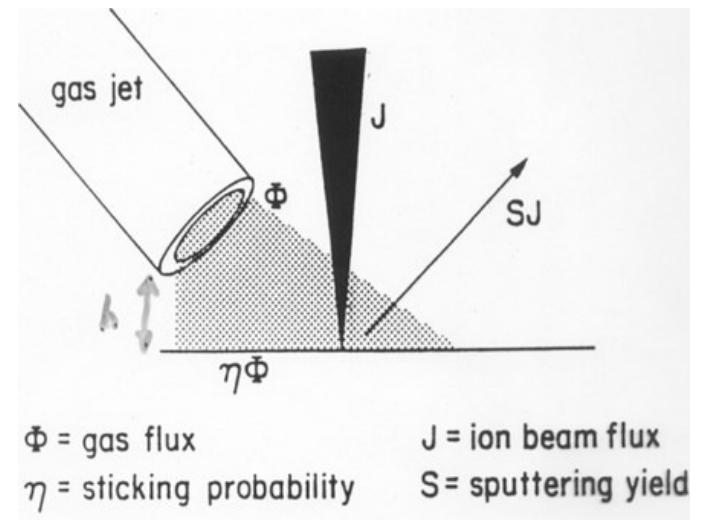
Refresh time: time between successive dwells at same point

Overlap: amount two consecutive points overlap to obtain uniform deposition.
typical 25% (positive overlap) to -100% (negative overlap)

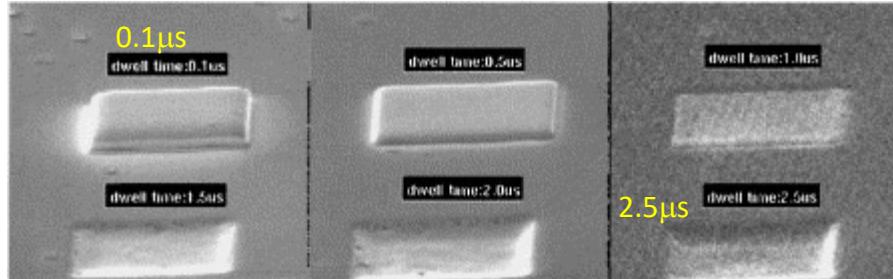
This is different from electron beam lithography, for which the beam stays at one point until this point received desired exposure does, then it moves to the next point. The beam never goes back to the same point again.

Here the beam stays at one point, then move to next point,... finally move back to the first point and start over again. However, this is not necessary if ion beam current is so low relative to the rate of mono-layer precursor gas formation.

Competition between deposition and sputtering



Net deposition



Net milling

Fig. 3. Deposited tungsten by FIB with different dwell times from 0.1 to 2.5 μ s, and the **same** ion dose 6nC/ μ m 2 , refresh time 1000 μ s, X and Y step size 71nm and 68nm, beam spot size 25nm.

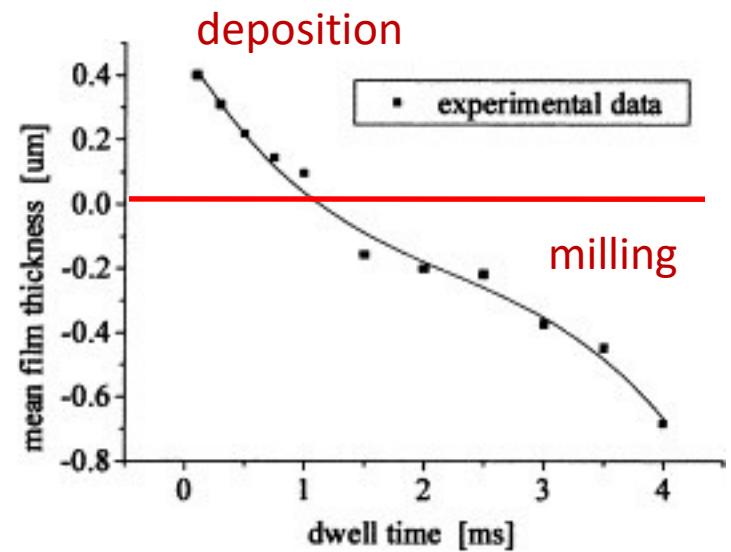
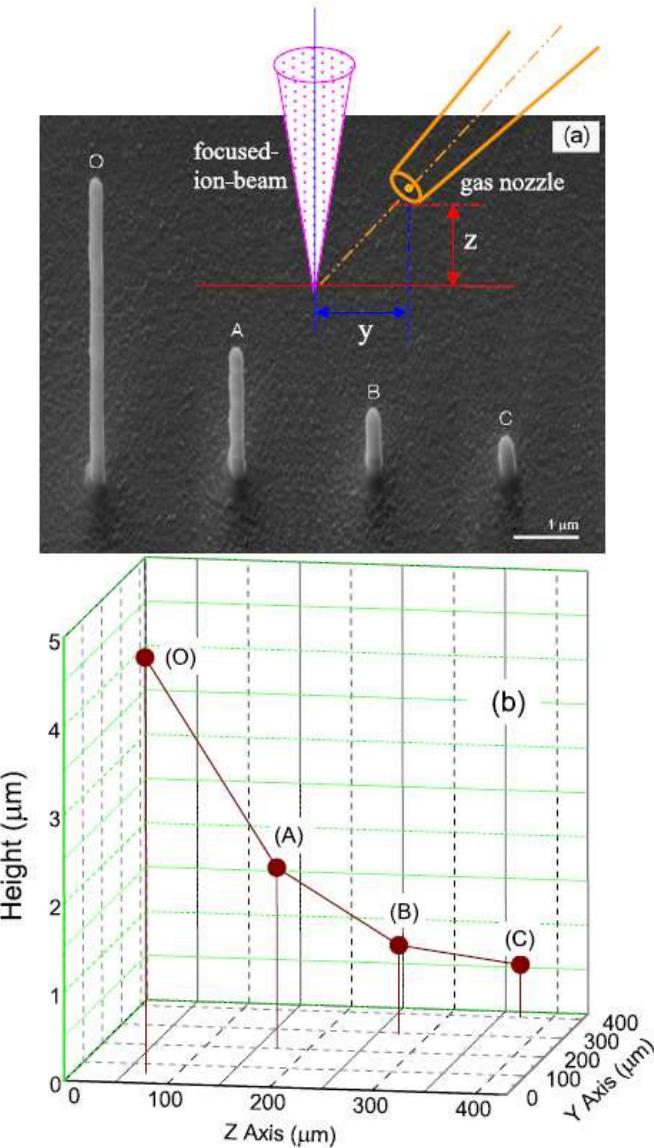


Fig. 4. Mean film thickness vs Dwell time under ion dose 3nC/ μ m 2 , spot size 25nm, current 207pA.
(Dwell time is μ s, NOT ms)

Deposition limited by gas diffusion and adsorption



Effect of the gas precursor nozzle position on nano-rod growth. Limited by diffusion.

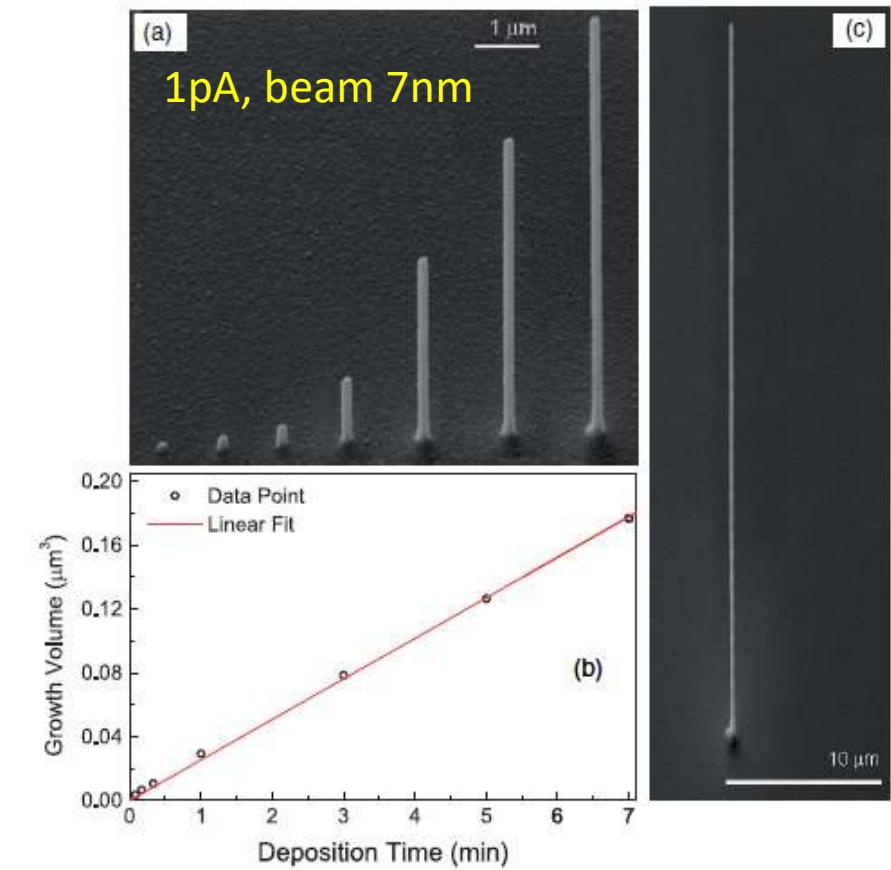
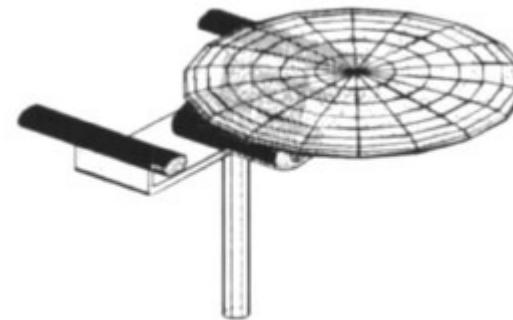
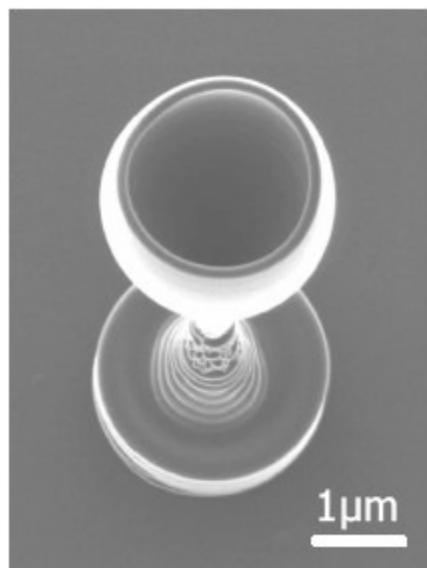
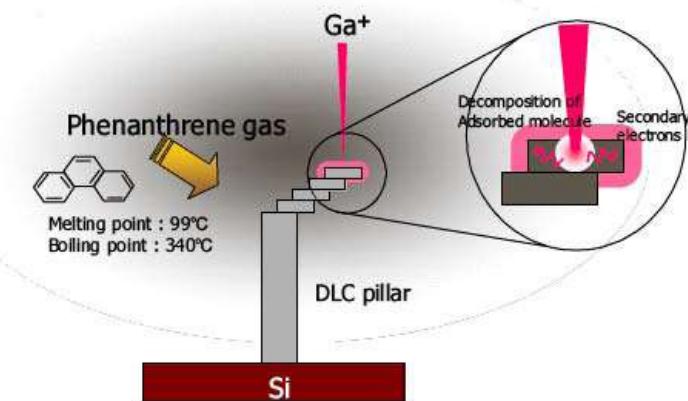


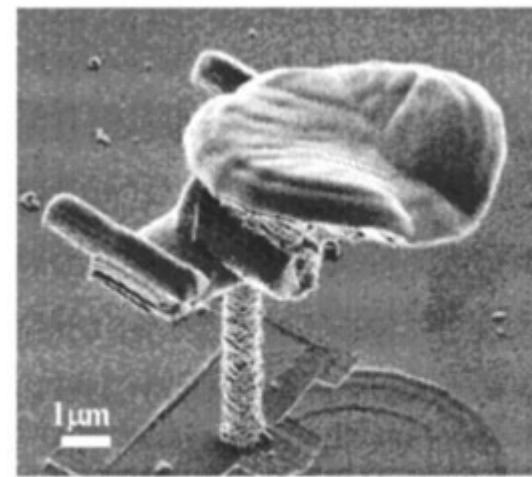
Figure 3. Nanorods deposited under optimized conditions with target cross-sectional size of $40 \times 40 \text{ nm}^2$: (a) SEM images of rods deposited for 5, 10, 20, 60, 180, 300 and 420 s (from left to right); (b) growth volume as a function of deposition time; (c) a very tall nanorod with a height up to 45 μm. SEM images were taken with a viewing angle of 54°.

Not limited by gas diffusion under optimal conditions.

3D structure by FIB deposition



(a) 3-D CAD model



(b) SIM image (tilt 45deg)

Diamond-Like Carbon Wineglass

Fujii et al, MRS Symp. Proc. 0983-LL08-08 (2007)

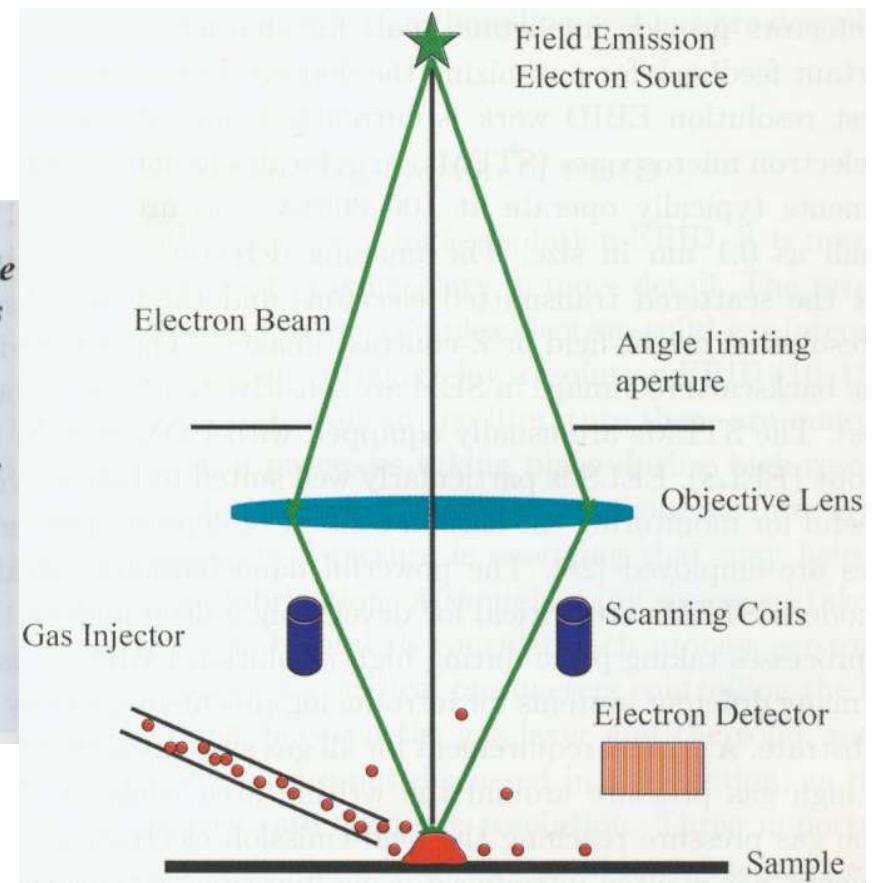
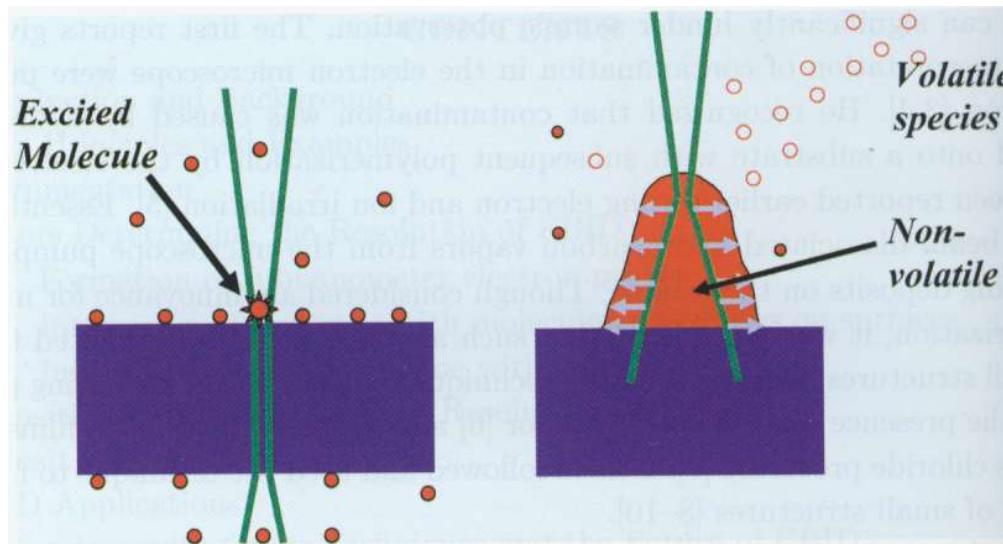
Hoshino et al, *J. Vac. Sci. Technol. B*, 21 2732 (2003)
(order of pixels matters)

Focused ion beam (FIB)

1. Overview.
2. Ion source and optics.
3. Ion-solid interaction, damage.
4. Scanning ion beam imaging.
5. FIB lithography using resist.
6. FIB milling, sputtering yield.
7. Redeposition.
8. Single line milling.
9. Other types of FIB lithographies (implantation, intermixing...).
10. Gas-assisted FIB patterning.
11. Focused ion beam induced deposition.
12. Focused electron beam induced deposition.
13. Deposition rate (electron and gas flux-limited regimes)
14. Deposit composition (carbon/metal)

Focused electron beam induced deposition

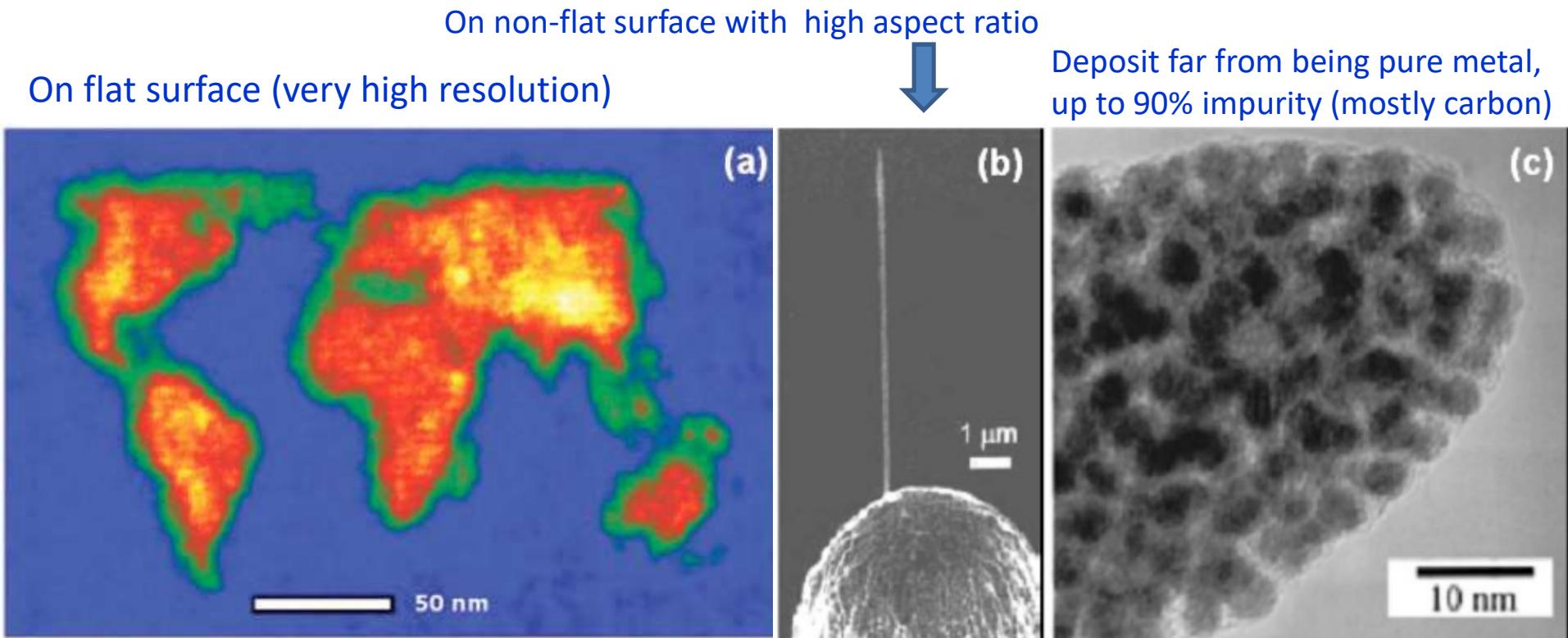
Tools: DualBeam FIB/SEM, SEM, Scanning TEM



The overall picture of deposition is similar to focused *ion* beam induced deposition:

- Fast electron excites an adsorbed precursor molecule.
- Excited molecule dissociates into volatile and non-volatile components.
- The volatile component escapes and leaves behind the non-volatile deposit.

Focused electron beam induced deposition: examples



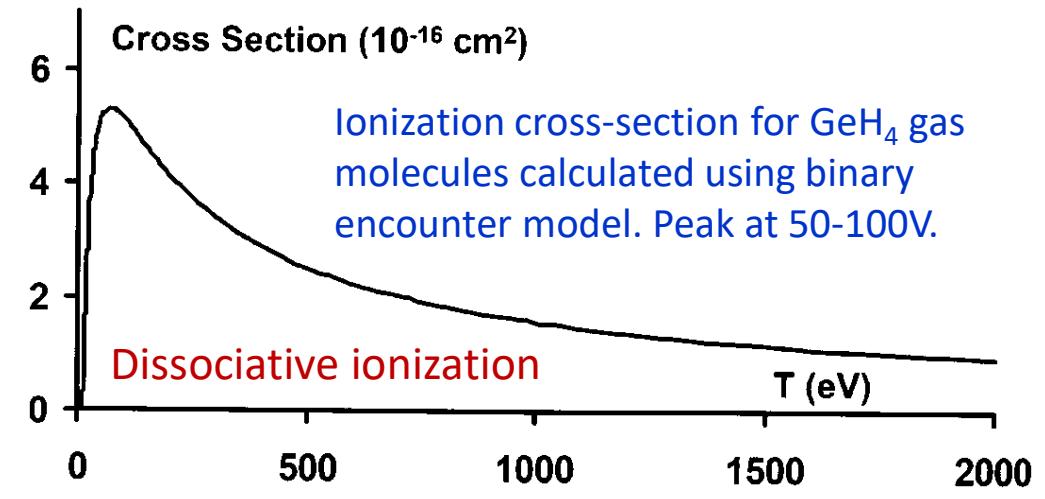
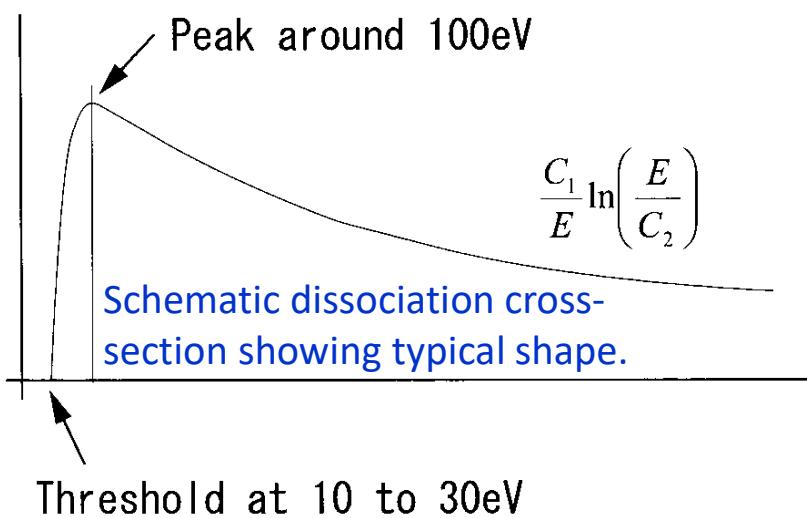
- a) A topographical map of the world on a flat substrate.
- b) A tip grown on a scanning tunneling microscopy probe.
- c) High-resolution TEM image of a typical deposit showing a nano-composite material - nanometer-sized metal crystals in an amorphous C matrix.

Comparison to FIB induced deposition

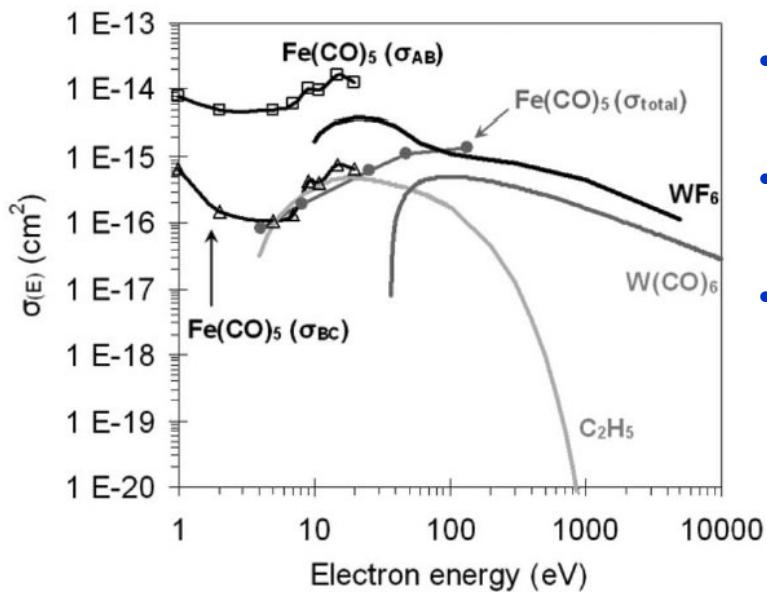
- No sputtering/material removal, so always pure deposition, unless reactive gas is introduced (then form volatile species) – gas assisted FEB (focused electron beam) etching similar to gas assisted FIB etching.
- Deposit has no Ga impurity, but a lot more amorphous carbon, thus more important to avoid carbon contamination component (C-H) in the precursor gas.
- Worse electrical conductivity.
- Deposition speed of FIB-ID is 10× that of FEB-ID for reasons not well understood yet.
- For high aspect ratio nano-rod deposition, FIB-ID is usually better because ion-solid interaction is well localized near the rod-apex, so is the deposition.
- Application side, FIB-ID is more mature and is widely used in industry; FEB-ID is essential for DUV mask repair because in IBID Ga^+ implantation into mask blocks DUV light.

ID = induced deposition, IBID = ion beam induced deposition, EBID = electron...

FEB-induced deposition mechanism



Dissociation ~ decomposition of precursor gas molecules

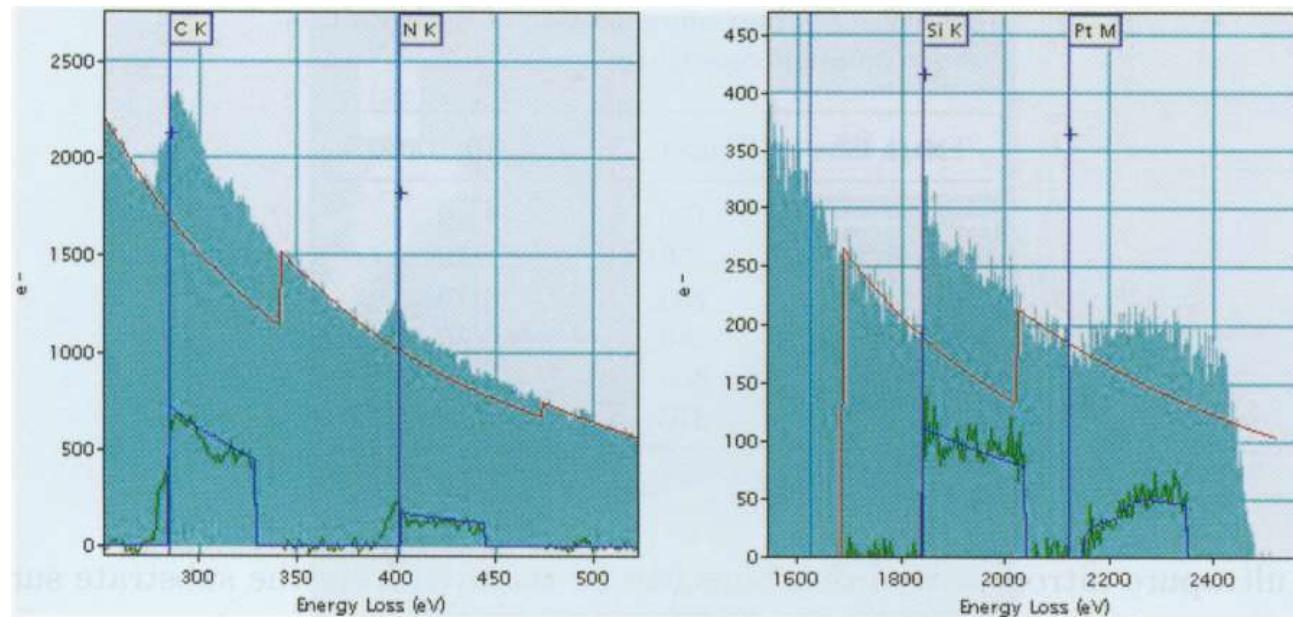


- It has generally been assumed that dissociation (e.g. $\text{GeH}_4 \rightarrow \text{GeH}_3 + \text{H}$) takes place after ionization of the precursor.
- Dissociate cross-section peaks at 50-100eV, so low-energy electrons such as secondary electrons play a central role.
- Contribution from primary electrons is important at the beam center.

Measured and estimated dissociation cross sections for few precursors. Two step dissociation for $\text{Fe}(\text{CO})_5$, through intermediate state B.

Deposit composition – carbon/metal

- For W deposition using $\text{W}(\text{CO})_6$, *thermal* decomposition (regular CVD process)
 $\text{W}(\text{CO})_6 + \text{heat} \rightarrow \text{W}(\text{CO})_{6-n} + n\text{CO}$, CO removed easily by heating to 200°C, leading to pure W.
- But for FEB induced deposition, *large* amount carbon (amorphous with high graphene component) *always* exists in the deposit when using carbonaceous precursors.
- Because electrons aggressively excite/activate many of the atoms in the precursor molecule.
- Even precursor is carbon-free, carbon gets into deposit *easily* from chamber contaminants.



Electron energy loss spectra recorded from Pt deposits on a thin film of Si_3N_4 , showing 90% of the deposit is carbon, the ratio is similar to C/Pt ratio in the precursor $\text{Pt}(\text{CH}_3)_3\text{CH}_3\text{C}_5\text{H}_4$. 21

Electrical properties of the deposit

Table 1. Electron conductivities of deposits fabricated by various precursors.

Typical pure metal resistivity $< 10 \mu\Omega \cdot \text{cm}$

	Material	Precursor	Resistivity	Reference
1.	W	W(CO) ₆	0.01 $\Omega \cdot \text{cm}$	[29,30]
2.	W	WF ₆ (no C, purer)	600 $\mu\Omega \cdot \text{cm}$	[31]
3.	Au	Me ₂ Au(tfac)	0.01 $\Omega \cdot \text{cm}$	[32]
4.	Au	AuClPF ₃	22 $\mu\Omega \cdot \text{cm}$	[33]
5.	Cu	HFA · ECu · EVTMS	3.63 $\Omega \cdot \text{cm}$ for 50 keV	[34]
6.	Pt	CpPtMe ₆	1 $\Omega \cdot \text{cm}$	[33]
7.	Co	Co ₂ (CO) ₈	2 k $\Omega \cdot \text{cm}$	[35]

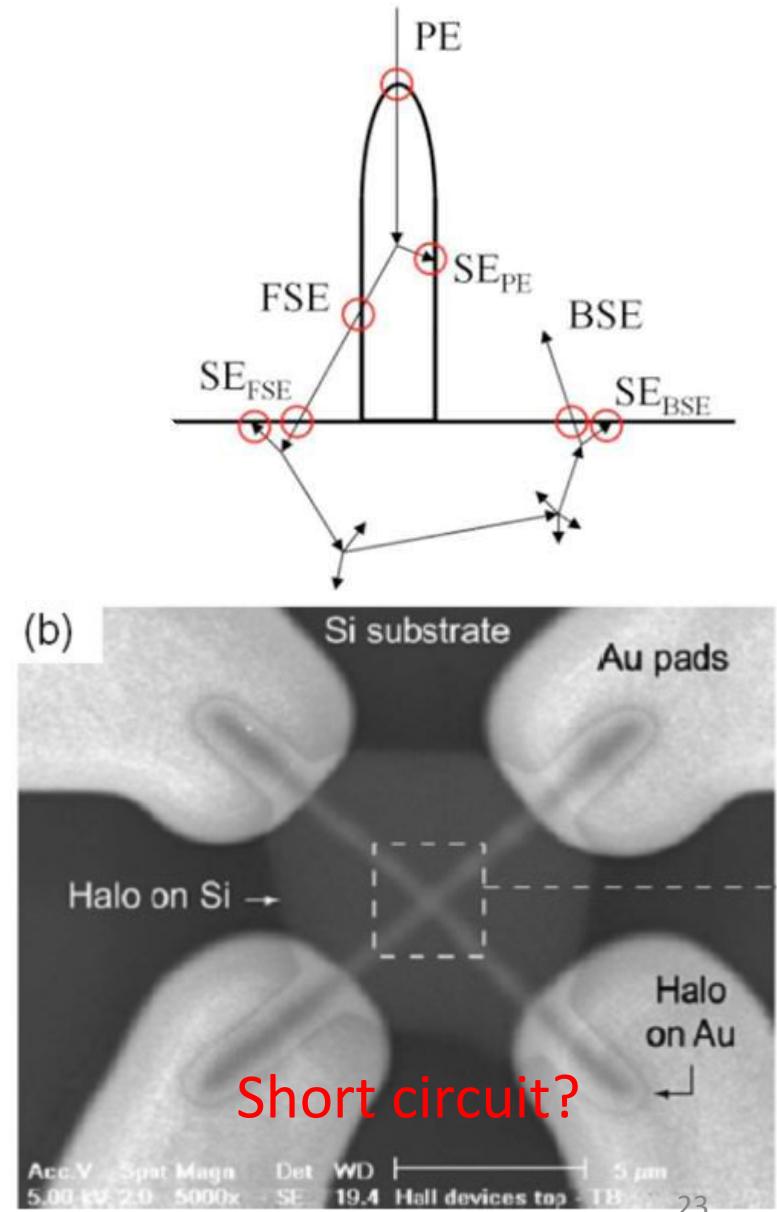
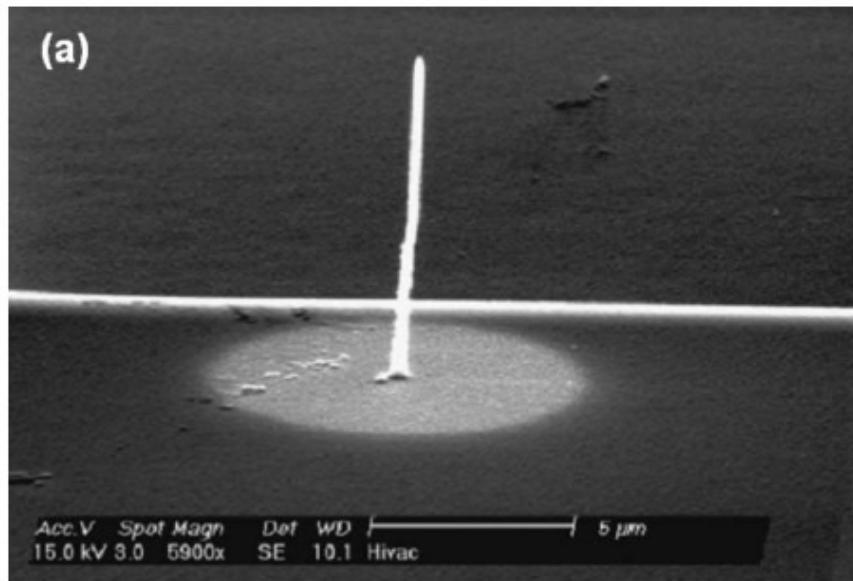
Table 2. References to deposits exhibiting non-Ohmic conductivity.

	Material	Precursor	Conductivity	Reference
1.	Au/Pt	Me ₆ Au(tfac)/CpPtMe ₆	Poole-Frenkel Formula	[37]
2.	Pt	C ₆ H ₁₆ Pt	Variable Range hopping	[38]
3.	Pt	Me ₃ Me	Variable Range hopping	[39]
4.	Pt	CpPtMe ₃	Coulomb blockade	[40]

Proximity effect

- Proximity effect is due to backscattering
- It leads to deposition over large surface area at the base.
- It may cause short circuit.

A halo around a deposited tip due to proximity effect and forward scattering .



High aspect ratio structures

- It is possible, but not as easy as FIB-induced deposition.
- Electron penetrate deep inside the nano-rod and can escape from a point far below the rod apex, causing continuous deposition at points well below the apex.

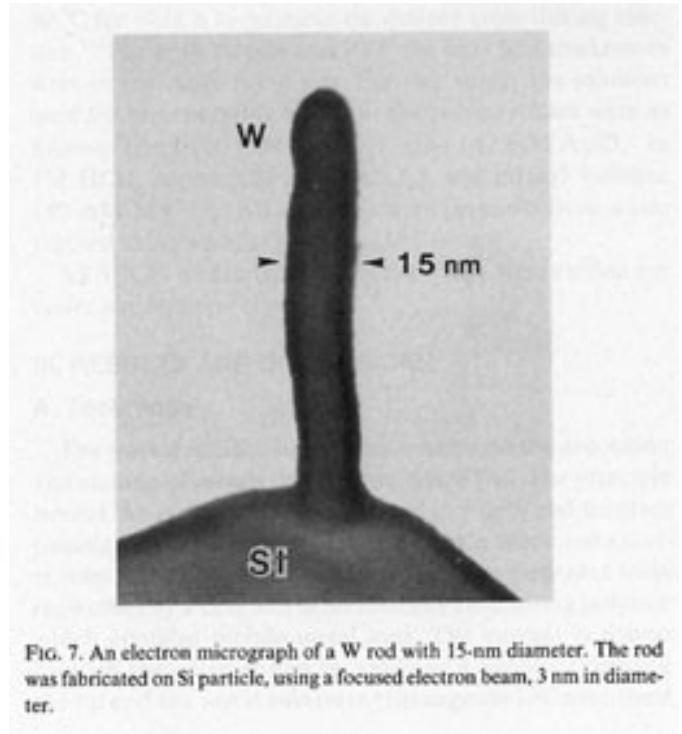
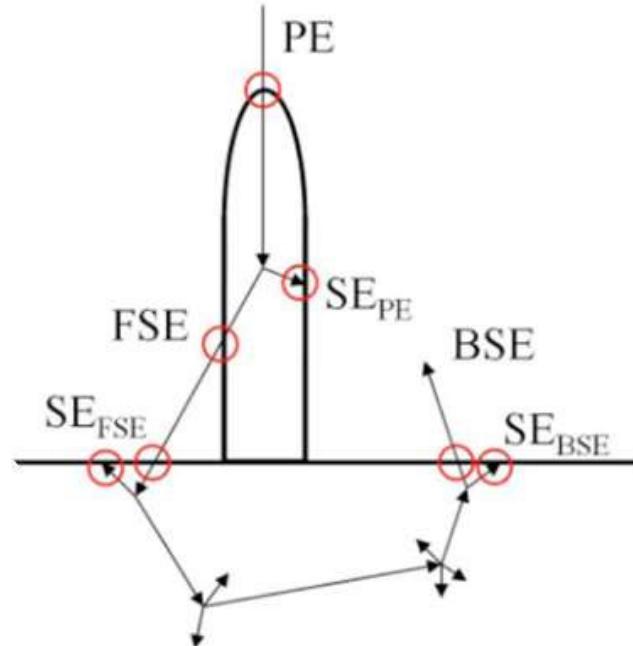


FIG. 7. An electron micrograph of a W rod with 15-nm diameter. The rod was fabricated on Si particle, using a focused electron beam, 3 nm in diameter.

Focused **electron** beam deposition
Tip diameter: 15nm (W-tip)
V=120kV, beam diameter = 3nm

Focused **ion** beam deposition,
high aspect ratio easy to achieve

Table 1. Typical Precursors Used in EBID/IBID Chemical formulae and corresponding names for EBID/IBID precursors, vapor pressure at room temperature (unless otherwise stated), and its phase (liquid L, solid S, gas G).

Material	Precursor chemical formula	Precursor name	Vapor pressure at 293 K	Phase
Al	Al(CH ₃) ₃ or AlMe ₃	trimethyl aluminum, TMA	8.4 m bar	L
	Al(C ₄ H ₉) ₃	tri-isobutyl aluminum	< 1 m bar	L
	AlCl ₃	aluminum trichloride	0.004 mbar at 323 K	S
Au	(CH ₃) ₂ Au(hfac) or Me ₂ Au (hfac)	dimethyl gold hexafluoroacetylacetone, DMG(hfac)	700 mTorr	L
	Me ₂ Au(acac)		8 mTorr	
	Me ₂ Au(tfac)	dimethyl gold acetylacetone	40 mTorr	
	AuCl ₃	dimethyl gold trifluoroacetylacetone		
	PF ₃ AuCl	gold trichloride gold trifluorophosphine chlride		G
C	C ₂ H ₄	ethylene		G
	C ₈ H ₈ or C ₆ H ₅ CH=CH ₂	styrene	10-25 Torr	
	C ₁₆ H ₁₀	pyrene		
	C ₁₆ H ₃₄	hexadecane		
	C ₁₂ H ₂₆ to C ₁₈ H ₃₈	liquid paraffin		L
	CH ₂ O ₂	formic acid		L
	C ₂ H ₄ O ₂	acetic acid		L
	C ₃ H ₄ O ₂	acrylic acid		L
	C ₃ H ₆ O ₂	propionic acid		L
	C ₅ H ₈ O ₂	methyl methacrylate (MMA)		
Co	Co ₂ (CO) ₈	dicobalt octacarbonyl		
Cr	Cr(CO) ₆	chromium hexacarbonyl	10 Torr	L
Cu	Cu(hfac) ₂	copper bis-hexafluoroacetylacetone	0.004 mbar	G
	Cu(hfac)(DMB)	DMB = dimethylbutene	1.3 mbar	
	Cu(hfac)(MHY)	MHY = 2-methyl-1-hexen-3-yne	0.2 mbar	
	Cu(hfac)(VTMS)	VTMS = vinyltrimethylsilane	0.1 mbar	G

Fe	Fe(CO) ₅ Fe(C ₅ H ₅) ₂	iron pentacarbonyl ferrocene or biscyclopentadienyl iron	3 Torr 0.04 mbar at 313 K	G/L S
GaAs	Ga(CH ₃) ₃ /AsH ₃	timethyl gallium/arsine		
Ga	D ₂ GaN ₃	perdeuterated gallium azide		
Mo	Mo(CO) ₆	molybdenum hexacarbonyl	78 mTorr	G
Ni	Ni(CO) ₄ Ni(C ₅ H ₅) ₂	nickel tetracarbonyl nickelocene	10 Torr 17 mTorr	S
Os	Os ₃ (CO) ₁₂	triosmium dodecacarbonyl		
Pd	Pd(OOCCH ₃) ₂ Pd(C ₃ H ₅)(C ₅ H ₅)	Pd-Ac, palladium acetate palladium allylcyclopentadienyl		
Pt	(C ₅ H ₅)Pt(CH ₃) ₃ or CpPtMe ₃ (CH ₃ C ₅ H ₄)Pt(CH ₃) ₃ Pt(PF ₃) ₄	cyclopentadienyl trimethyl platinum methylcyclopentadienyl trimethyl platinum trifluorophosphine platinum	54 mTorr 54 mTorr	G G
Re	Re ₂ (CO) ₁₀	dirhenium decacarbonyl		
Rh	[RhCl(CO) ₂] ₂ [RhCl(PF ₃) ₂] ₂	di- μ -chloro-tetracarbonyl-dirhodium di- μ -chloro-tetrakis-trifluorophosphine-dirhodium	0.25 Pa 55 mTorr	S
Ru	Ru ₃ (CO) ₁₂	triruthenium dodecacarbonyl		
Si	SiH ₂ Cl ₂	dichlorosilane		
SiO ₂	Si(C ₂ H ₅ O) ₄	tetraethoxysilane (TEOS)	1.5 Torr	
SiO _x	Si(OCH ₃) ₄	tetramethoxysilane (TMS)	420 Torr	L
W	W(CO) ₆ WF ₆ WCl ₆	tungsten hexacarbonyl tungsten hexafluoride tungsten hexachloride	17 mTorr	G

Focused ion beam (FIB)

1. FIB application: lithography using resist, milling, imaging.
2. FIB TEM sample preparation.
3. FIB circuit edit and photo-mask repair.
4. Other applications: superconducting, SPM tip, nano-pore.
5. Proton (hydrogen ion) beam writing.
6. Scanning Helium ion microscope
7. Ion projection and multi-beam lithography

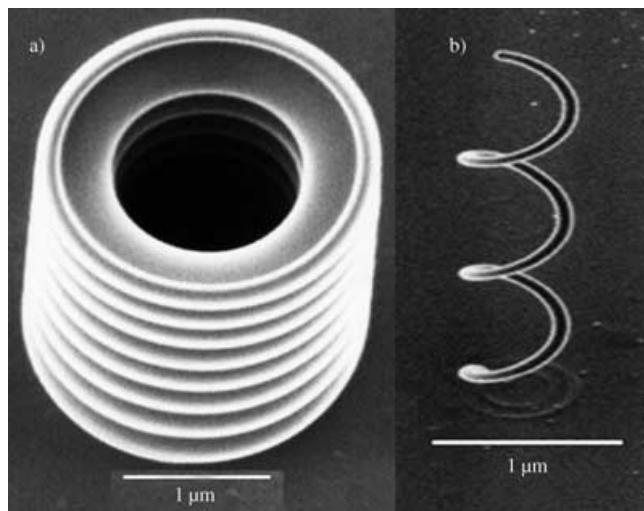
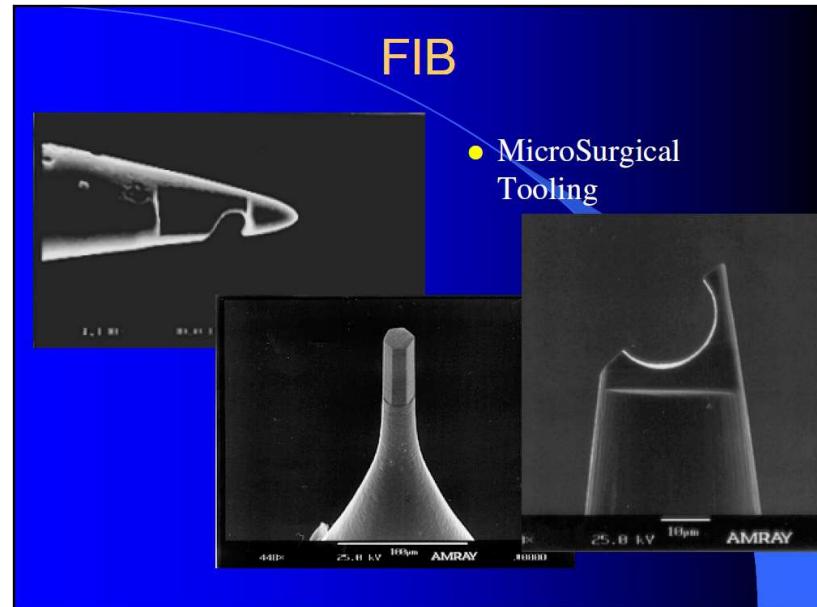
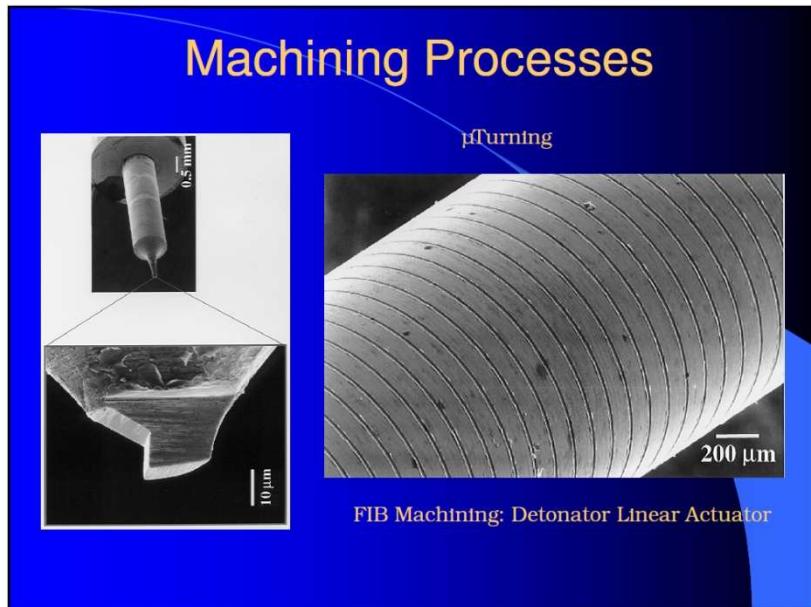
Note: topic 2 (TEM) will not be included in exams

FIB as a micro-nano-machining tool

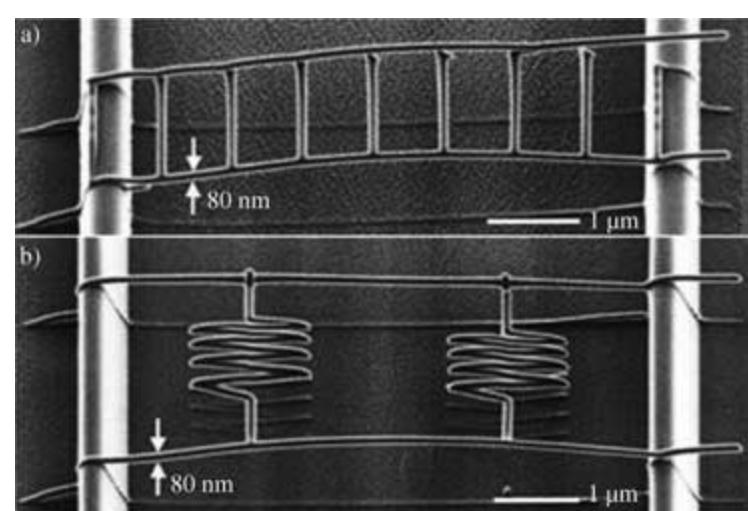


Micro diamond ring
milled from a 20 μm
diameter W wire.

More FIB milled and deposited structures



FIB-induced deposition: a) micro-bellows with 100nm thickness, 800 nm pitch; b) micro-coil with 80nm wire diameter.



SIM images of DLC (diamond like carbon) nanostructures prepared by FIB-induced deposition: a) free-space-wiring with a bridge shape; b) free-space-wiring with parallel resistances 3

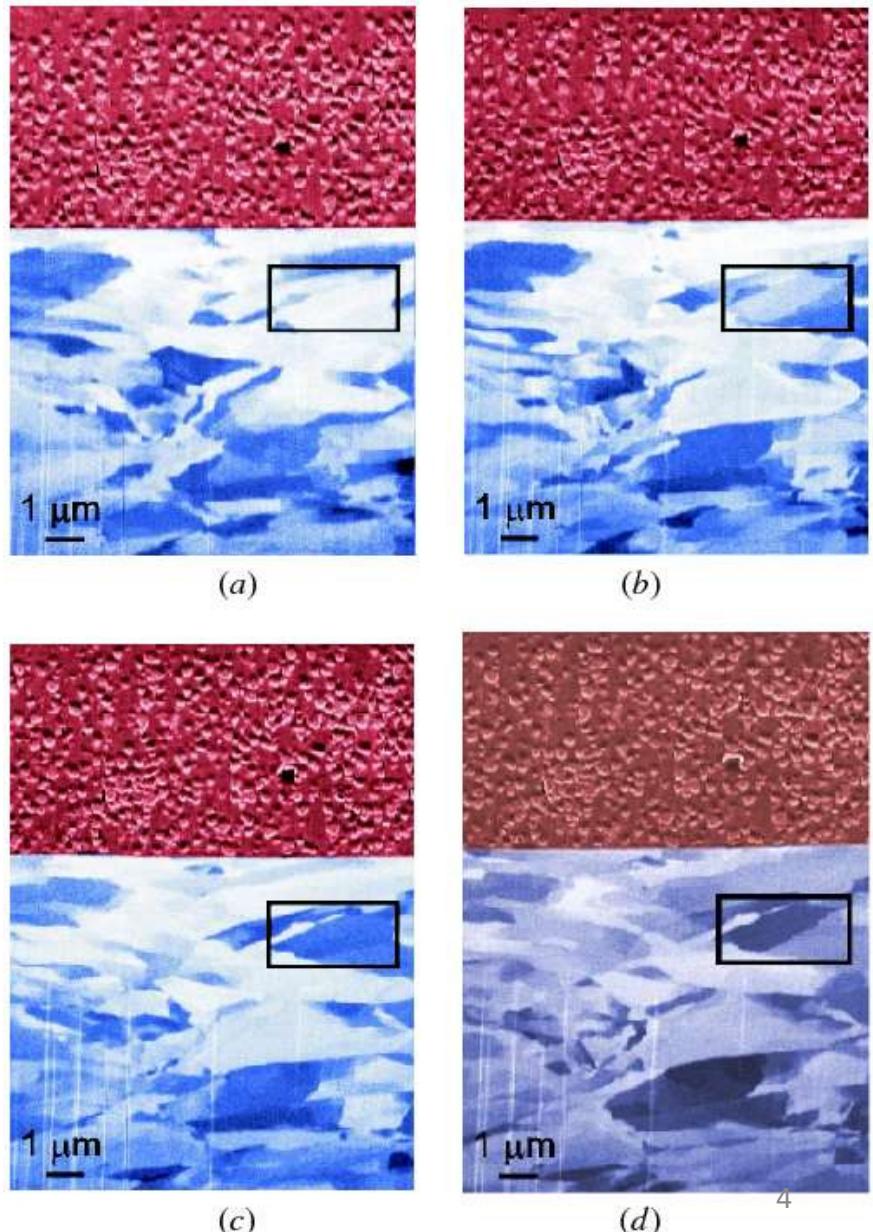
Tseng, "Recent developments in nanofabrication using focused ion beams", Small, 1(10), 924 – 939(2005)

See inside: section by milling, look by imaging

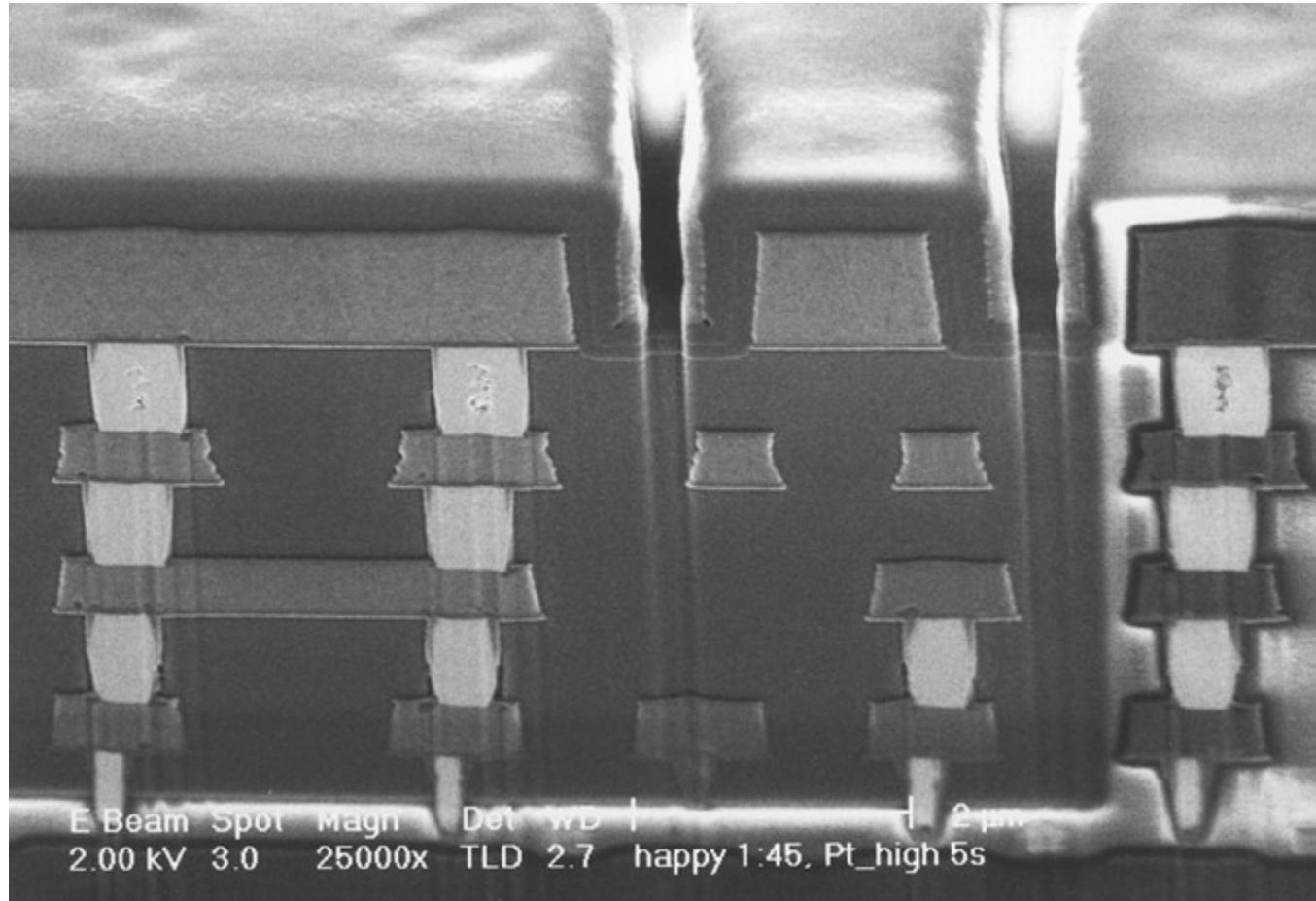


Figure 4. The beverage can that was cross sectioned for figure 5.

Figure 5. Cross section through an aluminum beverage can, visualized from various tilting angles: (a) 30° , (b) 35° , (c) 40° , and (d) 45° . The aluminum grains are clearly visible (lower part), as well as the polymer label (upper part). The tilt angle-dependent channeling contrast is clearly illustrated by the boxed grain.

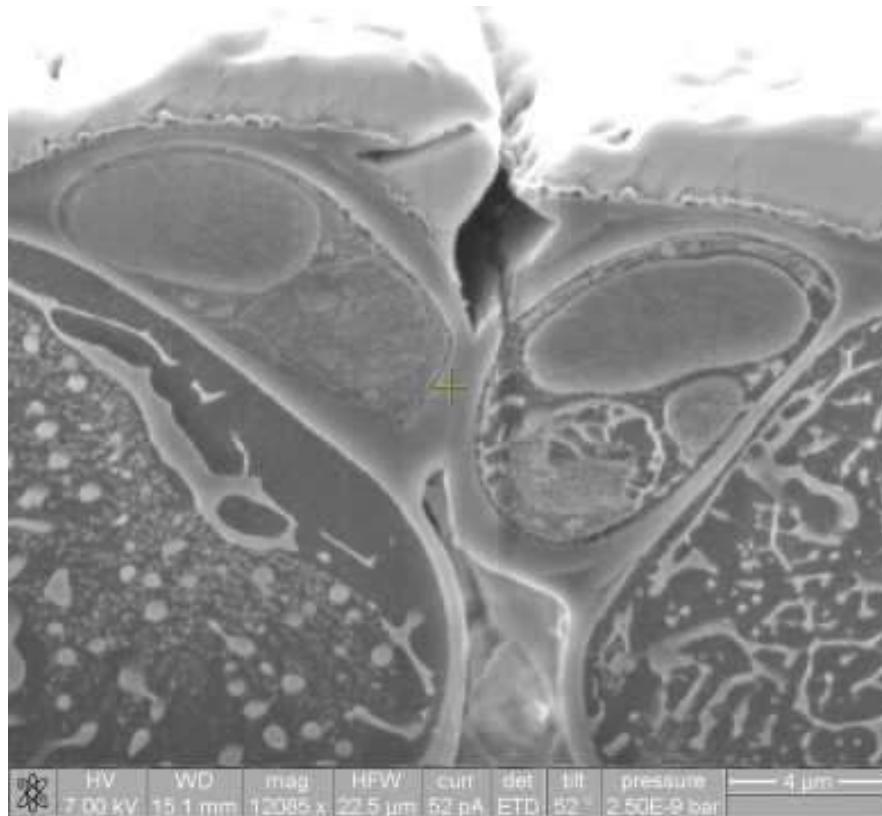


SEM image of integrated circuit cross-section milled by FIB

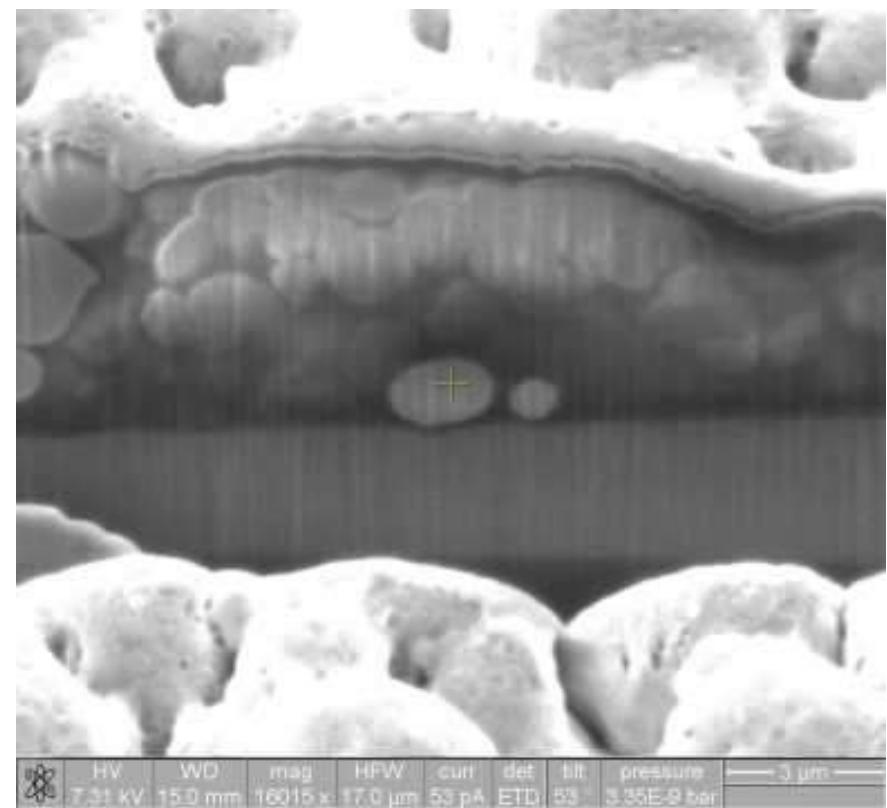


Biomaterial sectioned/milled at very low temperature

Stomata guard cells of frozen coriander leaf.



Cobalt particle in nucleus of frozen human fibroblast nucleus



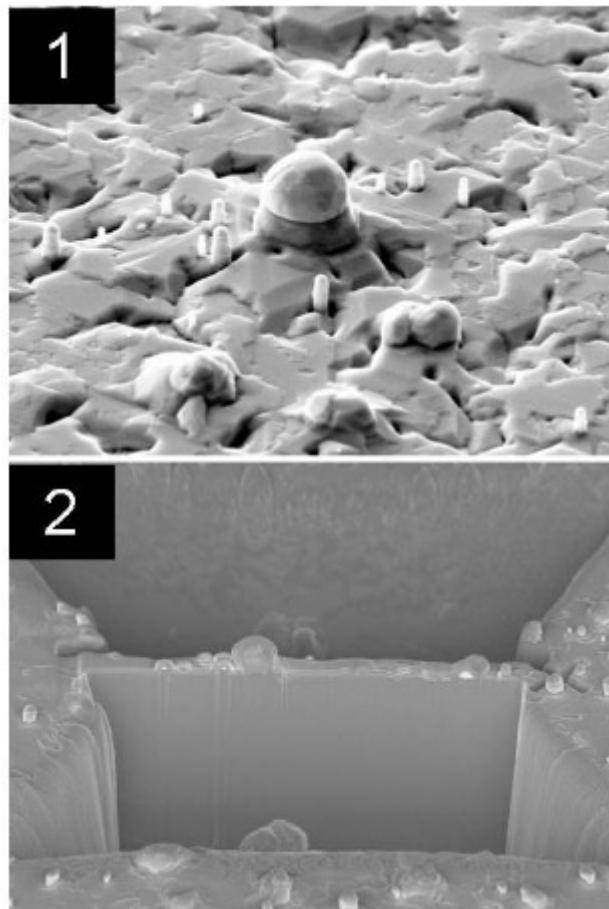
Focused ion beam (FIB)

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6. Scanning Helium ion microscope
7. Ion projection and multi-beam lithography

Note: topic 2 (TEM) and 4 (other applications) will not be included in exams

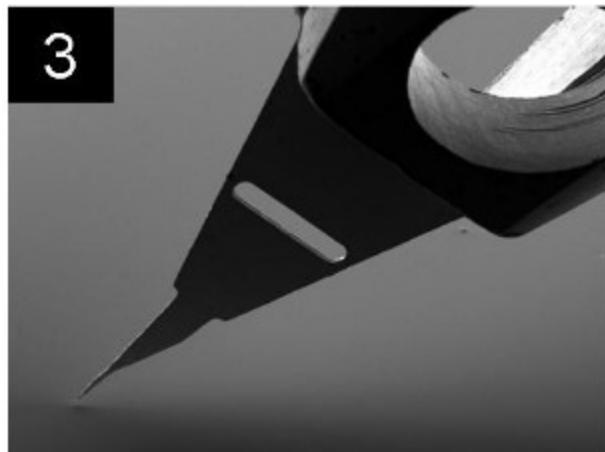
TEM sample preparation

FIB milling is a very powerful tool for preparing thin sections for electron microscopy analysis. In combination with the instrument's high resolution SEM imaging capabilities, one can prepare site-specific sections of sub-micron sized features.



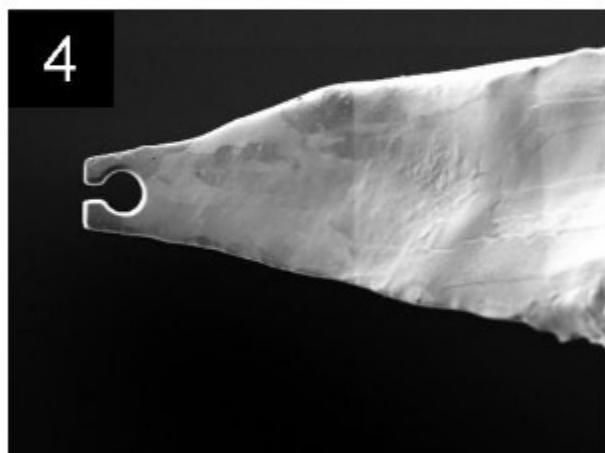
A feature of interest is located with the SEM in the FIB/SEM.

The region of interest is coated with platinum using ion-beam induced deposition. This layer protects the surface of the feature during subsequent FIB milling. The surrounding substrate is removed by FIB milling, leaving a $1\mu\text{m}$ -thick lamella containing the feature of interest.



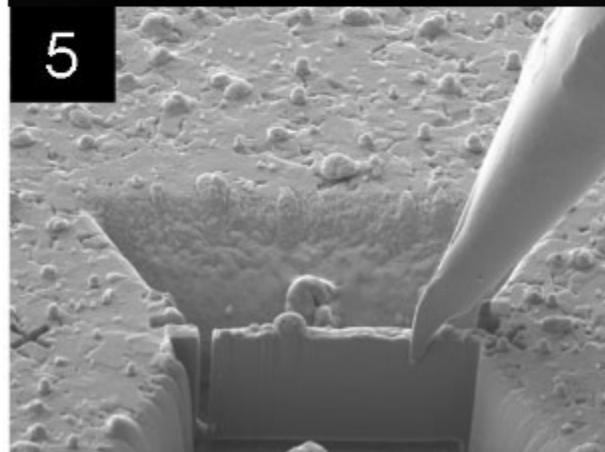
3

At the tip of nano-manipulator rod is mounted an “end effector” – a sharp Mo or Cu tip. The tip is positioned just above the region of interest on the sample.



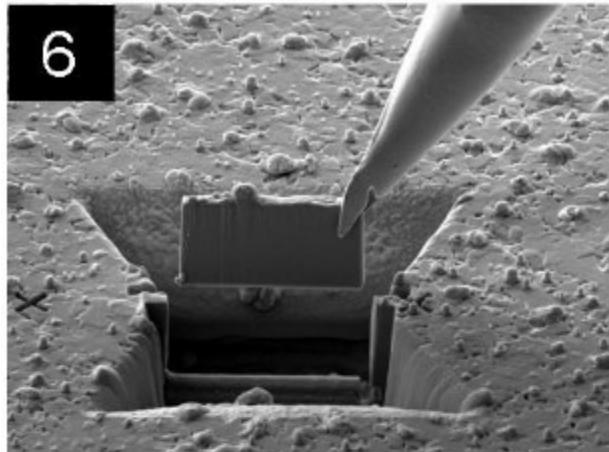
4

Using the FIB, a pair of tines are machined at the tip of the end effector. The spacing is slightly less than the thickness of the lamella prepared in step 2.



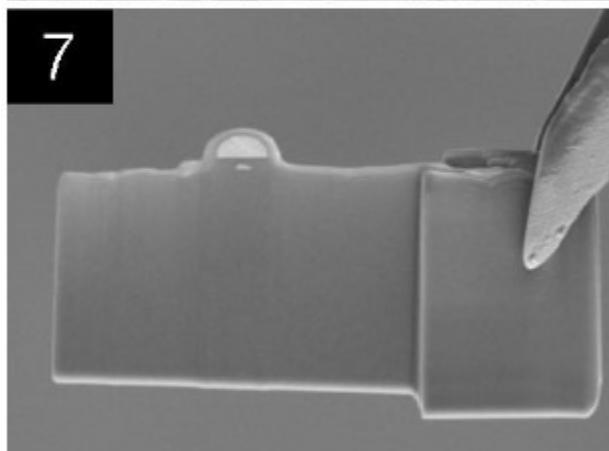
5

With the left and bottom sides of the lamella cut free, the end effector is positioned onto the right side of the lamella. This procedure is accomplished by viewing both the SEM and FIB secondary electron images while lowering the end effector onto the sample. The alignment of the tines with the sample in plane of the sample surface is observed and adjusted in the FIB image and the height is visualized in the SEM image. ⁹



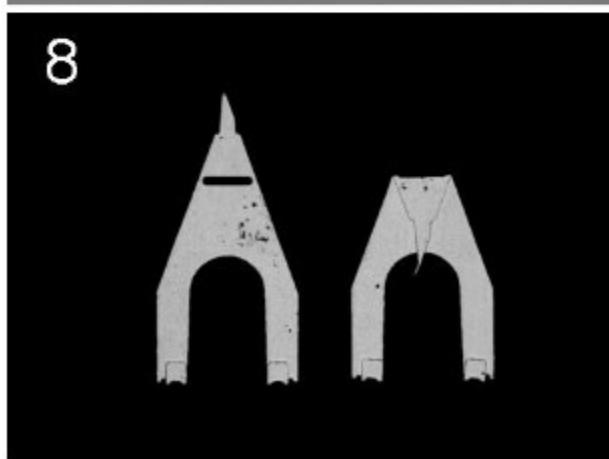
6

With the lamella securely held between the tines, the right side is cut free and the sample is lifted clear, again while monitoring the position with both the FIB and SEM electron images.



7

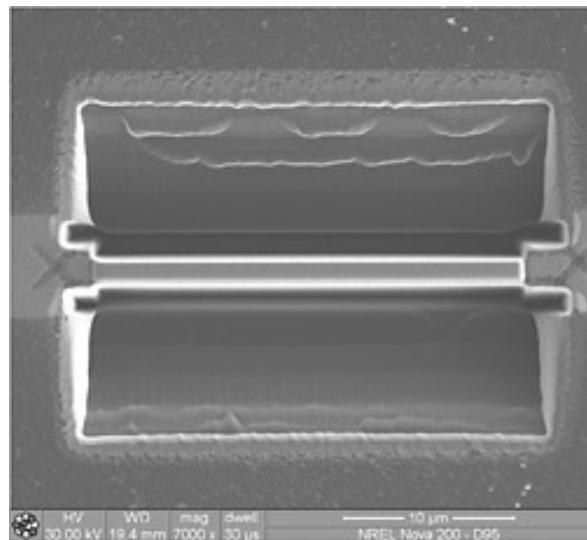
After the lamella is lifted clear of the substrate, the final thinning and polishing is performed by FIB milling. Progress is monitored in situ by SEM – the rod can be rotated to allow both front and back to be imaged and the thickness to be measured. A final thickness of 100nm is typical.



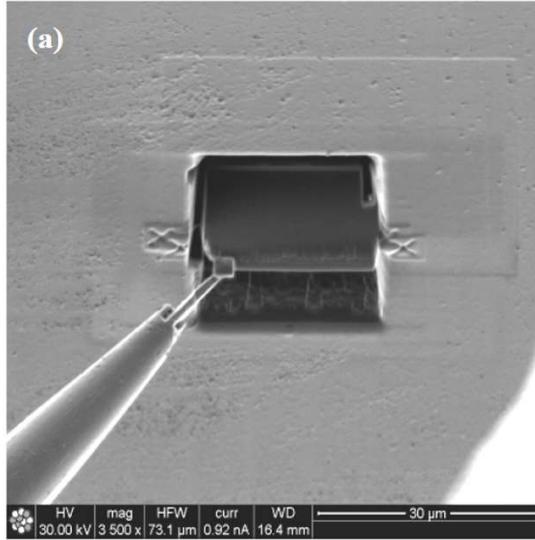
8

The nano-manipulator rod is withdrawn from the microscope through a load-lock without venting the microscope chamber. After the tip of the end effector is folded over and removed from the nano-manipulator rod, it can be directly mounted in a standard 3mm diameter TEM sample holder.

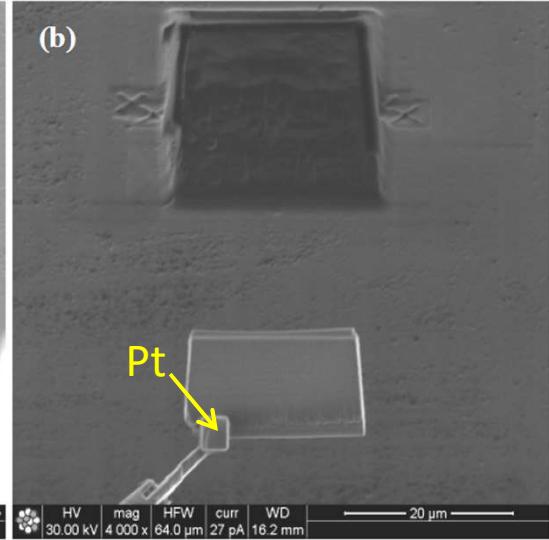
Milling a TEM lamella and lift out by nano-welding



Top view shows the width
of the lamella



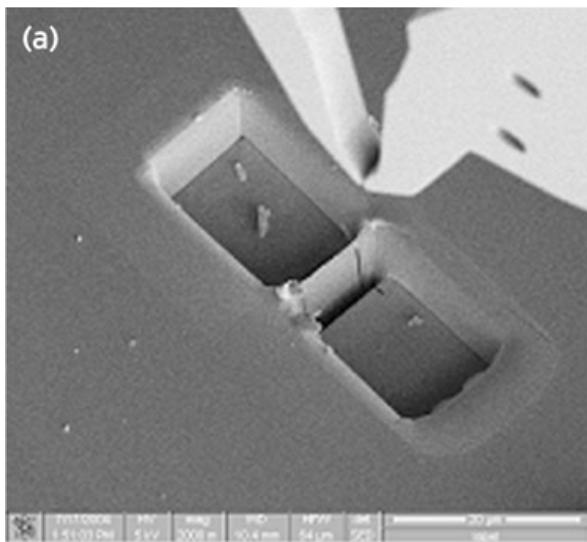
Weld and lift out by in-situ deposition of Pt



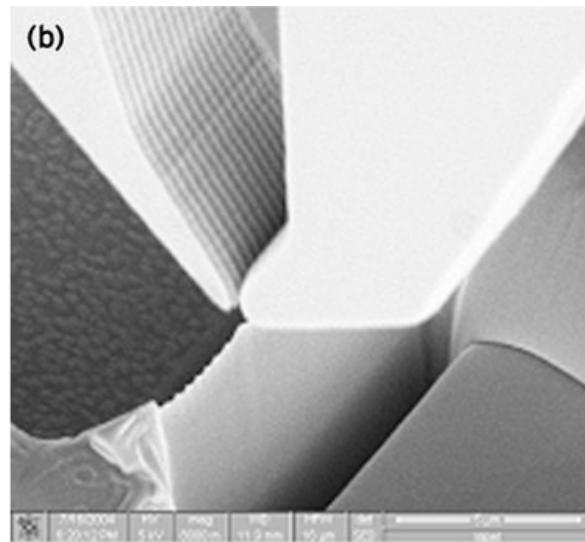
1. Opposing trenches are milled out and a 1-2μm thin section is left free standing in the wafer.
2. The section is welded to the micro-manipulator, extracted from the wafer then transferred and welded to a TEM grid post.
3. Final thinning down to a thickness of less than 100nm is achieved using low incident angles and low Ga ion current.

Lift out by nano-gripper

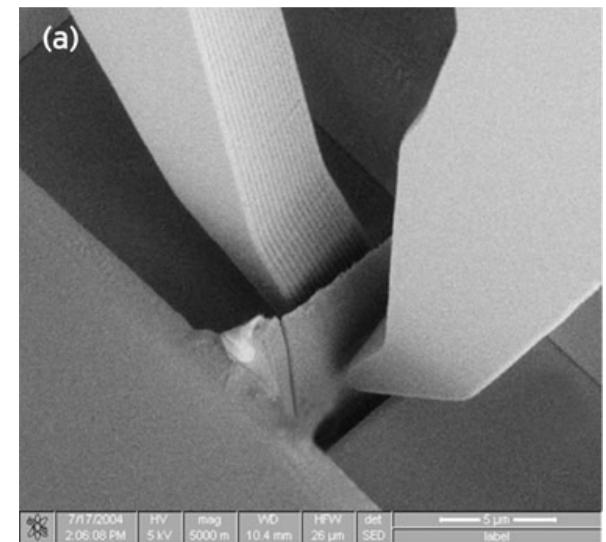
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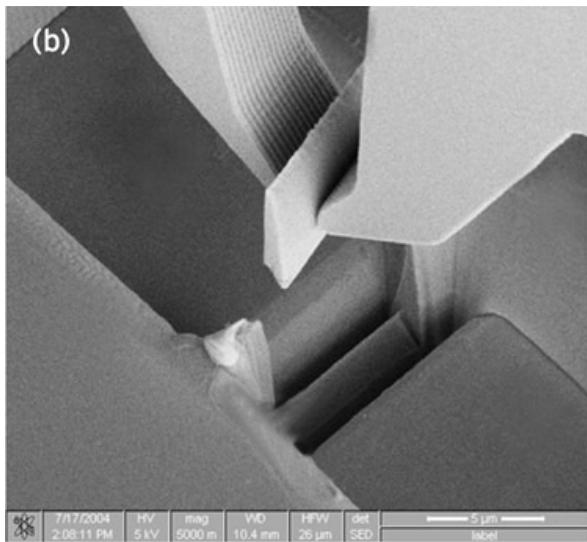
2



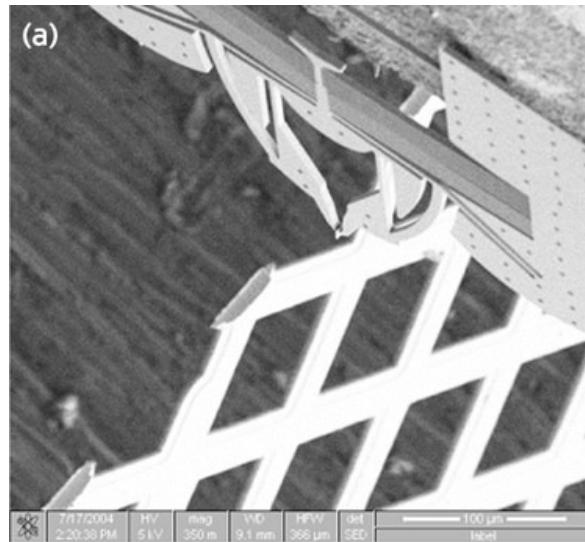
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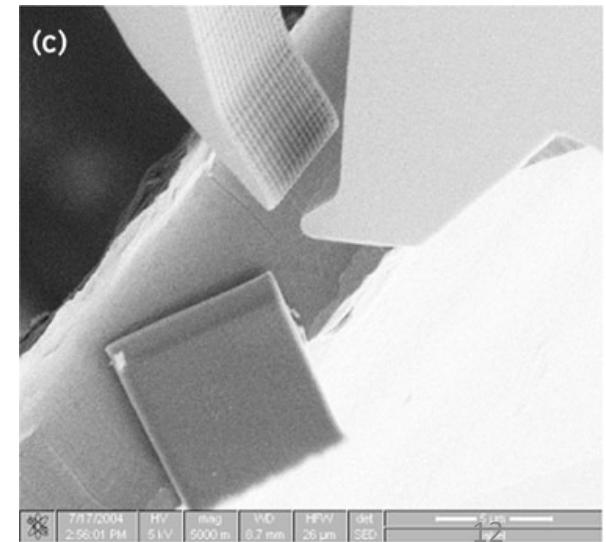
4



5



6

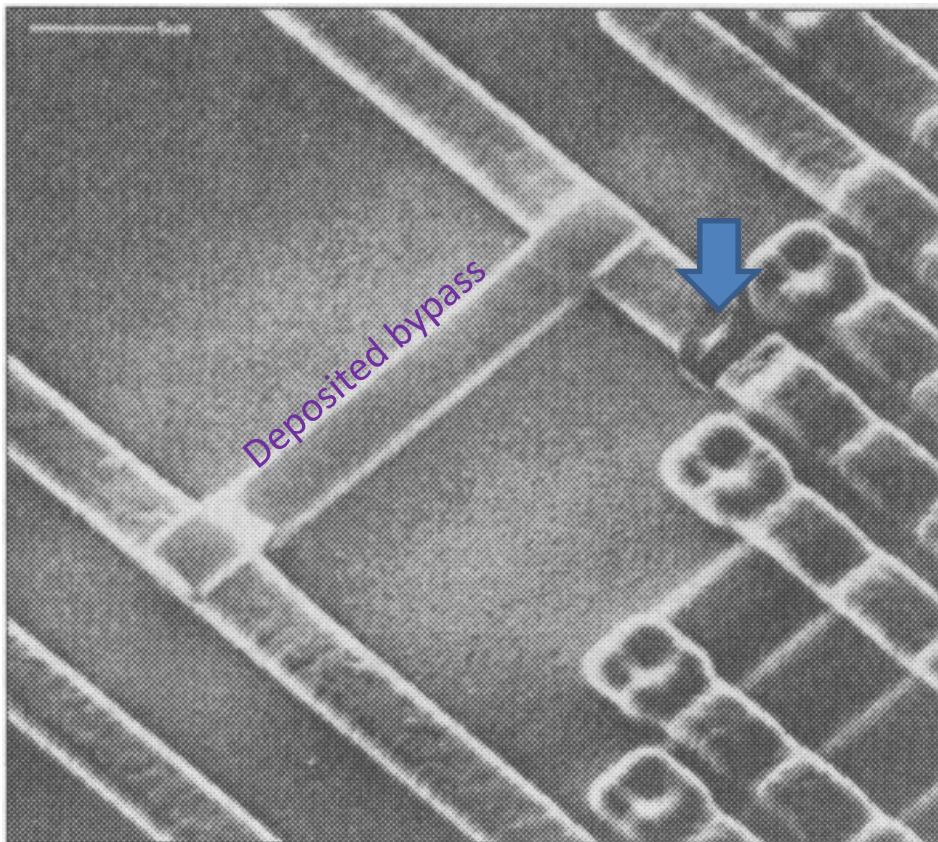


Focused ion beam (FIB)

1. FIB application: lithography using resist, milling, imaging.
2. FIB TEM sample preparation.
3. FIB circuit edit and photo-mask repair.
4. Other applications: superconducting, SPM tip, nano-pore.
5. Proton (hydrogen ion) beam writing.
6. Scanning Helium ion microscope
7. Ion projection and multi-beam lithography

Integrated circuit edit

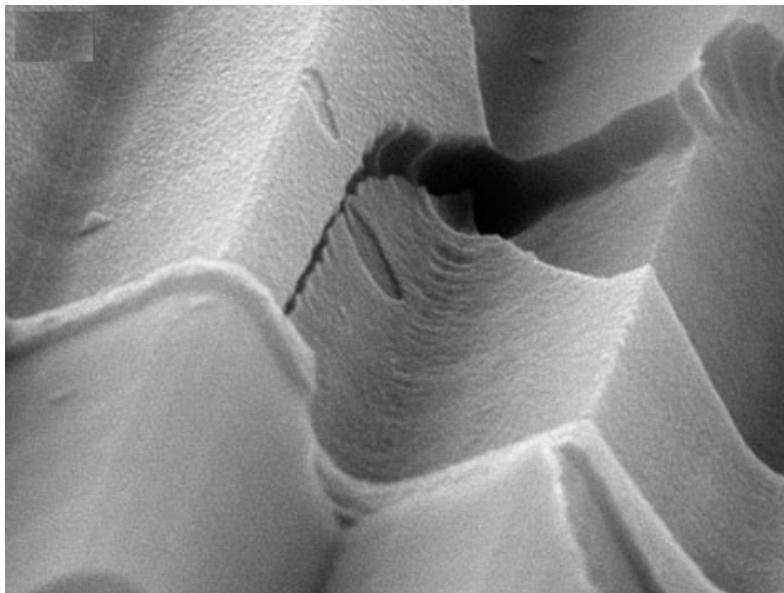
Errors in circuit design can be diagnosed (milling or sectioning by FIB, seeing by SEM/SIM), and corrected by disconnecting (milling) or connecting (deposition) some parts. After repair, protecting layer of SiO_2 can be deposited.



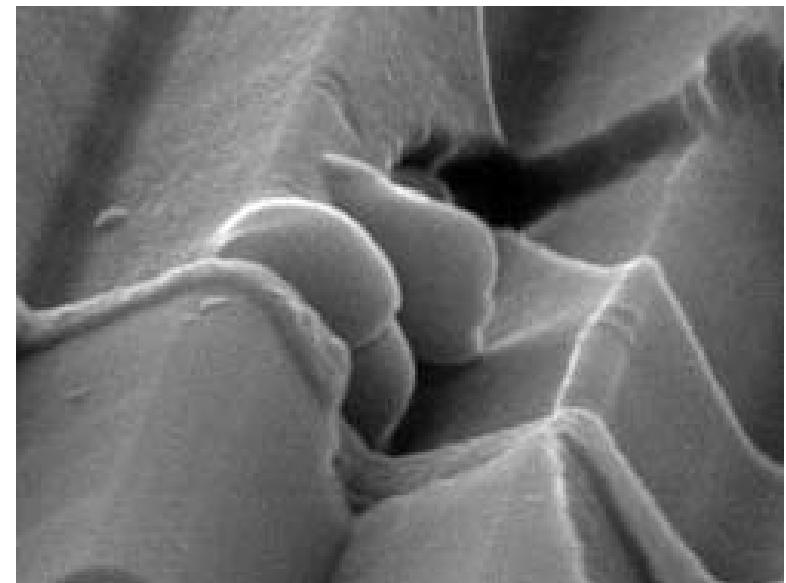
One metal track was cut and re-connected to the other metal track with a deposited bypass.

Electrical contact repair by FEB deposition

Electrical contact break

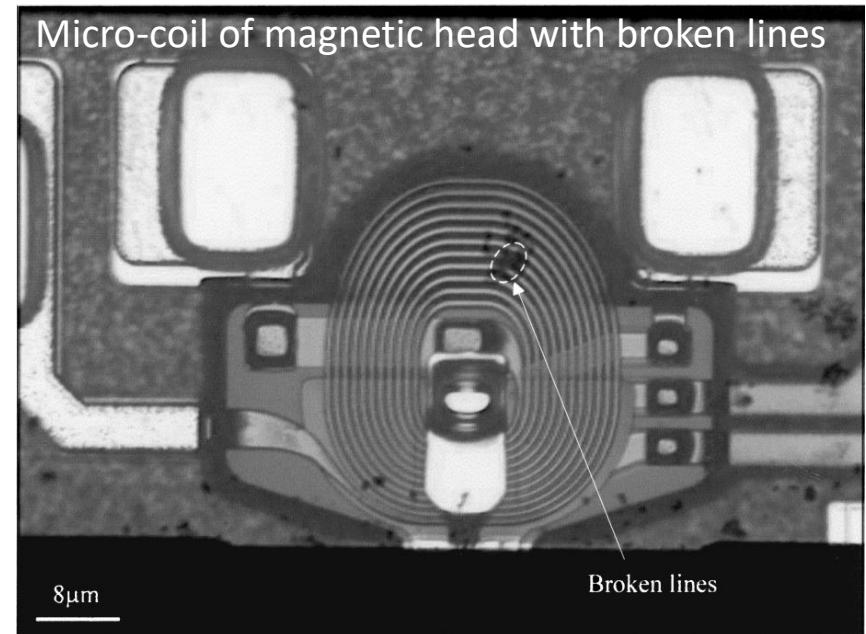


After FEB reparation



Even though the film is not pure with low conductivity, it is still quite conductive.

Repair of magneto-resistive (MR) head coil

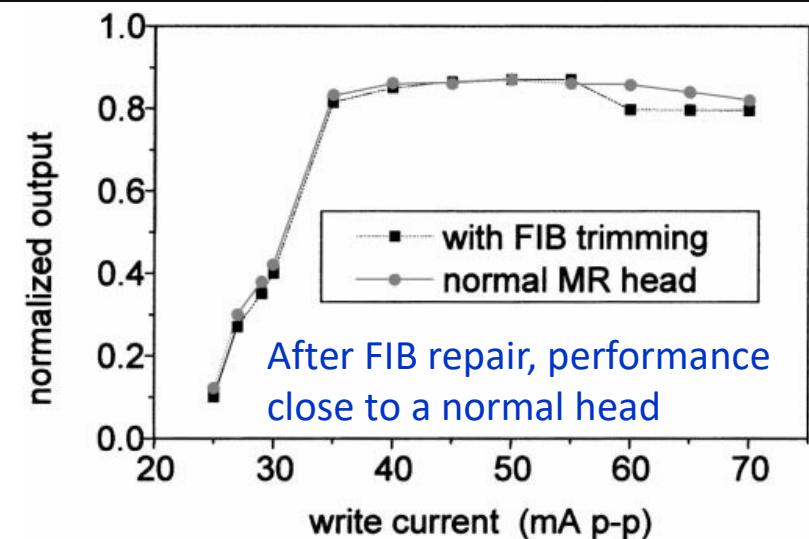


Process:

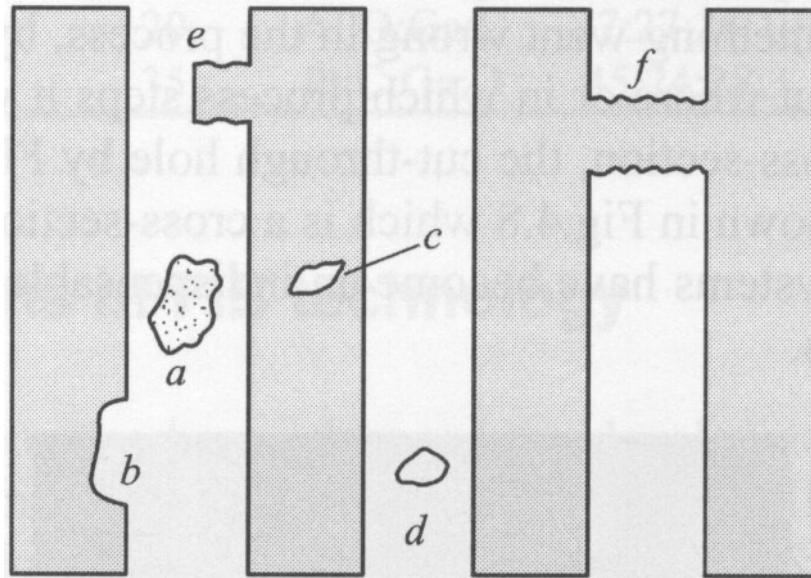
- FIB selective milling of polymer cover using XeF_2
- FIB deposition of W lines
- FIB deposition of SiO_2 protection layer

Optimal deposition parameters

dwell time: 0.5μs	spot size: 25nm
current: 400pA	refresh time: 1.5ms
ion dose: 0.6nC/mm ²	ion energy: 50keV
scanning mode: raster	
X and Y pixel space: 71nm and 68nm	



Optical mask defects repair



Types of mask defects: opaque defects a, e, d, f; clear defects: b, c

Clear defect can be easily repaired by FIB induced deposition of carbon (opaque) using hydrocarbon gas. Charge neutralization (“spray” electrons to surface) is needed to prevent ion charge accumulation, also need to minimize sputtering.

Opaque defects is more difficult to repair, will be addressed in the following slides.

Phase shifting mask even more difficult to repair, Cr removal (defect f in the figure) will cause additional phase shift.

Opaque defects removal by ion milling

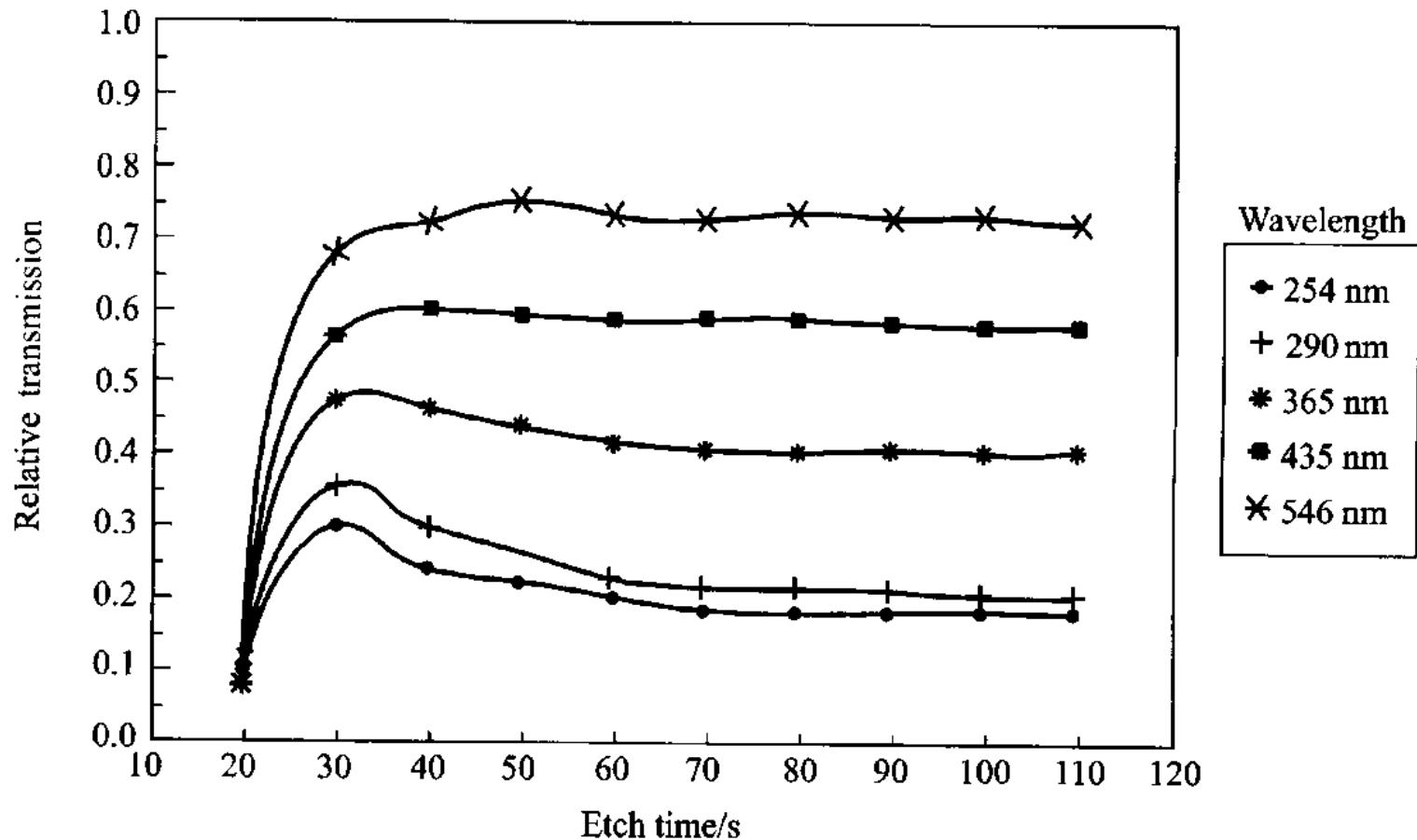
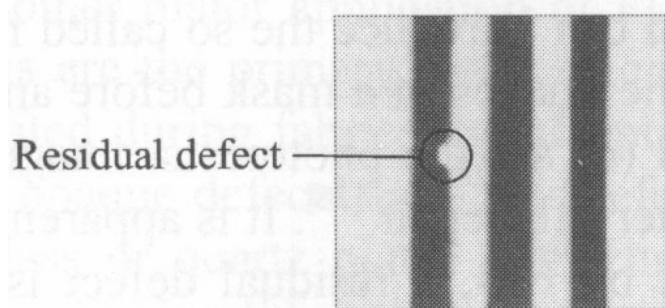


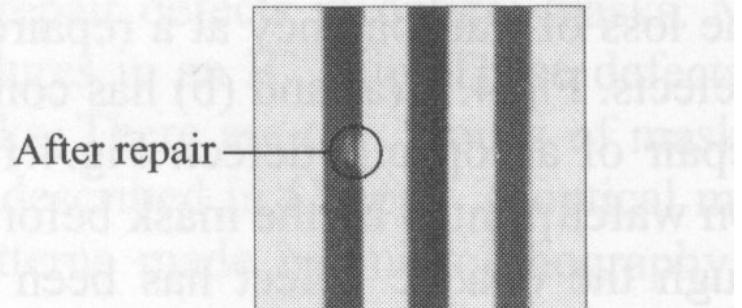
Fig.4.10. Transmission loss due to gallium staining in FIB repair of mask defects

Problem: Ga^+ implantation/staining reduces mask transmission to DUV light

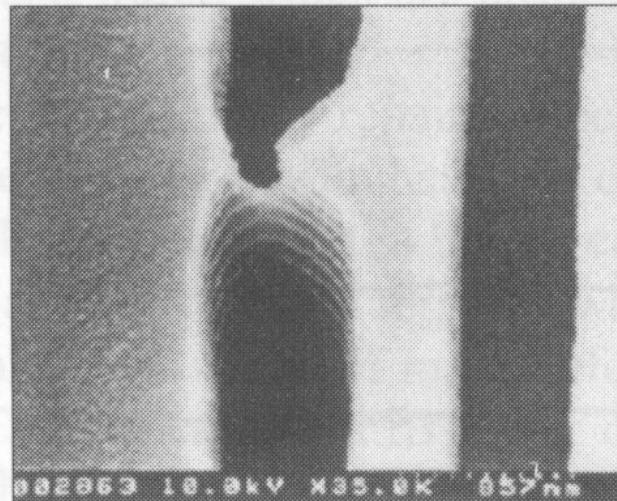
Gallium staining induced residual defect and printed photo-resist image



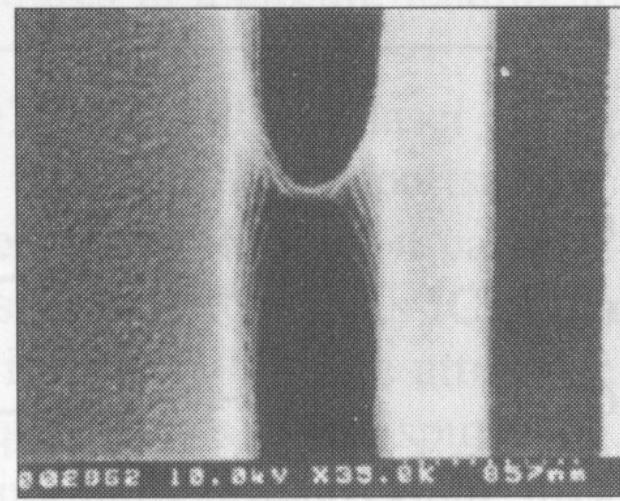
(a) Mask image before repair



(b) Mask image after repair



(c) Printed photoresist image before repair of the defect

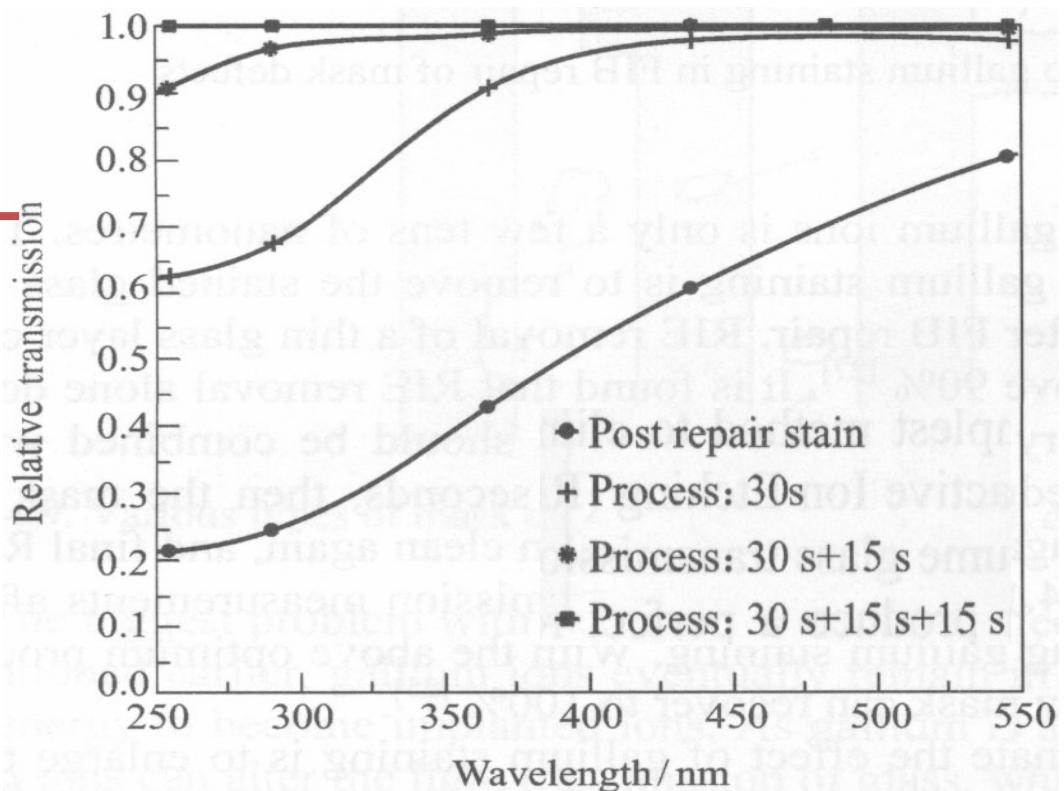


(d) Printed photoresist image after repair of the defect

How to reduce Ga⁺ staining effect while repairing opaque defects

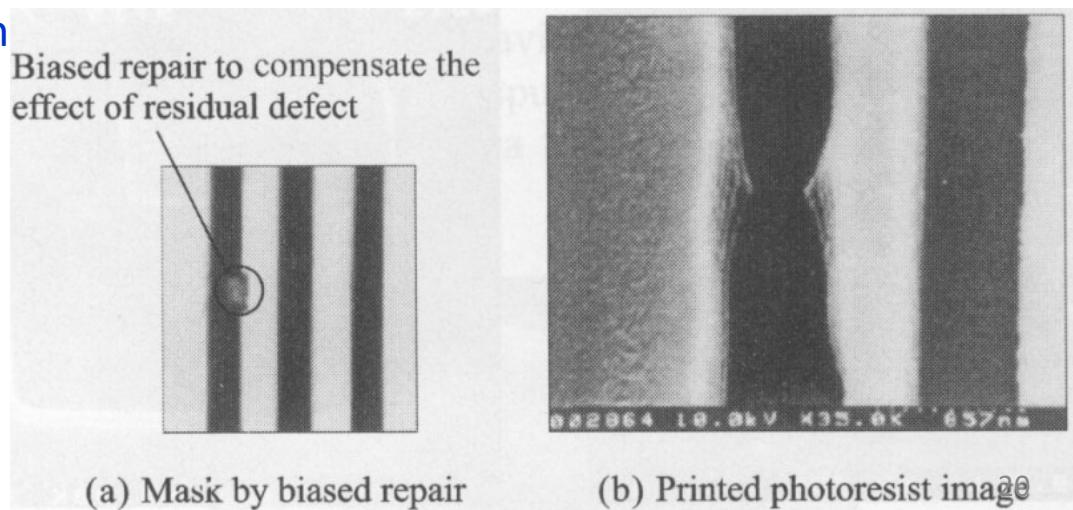
Recovery of transmission by RIE and cleaning to remove gallium staining.

1. RIE the glass using F-chemistry
2. Wet etch Ga by acid
3. Repeat with reduced RIE time.



Biased repair, over-etch to beyond defect area

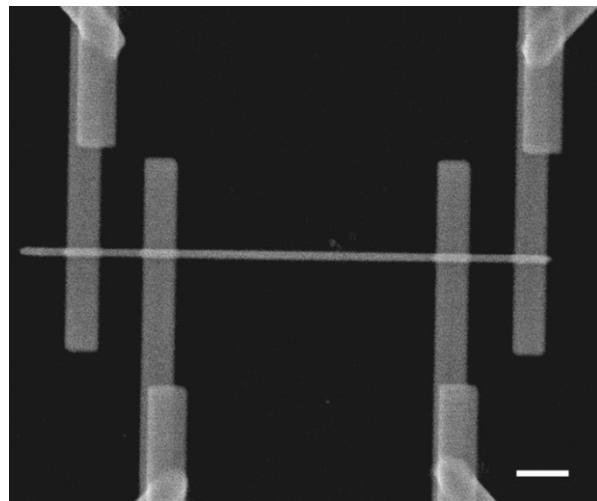
A third method: (to remove Cr) use focused *electron* beam with gas (Cl₂/O₂) enhanced etching to produce volatile compound (CrO₂Cl₂)



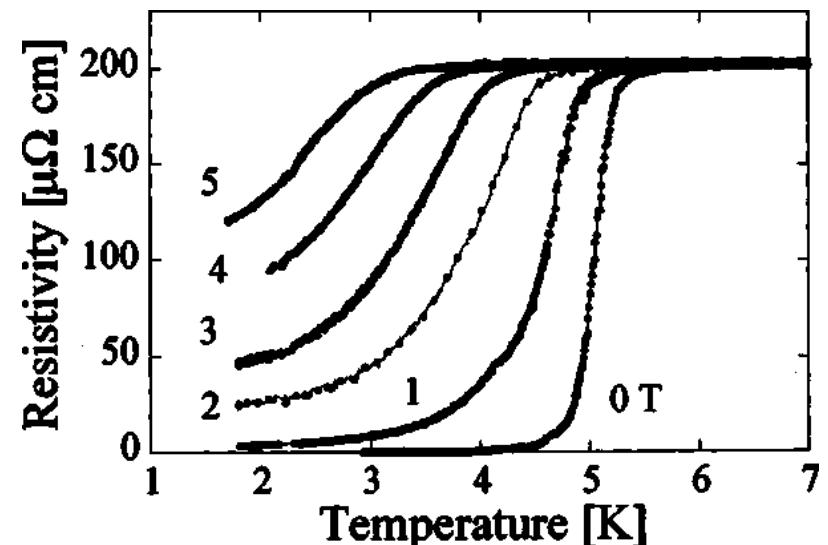
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Superconducting W nano-wires by FIB induced deposition



Superconducting wire in a four-point contact configuration for transport measurements.
Wire length 10 μ m, width 300nm, thickness 120nm



Resistivity vs. temperature for magnetic fields applied perpendicular to the wire from 0 to 5T.

Atomic ratio (%)	Carbon (C)	Tungsten (W)	Gallium (Ga)
Center	40.96	39.05	19.98
Edge	39.42	39.95	20.73
Average	40.19	39.45	20.36

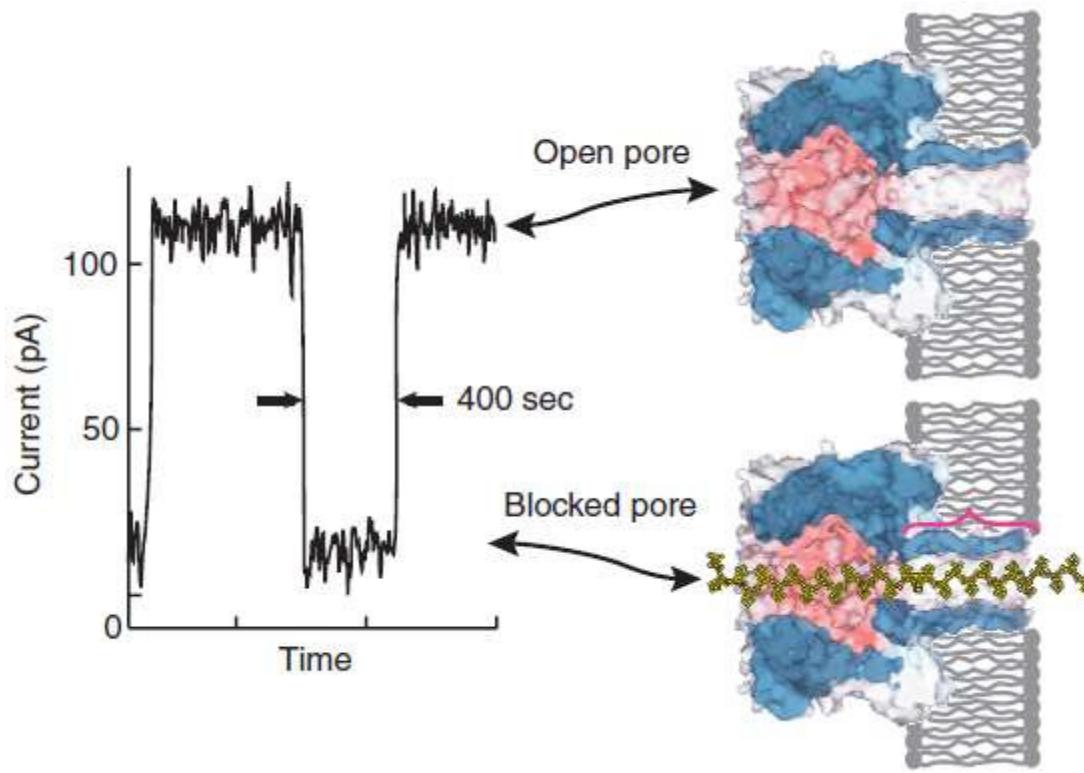
Single crystal pure W $T_c=0.01$ K,
here T_c much higher probably
because it is amorphous with
lots of C and Ga.

W(CO)₆ precursor, 30keV Ga⁺ ion, current 98pA, ion dose 1nC/ μ m².

Precursor temperature 61°C. During deposition, chamber pressure kept at 2.63×10^{-5} Torr.

Nano-pores for DNA sequencing

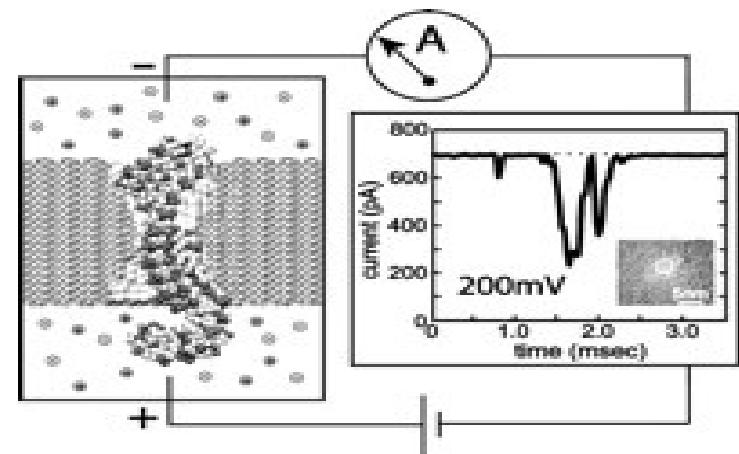
Translocation of a DNA through a *biological* channel



Strand-sequencing using ionic current blockage:

Typical trace of ionic current amplitude (left) through an α -hemolysin pore clearly differentiates between an open pore and one blocked by a strand of DNA.

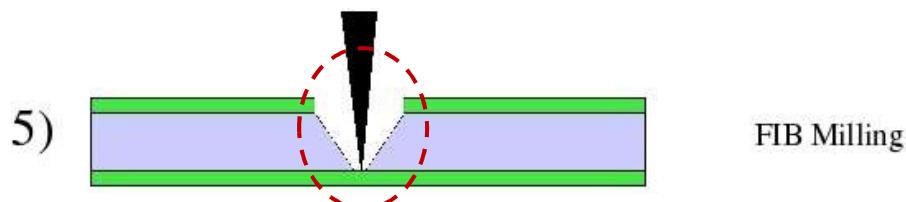
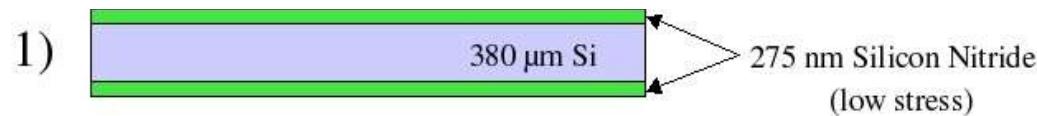
Translocation of a DNA through a *synthetic* channel



Application:

- DNA sequencing
- Separation of ssDNA and dsDNA in solution
- Determining DNA chain length

Fabrication of nano-pores for DNA sequencing



- 1) Si_3N_4 thin membranes are deposited by sputtering on a 4-inch Si wafer.
- 2) Photoresist (PR) is applied to the wafer.
- 3) Anisotropic RIE is used to remove the thin layer of Si_3N_4 not protected by the photoresist
- 4) Anisotropic wet etching uses KOH to remove bulk material from the wafer
- 5) Focused Ion Beam is used to drill a hole through the free standing membrane

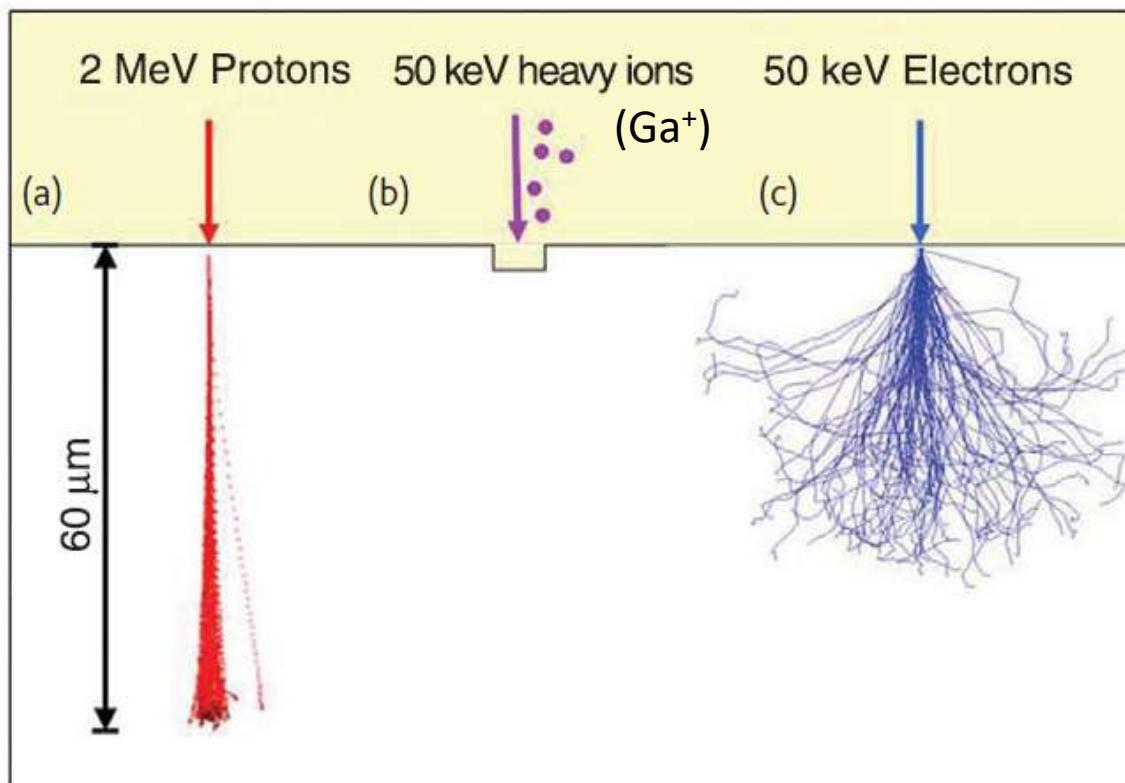
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Proton (p-) beam writing

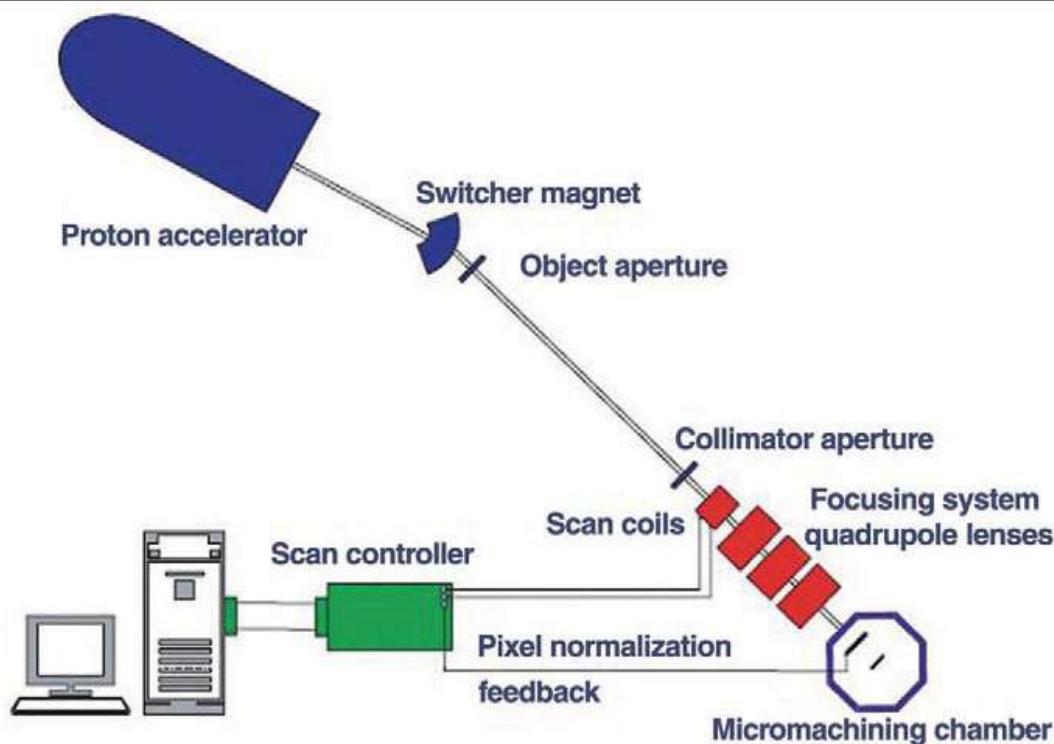
Compared to e-beam lithography:

- Proton (H^+) is heavier, with almost no proximity effect.
- In p-beam writing, typical energy is 0.5-2MeV (very high energy), thus deeper penetration in materials while maintaining a straight path.
- Hence it is capable of fabricating three-dimensional, high aspect ratio structures with vertical, smooth sidewalls and low line-edge roughness.



Proton (p-) beam writing

- For most of its path (except near its end), the probability of interacting with an electron is orders of magnitude larger than for nuclear scattering, so nuclear collisions have little effect on the trajectories.
- Due to high mass mismatch, p-e collisions do not significantly deviate proton's trajectory.
- Energy transfer in each p-e collision is also small, many 1000 collisions will occur before a proton comes to rest.
- Near its end (when p has low energy), nuclear collision becomes more important, thus more beam broadening.



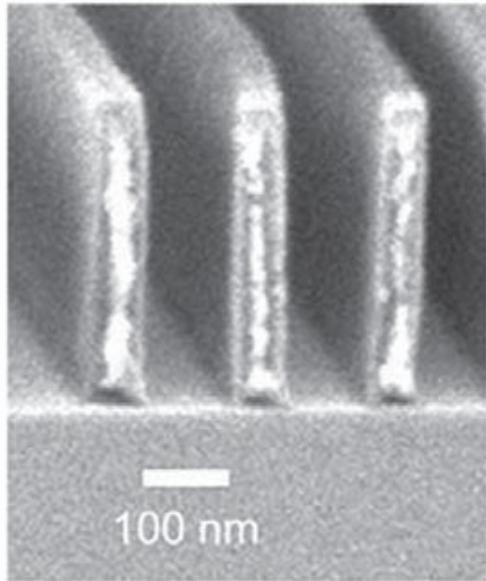
P-beam writing facility at
CIBA (Singapore).

MeV protons are produced in a proton accelerator, and a de-magnified image of the beam transmitted through an object aperture is focused onto the substrate material (resist) by means of a series of strong focusing magnetic quadrupole lenses.

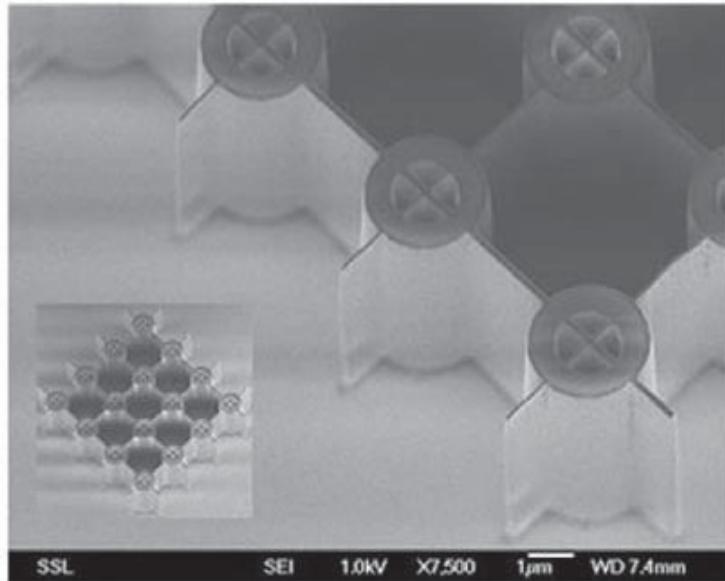
P-beam writing in PMMA, SU-8 and HSQ

Exposure is caused by proton-induced secondary electrons.

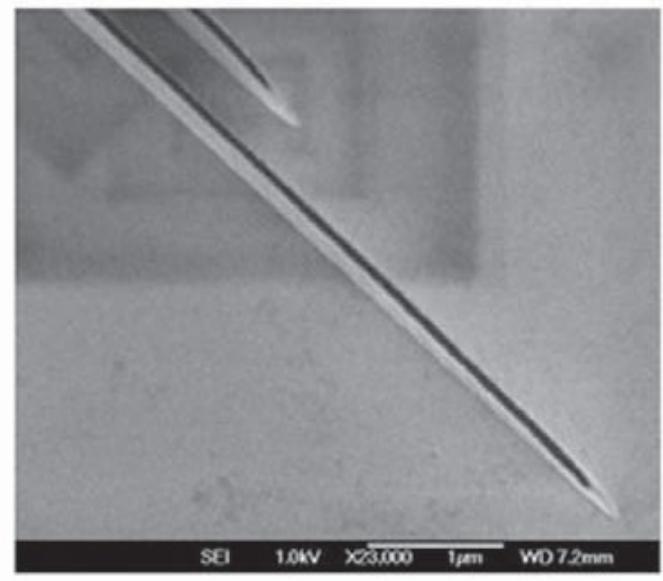
The proton dose required for exposure varies from $3\text{-}15\mu\text{C}/\text{cm}^2$ depending on the resist material, and is $\sim 50\times$ times faster than e-beam writing.



Parallel lines written in a 350nm thick PMMA layer using 2MeV p-beam

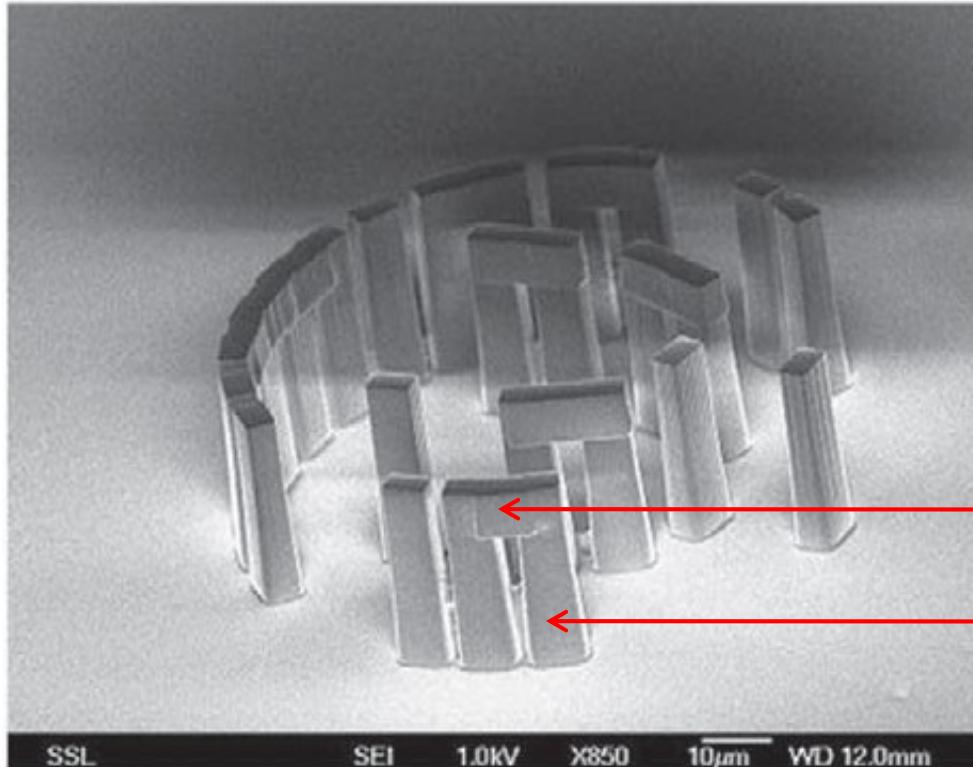


High aspect ratio structures in SU-8 resist showing 60nm wall structures that are 10μm deep



P-beam writing in hydrogen silsesquioxane (HSQ), high aspect ratio structures down to 22nm.

3D fabrication using proton beam



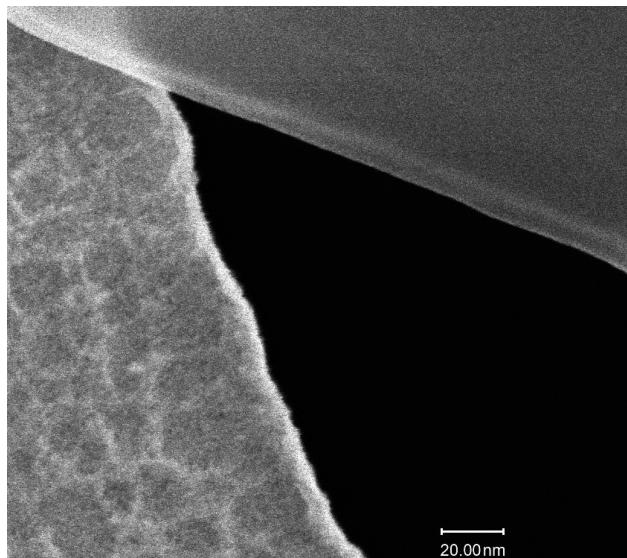
SU-8 is a negative resist,
positive resist won't work

Micro-sized copy of Stonehenge in the UK fabricated using p-beam writing in SU-8 resist.

Different depth exposure of two different proton energies, 500keV for fabricating the horizontal slabs and 2MeV for exposing the vertical supports.

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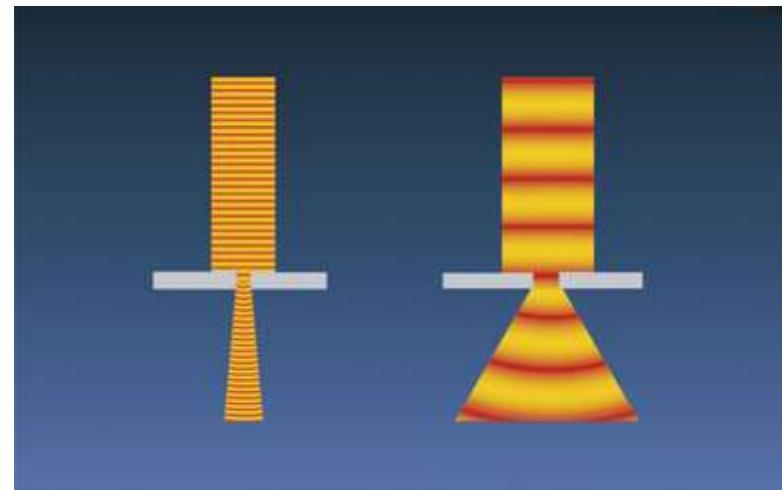
For demonstration of the image resolution of **0.24nm**, a line-scan over the very sharp edge of an asbestos fiber on a thin holey carbon foil is shown.

New trend: Scanning Helium Ion Microscope (SHIM)

Compared to SEM for high resolution *imaging*:

- Mass of He ion ($Z=2$, $M=4$) is $8000\times$, so $1/\sqrt{8000}$ shorter wavelength (for same eV), which leads to less diffraction for high resolution imaging.
- He ion has considerably smaller interaction volume (due to smaller penetration depth). This enables SHIM's resolution to be directly proportionate to its spot size which is not always the case with SEM.
- Like SIM using Ga^+ , SHIM has quite different material contrast than SEM.
- SHIM can produce $\sim 3\text{-}9$ secondary electrons per ion compared to ~ 1 per electron for SEM. Thus SHIM can image properly with ion currents $<1\text{pA}$ (small current – small aperture – small beam convergence angle α , so small beam size due to less chromatic and spherical aberration).
- Such small current also means little charging, thus SHIM can image insulating materials better.
- Higher depth of focus (by $\sim 5\times$).

He ion beam has a DeBroglie wavelength much smaller than an electron beam, resulting in much less diffraction.

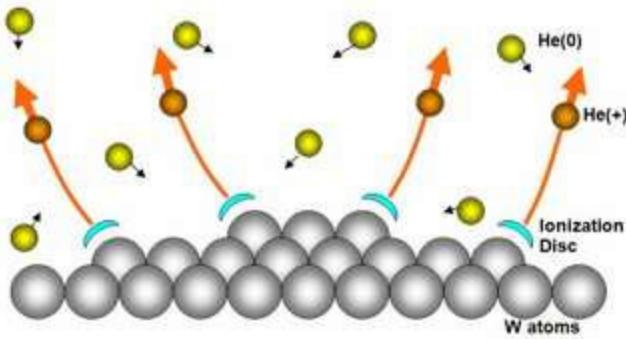


New trend: Scanning Helium Ion Microscope (SHIM)

Compared to FIB using Ga^+ ion:

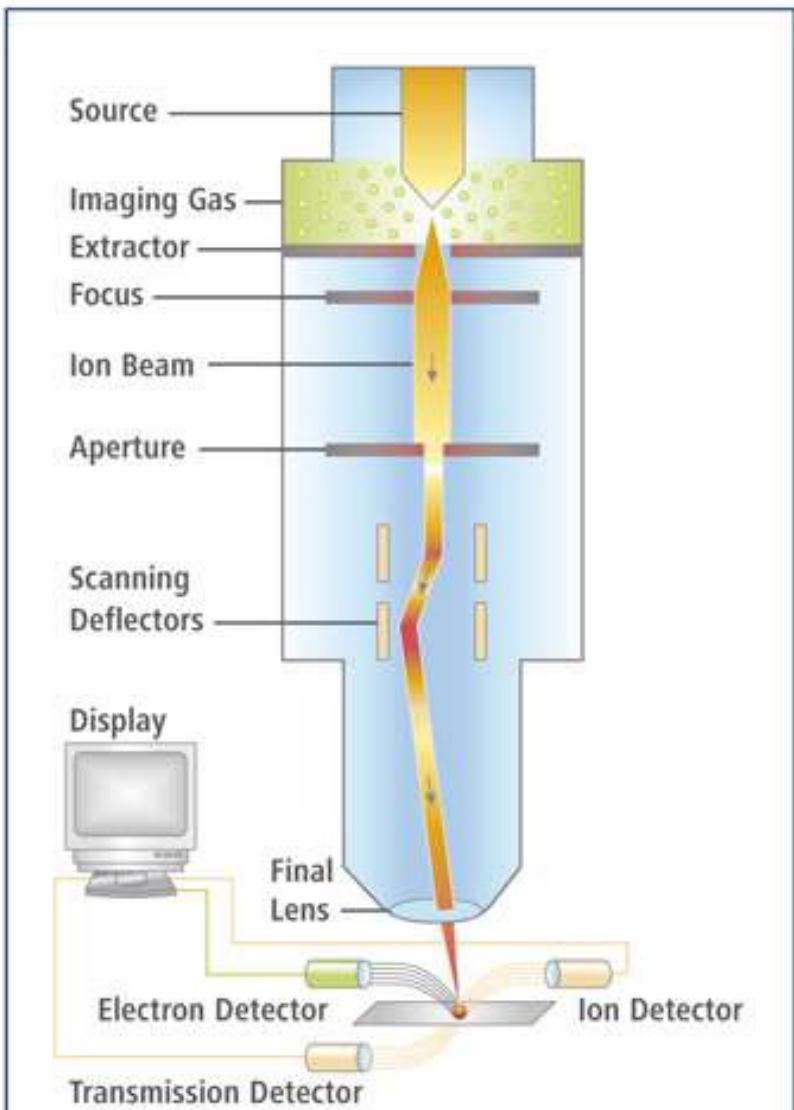
- He ion is much lighter, so much less damage and no “staining” by Ga.
- That is, He implantation doesn’t hurt much, whereas Ga does. At very high He dose, He bubble will form beneath sample surface, which may eventually blow off the surface.
- Little sputtering during imaging, so can image fine structures.
- It can still be used to mill material, yet milling is very slow (since He is light), though it can be chemically-assisted (add XeF_2 gas...) to get fast.
- It can also be used for material deposition, though in reality this is not a popular application for SHIM.

Gas field ion source (GFIS)



- GFIS has actually been researched on for longer than the LMIS. (liquid metal ion source, for Ga^+)
- But until ALIS (bought by Zeiss later on) came into the picture, nobody could achieve the stability, reliability and properties needed for a suitable helium ion beam that could match the spot size of a SEM.
- Like (cold) field emission SEM, electric field of $>10^8 \text{V/cm}$ is first achieved at the sharpest point of a W tip.
- Ionization can then take place at tip apex just like in field ion microscopy.
- He are accelerated away once they are ionized to form a beam that is accelerated by the ion column.
- Increasing He pressure increases the ion current proportionately, from 1fA to 100pA .
- Helium ion source has a very long lifetime due to the fact that the source tip is always kept at a positive potential. The only things attracted to the tip are electrons, which do not cause any ill effects. Positively charged ions are repelled from the tip and other gasses will be ionized before they have a chance to strike the source tip. For this reason, the source lifetime for the helium ion source is well over 1000 hours.

SHIM structure



Detectors:

Ion (backscattered He); Electron (secondary electron)
Transmission detector (for thin sample, He gets through)

The “trimmer”: for extremely sharp tip

- A finely sharpened needle is made even sharper - individual atoms are stripped away from the source until an atomic pyramid is created with just three atoms (trimmer) at the very end.
- This repeatable process can be accomplished in-situ. Once the trimmer is formed, the tip is maintained under high vacuum and cryogenic temperatures.
- The helium gas is attracted to the energized tip where it is ionized.
- With ionization happening in the vicinity of a single atom, the resulting ion beam appears to be emanating from a region $<1\text{\AA}$ in size.
- This produces an extremely bright beam that can be focused to an extraordinarily small probe size.

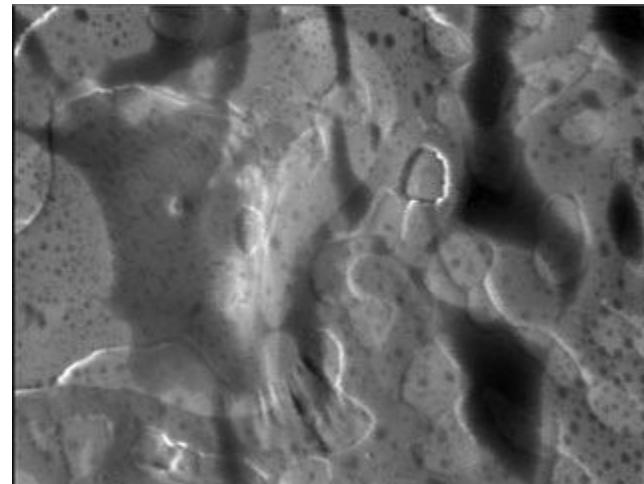
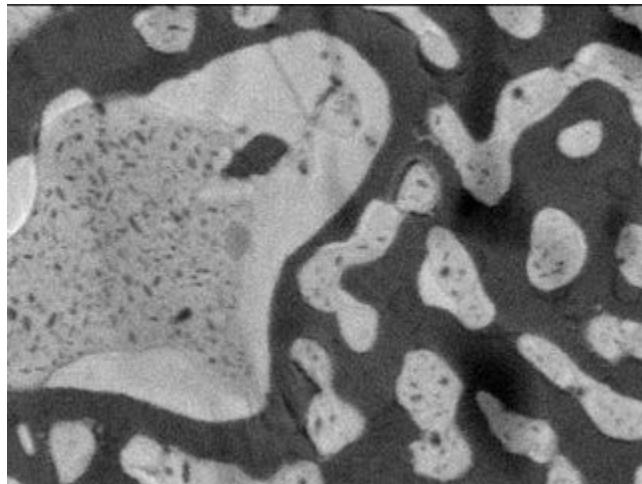


Image of the atoms at the end of the source tip emitting helium ions. Since each atom can be individually seen, the virtual source size must be much smaller.

34

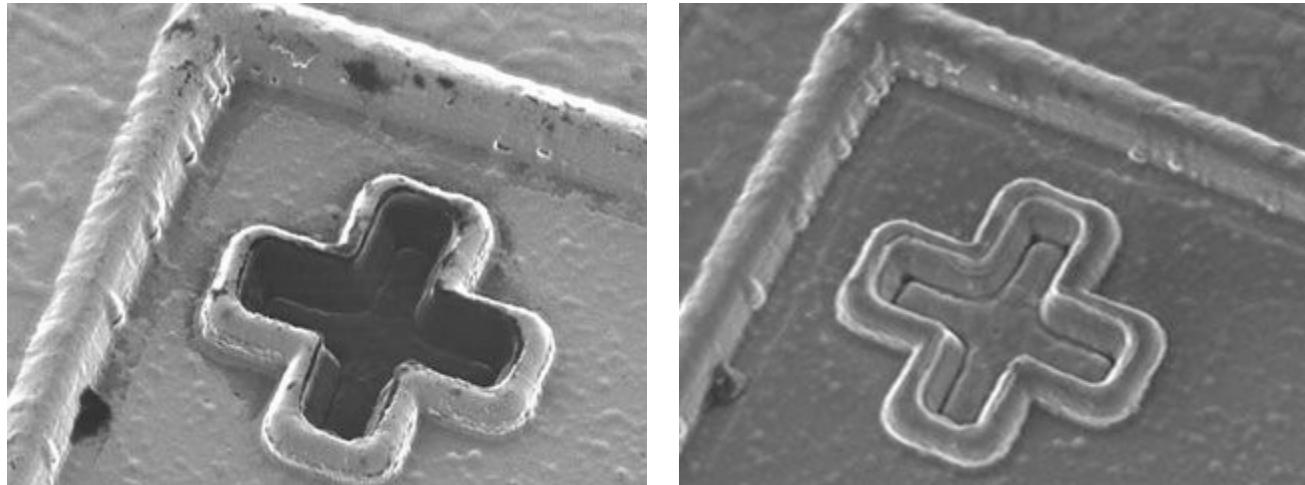
Application of SHIM

“(SHIM) is clearly a serious and major breakthrough in “seeing” things. The applications of this technology are immense. Imagine, a microscope, with the resolution of (close to) a TEM, does not require sample preparation, provides higher voltage and material contrast information, inert ion beam with much less volume interaction leaving no artifacts. And to top it all off, it’s still the start whereas electron microscopy and focused ion beam microscopy has been under development for over 40 years.”

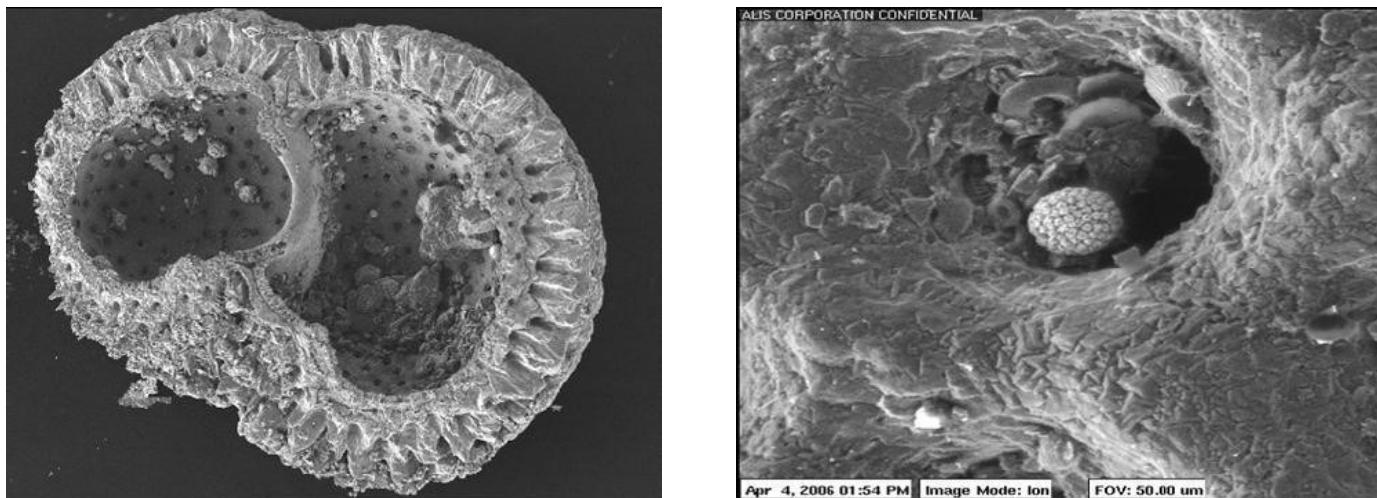


Left: SHIM image of a solder bump showing the difference in the lead and tin sections. Right: SEM image of the same sample.

Application of SHIM



SHIM image of a sample. It is discernible that the material in the cross is different from the outside. Some of the dark specks are actually material from the inside scattered on the outside. Right: SEM image of the same sample.



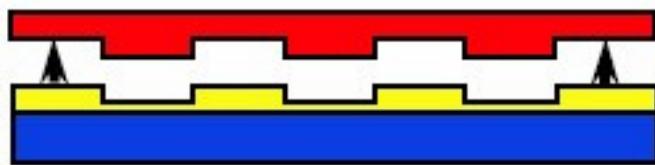
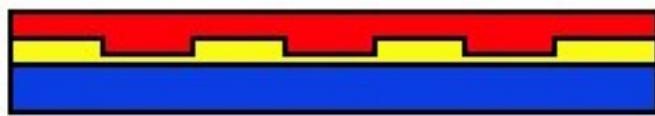
Left: SHIM *backscattered* (He ion) image of Benthic Foraminifera. Right: Benthic Foraminifera. Note that both of these samples are insulators and no sample preparation was made.

Nanoimprint lithography (NIL)

1. Overview and thermal NIL resists.
2. Residual layer after NIL.
3. NIL for large features (more difficult than small one).
4. Room temperature NIL, reverse NIL, NIL of bulk resist (polymer sheet, pellets).

Two NIL approaches

Thermal NIL

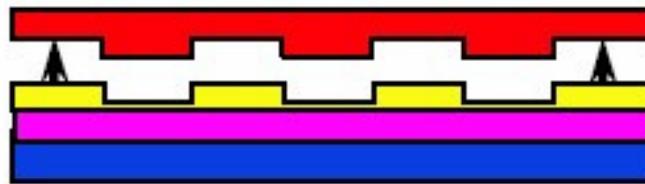
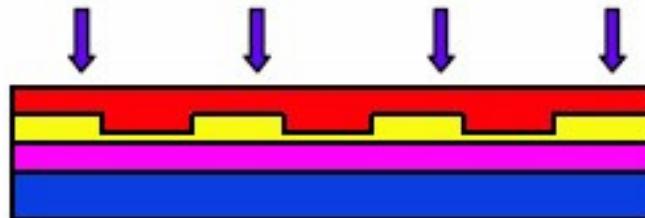
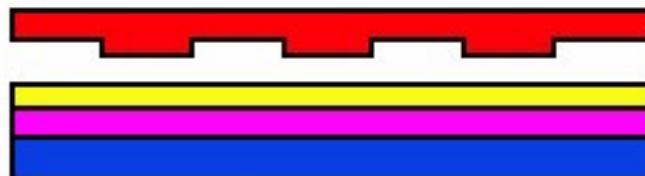


RIE residual layer

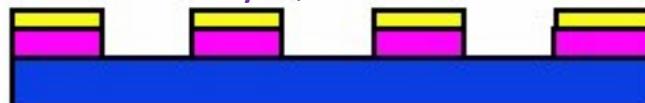


Heat up to soften the resist, imprint,
cool down and separate

UV-curing NIL



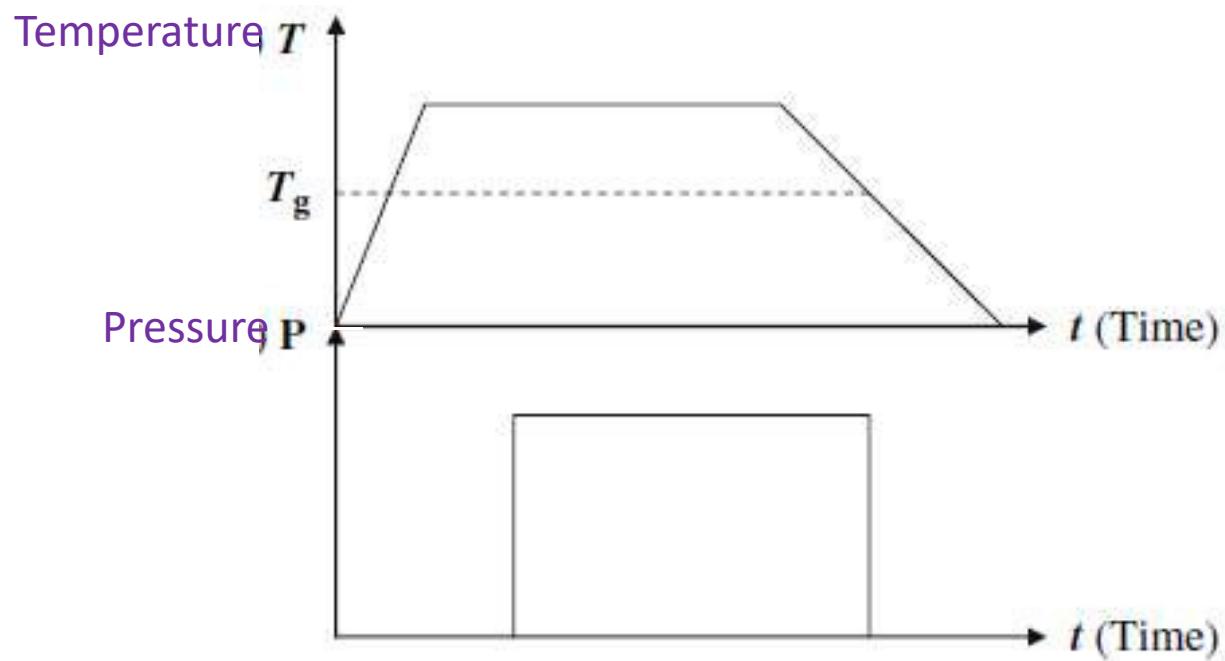
RIE residual layer, transfer into under-layer



Liquid (soft) resist, hardened by UV
irradiation due to cross-linking

Thermal nanoimprint

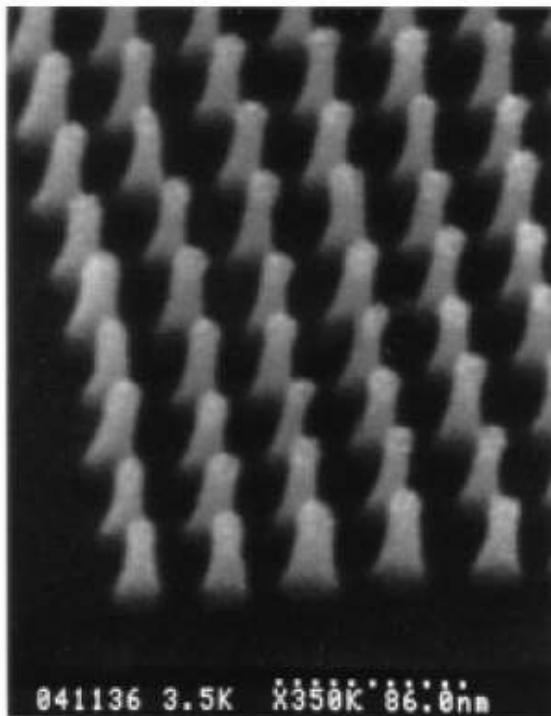
Temperature and pressure evolution during thermal press nano-imprinting



- Typical temperature is $100^{\circ}\text{C} – 200^{\circ}\text{C}$, $\sim 30\text{-}50^{\circ}\text{C}$ above resist's glass transition temperature.
- Typical pressure is about 20-50 atm, depends on resolution and pattern in the mold (easy for protruded feature, higher pressure for recessed feature in mold)

Key advantage of NIL: highest resolution

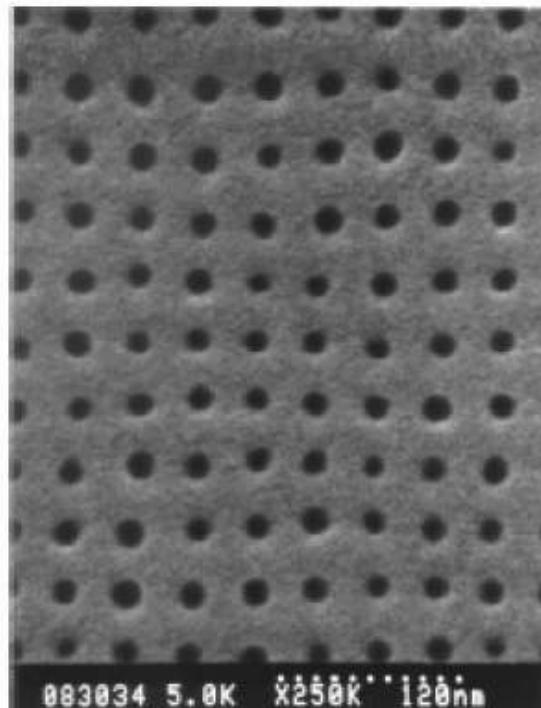
Mold



041136 3.5K X350K i86.0nm

10 nm dia pillar mold

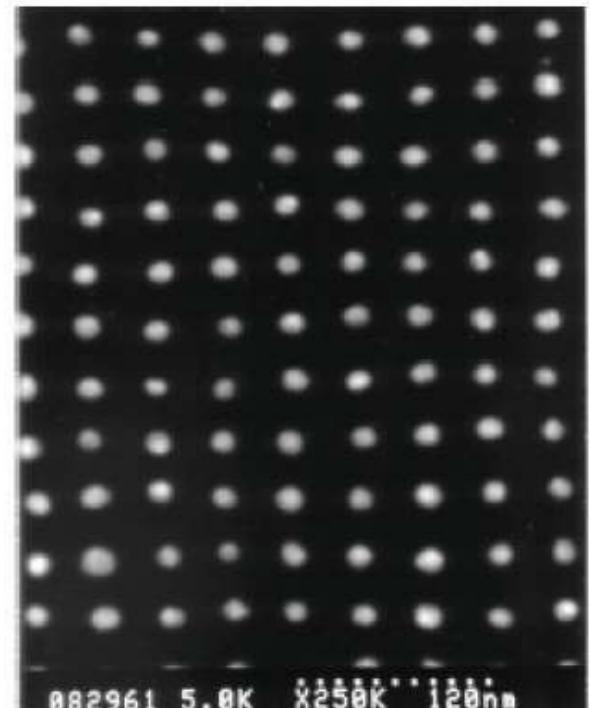
Resist



083034 5.0K X250K i120nm

10 nm dia resist holes
by imprinting

Lift-Off



082961 5.0K X250K i120nm

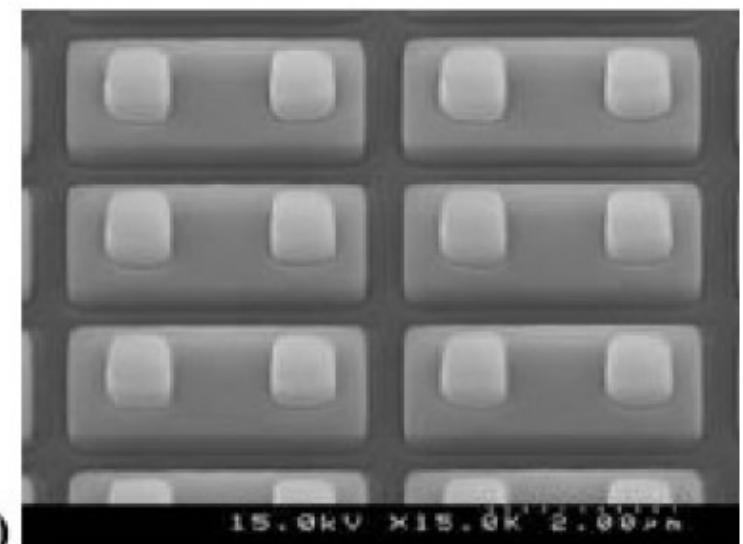
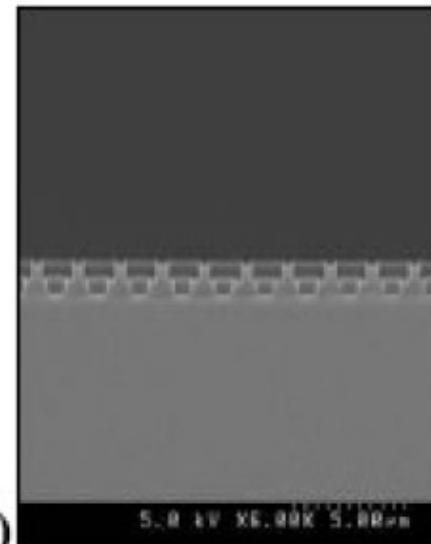
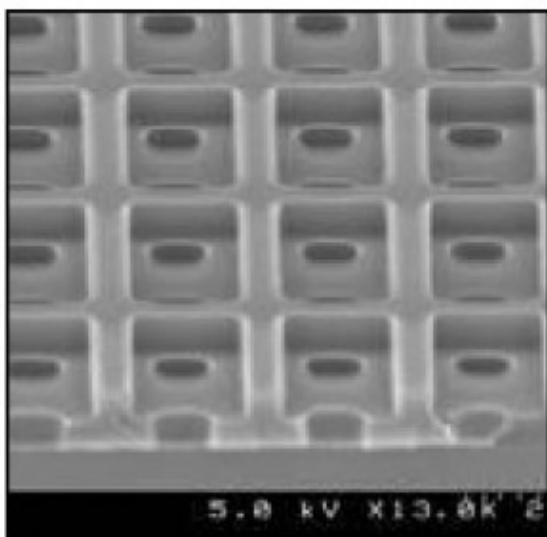
10 nm dia metal dots
by imprint and lift-off



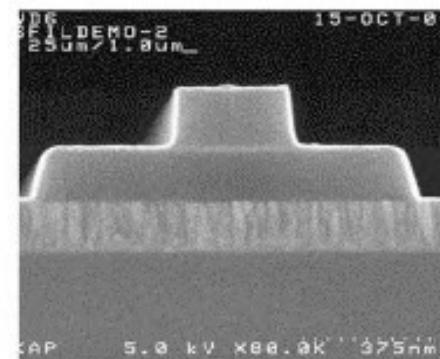
NanoStructure Laboratory

PRINCETON UNIVERSITY

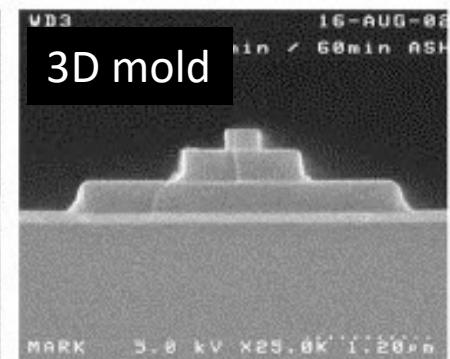
Another key advantage: 3D imprinting



- Patterning of the via and interconnect layers simultaneously, in CMOS BEOL .
 - Thus potentially reduces the number of masking levels needed in BEOL.
- (BEOL: back end of line)



2 tier, using oxide/ITO



3 tier using oxide/ITO

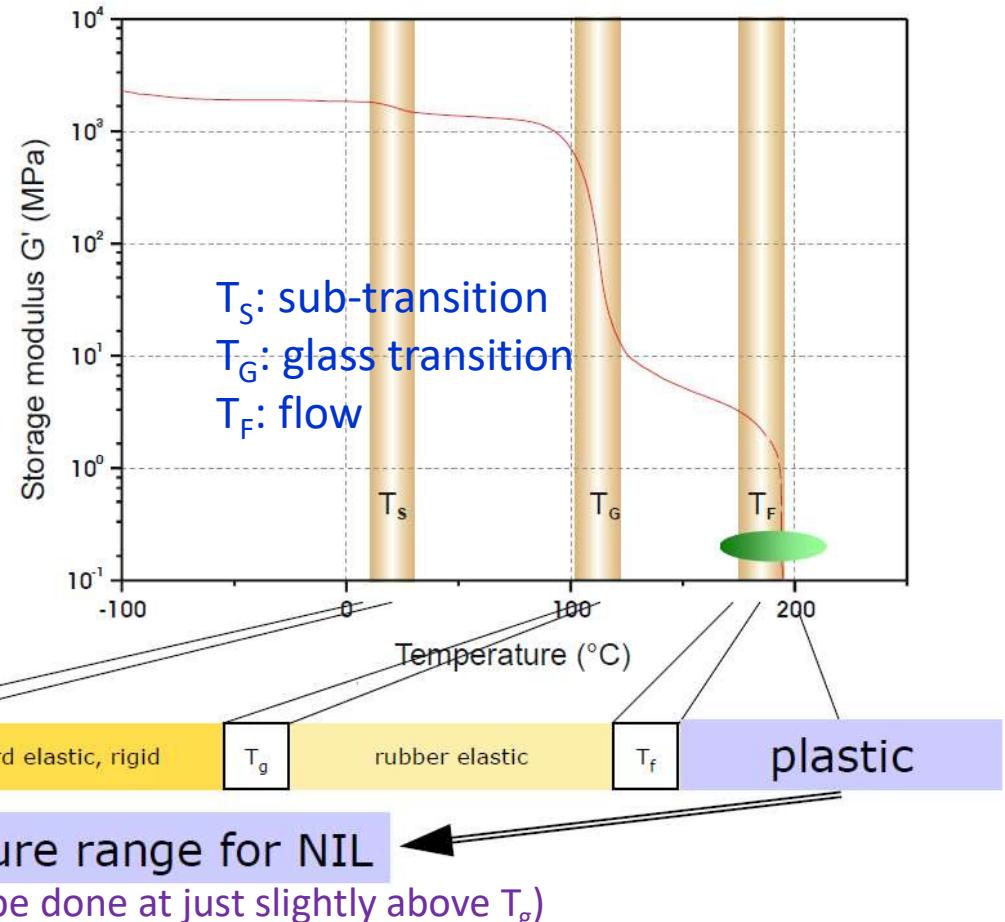
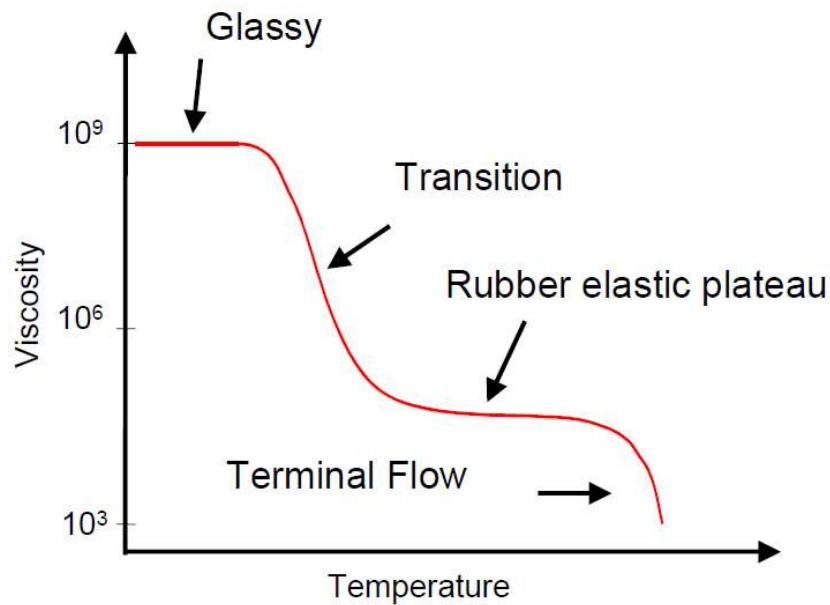
Wikipedia: **Back end of line (BEOL)** is the portion of integrated circuit fabrication line where the active components (transistors, resistors, etc.) are interconnected with wiring on the wafer. BEOL generally begins when the first layer of metal is deposited on the wafer. It includes contacts, insulator, metal levels, and bonding sites for chip-to-package connections.

Nanoimprint lithography (NIL)

1. Overview.
2. Thermal NIL resists.
3. Residual layer after NIL.
4. NIL for large features (more difficult than small one).
5. Room temperature NIL, reverse NIL, NIL of bulk resist (polymer sheet, pellets).

“Standard” resist for NIL: PMMA

Glass transition and flow temperature of PMMA



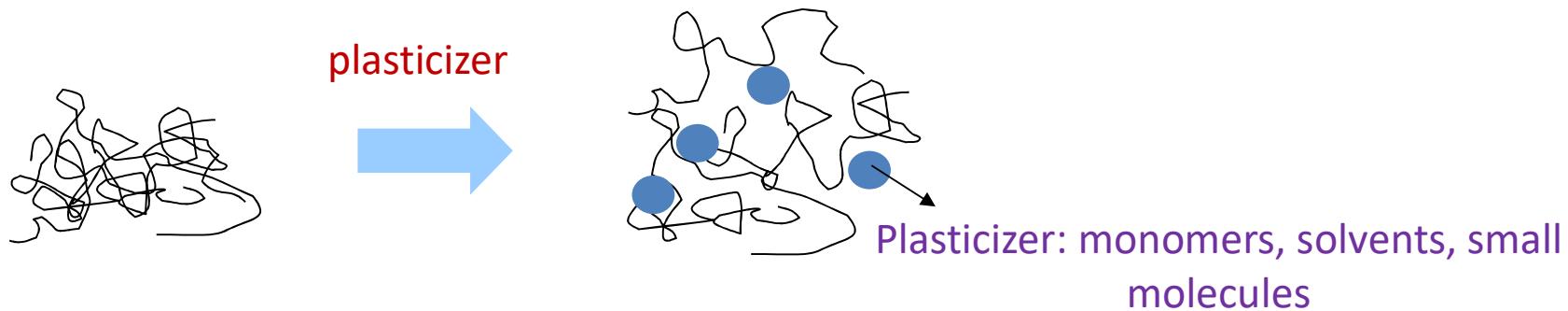
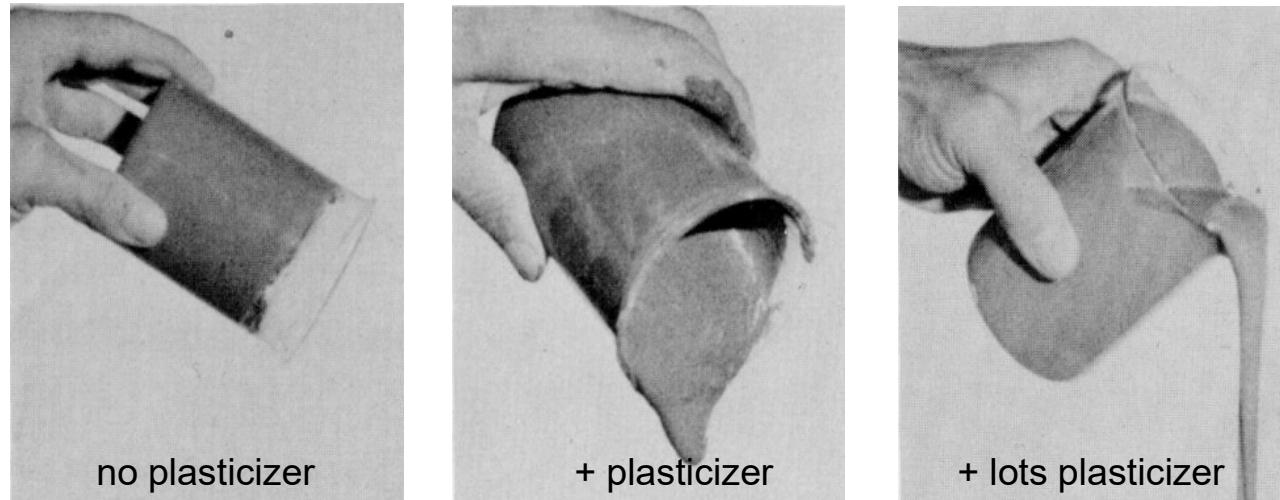
Comments:

PMMA is the choice for beginners, not optimized for NIL. $T_g = 105^\circ\text{C}$, NIL at $> 150^\circ\text{C}$.

Polystyrene (T_g close to PMMA) is slightly better – easy separation due to lower surface energy.

Poly(vinyl phenyl ketone) is comparable to polystyrene but with T_g only 58°C . NIL at 95°C . ⁷

T_g can be lowered by adding plasticizer into the resist

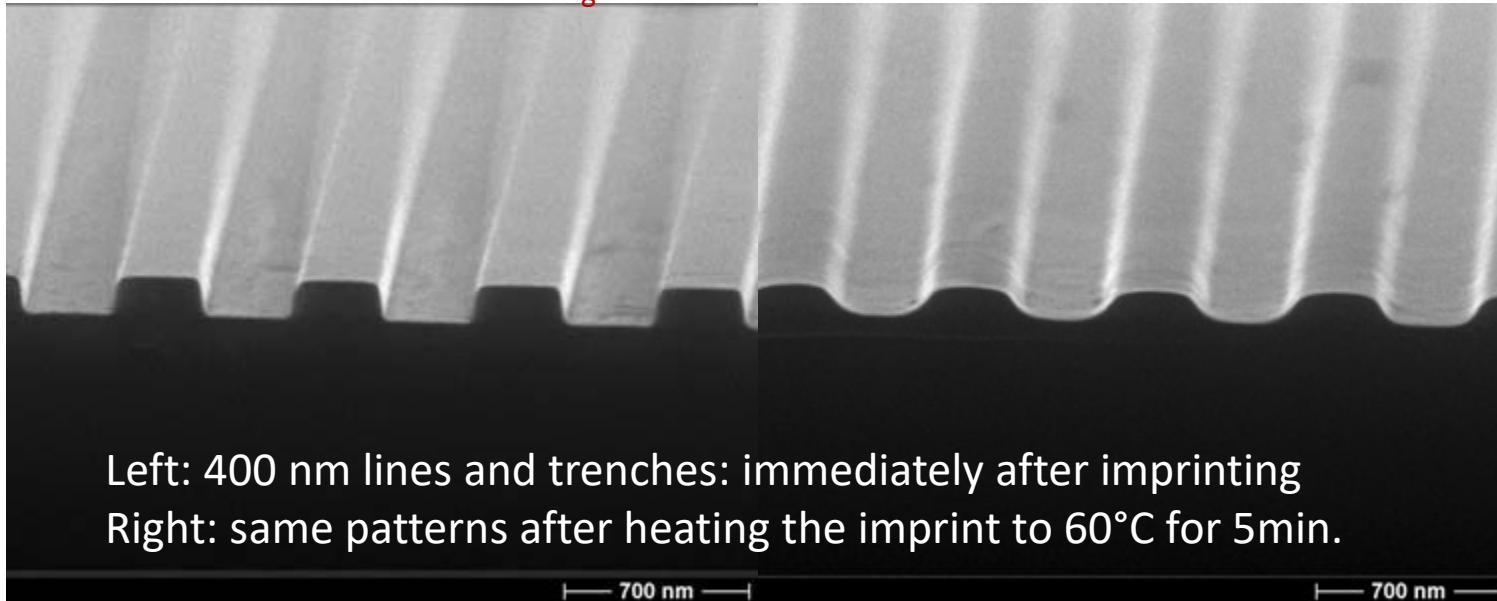


Plasticizer: decreased chain entanglement, increased chain motion.

Polymer with low T_g

- Low imprint temperature
- Good polymer flow at moderate temperature
- Less problems with thermal expansion
- Shorter thermal cycle time

Example: thermoplastic with T_g 40 °C



Left: 400 nm lines and trenches: immediately after imprinting

Right: same patterns after heating the imprint to 60°C for 5min.

- Thermal stability of imprinted patterns (deterioration by thermal flow) is determined by the glass transition temperature.
- Sufficient thermal stability of imprinted patterns is necessary in subsequent processes such as metal evaporation for liftoff or plasma etching.

Approach to thermal stability

Imprinting at low/
moderate temperature

Imprints with
sufficient thermal
stability

Low T_g (pre)polymers

Curing of the
imprinted polymer

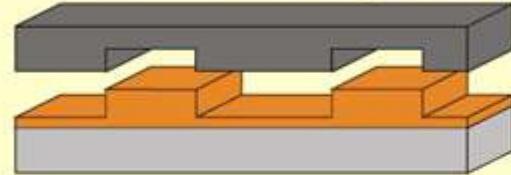
Spin coating and prebake



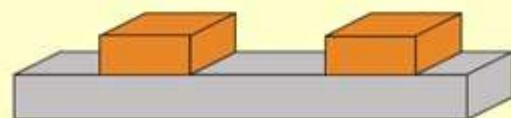
Nanoimprinting @ $T > T_g$ and
thermal curing ($T_g \nearrow$)



Mould detachment @ $T < T_g$



Anisotropic plasma etch

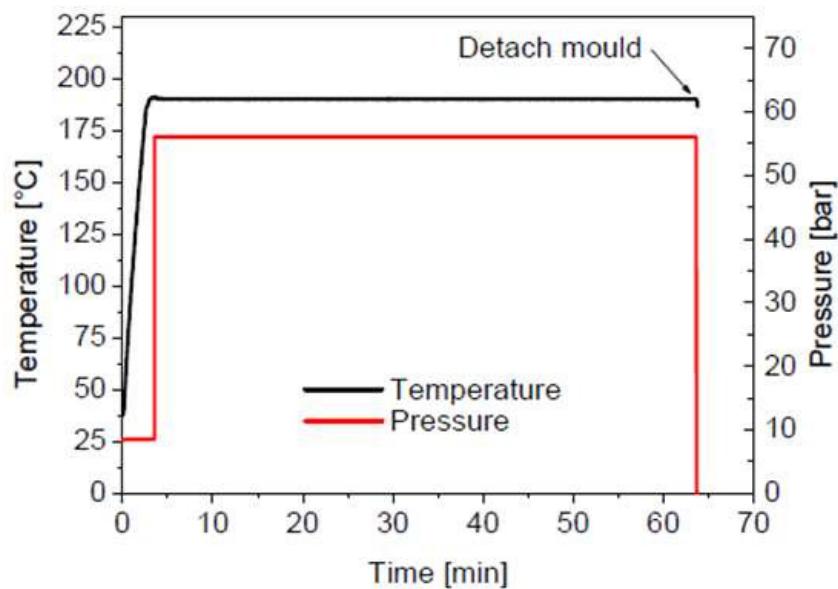


Thermal-set/curable resist:

(low T_g pre-) polymer is cured (cross-linked) upon heating, making it stable at very high temperatures.

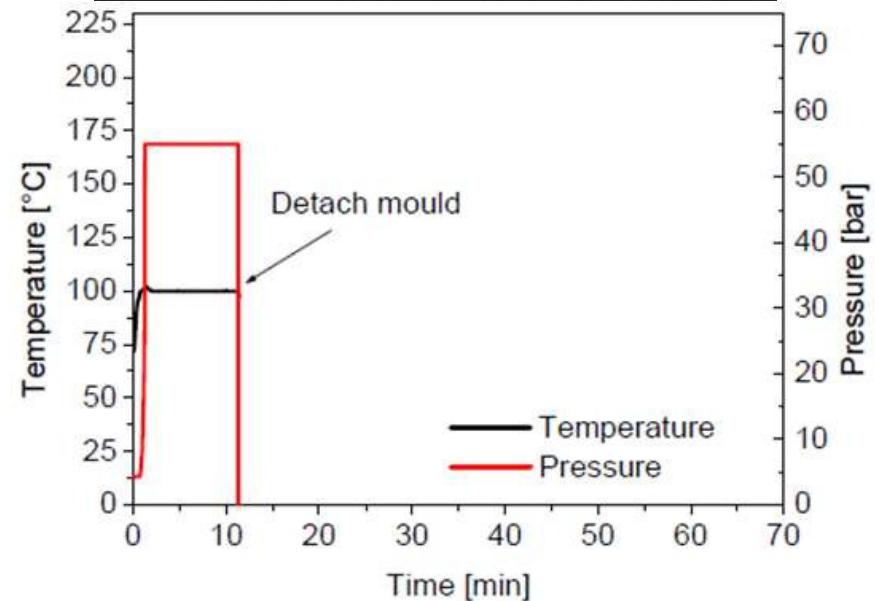
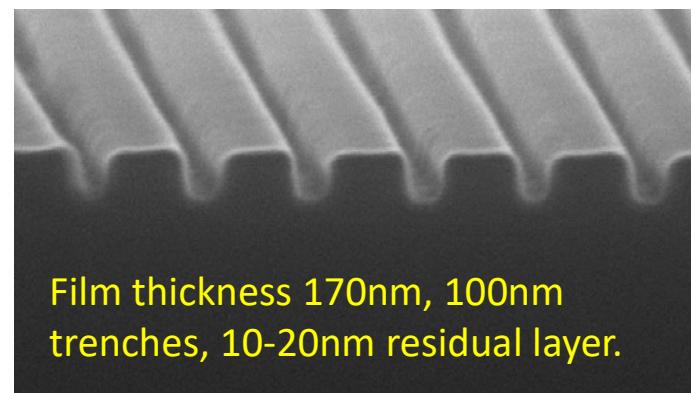
Fast iso-thermal (no thermal cycle, no cooling) nanoimprint

- Isothermal imprinting due to increase in T_g during imprinting (so no need to cool down).
- Reduce issues of thermal expansion.
- Decrease considerably imprint time (since no cooling).



Starting model system:

NIL at 190°C for 1 hour for sufficient curing.



Add initiator + plasticizer:

Imprint at 100°C for 10min, no cooling.
(Initiator to increase curing speed;
plasticizer to lower imprint temperature)

Functional “resist”: nano-crystal (NC)/polymer based materials

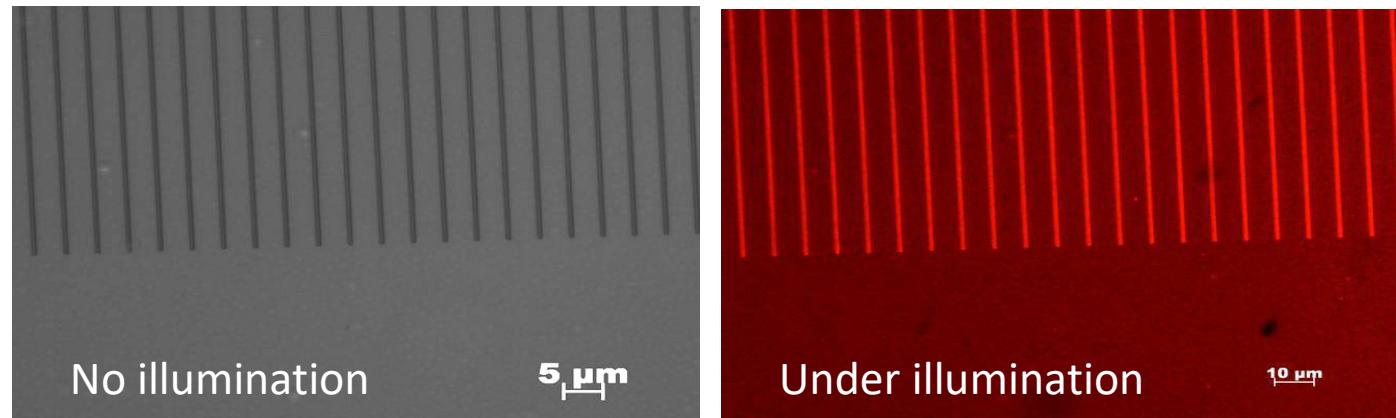
Synthesis and functionalisation of colloidal nanoparticles for incorporation into thermoplastic or thermal-curing (i.e. thermal-set) polymers.

Tuning of functional properties:

- Optical absorption and emission
- Mechanical Stability
- Conductivity...



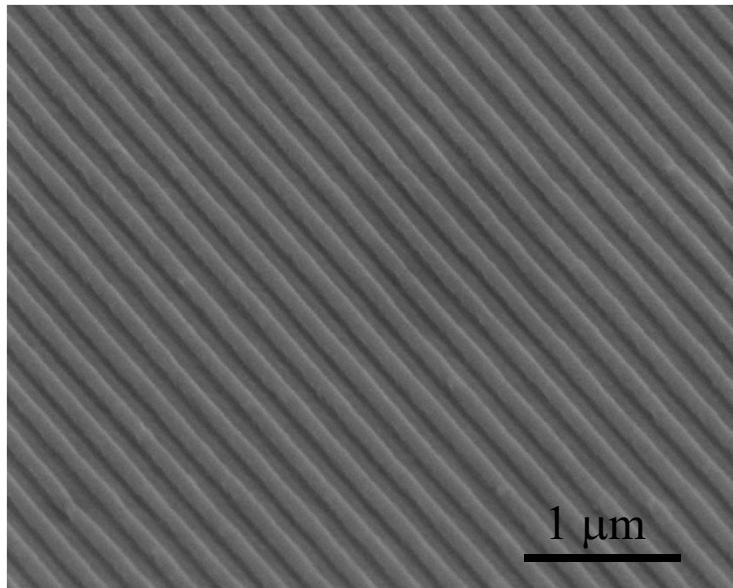
Size dependent luminescent CdSe NCs (quantum dot)



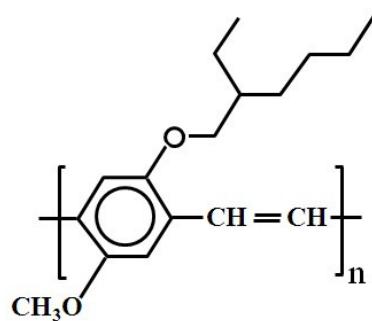
CdSe@ZnS nano-crystals (NC) in PMMA modified co-polymer.
Homogeneous distribution of NCs inside the polymer matrix.

Functional “resist”: semiconducting polymer

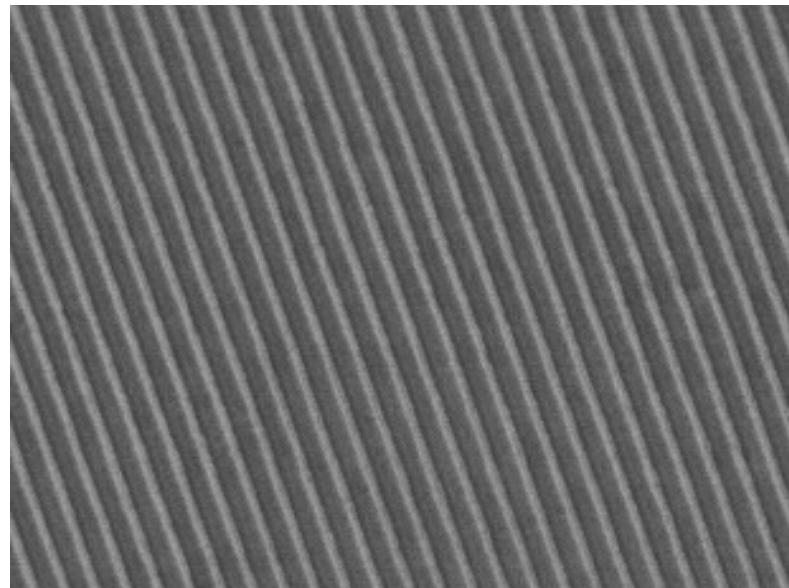
SEM image of 200nm period MEH-PPV grating



MEH-PPV $T_g=65^\circ\text{C}$.
Hot embossing at 120°C and 20bar.
MEH-PPV spun on a PEDOT/ITO/glass.



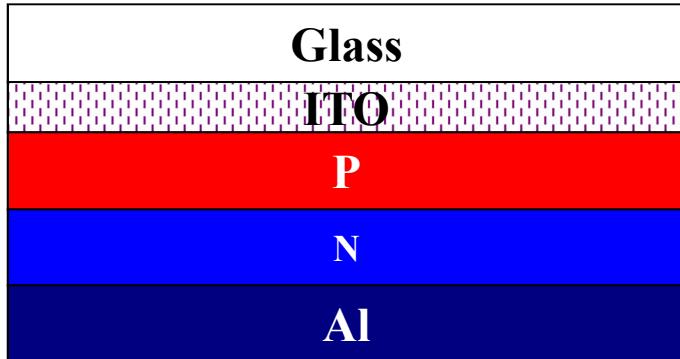
R-P3HT grating with 200nm period



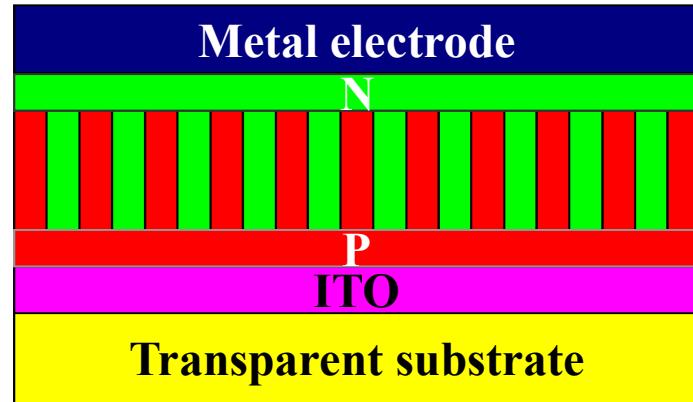
R-P3HT 200nm period grating.
NIL at 160°C and 35 bar.
Strong physical bond, high transition temperature.

Application: nanostructured plastic solar cell

MEH-PPV is a popular p-type semiconducting polymer for plastic solar cell.
(The n-type material is Alq₃, [http://en.wikipedia.org/wiki/Tris\(8-hydroxyquinolinato\)aluminium](http://en.wikipedia.org/wiki/Tris(8-hydroxyquinolinato)aluminium))



Classic planar p-n junction, low junction area, low efficiency



Nanostructured junction, high junction area, high efficiency

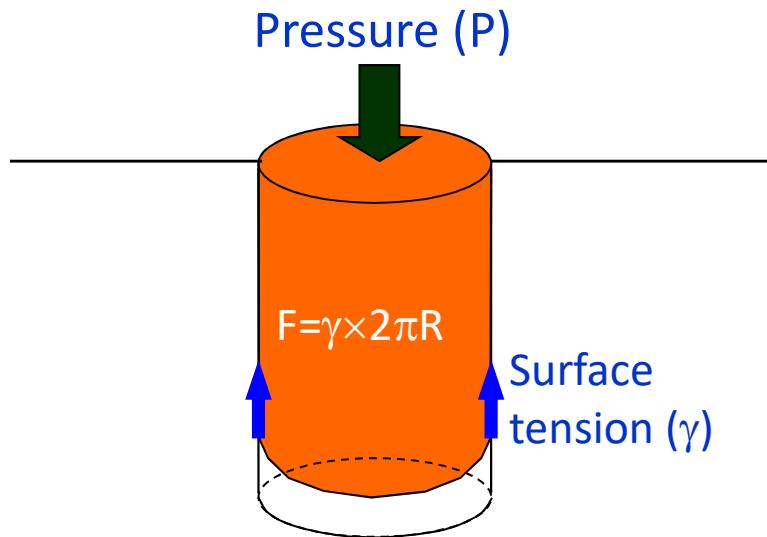
- Plastic solar cells: flexible, light weight, tunable electrical properties, and potential lower fabrication cost.
- Limitation: low energy conversion efficiency due to low carrier mobility.
- One method to increase efficiency: increase the interface area by nano-patterning the p-n junction.

Nanoimprint lithography (NIL)

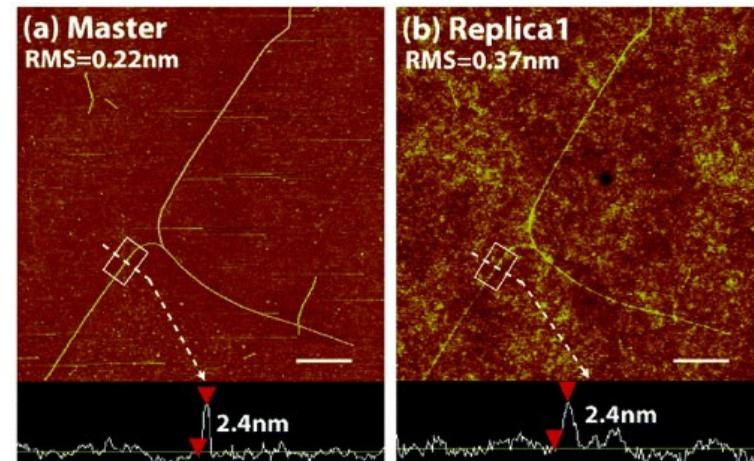
1. Overview.
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NIL for small features/high resolution (<10nm)

Press liquid into a nano-hole



$$P = \frac{\gamma \times 2\pi R}{\pi R^2} = \frac{2\gamma}{R} \propto \frac{1}{R}$$



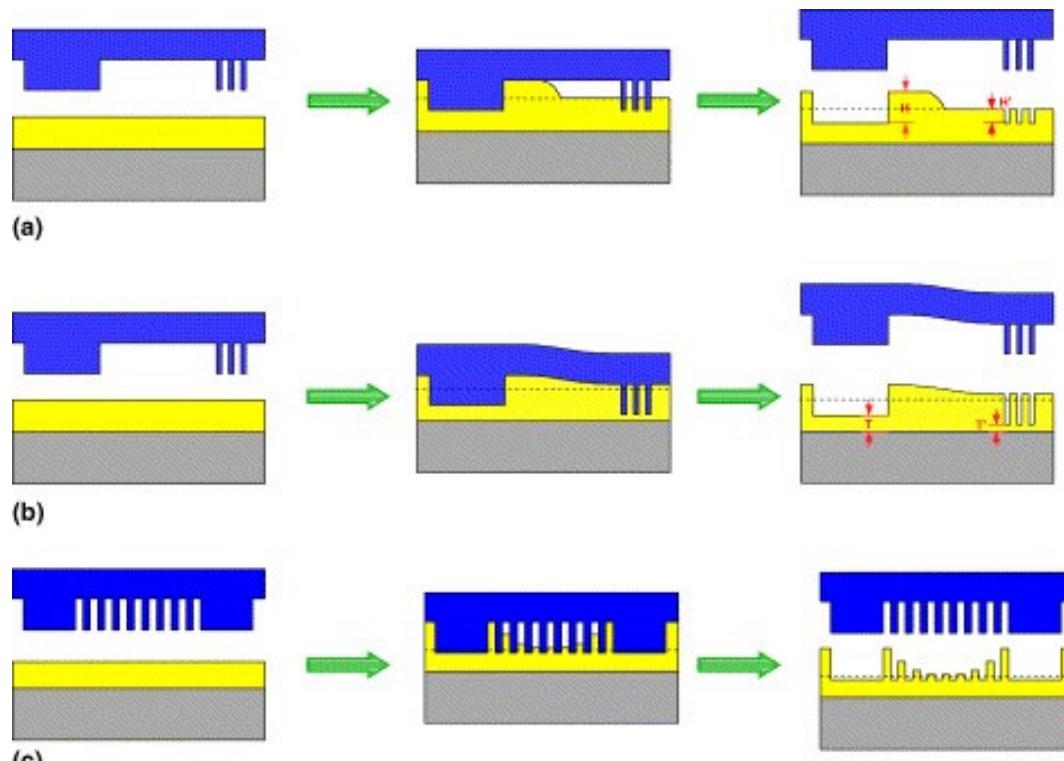
UV-curable NIL, **2nm** carbon nanotube mold

- Pressure \propto 1/diameter.
- But for protruded mold features (pillars...), local pressure at the pillar is much higher than average - easy to imprint.

NIL for large features ($>100 \mu\text{m}$) - simultaneous pattern duplication of large and small features

- Application: large features are needed to connect small ones to the outside world (electrodes...).
- Challenge: more polymer must be displaced over longer distances.
- A popular approach: two-step process - small features by NIL, large ones by photolithography with alignment.

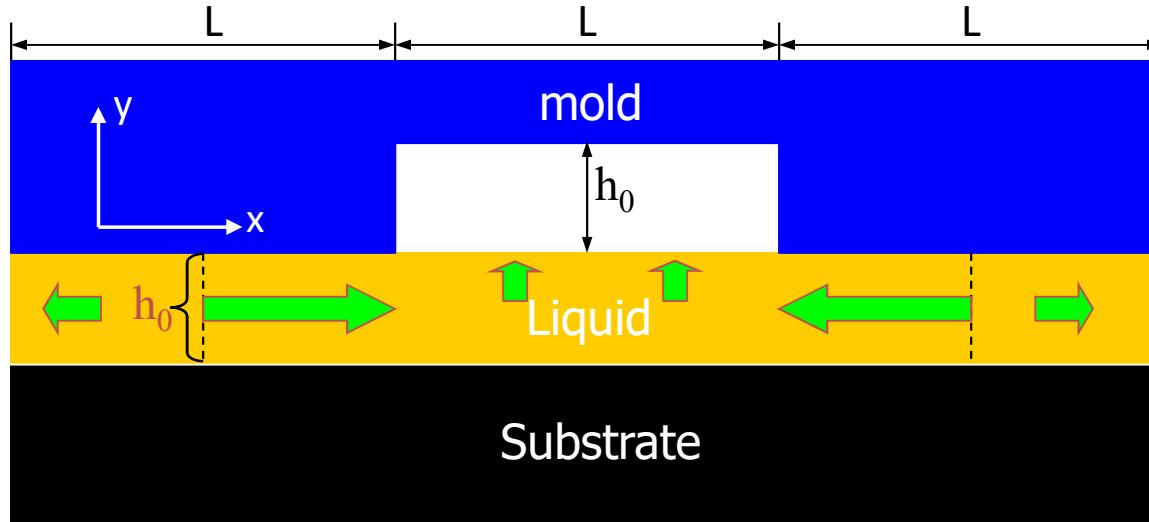
Problems when both small and large features are present



Schematics of pattern failure mechanisms in NIL as a result of: (a) non-uniform pattern height; (b) non-uniform residual layer thickness; (c) incomplete nano-pattern replication.

Cheng, "One-step lithography for various size patterns with a hybrid mask-mold", Microelectronic Engineering 71, 288–293 (2004).

Modeling of liquid flow for large features (>>pattern depth)



Assumptions:

- Periodic mold structure (period $2L$)
- Ignore inertial, gravitational force and surface tension
- Resist film thickness = mold trench depth = h_0

$$L = \frac{2h_0}{3} \sqrt{\frac{p\tau}{\mu}} \propto \left(\frac{p\tau}{\mu} \right)^{1/2}$$

L: achievable feature size

p: pressure

τ : imprinting time

μ : viscosity

h_0 : film thickness

Strategy to imprint large features (mm)

$$L \propto \left(\frac{p \tau}{\mu} \right)^{1/2} \propto \frac{1}{\sqrt{\mu}}$$

For thermoplastic polymer PMMA at $T > T_g$

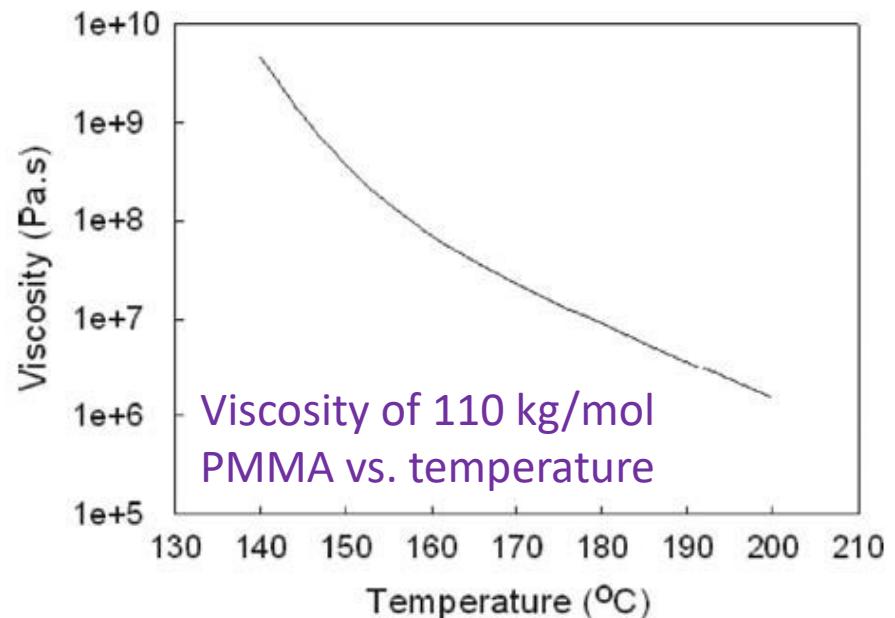
$$\log \mu = n \log M_w - \frac{12.21(T - T_g)}{70.1 + (T - T_g)} + const$$

M_w : molecular weight

$n=1$ for $M_w < M_c$, un-entangled molecules

$n=3.4$ for $M_w > M_c$, entangled molecules

The constant in the equation is also different for the two cases!!



Viscosity for PMMA ($M_c=30\text{kg/mol}$)

a) 12 kg/mol, 200°C; b) 12 kg/mol, 150°C; c) 120 kg/mol, 200°C

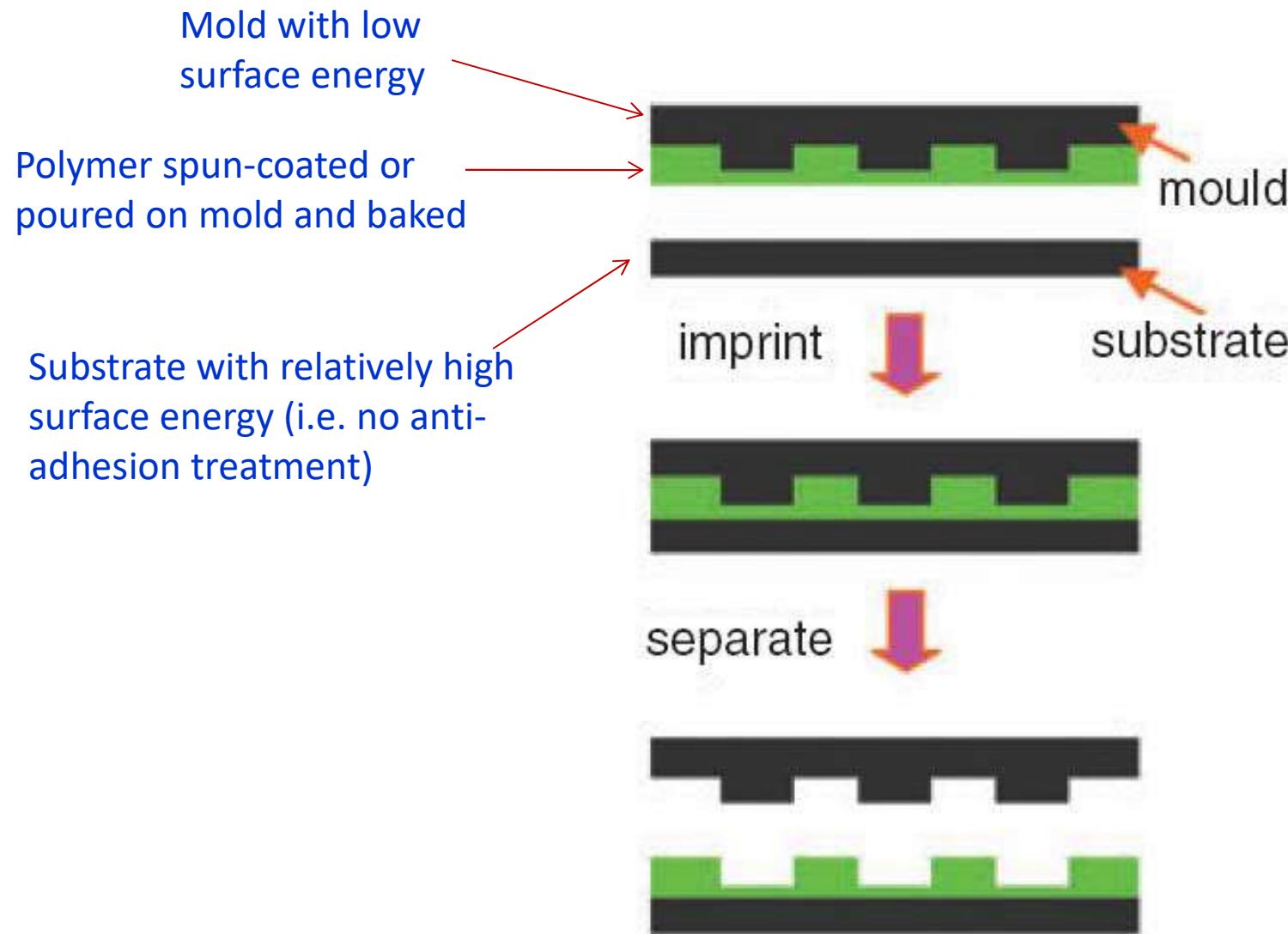
$\mu_a : \mu_b : \mu_c = 1 : 126 : 278$

Therefore, use low molecular weight PMMA and imprint at high temperature

Nanoimprint lithography (NIL)

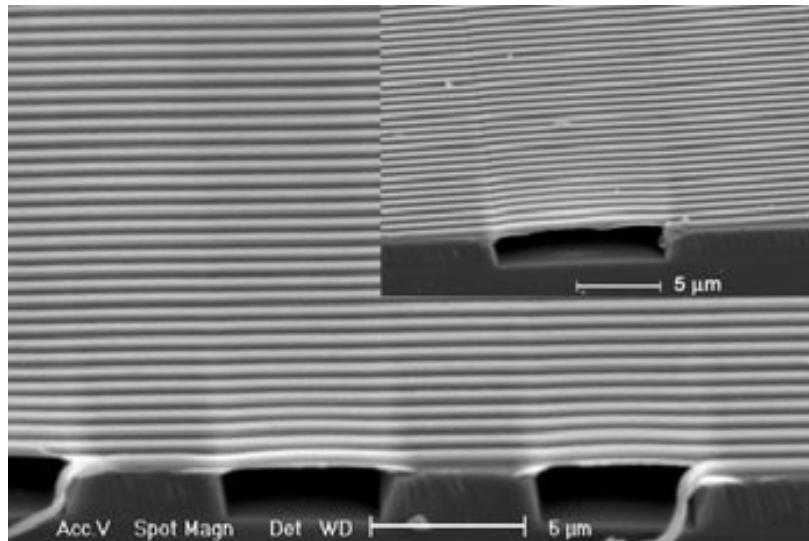
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Reverse NIL

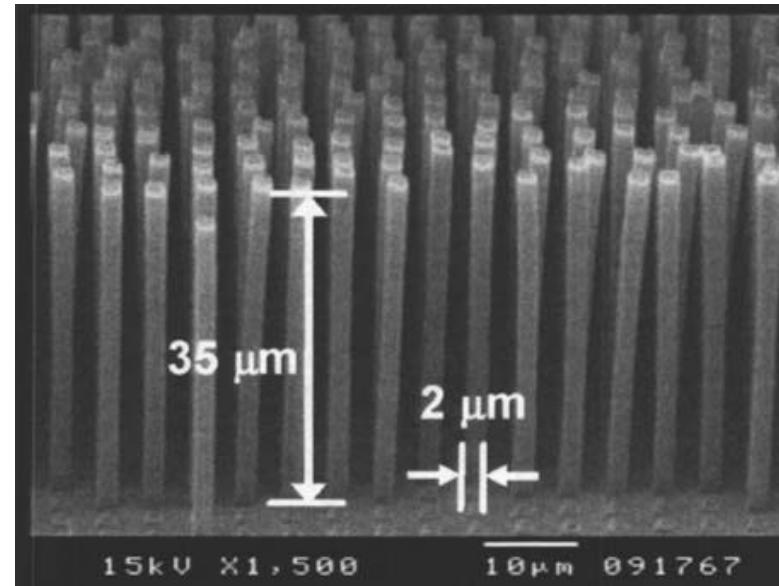


L. J. Guo, J. Phys. D 37, R123 (2004)

Reverse NIL: result



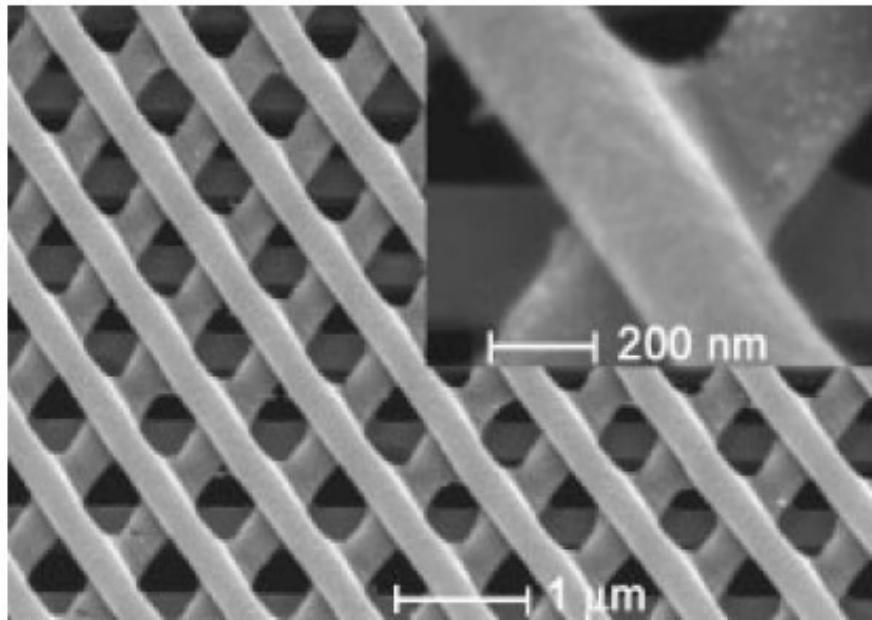
Polycarbonate grating imprinted across 5 μm and 10 μm (insert) gaps in silicon.



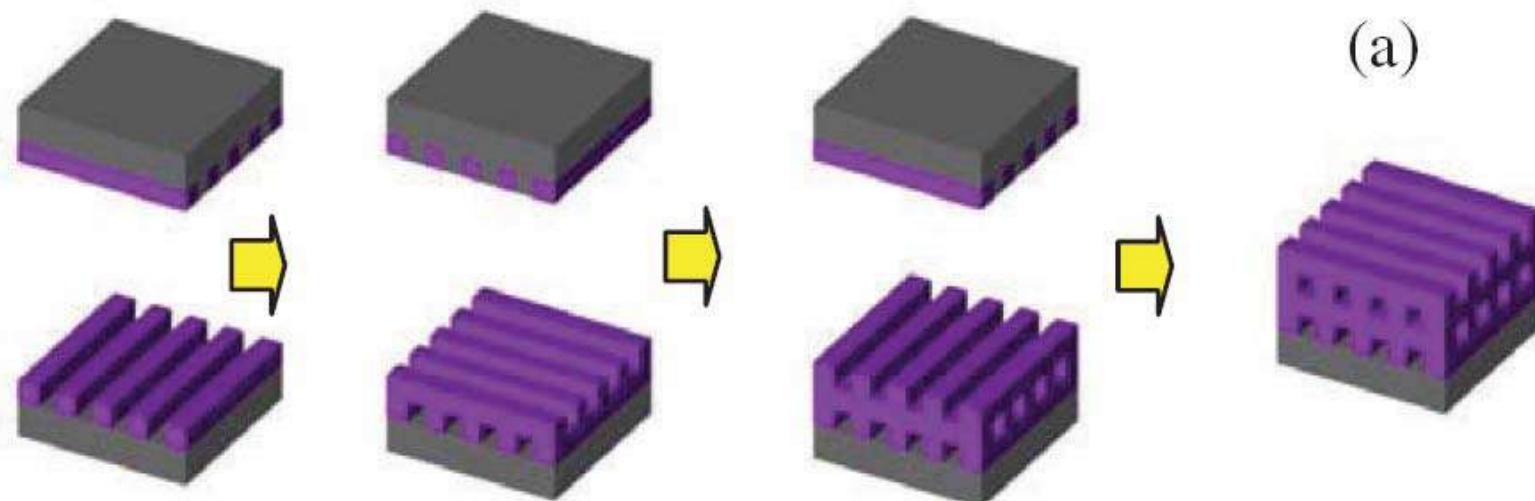
High-aspect-ratio PMMA pillars replicated by cast molding (reverse NIL).

- PMMA is dissolved in toluene (or chloroform) that “wets” the mold treated with anti-stick low surface energy layer.
- Since they wet each other, resist solution goes into the mold pattern by capillary force.
- The separation (de-molding) is actually easier than regular imprint, since now there is no external force applied to squeeze the polymer into cavity, and thus there is no shear stress in the molded polymer structures. (shear stress makes separation more difficult)

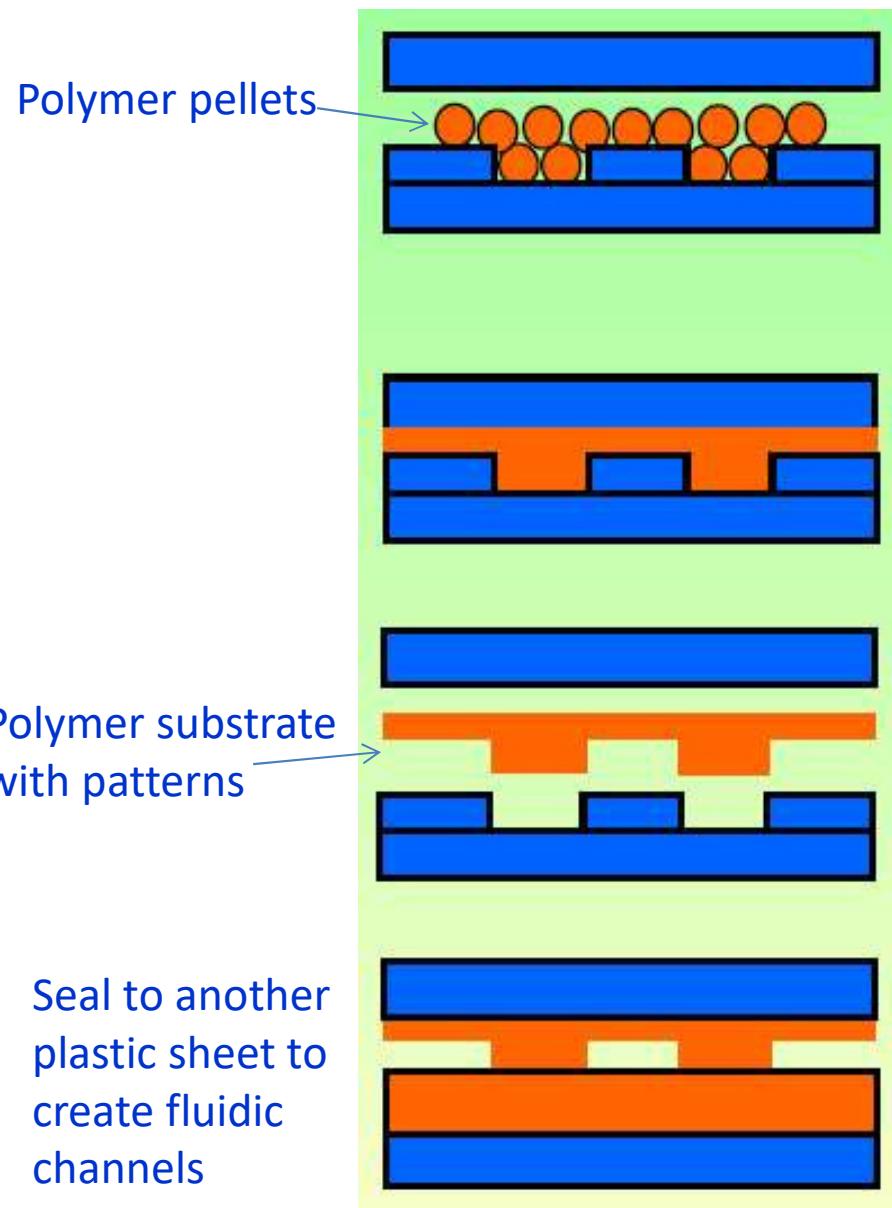
Layer-by-layer NIL (repeated reverse NIL)



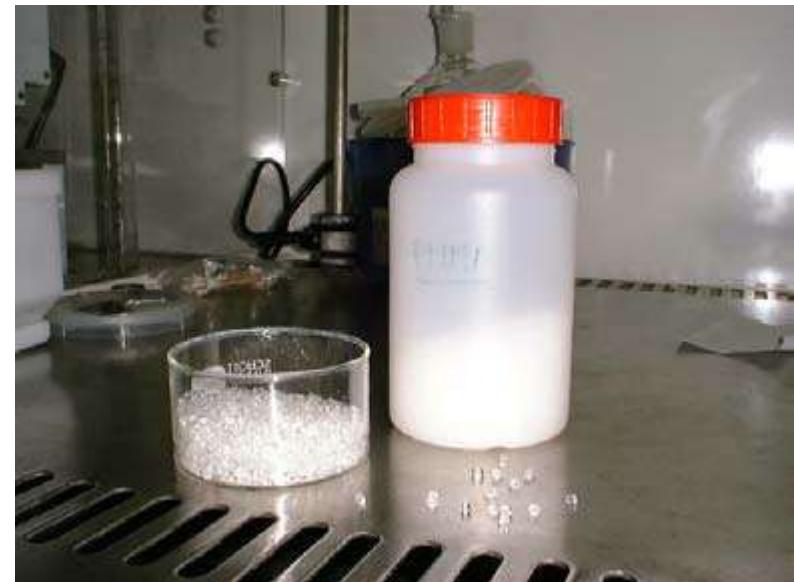
The glass transition temperatures of the polymers must be lower for later/upper layers. Here the residual layer has been dry-etched.



Hot embossing pellets

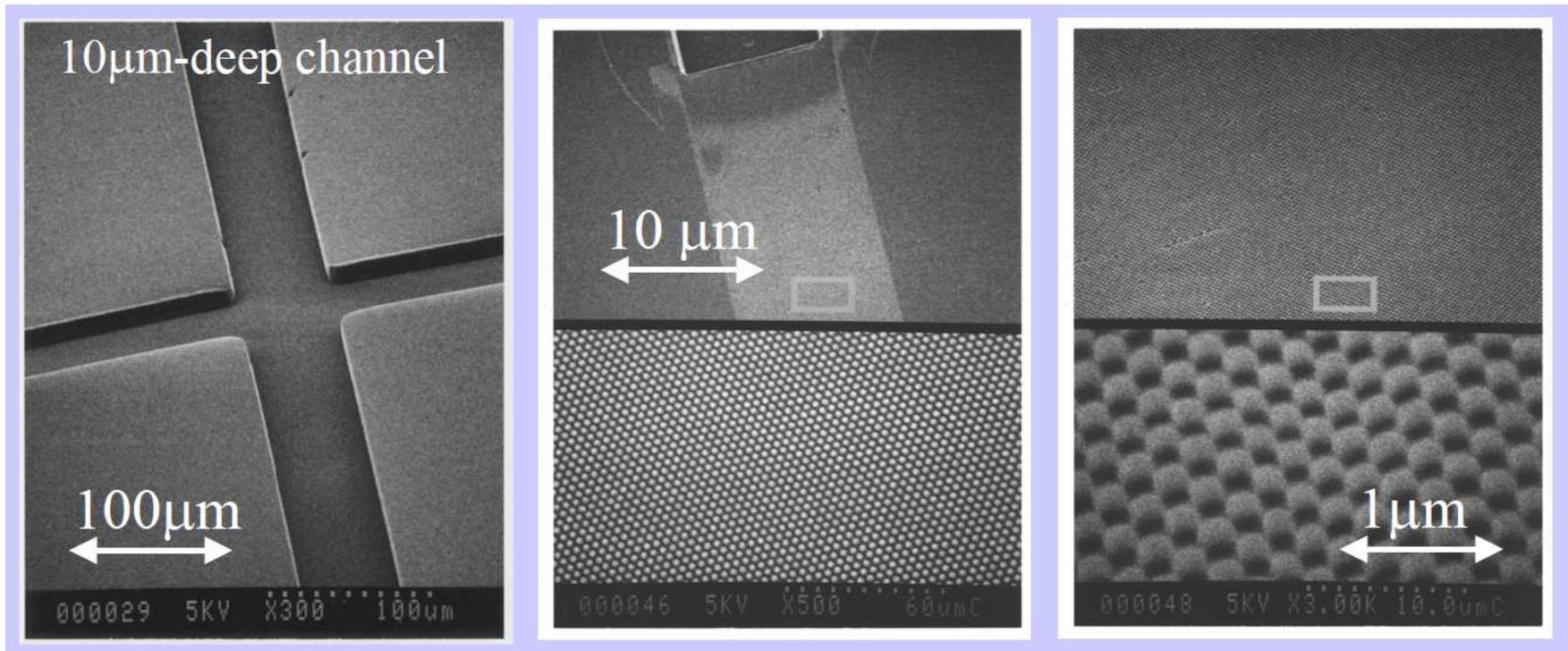


V. Studer, A. Pépin, Y.Chen, Appl. Phys. Lett. 80, 3614 (2002)



Hot embossing PMMA pellets: result

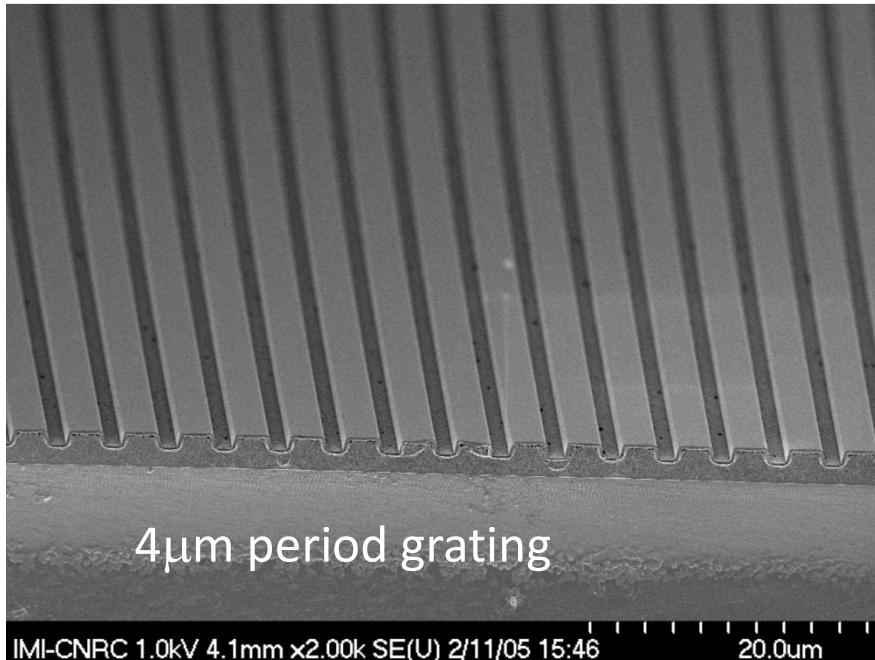
NIL at 180°C, 50bar pressure for ~10 min



For fabricating micro- and nano-fluidic channels in thermoplastic polymers.

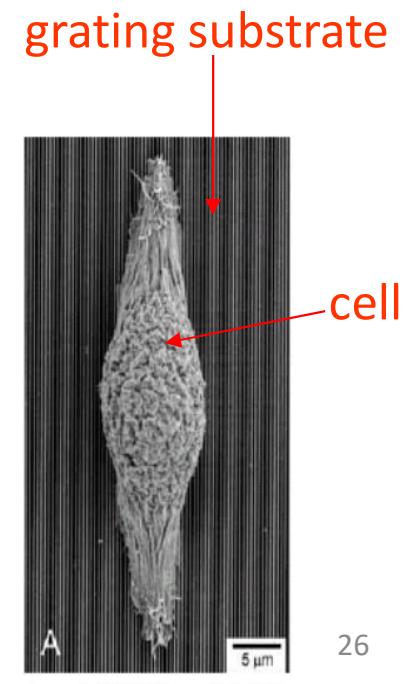
Hot embossing polystyrene pellets

Polystyrene is bio-compatible (cell culturing Petri-dish is made of polystyrene, perhaps plus some additives).

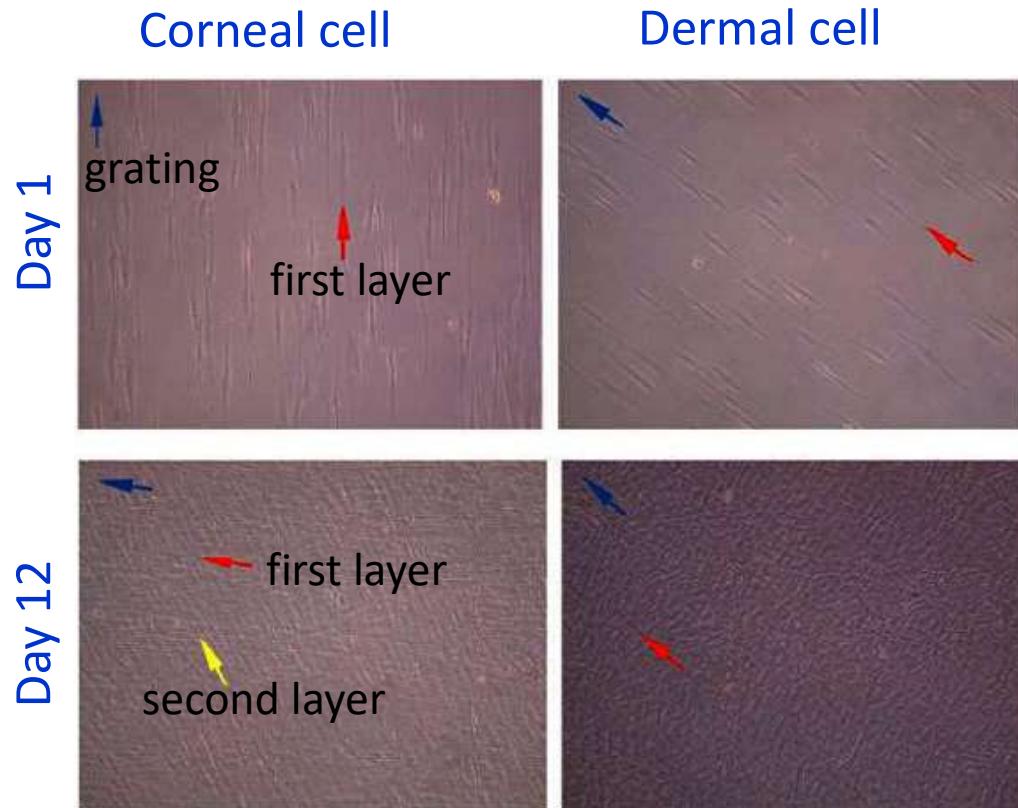


Application: contact guidance of cell growth

- Definition: anisotropic topographic features induce cells to align along the direction of the anisotropy.
- Importance: in tissue engineering, if tissue is to be repaired, the new cells must be aligned and positioned correctly.



Tissue engineering: corneal and dermal cell growth



- First layer: both cells aligned with the grating (as expected).
- Second layer:
 - Corneal cells - oriented at 60° relative to first layer, as in a native cornea
 - Dermal cells - no orientation

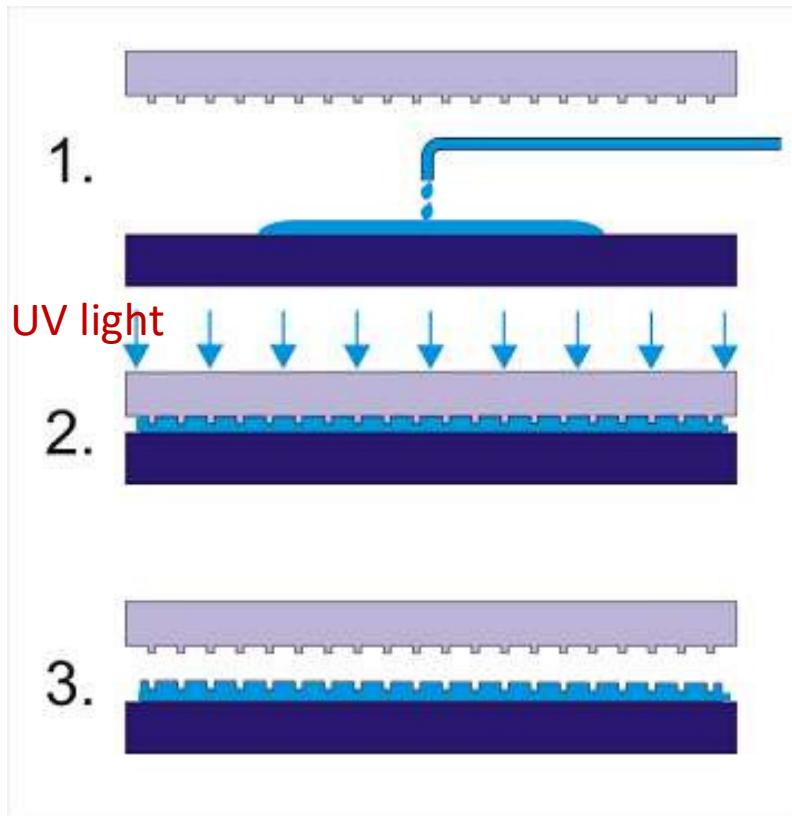
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6. UV-curing NIL.
7. Resists for UV-NIL.
8. Mold fabrication for thermal and UV-NIL.

UV-curing NIL

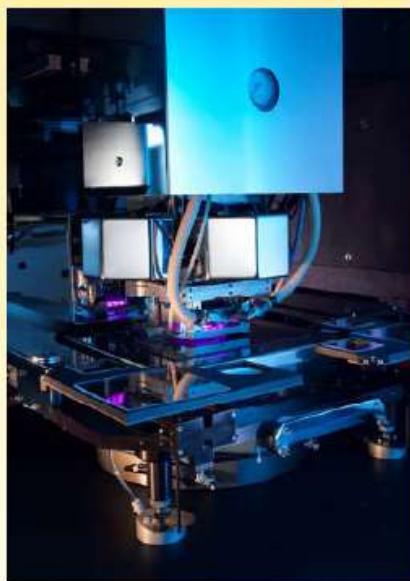
UV-curing NIL is a mechanical molding process, like thermal NIL; but very different from photolithography that is a chemical process, though they both use UV light.

UV-NIL using dispensing resist

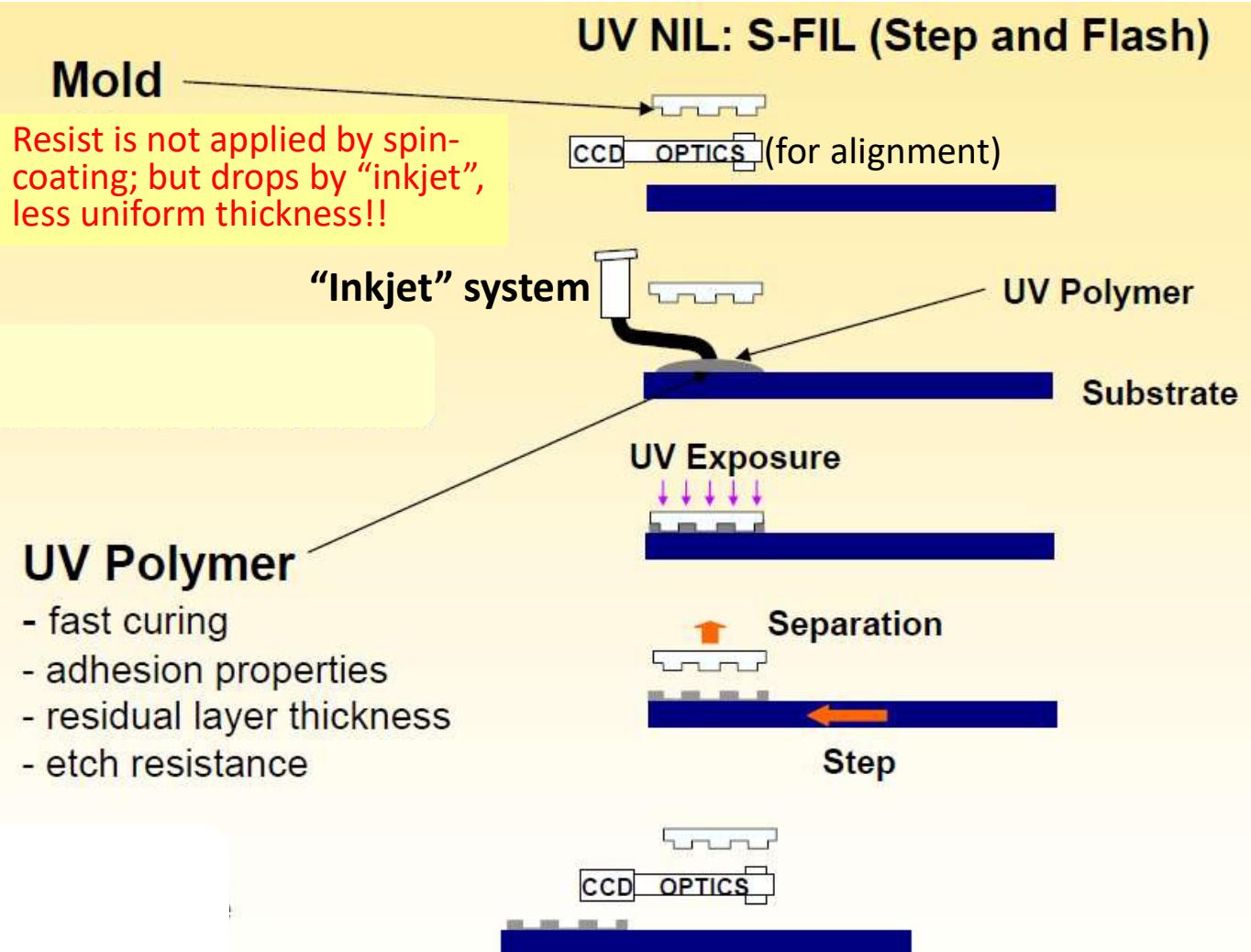


- Room temperature, low pressure (1 - few atm).
- *Liquid* resist consisting monomer, photo-initiator, coupling agent, surfactant, solvent...
- Resist cross-link (become solid) upon UV illumination.
- Mold (or substrate) must be transparent to UV. Most popular mold material is quartz.
- Easier for alignment than thermal NIL (thermal expansion destroys alignment), closer to optical lithography.
- But resist side, thermal NIL resist is closer to optical lithography resist. For example, PMMA and SU-8 is both a photo-resist (PMMA for DUV lithography) and thermal NIL resist.
- In fact, UV-NIL resist is closer to UV-curable glue.

Step and flash UV-NIL

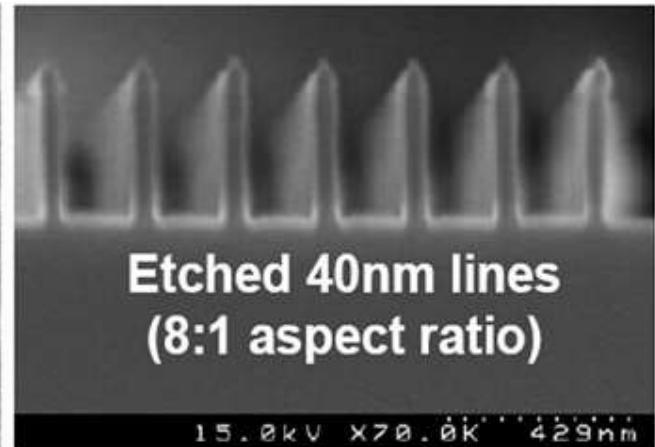
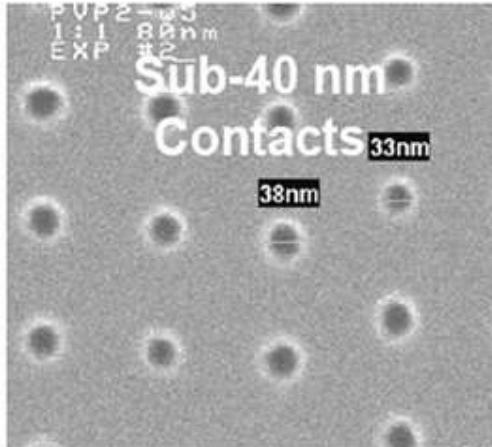
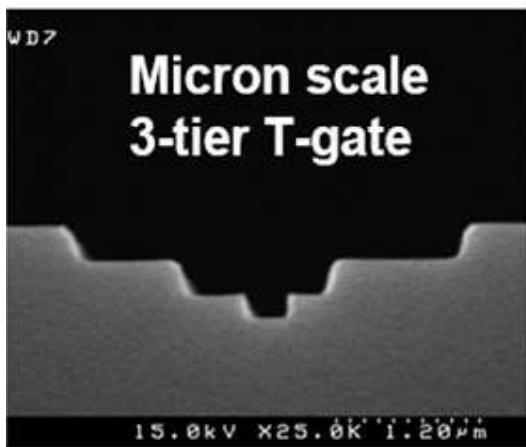
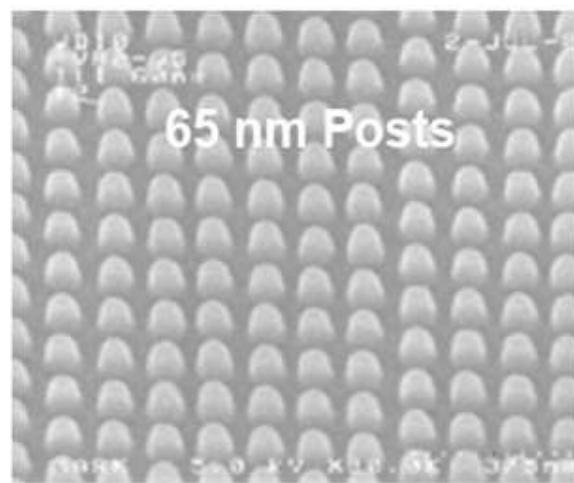
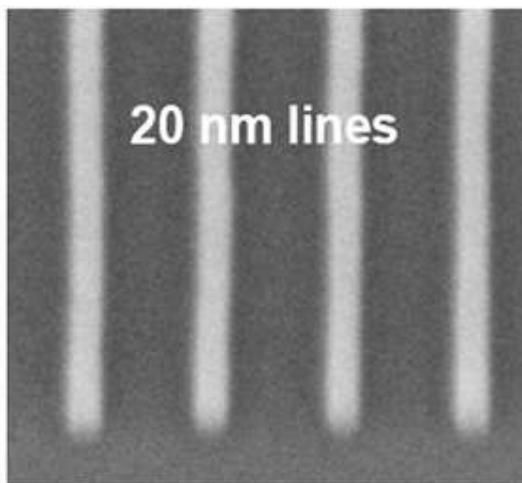
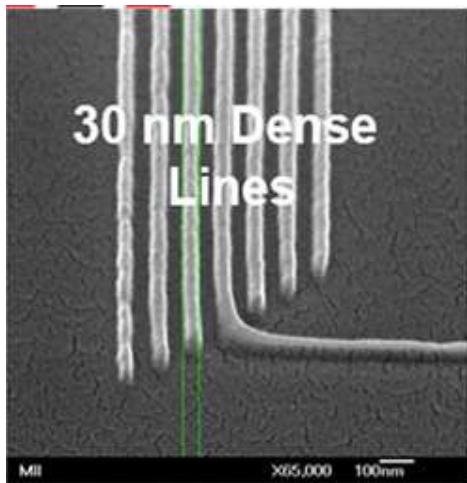


Source: Suss MicroTec



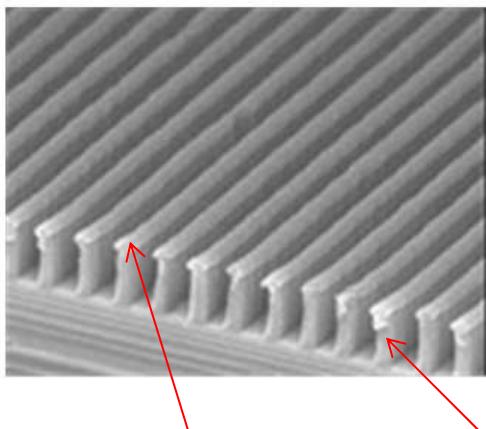
- Technology commercialized by Molecular Imprint Inc.
- Resembles deep UV stepper, die by die patterning (no need of a BIG expensive mold).
- Favored by the semiconductor industry or wherever mold is too expensive.

Some examples of step and flash NIL



In principle, UV-NIL has lower resolution than thermal NIL due to resist shrinkage (~10%) upon cross-linking. In practice, UV-NIL has demonstrated similar resolution to thermal NIL.

UV-NIL using spin-on resist (uniform thickness)



UV-resist

Under-layer (PMMA, ARC..., also called transfer layer)

NXR-2000 Series, Photo-Curable Resists

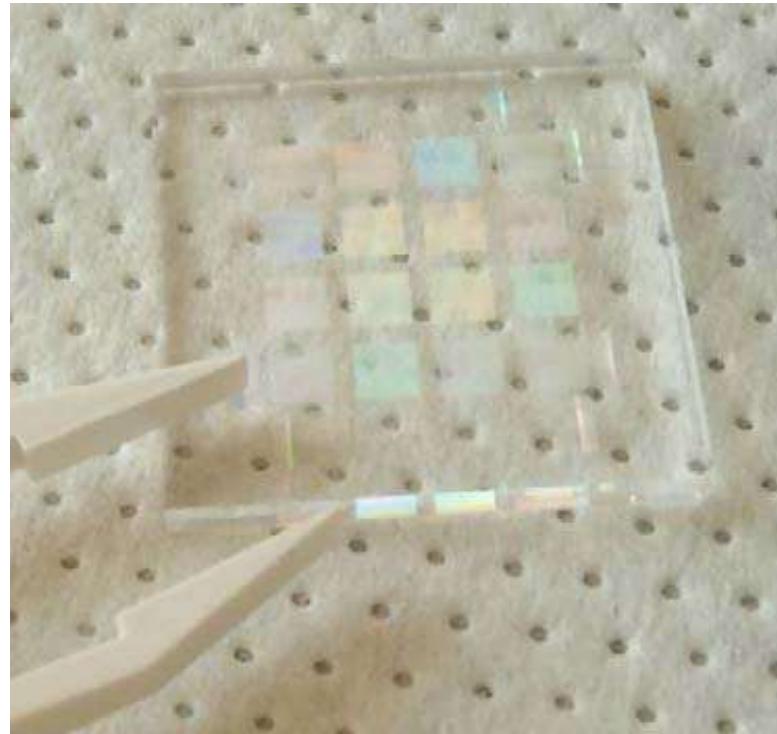
- Sub-5 nm demonstrated resolution and wafer-scale uniformity
- Room temperature operation
- Super-low viscosity
- Spin-on or resist-drop dispensing
- Excellent etching resistance
- Low UV-curing dosage



- Typically bi-layer system, thin UV-resist layer to minimize shrinkage effects.
- Resist contains Si, so can be used as a hard mask for etching under-layer with O₂ plasma.
- Spin-on resist is not suitable for step-and-flash NIL, because the entire film must be imprinted quickly in one shot (liquid resist not as stable as thermal NIL resist in air, and it takes in dust quickly).
- For R&D, spin-on resist is much more reliable than step-and-flash NIL, because the amplitude and uniformity of residual layer thickness is a big issue for drop-dispensed resist.

PDMS mold for UV-NIL

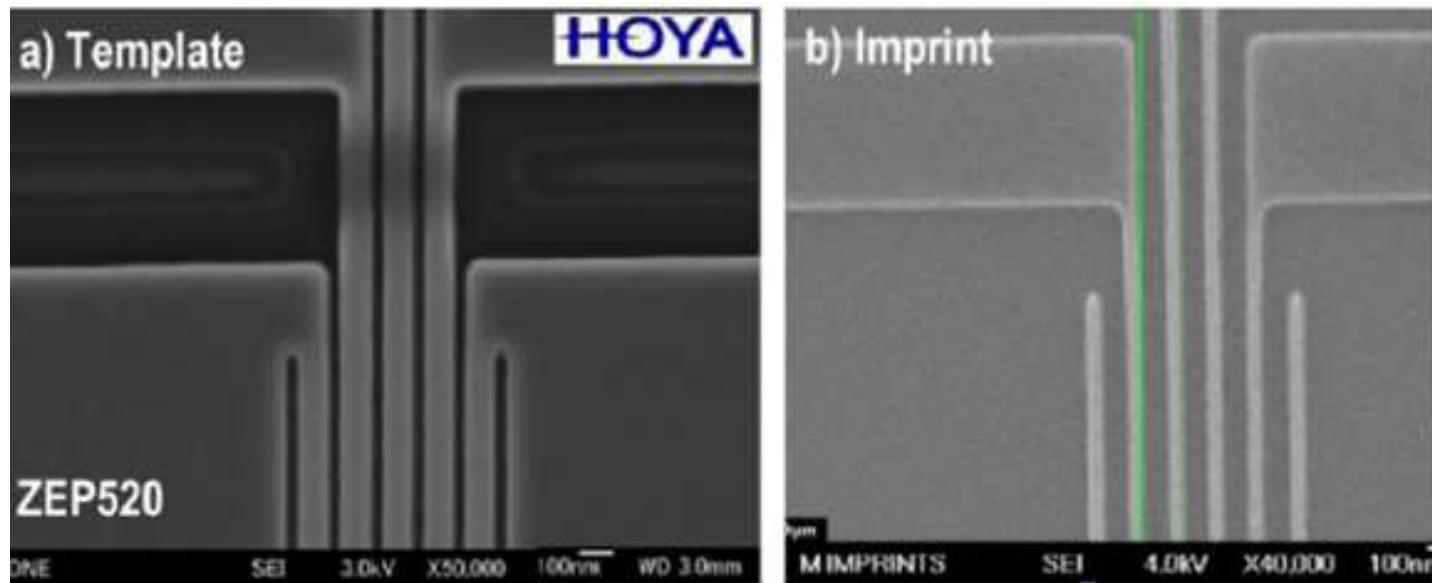
Transparent mold (also called stamp or template) in PDMS



- Unlike quartz, PDMS is flexible and soft for conformal contact to non-flat substrate.
- But not for high resolution (<100nm), because PDMS is not hard enough and thus its nanostructure will deform under pressure.
- One solution is using bi-layer, pattern in *hard*-PDMS or PMMA, which is spun on (regular soft) PDMS.
- After oxygen plasma treatment, PDMS surface is like SiO_2 , so it is easy for silane anti-sticking treatment.

ZEP-520 mold (ZEP is an e-beam lithography resist)

- Because UV-NIL uses low pressure and room temperature, thermoplastic EBL resist such as PMMA and ZEP-520 can be used as a mold right after EBL and development.
- However, one may need anti-sticking surface treatment with silane, yet the silane treatment is not reliable on ZEP or PMMA, or other thermoplastic polymers.
- Therefore, thermoplastic polymers are not popular mold materials.



Mold in ZEP-520 with line-width 50nm

Imprint result into a UV-curing resist

Summary: comparison between thermal and UV NIL

	Thermal	UV
Resist material	Thermoplastic or thermal-set (i.e. cured upon heating)	Monomer, photo-initiator plus various additives
Resolution	Sub-5nm	2nm demonstrated, but volume shrinkage after cross-linking
Temperature	30-100°C above T_g	Room temperature
Pressure	Normally over 10 bar	~1 bar, or higher
Resist application	Spin coating, easy	Spin coating or drop
Resist thickness	Up to many μm , easy for pattern transfer	Typically < 100nm, need an extra transfer layer
Cycle time	1-30 min, slow	~1 min
Large features	~100 μm , difficult	Relatively easy, since low viscosity
Alignment	~ 1 μm , difficult; CTE mismatch	20nm demonstrated
Application	Broad range, simple and work with many materials	Targeted for semiconductor industry with alignment

T_g : glass transition temperature

CTE: coefficient of thermal expansion

Resist for UV-NIL

Overview:

- UV-NIL resist has little in common with photo-resist, which resembles more thermal NIL resist.
- In principle, any material that is soft (thus can be imprinted) and becomes hard upon UV exposure, can be used as UV-NIL resist.
- For example, UV-glue and dental UV sealant, are UV-NIL resists.

Component of UV-NIL resist:

- Vinyl ethers that are the key ingredient for photopolymerization.
- Organic acrylate monomer that provides low viscosity.
- Organic cross-linker for thermal stability and mechanical strength.
- Additives: silicon-containing acrylate monomer (to increase dry etching resistance), flourinated compounds (to lower surface energy for easy separation).
- Photoinitiator: cationic or free radical photoinitiator.

Photoinitiators:

(dissociate upon UV irradiation to form radicals that promote polymerization process)

- Cationic photoinitiator:
Insensitive to oxygen, but low curing rates; and acids and heavy metals are harmful to semiconductors.
- Free radical photoinitiator: (more popular at present)
Great variety, high curing rates, but sensitive to oxygen, need vacuum or N₂ environment curing.

Nanoimprint lithography (NIL)

1. Overview.
2. Thermal NIL resists.
3. Residual layer after NIL.
4. NIL for large features (more difficult than small one).
5. Room temperature NIL, reverse NIL, NIL of bulk resist (polymer sheet, pellets).
6. UV-curable NIL.
7. Resists for UV-NIL.
8. Mold fabrication for thermal and UV-NIL.

Mold for thermal and UV-curing NIL

Mold: also called template, stamp, master.

Mold release agent: also called releasing layer, anti-sticking coating.

Separation: also called de-molding, de-embossing, release.

Overview:

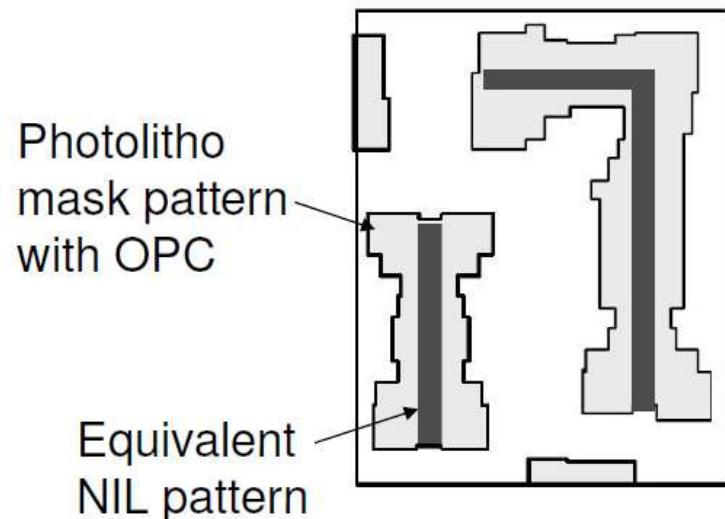
- Usually fabricated from Si, quartz or nickel, though polymer mold is becoming more popular and available.
- Feature fabrication at 1x vs. 4x for optical projection lithography.
- For instance, photomask needs ~250 nm resolution to print 65 nm features; NIL mold needs to be 65nm.

Desired properties:

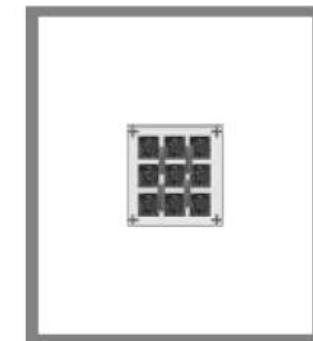
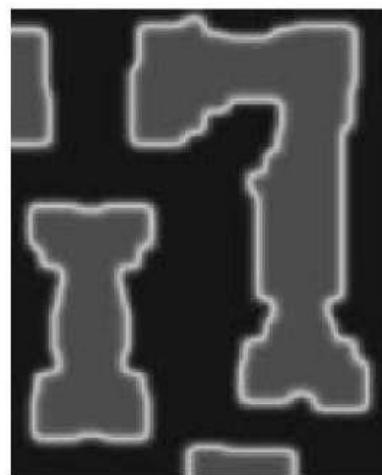
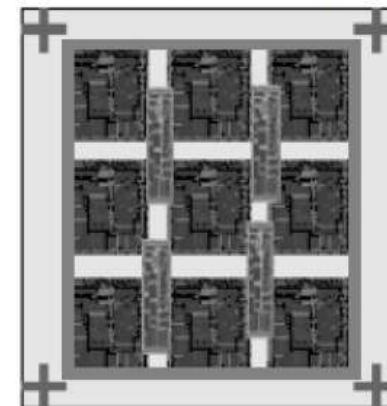
- Compatible to mold release agent coating.
- Mechanically durable (for reuse).
- Chemically durable (for cleaning).
- Low CTE mismatch with substrate (coefficient of thermal expansion).

Comparison with photomask

Optical projection lithography mask with OPC & equivalent NIL mold.



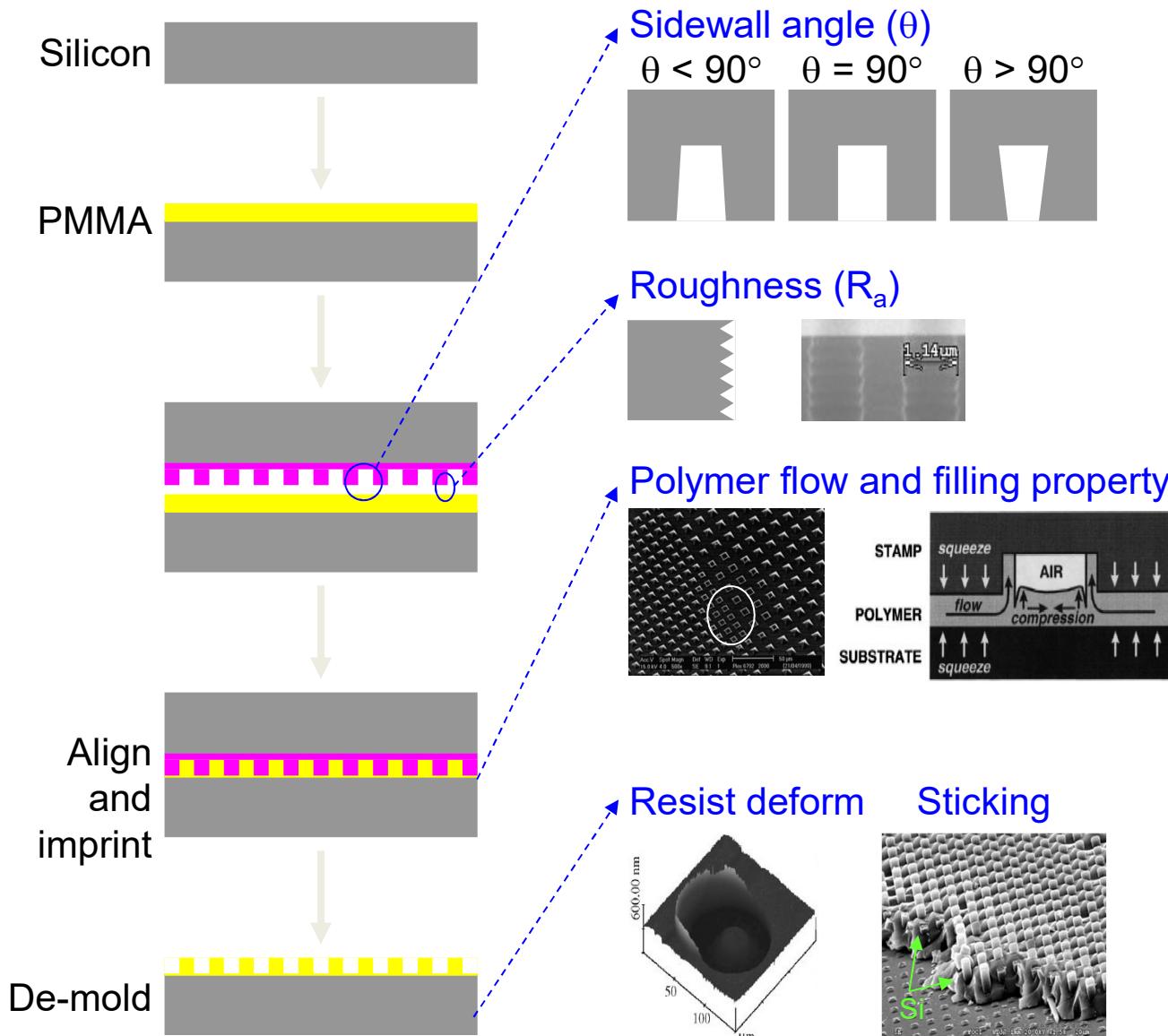
Photomask (4X)



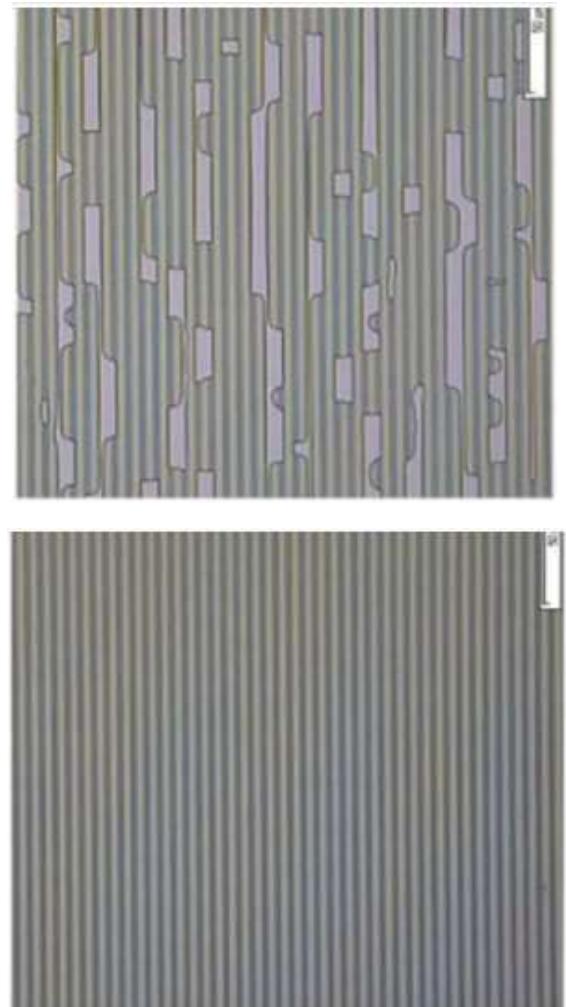
NIL Template (1X)

OPC: optical proximity correction

Mold issues: profile, roughness, sticking



NIL using a mold without (top) and with (bottom) anti-stick coating



Mold release agent: teflon-like coating

Same idea as anti-stick cooking ware coating, but mono-layer.

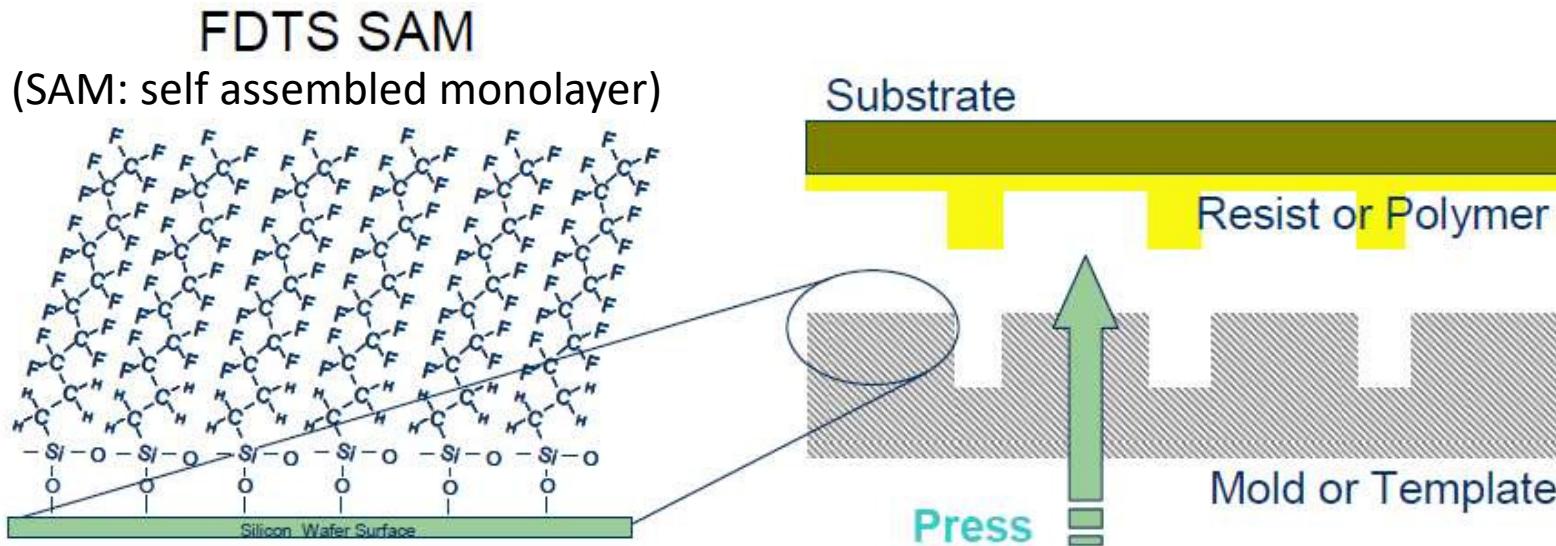
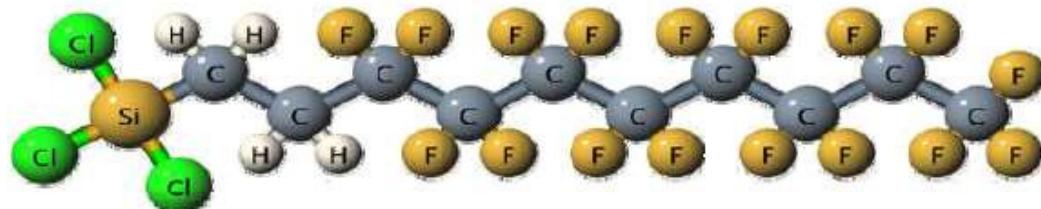


Fig. 2 SAMs used as a low energy release layer

FDTs: (1H,1H,2H,2H)-Perfluoro decyl trichloro silane, works with SiO_2 surface



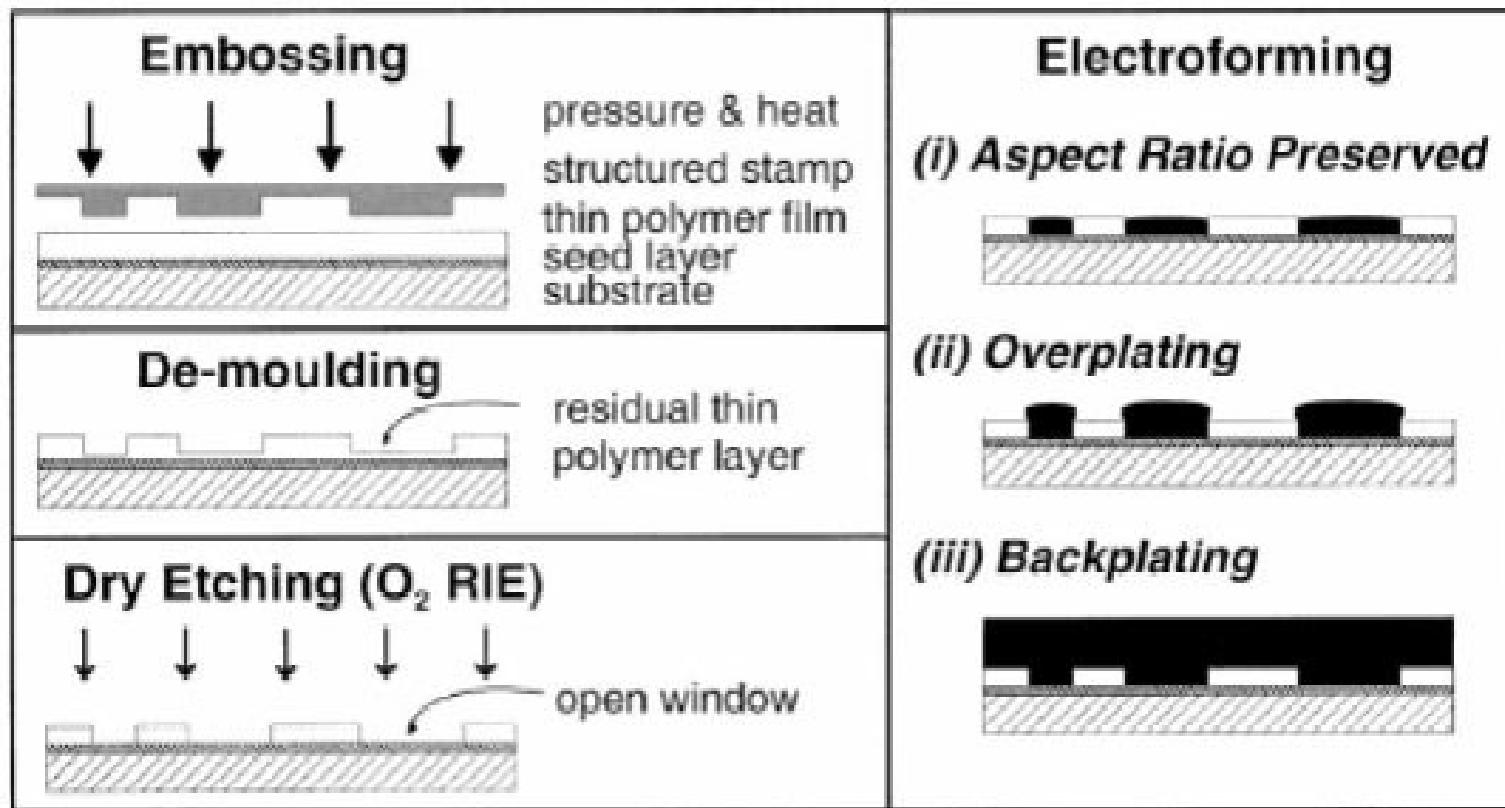
Coatings are 100%
conformal and
extremely uniform.

Silane treatment by simple vacuum coating:

Clean wafer by oxygen plasma, put wafer and a drop of silane inside a container, and vacuum the container. After >5 hours, take wafer out and bake 150°C for 20min to stabilize the silane coating.

Ni mold

- Si or SiO₂ mold is most popular, but they are brittle.
- Metal mold is more robust and durable, used for making CD/DVDs.
- More difficult to fabricate, takes days for electroplating to 100s μm thick.
- Thickness is not uniform: much thicker (>2×) plating near wafer edges, need polishing back.
- Direct silane anti-stick coating to Ni not working well, needs sputtering a thin (10nm) SiO₂.
- More used for hot-embossing onto thick plastic sheets for micro/nano-fluidics applications.



Source: Microelectron. Eng. 57-58 (2001) 375-380

Soft PDMS/PMMA (rigid) mold for UV-NIL

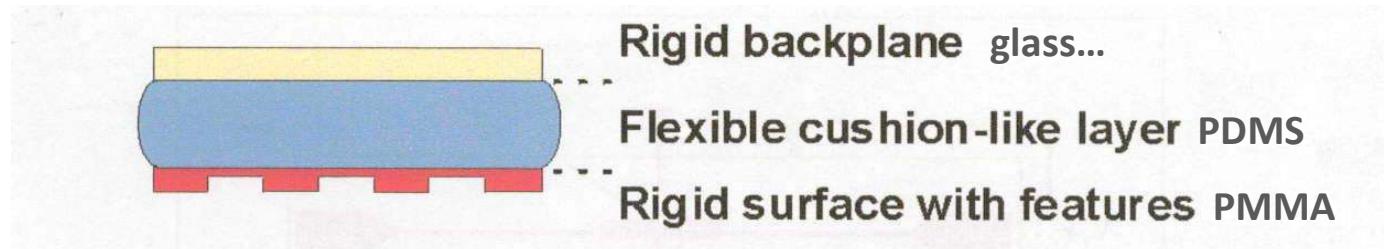
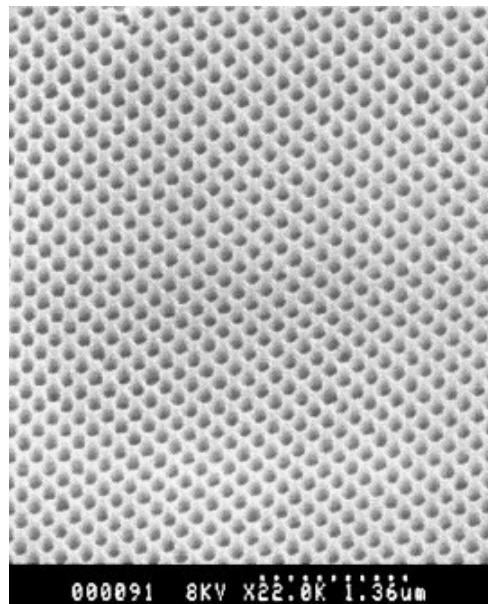
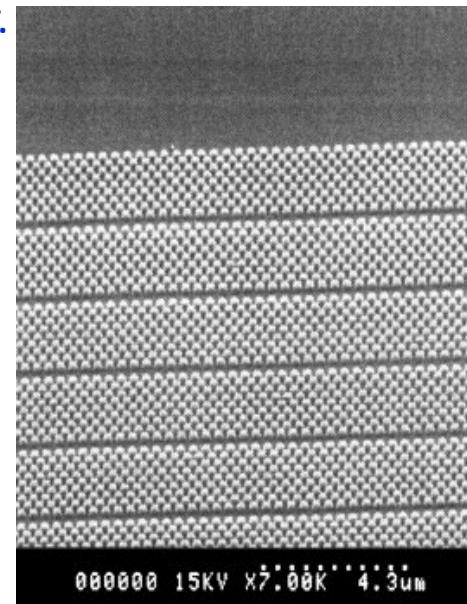


Figure 7: schematic overview of a possible multi-layer-stamp design, a flexible cushion like layer between a rigid backplane and a thin, rigid surface with the imprint structures

Mold: PMMA top layer cast and bonded on a PDMS buffer and a glass carrier.



Resist pattern: 0.1atm imprint pressure, triangular lattices of 300nm period and 200nm pillar diameter.

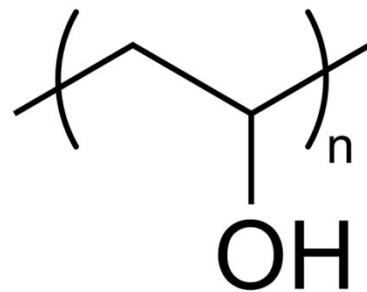


PDMS alone can be used as UV-NIL mold, but its nanostructure is not hard enough and will bend/collapse during NIL even at low pressure. It is good for μm -feature size UV-NIL.

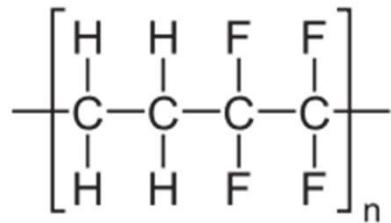
43

Other polymer mold materials

PVA (polyvinyl alcohol): water soluble, can be one-time use mold (imprint and dissolve the mold with water)

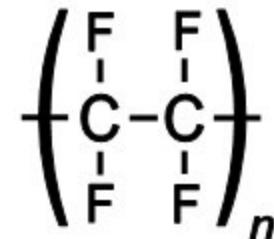


ETFE (ethylene tetrafluoroethylene): similar to PTFE, but mold is easier to fabricate from a master mold.

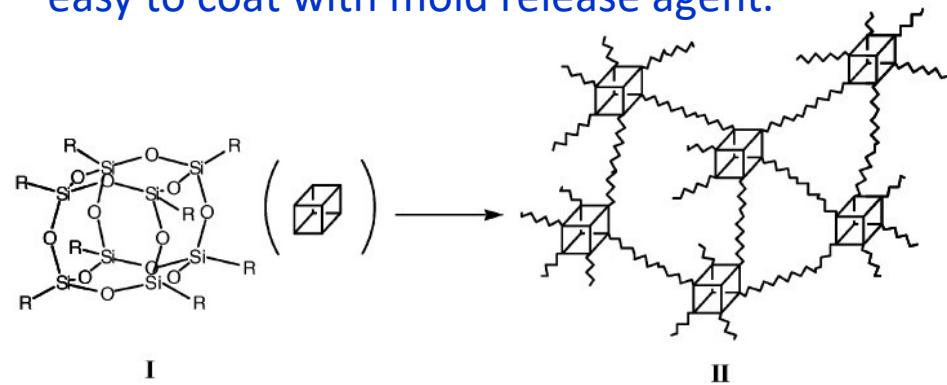


In principle, all cross-linked polymer can be used as NIL mold; however, most of them cannot be treated with mold release agent.

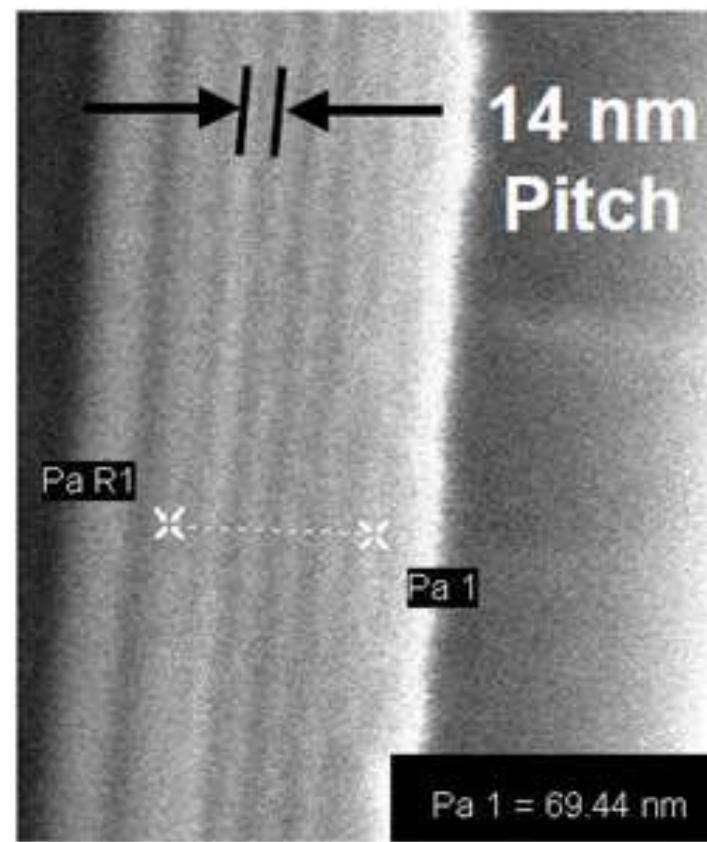
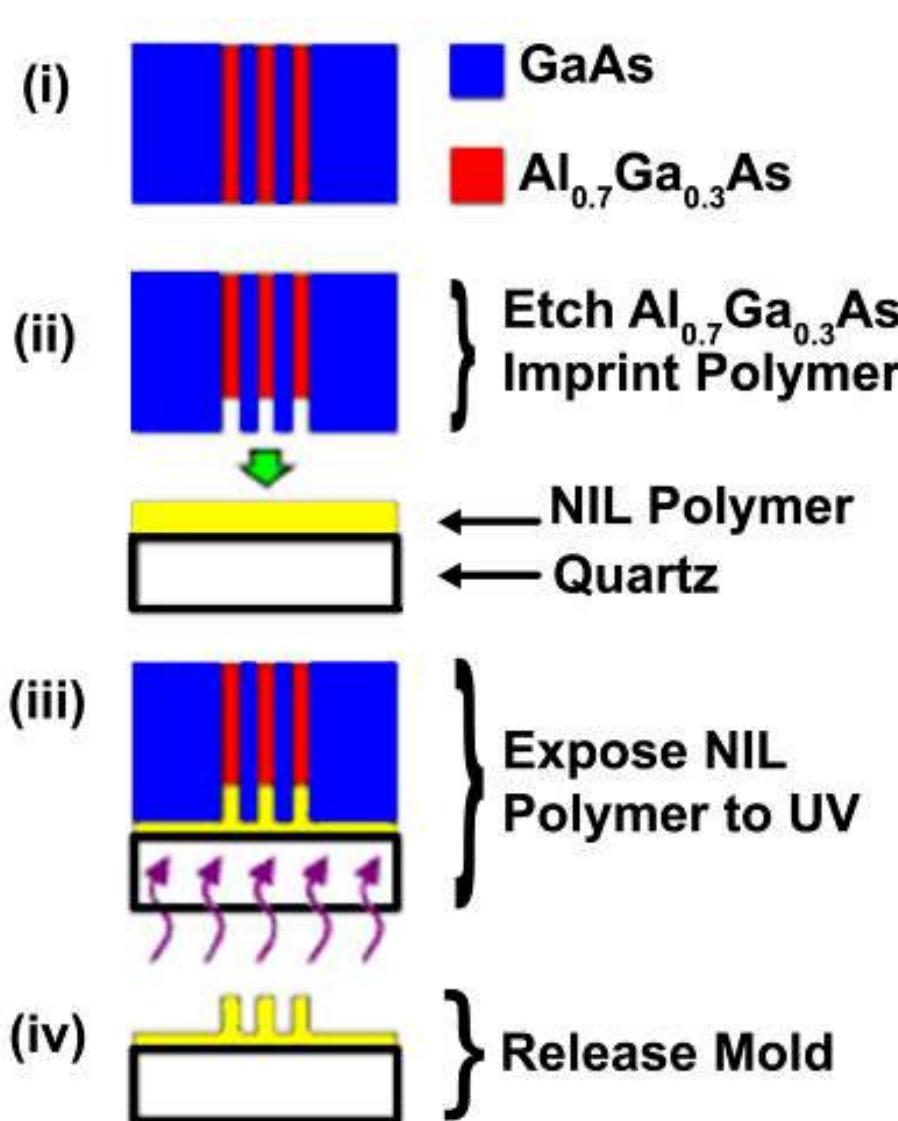
PTFE (Teflon, polytetrafluoroethylene): can be molded using a silicon mold at high temperature ($>250^{\circ}\text{C}$). Low surface energy (no need for mold release agent), high strength, can do thermal NIL at high temperature.



SSQ (silsesquioxane): similar to HSQ. After cross-linking the material is like SiO_2 , which is easy to coat with mold release agent.



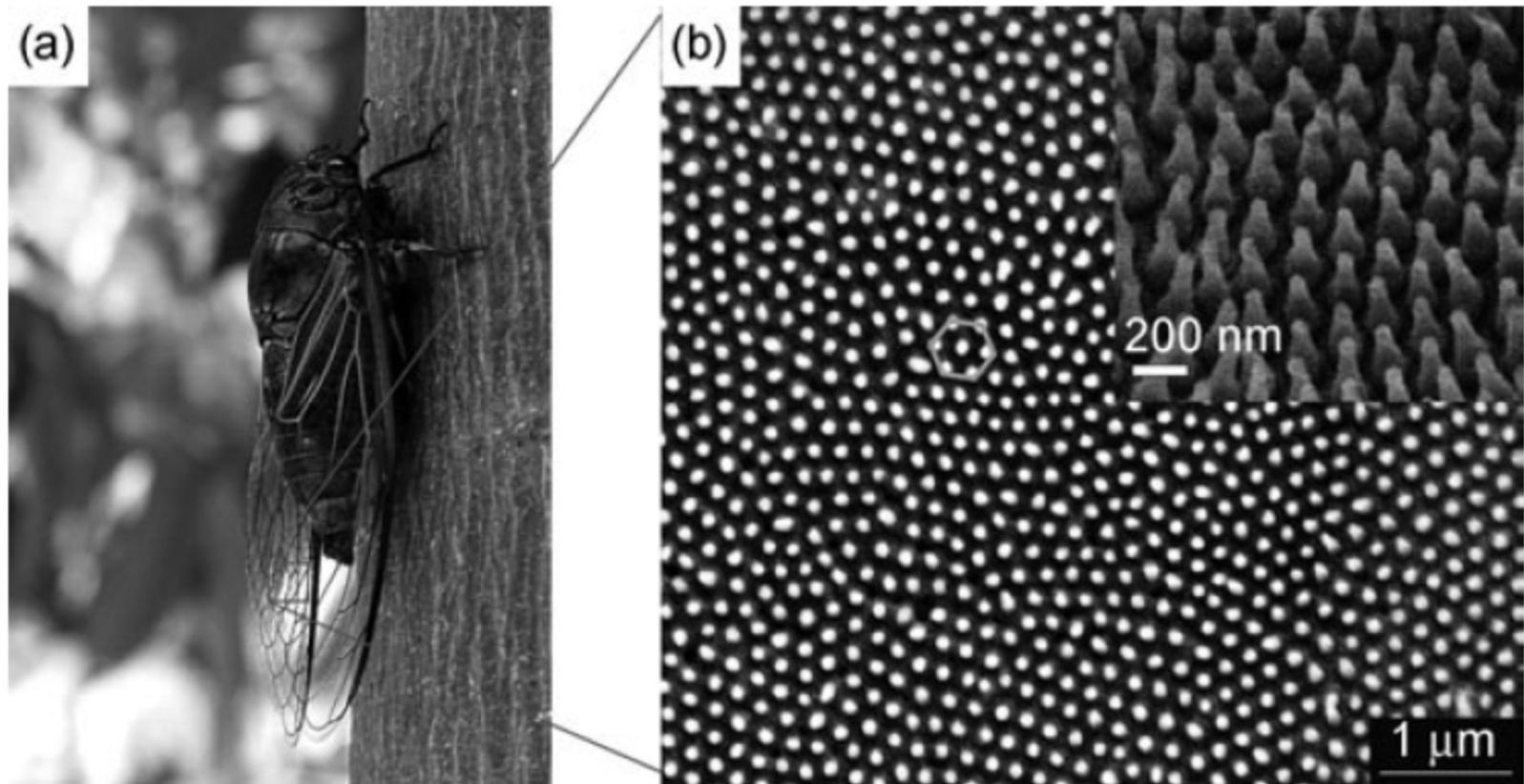
Mold by MOCVD and selective wet-etching



Precise control of pitch and line-width.
By far the highest resolution (~6nm) NIL is demonstrated using such a mold.

Mold fabricated by nature

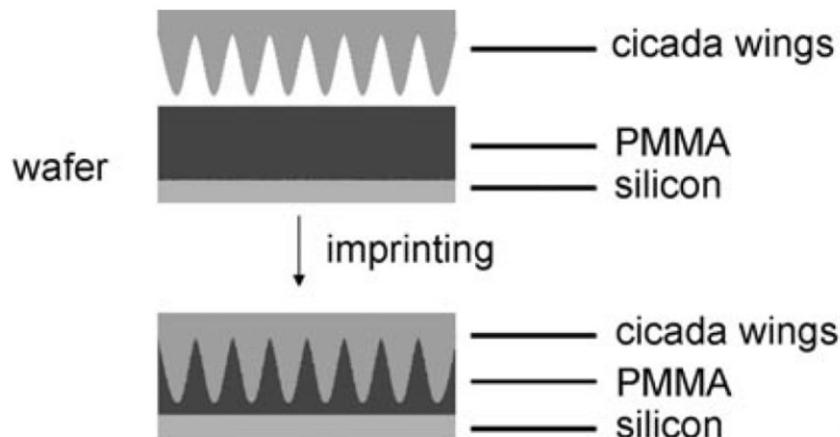
Cicada Wings: a mold from Nature



The cicada wings consist of ordered hexagonal close-packed arrays of pillars with a spacing of about 190nm.

The height of the pillars is about 400nm and the diameters at the pillar top and bottom are about 80nm and 150nm, respectively.

Results of NIL using cicada wing mold



Pressure ~40 bar; temperature
~190°C, 70°C higher than the T_g of
PMMA; imprint time 3min.

The pitch between the wells is about 190nm, the well diameter is about 150nm, and the depth is found to be about 400nm; these are consistent with the mold.

- The Young's modulus of cicada wings can be as high as 7–9GPa, sufficient for imprinting into PMMA.
- There is a layer of wax on the surface of the wings, which contains esters, acids, alcohols, and hydrocarbons. This layer gives low surface tension, so no need of anti-stick coating.

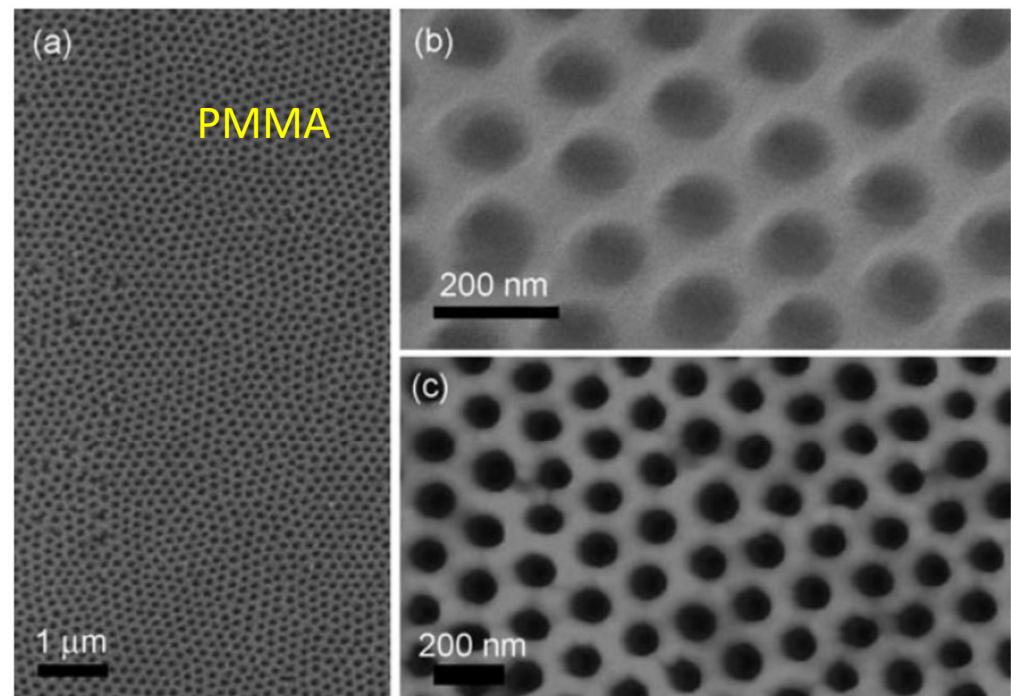


Figure 3. Results after imprinting using cicada wings as the stamp. (a) and (b) are SEM images of patterned PMMA with different scales. (c) is an AFM image of the patterned PMMA surface.

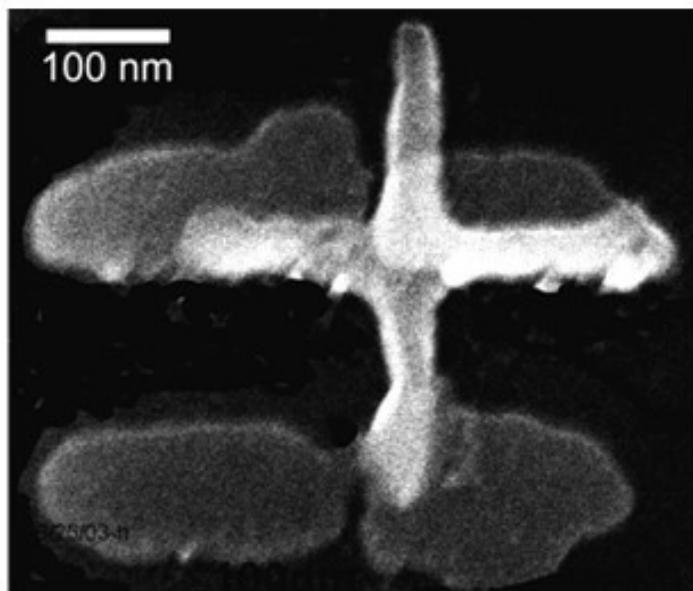
Nanoimprint lithography (NIL)

1. UV-curable NIL.
2. Resists for UV-NIL.
3. Mold fabrication for thermal and UV-NIL.
4. Alignment.
5. NIL into metals.
6. NIL systems (air press, roller, roll-to-roll, EFAN...)
7. NIL applications

Alignment (overlay)

Challenges for sub-100nm alignment:

- Smaller error budget for mold pattern placement since it is 1 \times (rather than 4 \times reduction as is the case for photolithography).
- Mold distortion/drift due to pressure, temperature and defects is big problem.
- Generally, alignment for NIL is much more difficult than other lithographies.
- Thermal NIL is worse due to thermal expansion mismatch.

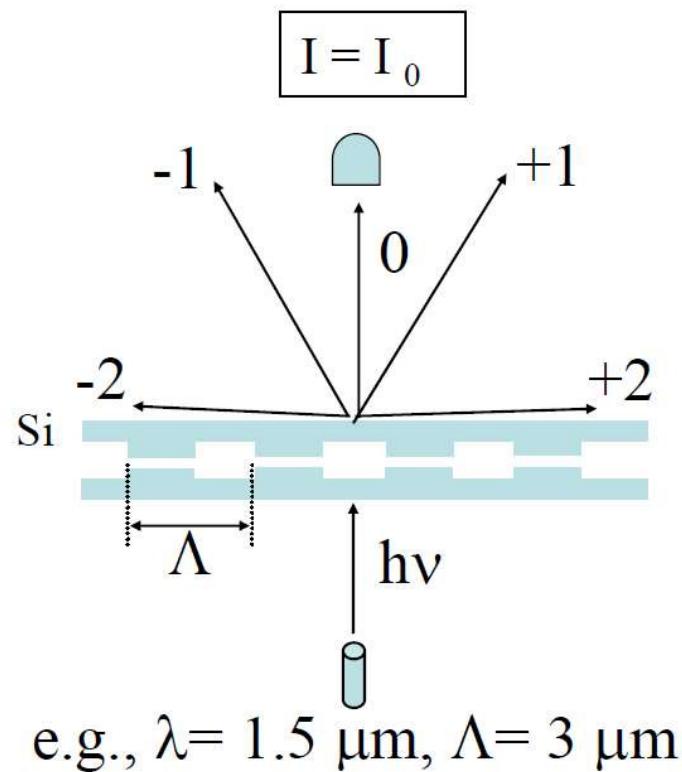


For UV-NIL, sub-100nm alignment can be achieved readily, but this is still too far away from requirement for IC production (few nm).

"Sub-20-nm Alignment in Nanoimprint Lithography Using Moiré Fringe", Li, Nano Lett., 2006.

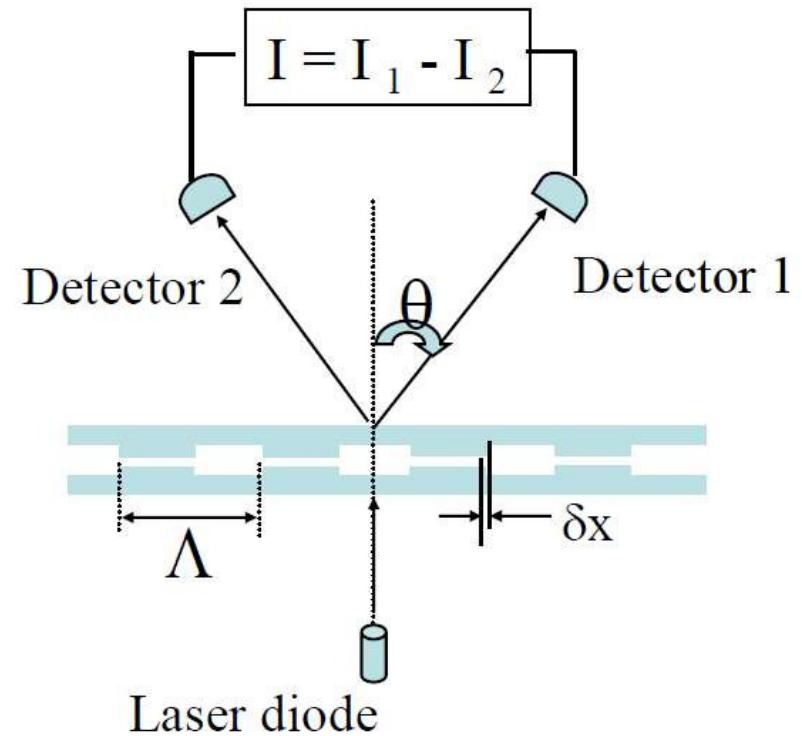
Amplitude sensitive alignment scheme

- **Method-1:** Measure the **zero** order diffraction patterns of two gratings with the same period



Maximum signal when aligned.

- **Method-2:** Measure the **first** order diffraction patterns of two gratings with the same period



Minimum signal when aligned ($I_1=I_2$)

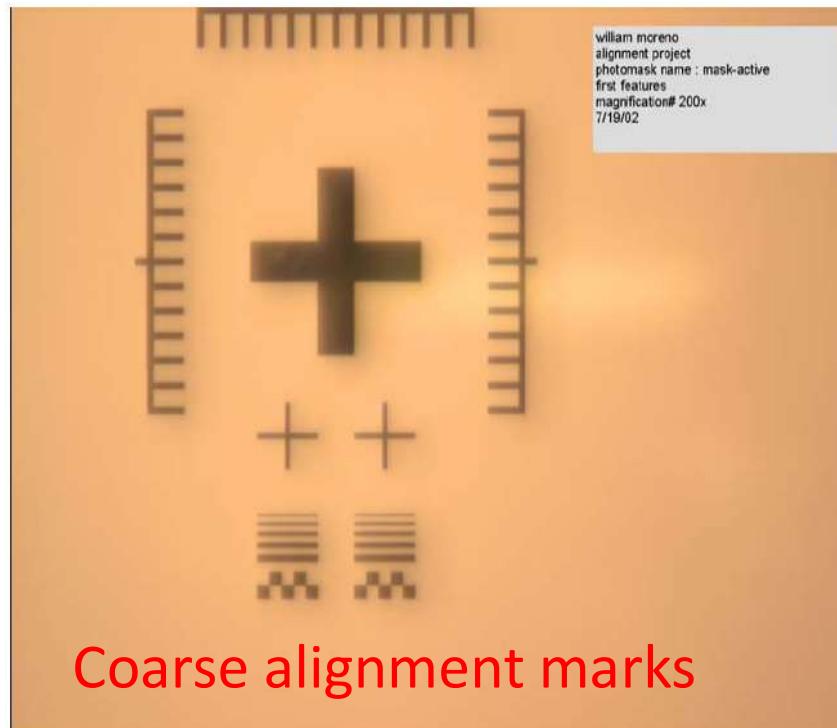
Two step alignment using cross marks and Moiré patterns

For sub-100nm alignment:

- Coarse alignment using cross marks and boxes or circular gratings, just like regular optical lithography.
- Fine alignment using Moiré pattern.

Moiré patterns: optical image of superposition of two patterns.

Advantage: slight displacement of one of the objects creates a magnified change in their Moiré patterns.

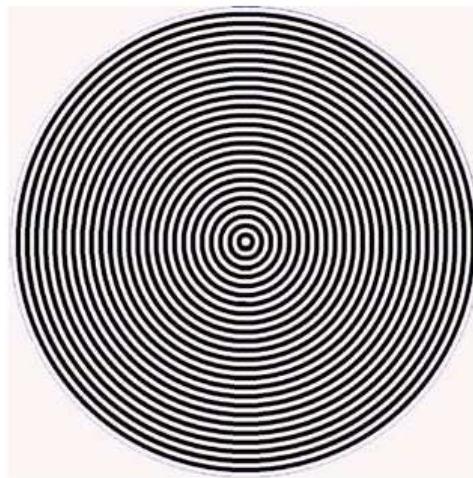


Optical image (200x)

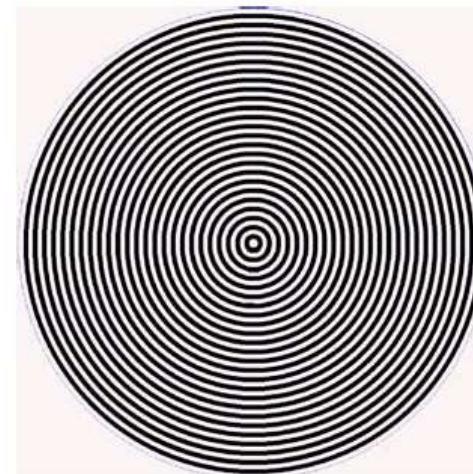
- Same as alignment in contact/proximity optical lithography.
- Cross mark provide alignment of $\sim 0.5\mu\text{m}$.
- Cross marks are relatively big and easy to locate.

Circular gratings

p1

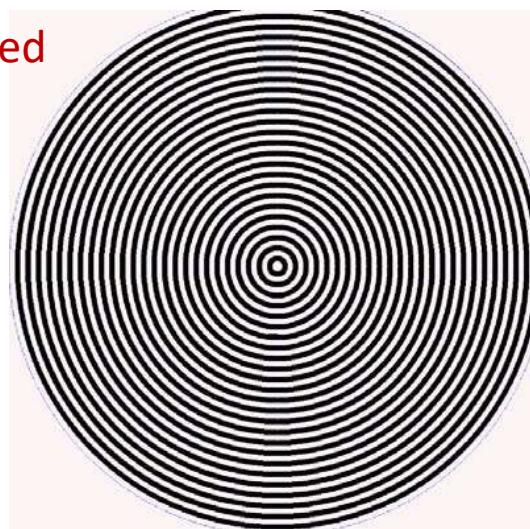


+ p1

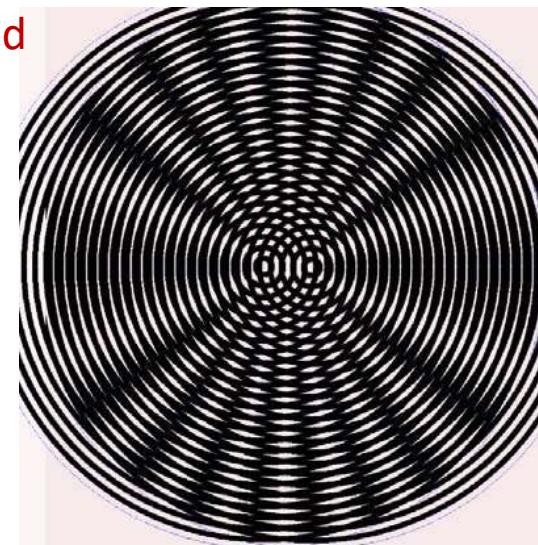


=

Aligned



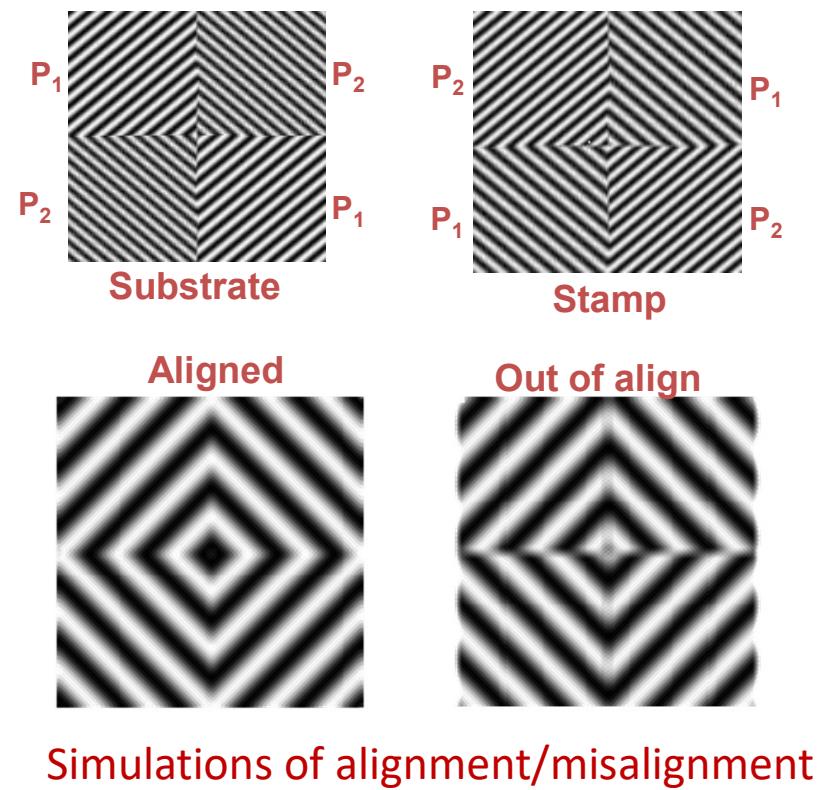
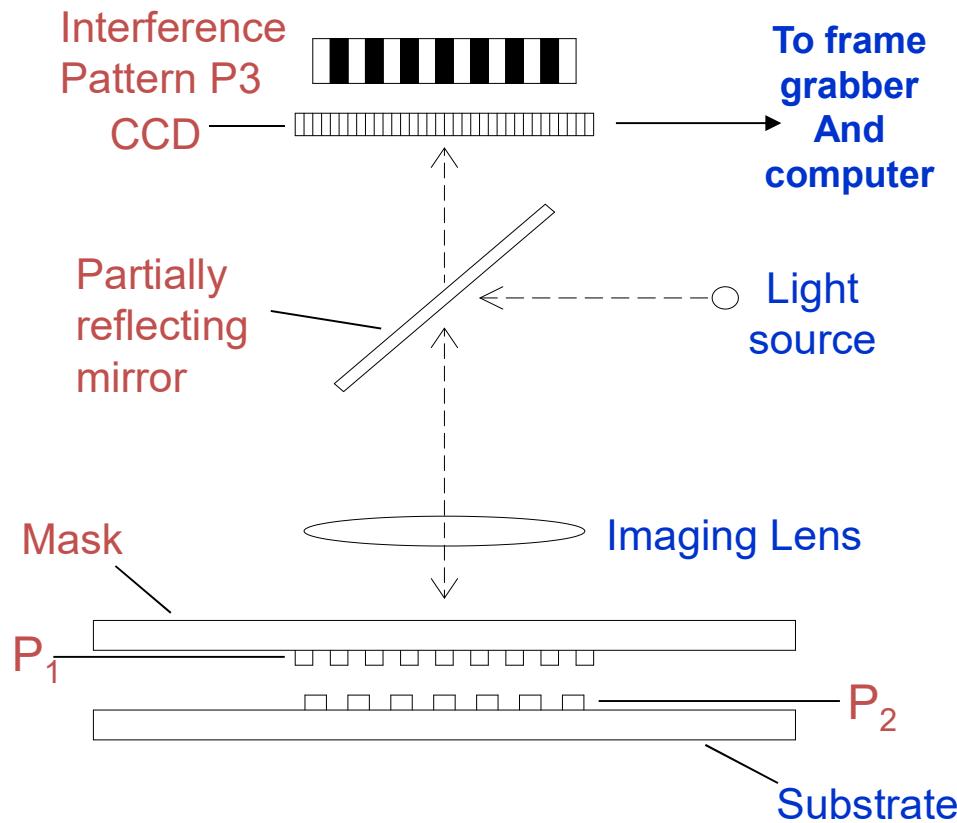
Misaligned



M. King and D. Berry were the first who start alignment using moiré concentric circles in 1972 (Appl. Opt.11. 2455).

Fine alignment using Moiré: concept and simulation

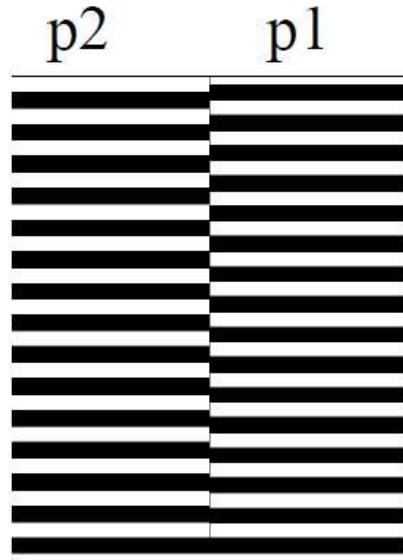
Sub-10 nm alignment accuracy



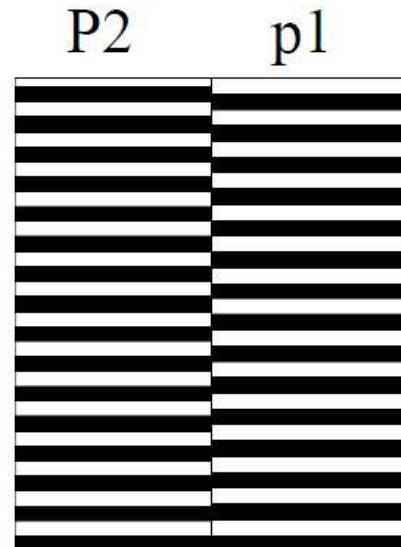
Simulations of alignment/misalignment

$$P_3 = (P_1 \times P_2) / |P_1 - P_2|$$

Interferometric spatial phase matching of linear gratings



mask



substrate

Pre-alignment $< P_{1,2}/2 \sim 2\mu$

is required

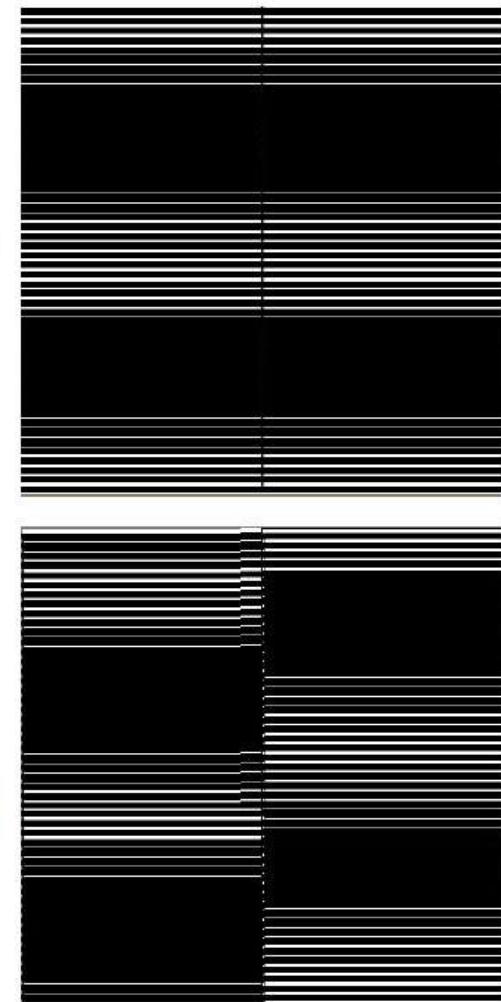
$$p_3 = (p_1/p_2)/|p_1 - p_2|$$

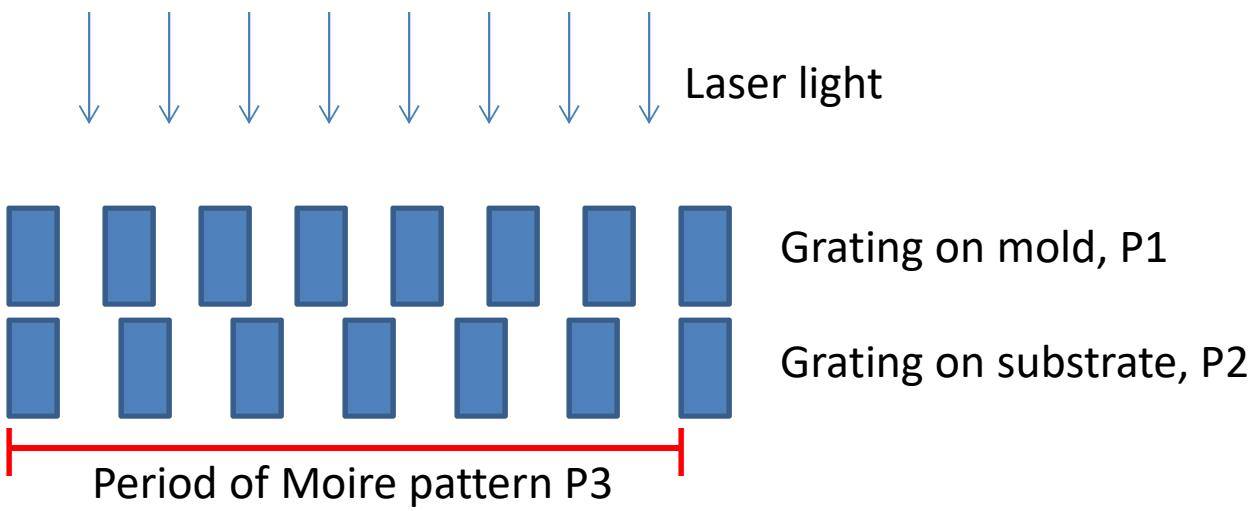
aligned

P_3

Not
aligned

p_3





Here, $P_3 = 7P_1 = 6P_2$

In general, $P_3 = nP_1 = (n-1)P_2$

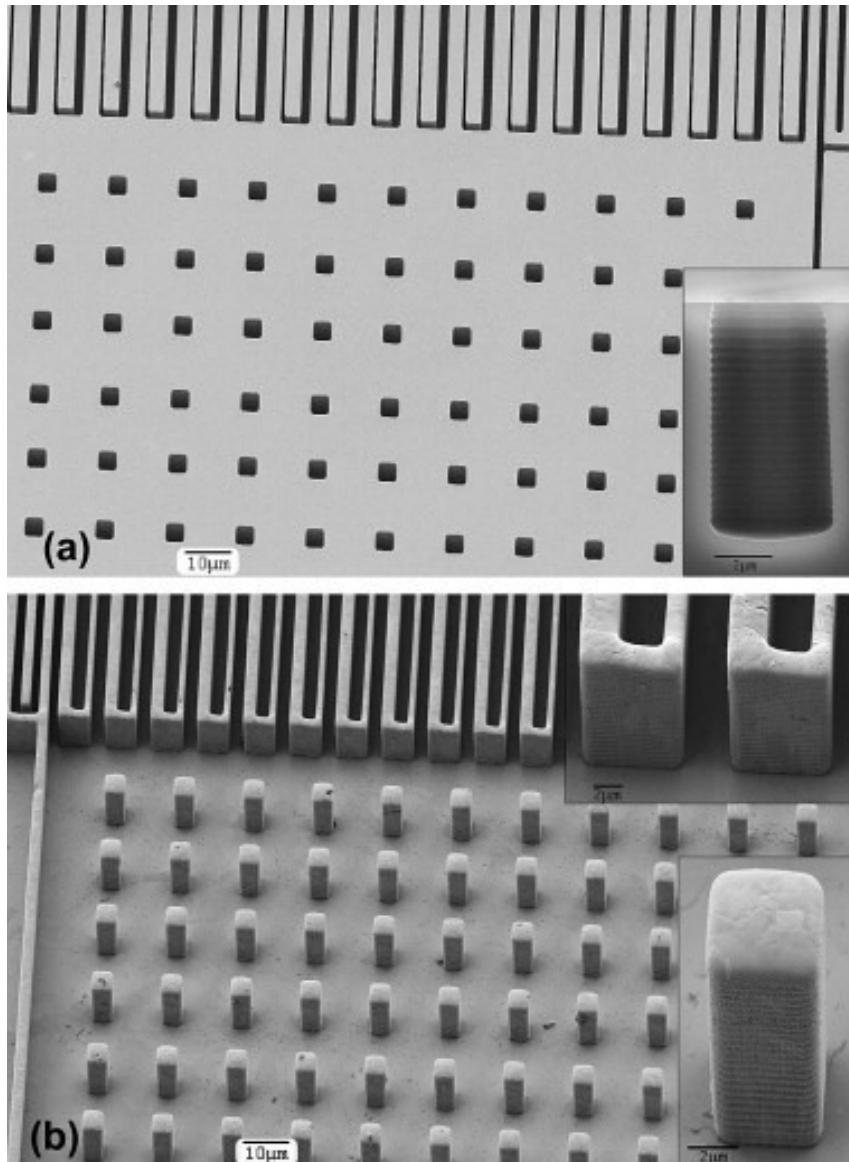
Then $n = P_2 / (P_2 - P_1)$

Then $P_3 = nP_1 = P_1 P_2 / (P_2 - P_1)$

Nanoimprint lithography (NIL)

1. UV-curable NIL.
2. Resists for UV-NIL.
3. Mold fabrication for thermal and UV-NIL.
4. Alignment.
5. NIL into metals.
6. NIL systems (air press, roller, roll-to-roll, EFAN...)

NIL directly into metals



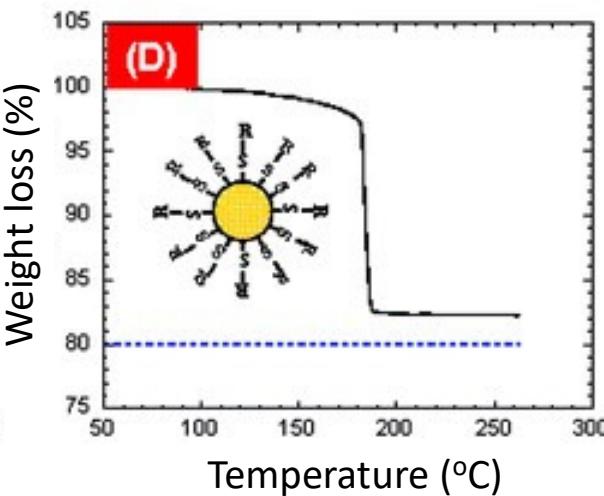
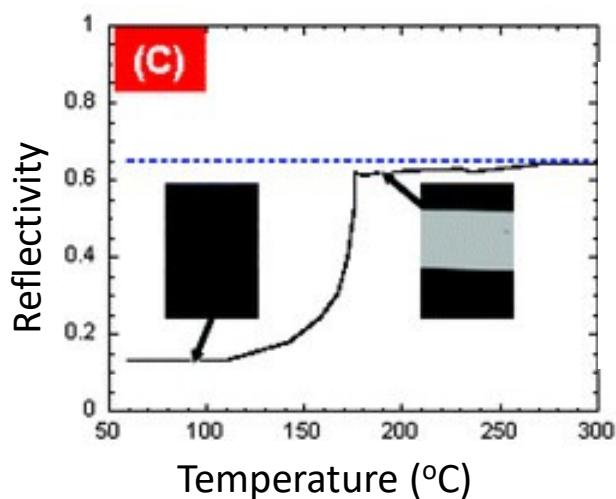
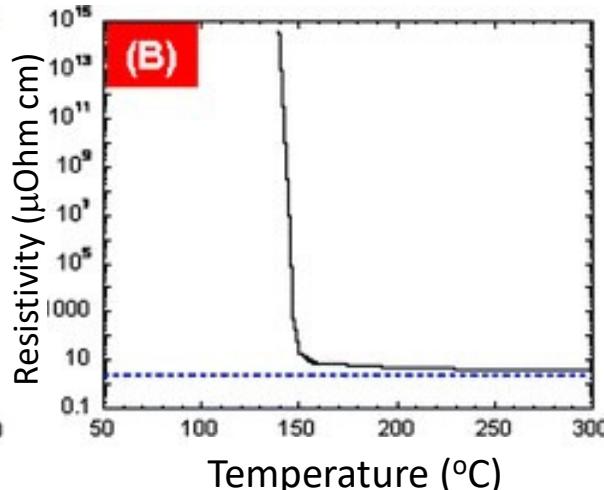
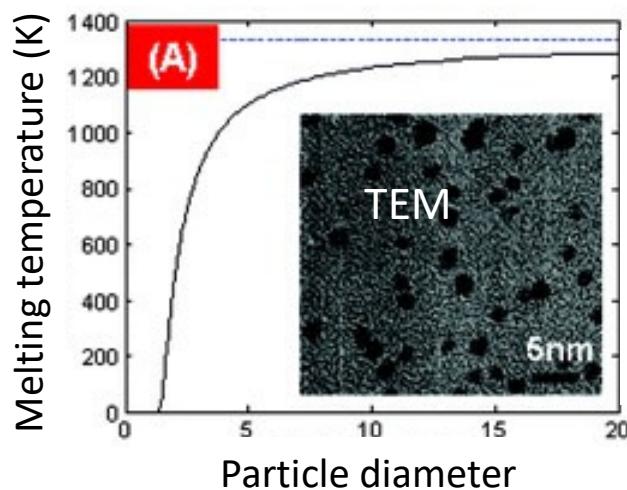
Silicon mold (inset: cross-section) produced by ICP-DRIE (26 cycles), with line-width 1 or 2 μm (depth 6 μm) and holes with edge length 4 μm (depth 8 μm).

Microstructured silver plate after forming at 400°C with a pressure of 300MPa, and Si mold removal by KOH etching.
(Typical thermal NIL pressure is 2MPa)

NIL into metal nano-particles at low temperature & pressure

Thermal (melting) characteristics of SAM-protected Au nano-particles (NPs).

NP can be melted/imprinted at rather low temperature. (SAM: self assembled monolayer)



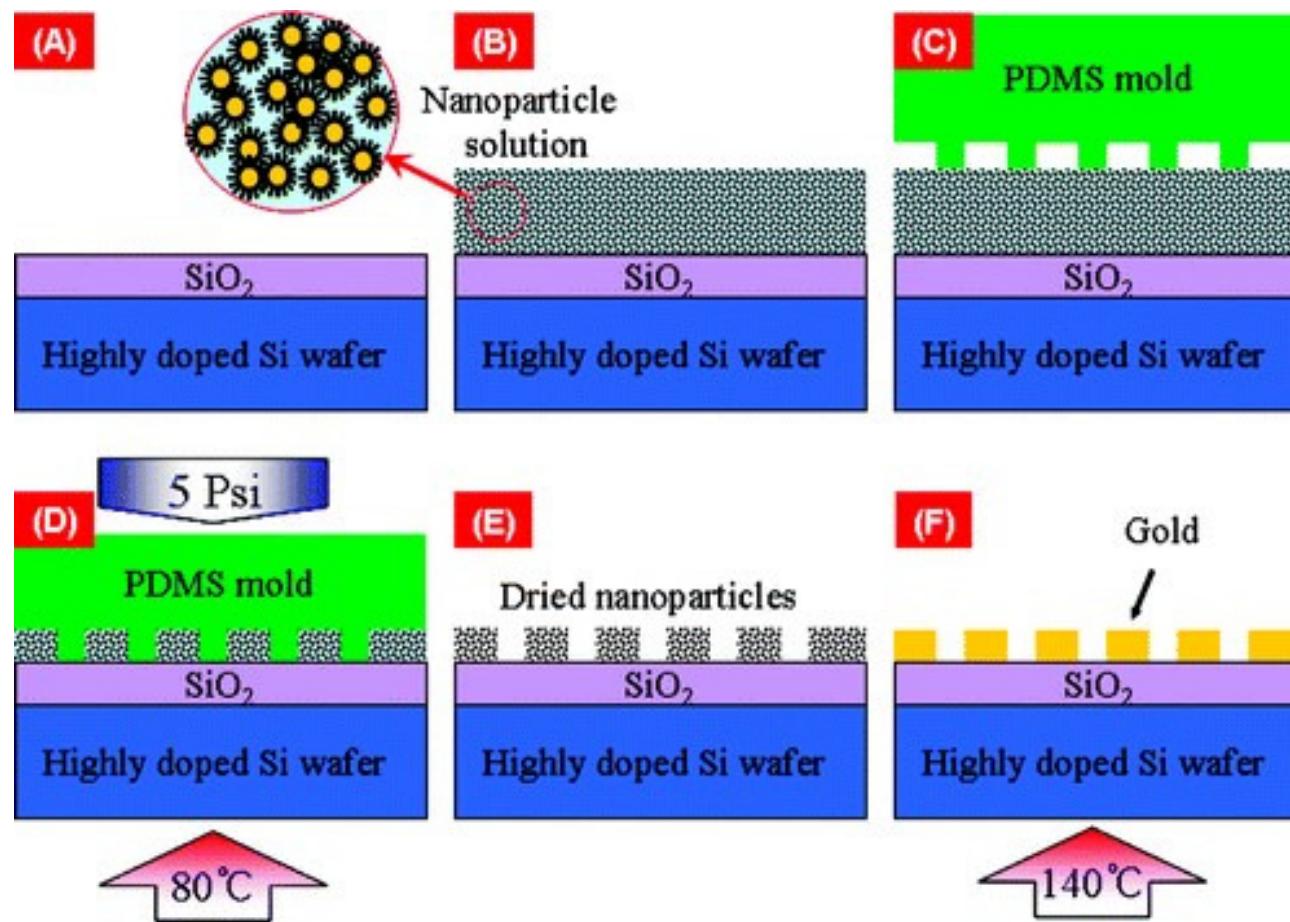
(A) Melting temperature of Au NPs with different sizes.

(B) Resistivity (dotted line represents bulk gold resistivity $2.65 \mu\Omega \cdot \text{cm}$). Melt to form continuous film with low resistivity.

(C) Reflectivity at 514.5nm wavelength. Insets represent the optical images of NP film before (left) and after (right) the melting.

(D) Mass change at various heating temperatures.

NIL into Au nano-particles and melting of NPs



(A, B) Dispensing NP solution on Si wafer.

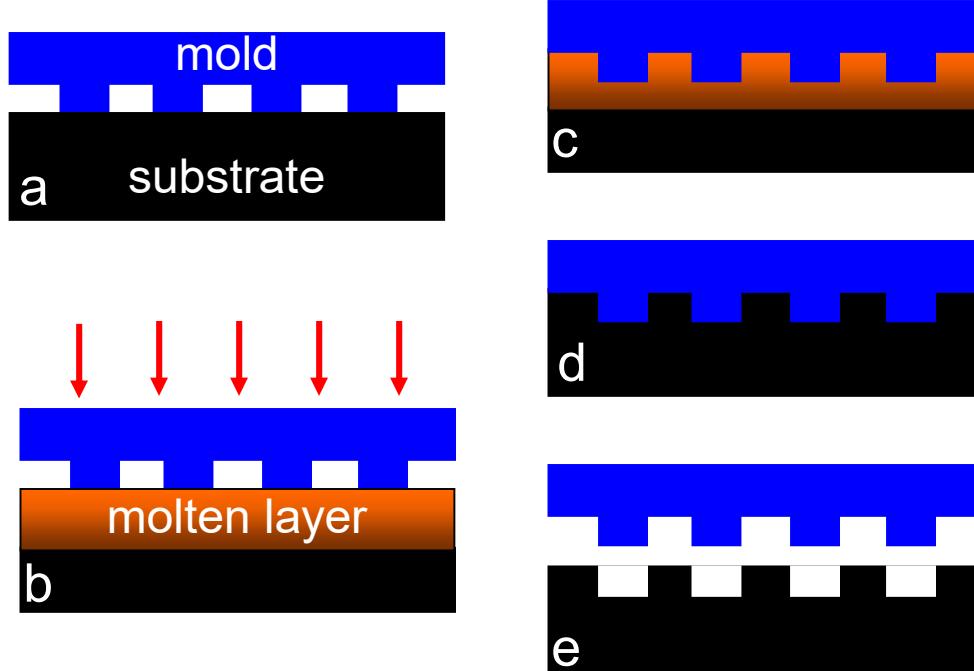
(C, D) Pressing PDMS mold on NP solution under 5psi pressure at 80°C (1atm=14psi).

(E, F) Removal of mold and induce NP melting on hot plate at 140°C.

The SAM-protected NPs are suspended in an organic solvent that is extremely viscous (like a solid) at room temperature, but its viscosity drops drastically with temperature.

Laser-assisted direct imprint (LADI) of metals

Metal can be easily melted and patterned by a pulsed laser.



One-step patterning process:

Replaces the steps of resist patterning, pattern transfer by etching, and resist removal all into one single step. And this step takes only order 100 ns!

Minimal heating of the substrate

Mold and substrate can have different thermal expansion.

Application:

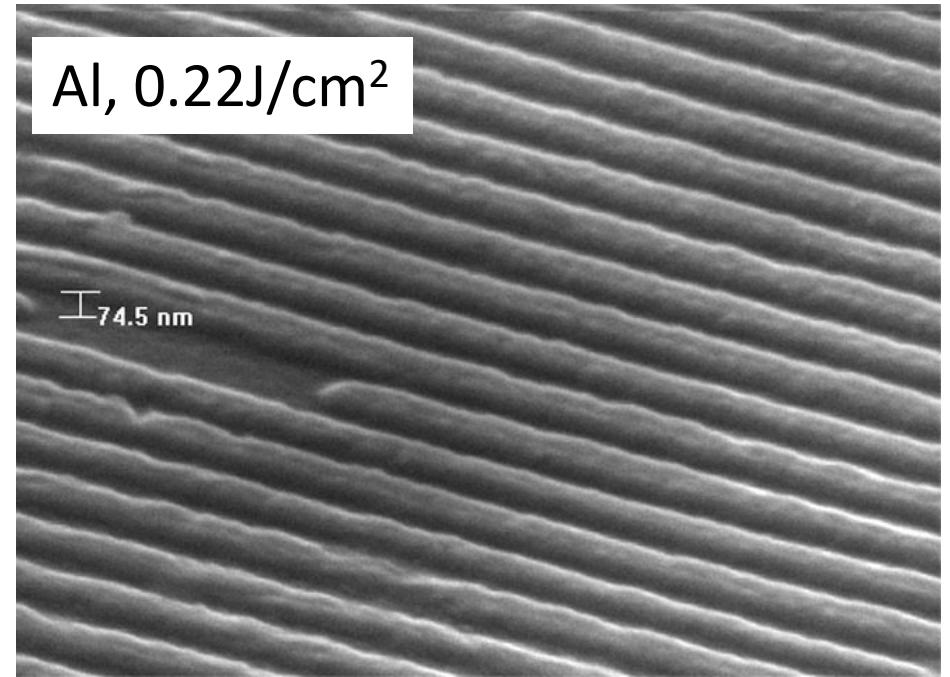
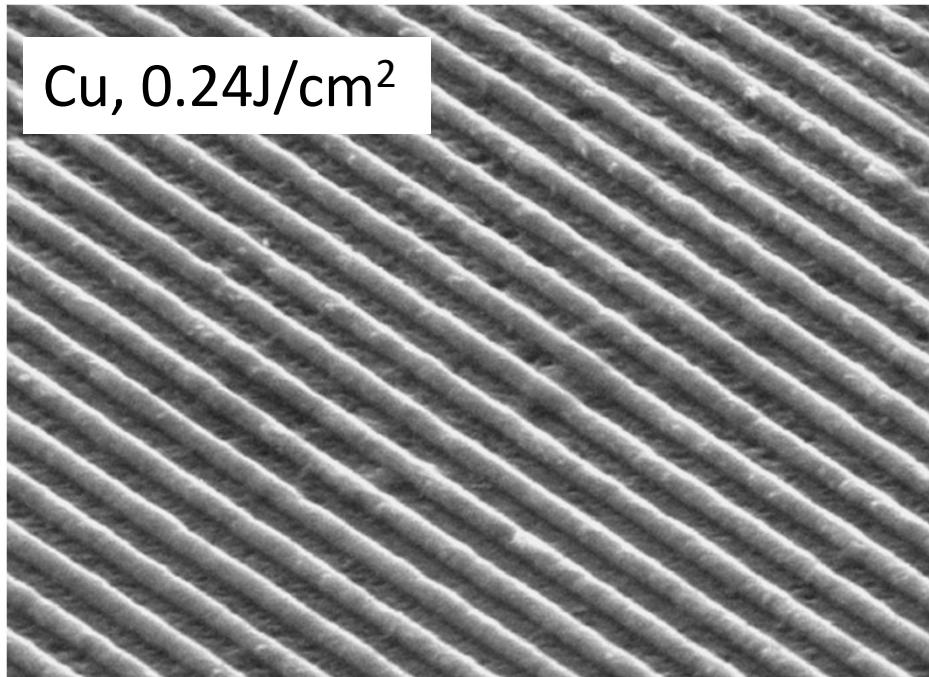
IC interconnect, flexible/durable NIL metal mold.

Here the drawing shows imprint into bulk silicon substrate (no metal film on it). Next slide is imprint into metal film coated on quartz wafer.

Laser-assisted direct imprint (LADI) of metals

Metal can be easily melted and patterned by a pulsed laser.

200 nm period grating patterned by LADI

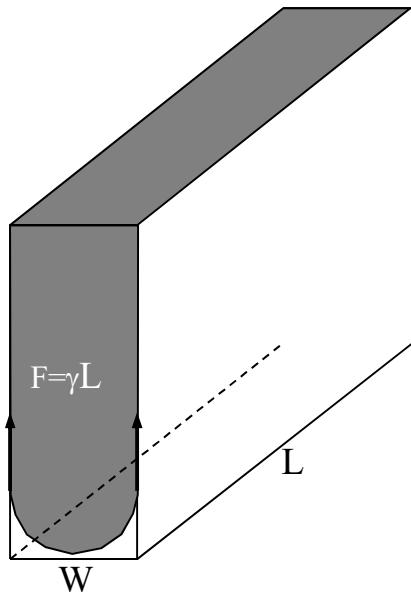


Pattern height: 100 nm.

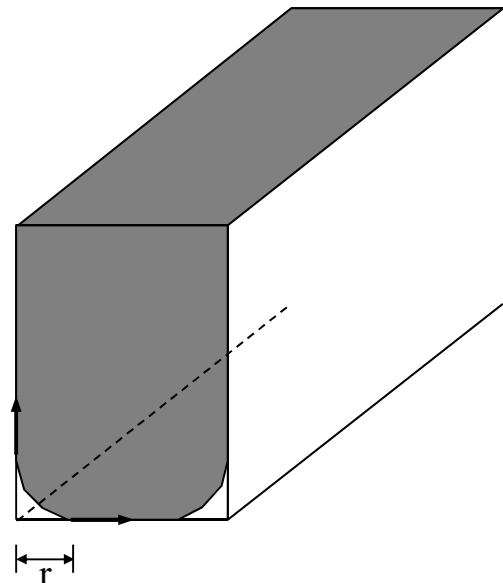
XeCl excimer laser, $\lambda=308\text{nm}$, 20ns pulse, laser fluence $0.24\text{J}/\text{cm}^2 = 12\text{MW}/\text{cm}^2$

Line was rounded due to surface tension and volume shrinkage upon solidification.

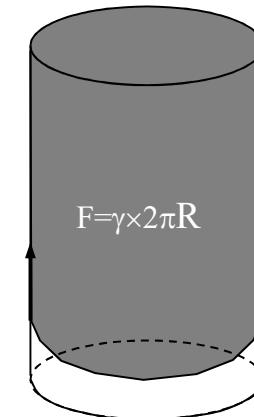
How much pressure needed



$$P = \frac{2\gamma L}{WL} = \frac{2\gamma}{W}$$



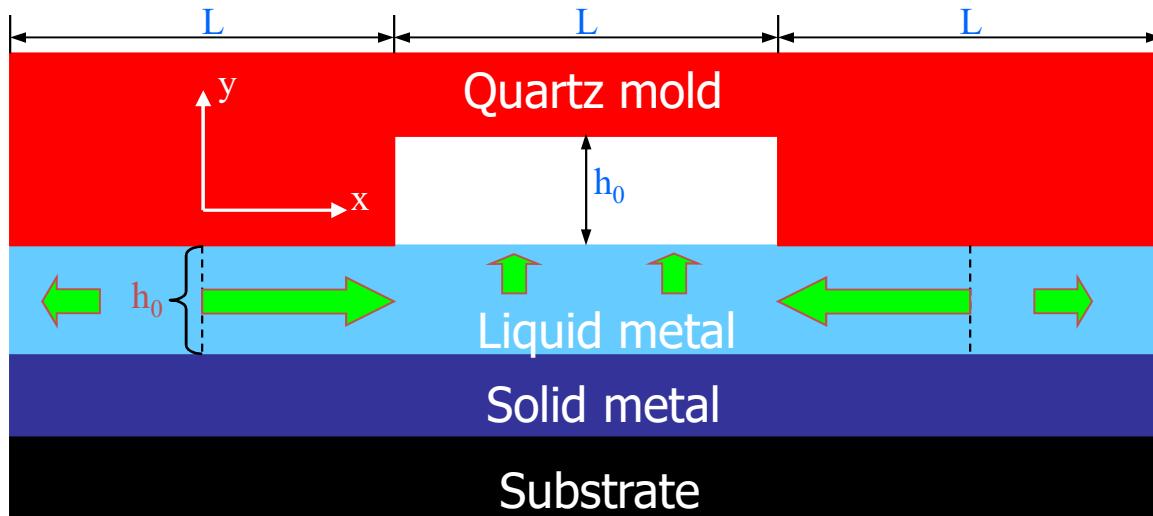
$$P = \frac{2\gamma L \cos 45^\circ}{\sqrt{2}rL} = \frac{\gamma}{r}$$



$$P = \frac{\gamma \times 2\pi R}{\pi R^2} = \frac{2\gamma}{R}$$

- Pressure \propto surface tension / dimension.
- Order 10^2 atm is needed for 100 nm feature size, due to the high surface tension of metals.
- The surface tension of metals are order 1N/m, as compared to 0.07N/m for water.

How big feature can be patterned (how far the liquid can flow before it freezes)



$$L = \frac{2h_0}{3} \sqrt{\frac{p\tau}{\mu}}$$

Inertial force is ignored.
p: pressure.
 τ : melting time.
 μ : viscosity.

Material	L	Assume:
Cu	4.9 μm	P=400atm
Ni	4.2 μm	$\tau=100\text{ns}$
Si	12.0 μm	$h_0=200\text{nm}$

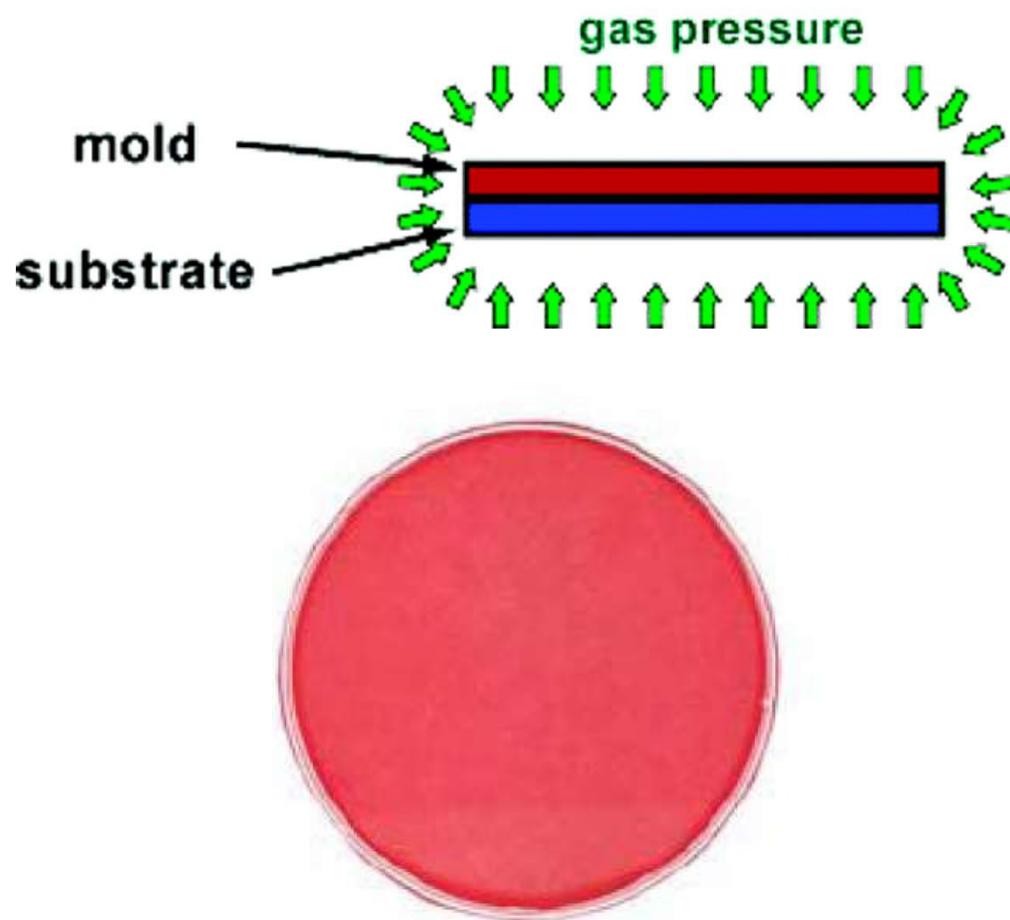
Experiment: 17 μm Si has been patterned, but failed for several tens of μm .

Viscosity for molten metals are comparable to that of water at room temperature (0.00091 Pa·sec, or 0.91 centipoises), much lower than polymer.

Nanoimprint lithography (NIL)

1. UV-curable NIL.
2. Resists for UV-NIL.
3. Mold fabrication for thermal and UV-NIL.
4. Alignment.
5. NIL into metals.
6. NIL systems (air press, roller, roll-to-roll, EFAN...)

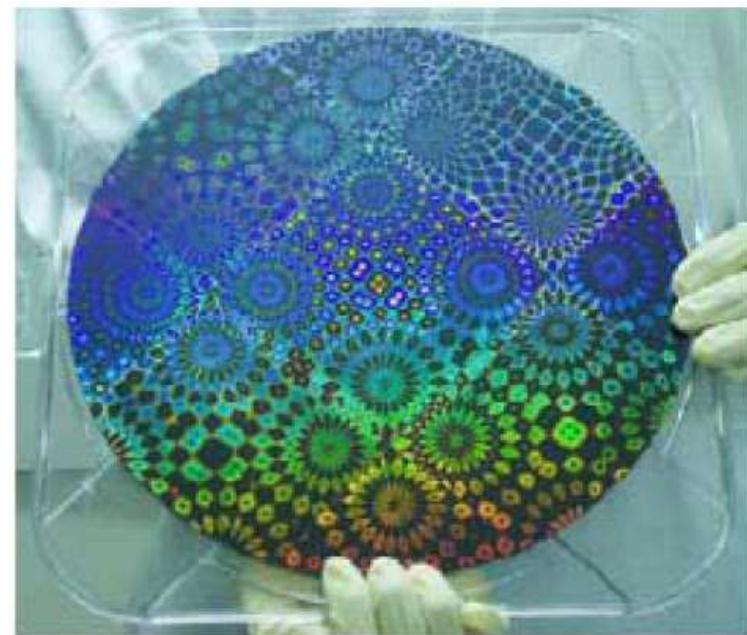
Air cushion press (ACP) nanoimprint



8-in pressure indicating papers (gas pressure= 5kg/cm²). Uniform color means uniform pressure.

One can get similar imprint result using solid plate press, but needs higher pressure to make sure the pressure is high enough everywhere across the wafer.

Mold/substrate sealed between plastic sheets/membranes



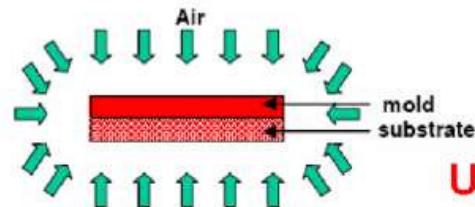
A 12-inch imprinted wafer

NIL tools: air-press



- * Full-wafer (up to 4") nanoimprinting tool
- * Sub-micron overlay alignment accuracy

Air Cushion Press™ (ACP)
for ultimate nanoimprint uniformity



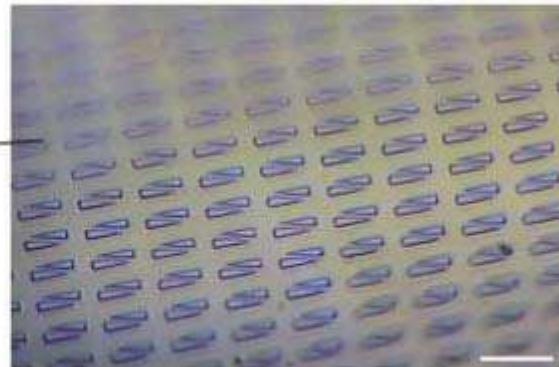
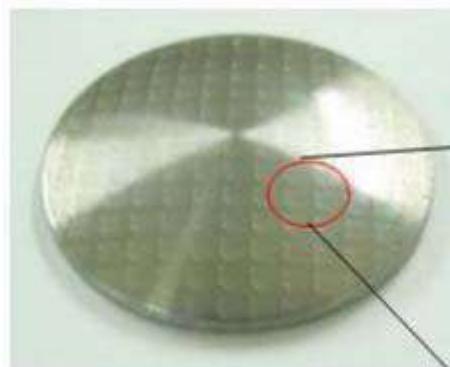
Uniform pressure applied by the 2 membranes



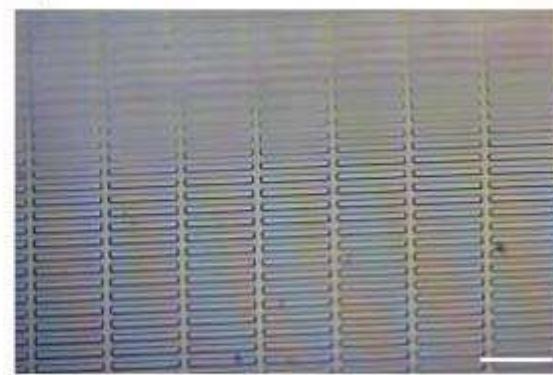
Air press has uniform pressure, but for most applications parallel plate press can also achieve good result (may need something soft like a paper for more uniform pressure).

"Air Cushion Press for Excellent Uniformity, High Yield, and Fast Nanoimprint Across a 100 mm Field", Nano Lett. 2006.

NIL onto curved surface



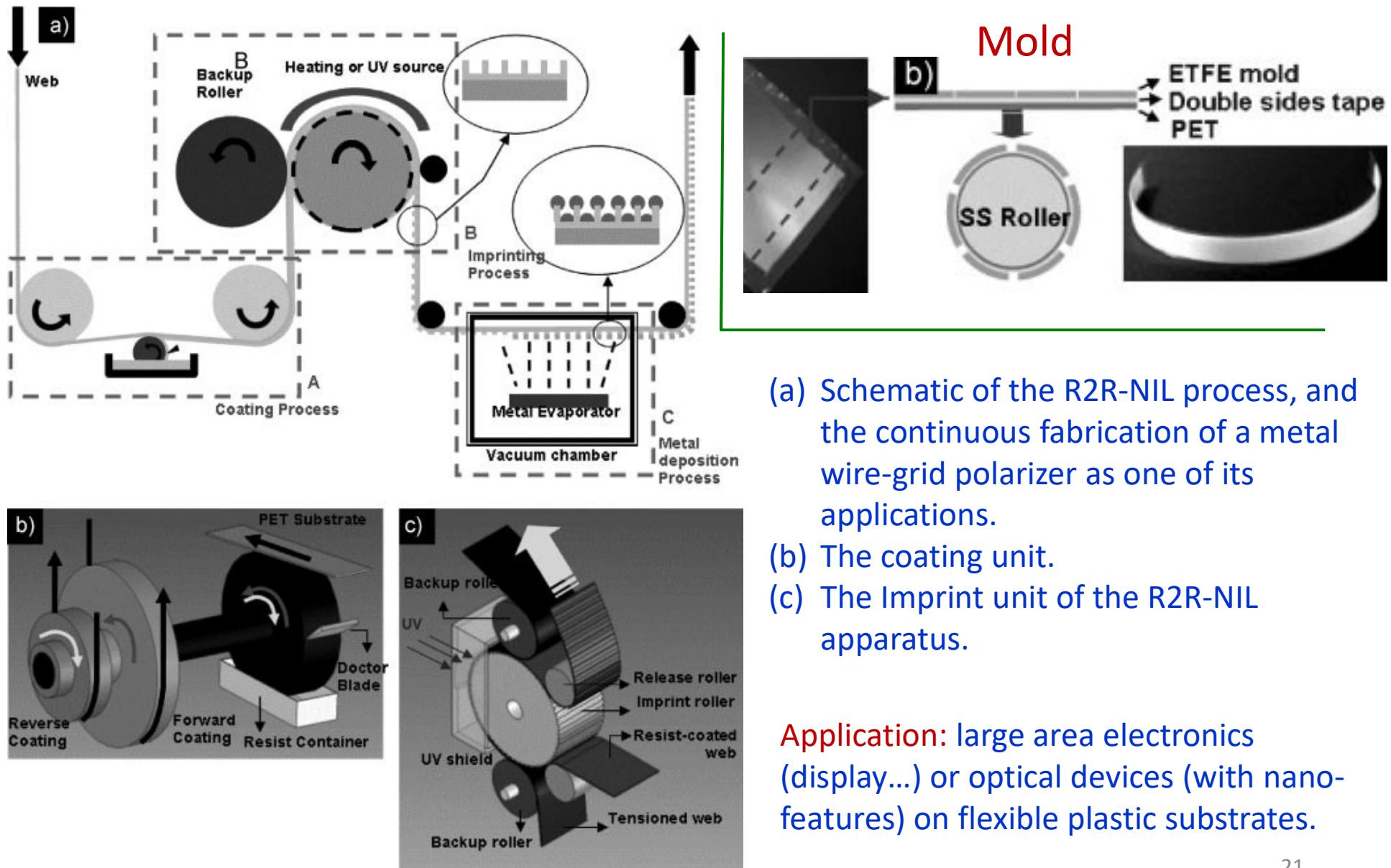
(a) photograph images



(b) OM images, scale bar is 15 μm

- Imprinted patterns on 2-inch convex surface.
- Using flexible PDMS mold and uniform gas pressure, the patterns can be transferred onto curved surface successfully.

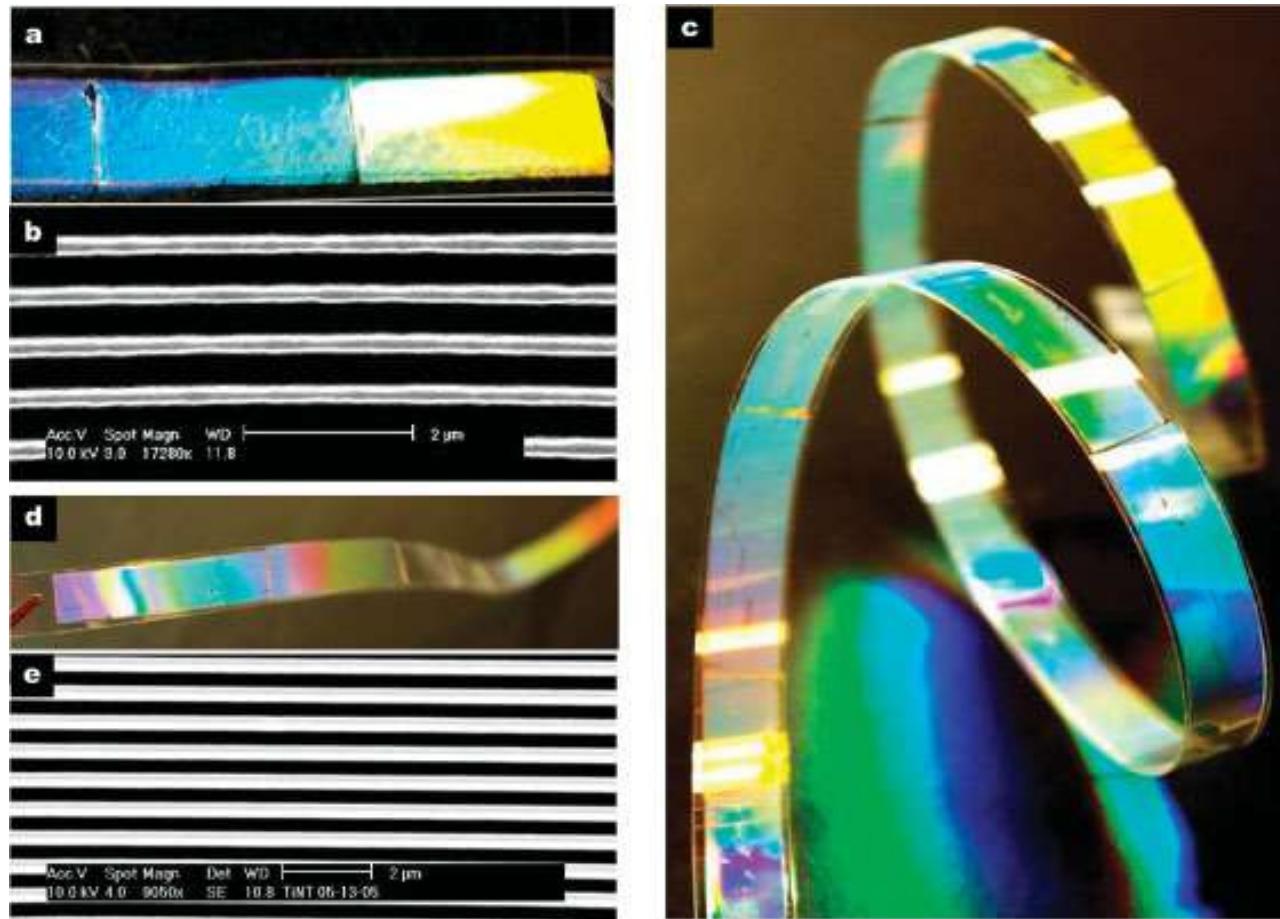
Roll-to-roll (R2R) nanoimprint lithography



- Schematic of the R2R-NIL process, and the continuous fabrication of a metal wire-grid polarizer as one of its applications.
- The coating unit.
- The Imprint unit of the R2R-NIL apparatus.

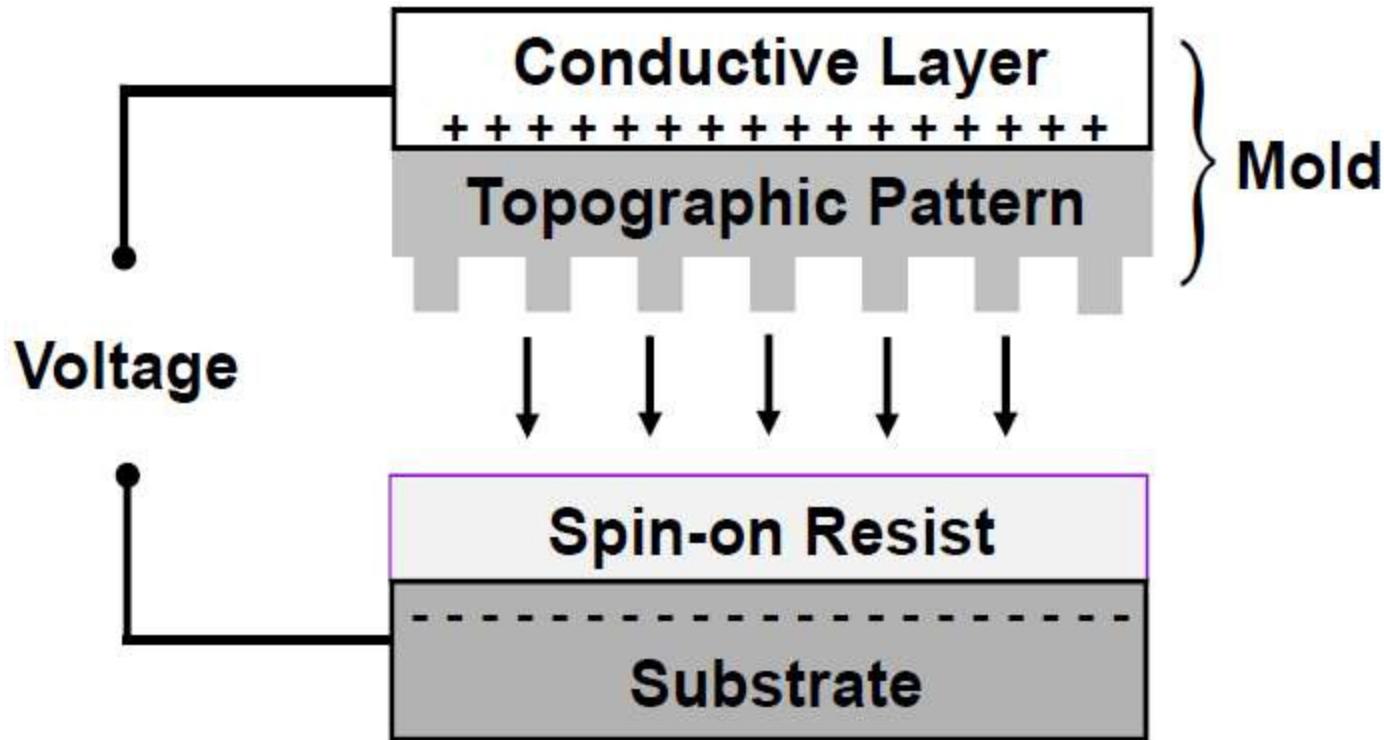
Application: large area electronics (display...) or optical devices (with nano-features) on flexible plastic substrates.

Results of roll-to-roll imprint



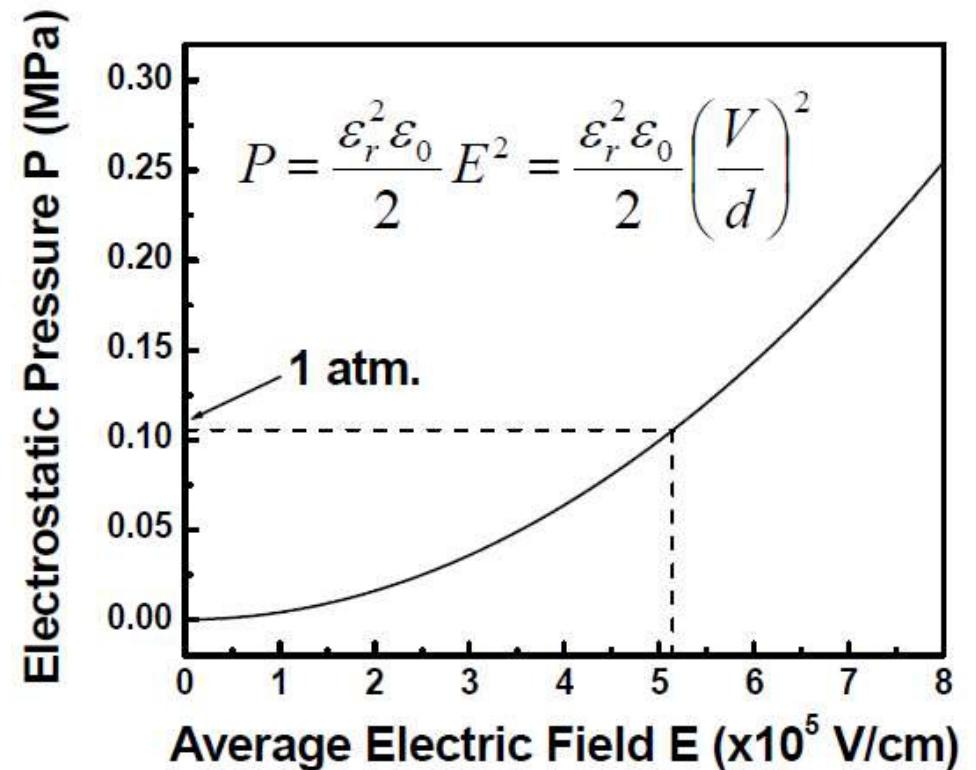
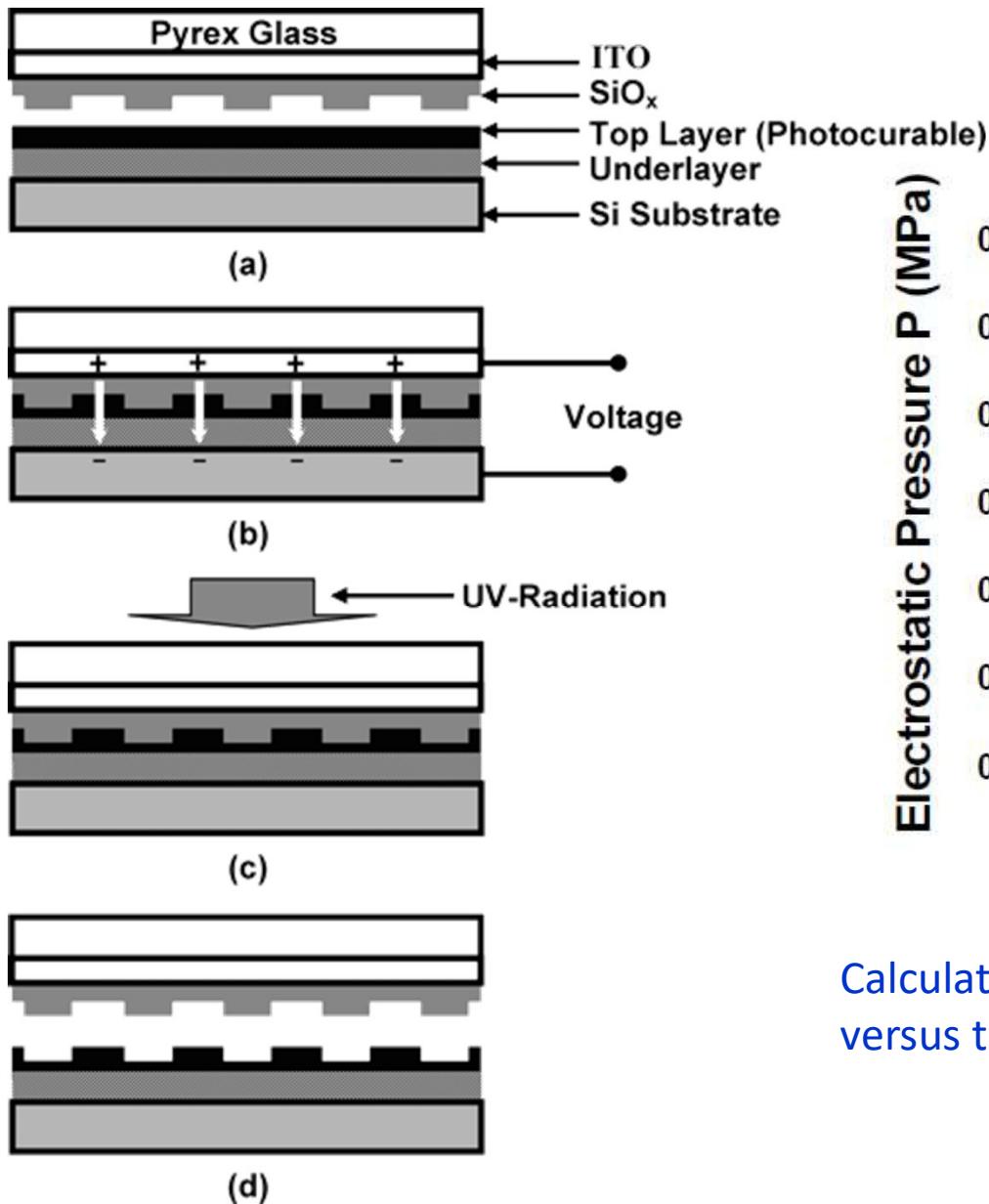
- Thermal R2R-NIL results: a-b) photograph and SEM of a 700nm period 300nm line-width PDMS grating pattern imprinted on PET strip.
- UV R2R-NIL results: c-e) photographs and SEM of 700nm period 300nm line-width epoxy-silicone grating pattern imprinted on PET strip, showing bright light diffraction. Total length is 570mm.

Electric field assisted NIL (EFAN)



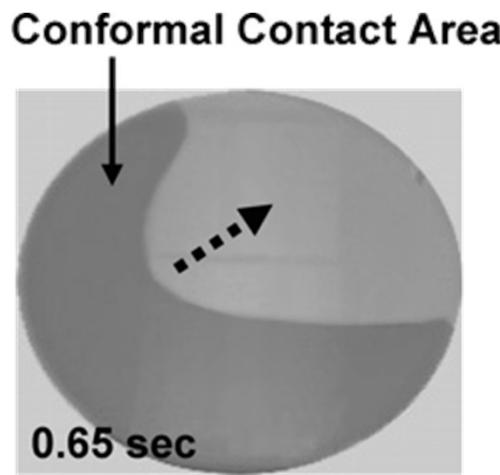
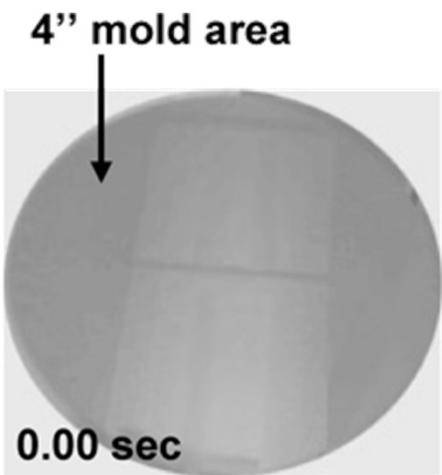
Principle of EFAN: a voltage is applied between the conductive layers on the mold and the substrate, generating an electrostatic force to press the mold into the resist layer.

EFAN process flow

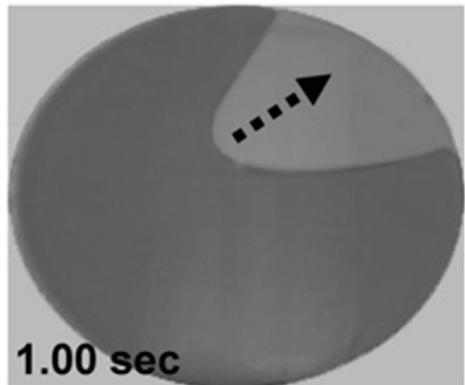


Calculated effective electrostatic pressure (P) versus the required strength of the electric field.

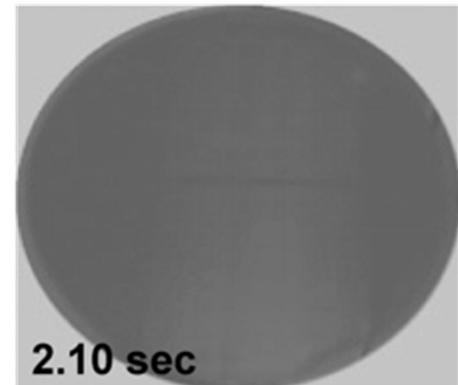
Propagation of contact area and imprint results



No conformal contact

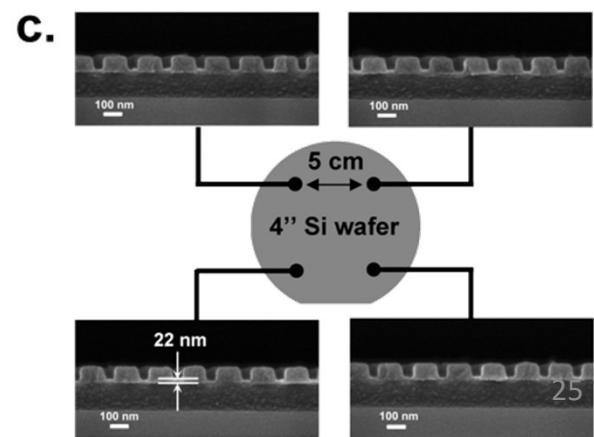
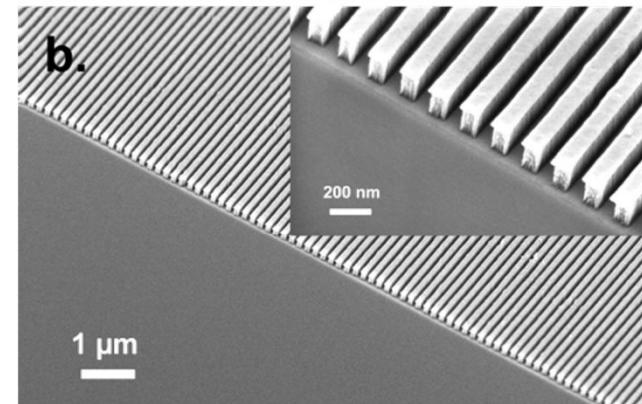
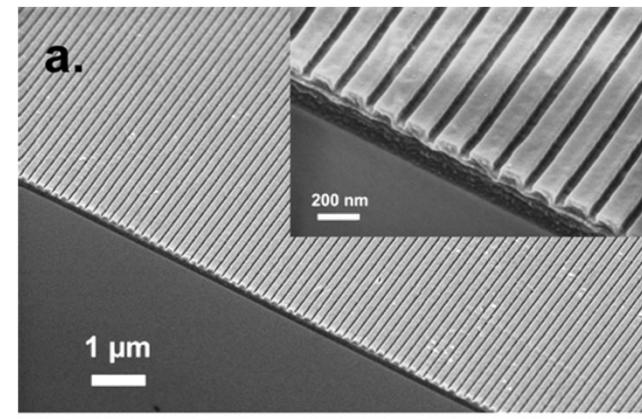


Propagation of the conformal contact area



Propagation at t = 1 sec

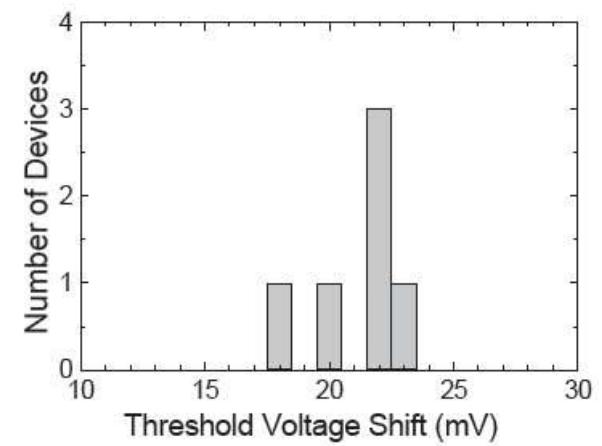
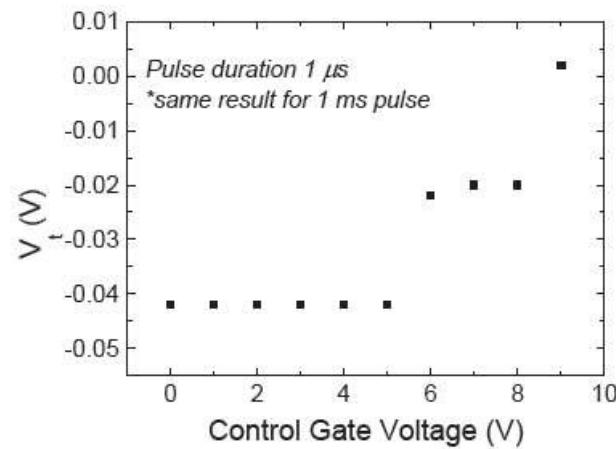
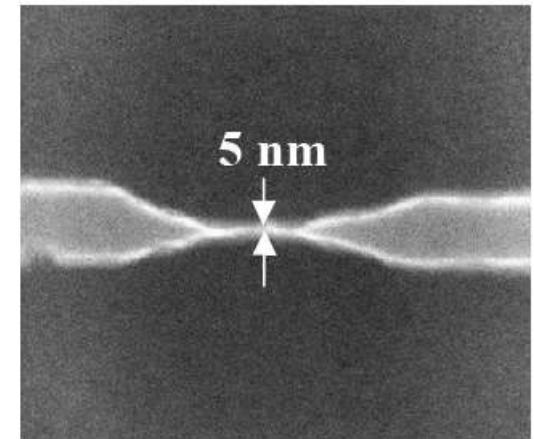
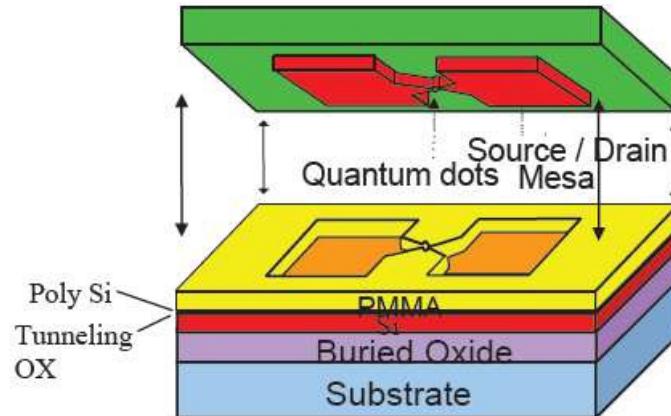
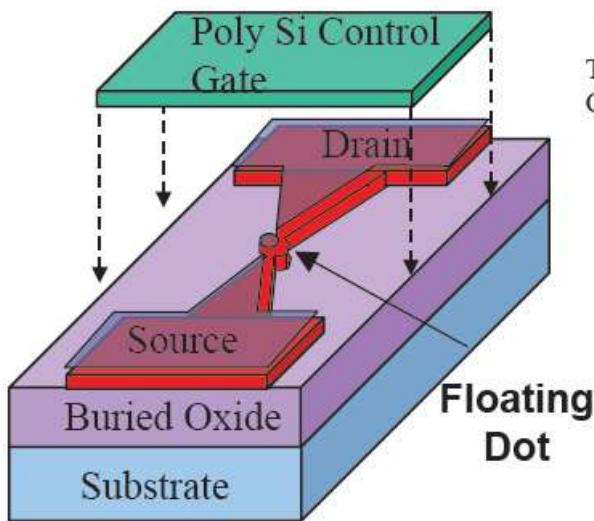
Fully imprinted wafer at t = 2.1 sec



Nanoimprint lithography (NIL)

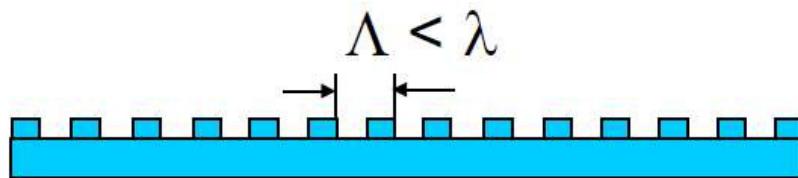
1. UV-curable NIL.
2. Resists for UV-NIL.
3. Mold fabrication for thermal and UV-NIL.
4. Alignment.
5. NIL into metals.
6. NIL systems (air press, roller, roll-to-roll, EFAN...)
7. NIL applications

First single-electron memory with 8nm dot using NIL



For single electron devices, the size of the quantum dot is very critical. It is achieved by e-beam lithography and size shrinkage techniques, which has very low yield. By using NIL, once the “right” size is achieved, it can be duplicated many times faithfully.

Sub-wavelength optical elements – optical chips by NIL

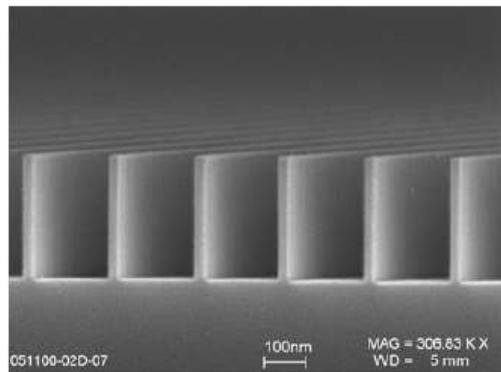


Key Uniqueness:

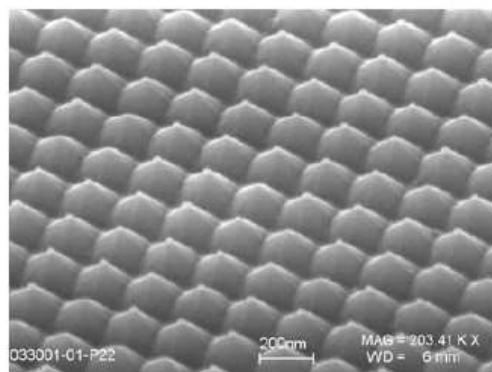
- New functions unavailable in bulk optics
- Ultra-thin (e.g., $< 1 \mu\text{m}$)
- Different optical functions by the same materials but different nanopatterns
- Large-scale monolithic integration on-chip
- Low cost, mass production

Examples of SOEs

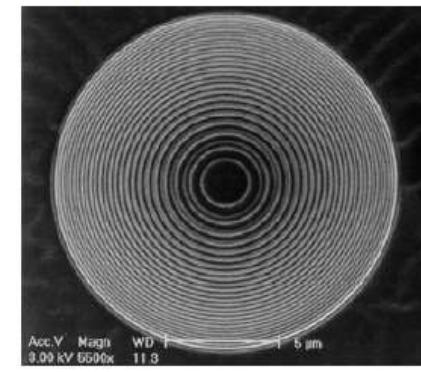
- Antireflective surfaces
- Waveplates
- Polarizers
- Filters
- Add/drop channel switches (tunable)
- Couplers
- Subwavelength binary lenses and zone plates
- Photonic crystals
- High-speed photodetectors
- High-speed lasers
- And much more



Waveplate with 20 nm fins

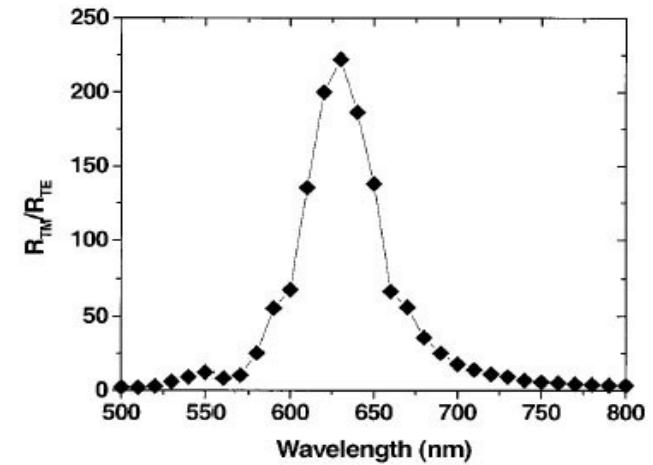
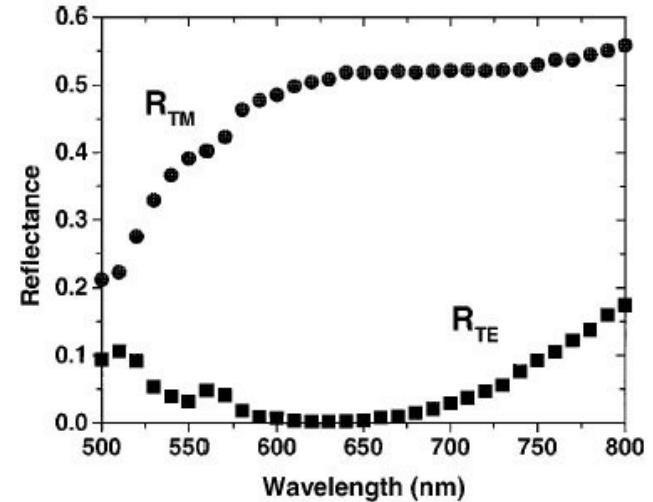
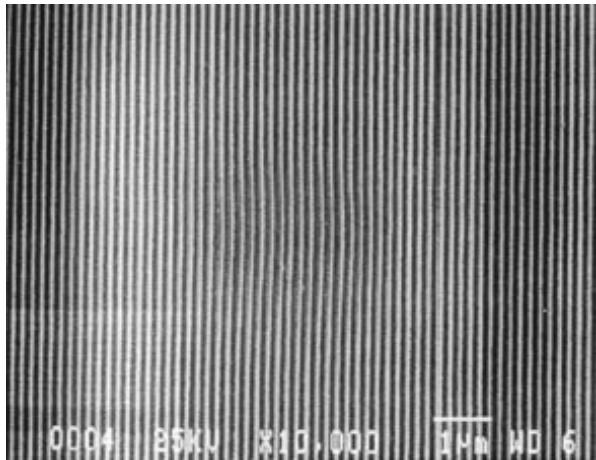
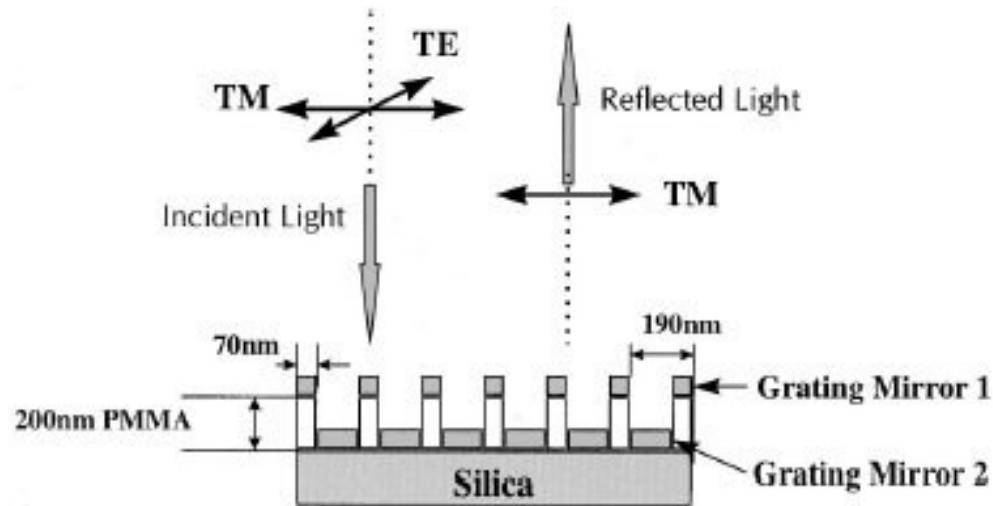


Antireflection of 200 nm pitch



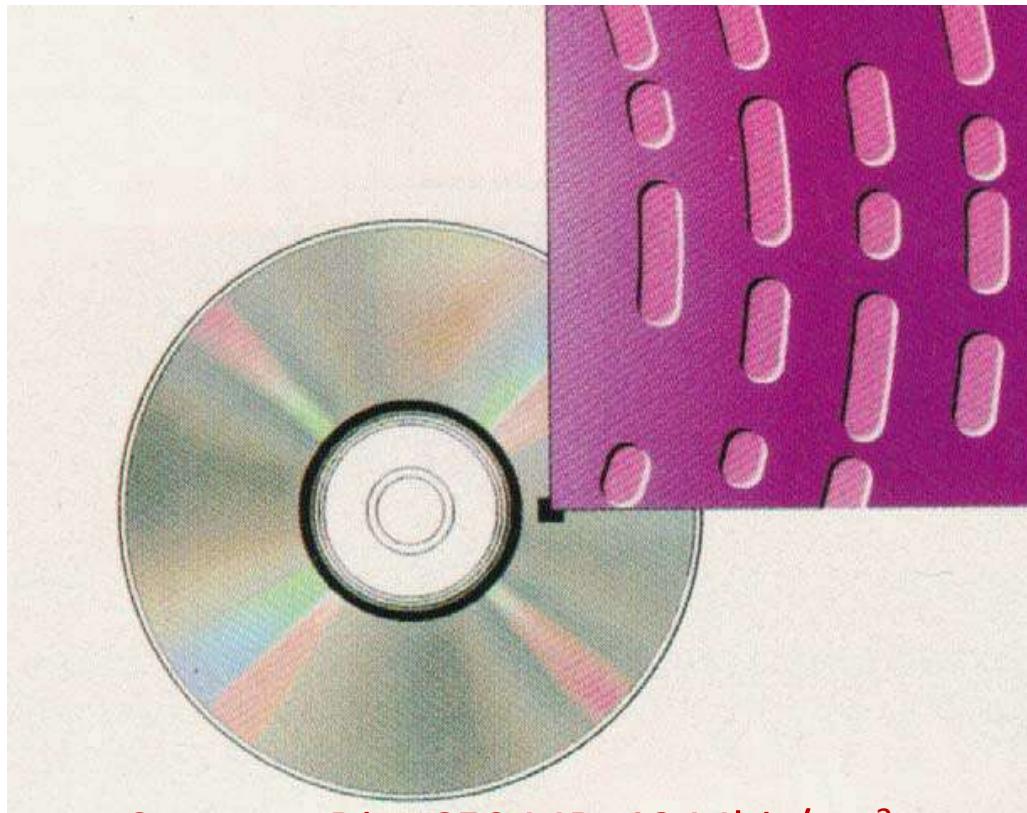
Zone plate of 70 nm min. feature

Thin film reflective polarizer

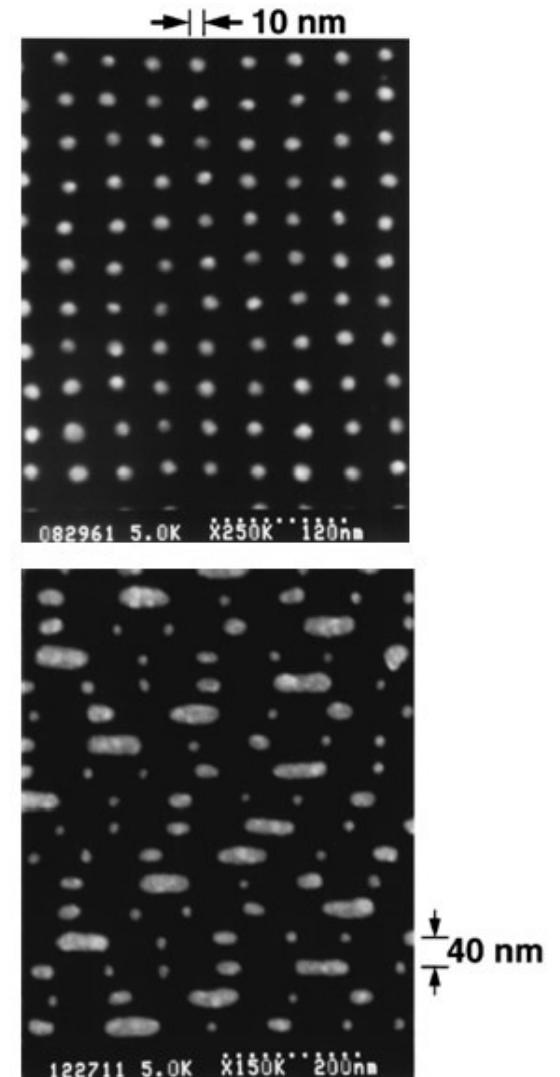


Commercial CD and nano CD

CD is made by injection molding
into polycarbonate using a Ni mold,
similar to NIL.



Compact Disc 650 MB, 48 Mbit/cm²



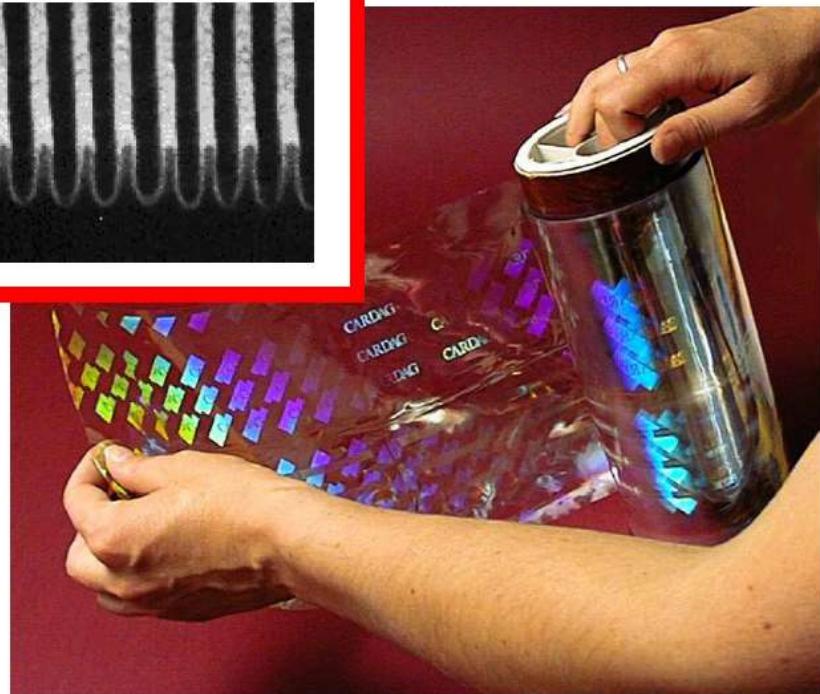
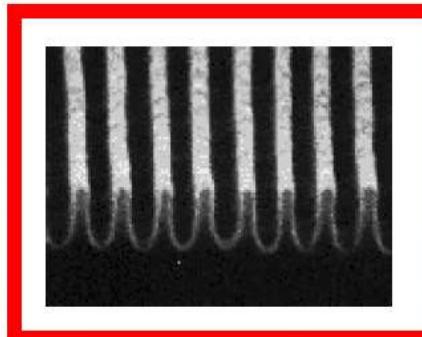
CD areal density: 400 Gbit/in²

Krauss and Chou, "Nano-compact disks with 400 Gbit/in² storage density fabricated using nanoimprint lithography and read with proximal probe", Appl. Phys. Lett. 71, 3174-3176 (1997).

Application: diffractive security elements

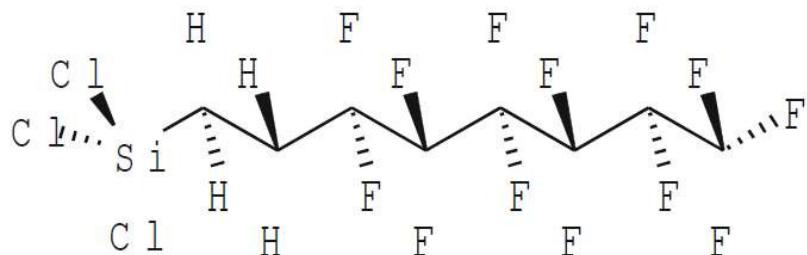
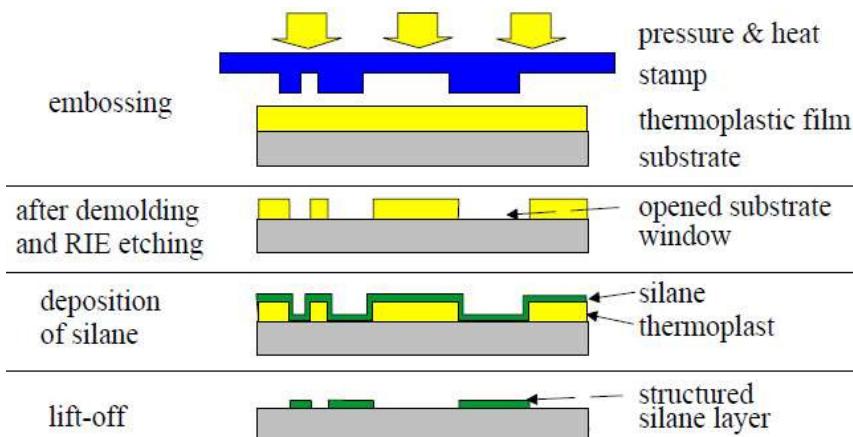


Example for diffractive colors:
Tropical butterflies



Periodic diffractive elements produced
by “roll-embossing” to be laminated into
credit cards, bank notes etc.

Chemical patterning by liftoff for liquid crystal displays



tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (TFS)

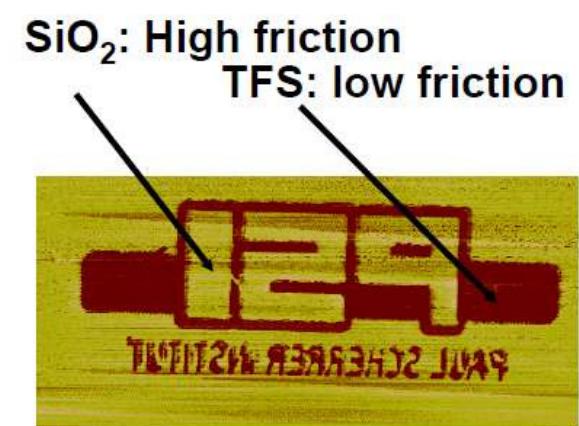
Stamp:
AFM image



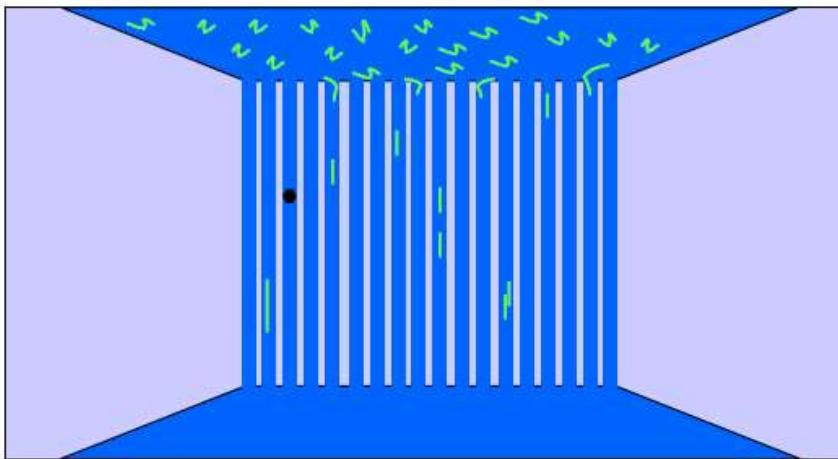
Embossed structure:
AFM image



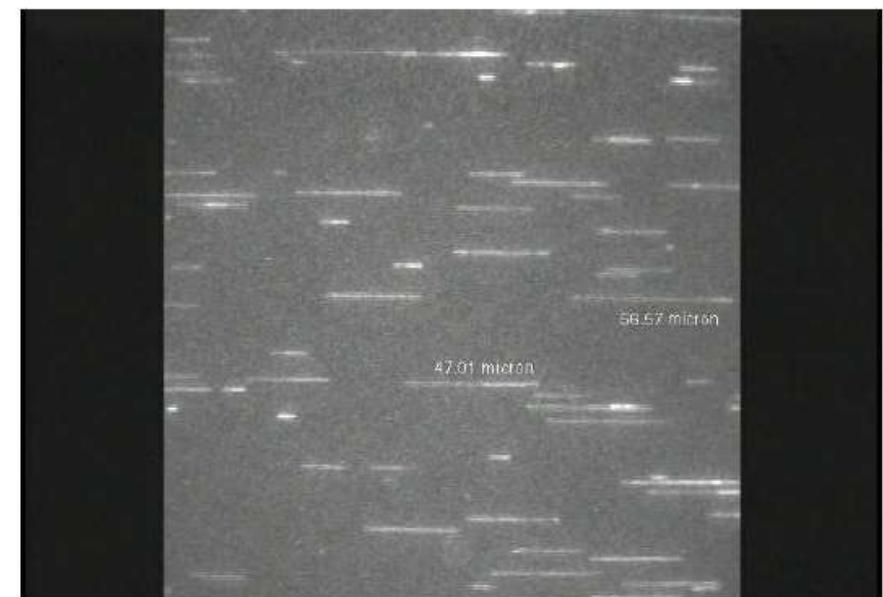
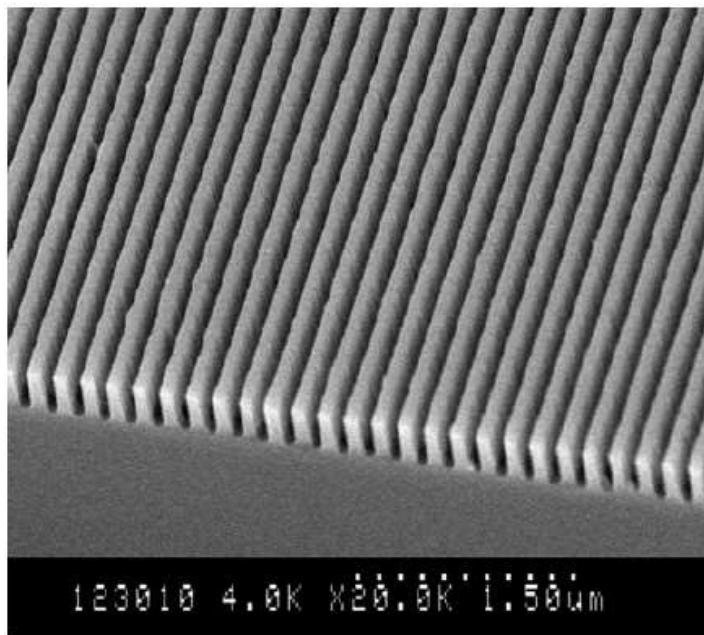
Chemical patterns after lift-off:
LFM image



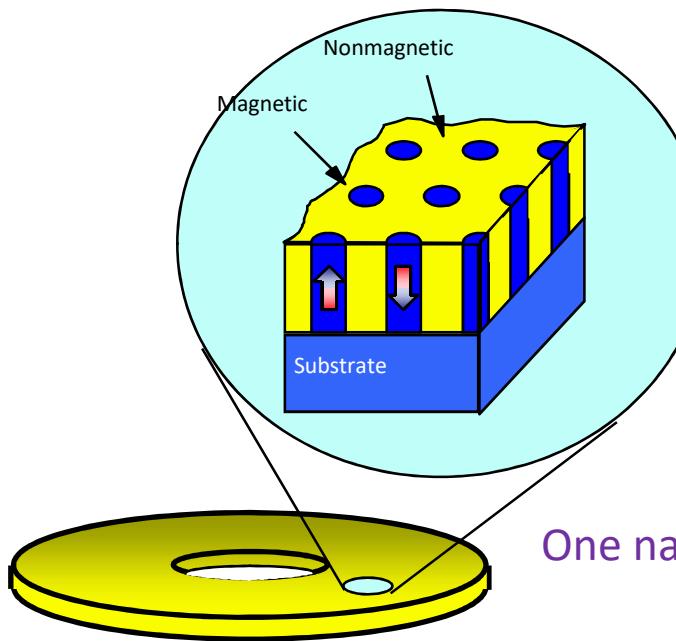
Nano-channel DNA sorter by NIL



- Channel width (>50 nm)
- Narrower than DNA Persistent length
- DNA automatically stretch DNA molecules straight
- DNA length = DNA molecular weight



Bit-patterned magnetic recording media



Advantage over conventional thin film disk:

- Overcome super-paramagnetic limit thus capable of ultra-high density recording.
- Smooth transition hence low media noise
- All-or-nothing writing process, thus can tolerate large head-field gradient.
- Robust and precise tracking through patterning.

- Nanoimprint lithography is invented when Dr. Chou was asked how to make patterned magnetic media in a cheap way.
- Interestingly, first large scale application for NIL is likely on magnetic data storage. (or it may be on large area electronics for display, but then it is not very “nano”)
- This is because no other lithography can do the job ($25\text{nm} \times 25\text{nm}$ for 1Tbits/in^2).
- Currently, data storage companies like Seagate is working on this.
- The most likely solution for even higher density ($>4\text{Tbits/in}^2$) is guided self-assembly, where self-assembly is guided by NIL-created patterns.
- However, the mold still need to be made by the slow e-beam lithography, take ~month to fabricate.

Who invented nanoimprint lithography?



- It is well recognized that Dr. Stephen Chou invented nanoimprint lithography in 1995 (result published in Science in 1996).
- Dr. Grant Wilson from University of Texas at Austin invented what is now called as UV-curing NIL.
- However, it is recently revealed that Japanese scientists invented NIL (both thermal and UV-curing) in 1970s, with a few patents and publications (all in Japanese) covering many aspects.
- But 30 years ago, nobody noticed or cared about this invention.

Dr. Chou from Princeton

Japanese Journal of Applied Physics 48 (2009) 06FH01

REVIEW PAPER

Fine Pattern Fabrication by the Molded Mask Method (Nanoimprint Lithography) in the 1970s

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Received November 28, 2008; accepted February 9, 2009; published online June 22, 2009

Nanoimprint lithography has recently been attracting the attention of many researchers in the field of nanofabrication technology. Although the study of nanoimprint lithography was initiated by Chou *et al.* around 1995, a fine-pattern fabrication technology, whose concept is similar to nanoimprint lithography, had been proposed and studied at NTT Laboratories in Japan as early as in the 1970s. The technology was based on the combination of the molding of plastic film on a substrate and dry etching of the molded film and substrate surface. It is considered that most of the basic concepts in current nanoimprint lithography were included in this early study. Some demonstration experiments using diffraction gratings, micro-sized test patterns, LSI patterns and microlenses were carried out to verify the feasibility of the technology at that time. The key point of the technology to fabricate fine patterns accurately was the fluidity of the plastic film. It was called the "Molded Mask Method" and this paper introduces the study on the molded mask method of those days.

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“Soft” lithography

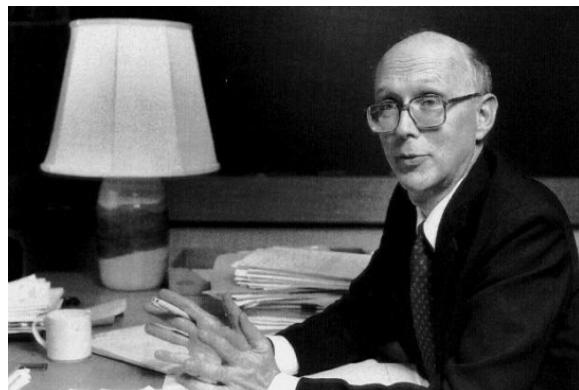
1. Soft lithography and PDMS.
2. Micro-contact printing.
3. Replica molding.
4. Micro-molding in capillary.
5. Micro-transfer molding/printing.
6. Solvent assisted microcontact molding.

Soft lithography

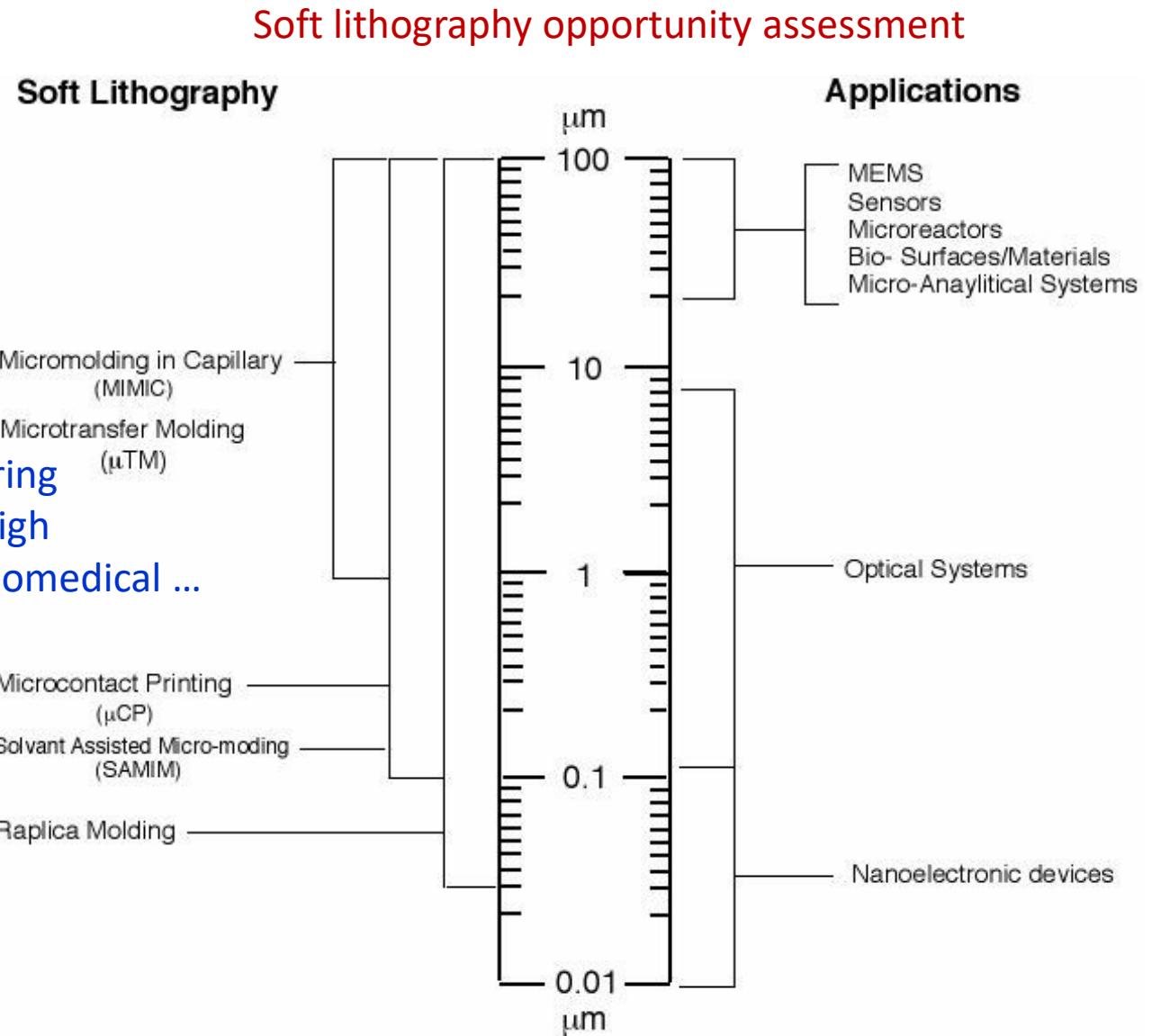
“Soft” means no energetic particles (electron, ions) or radiation (UV, X-ray) is involved. Instead, soft elastomeric stamp is used.

Soft lithography:

- Low cost
- Molding, printing or transferring
- Resolution usually not very high
- Application in microfluidic, biomedical ...



George M. Whitesides (Harvard)

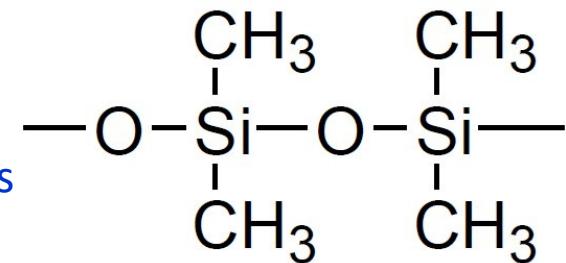


“Size is not the only thing that matters, function is more important” (something like this), Whiteside 2

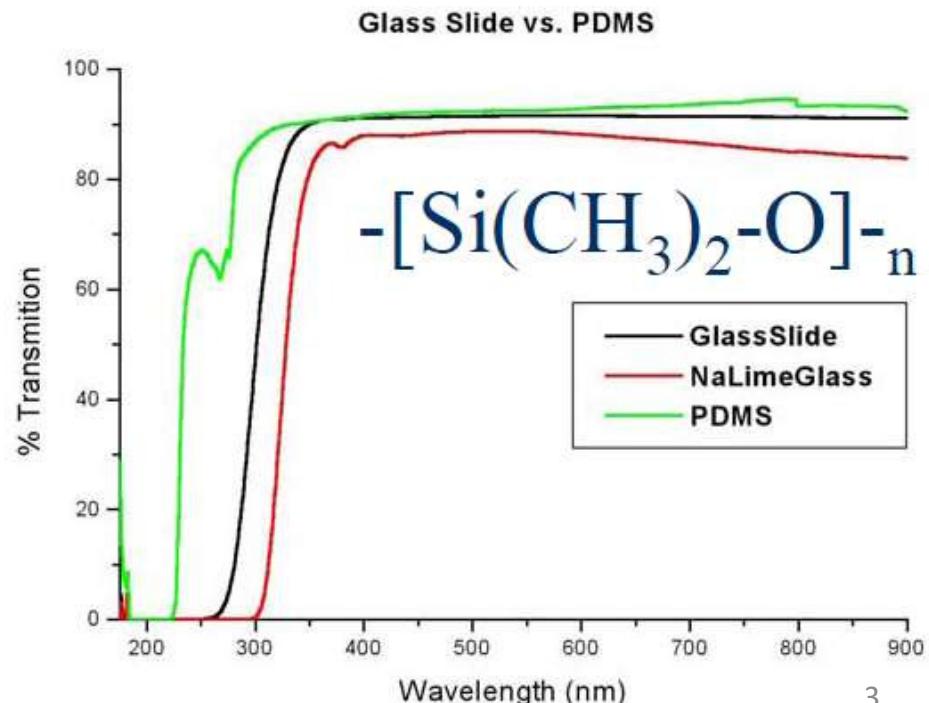
PDMS: poly(dimethyl-siloxane)

PDMS properties:

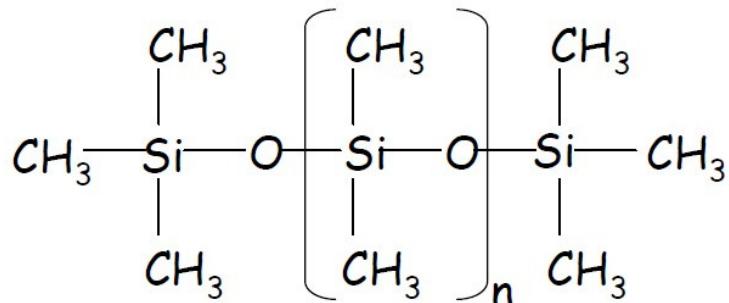
- Silicone elastomer with a range of viscosities
- Flexible (1 MPa Young's modulus, typical polymer 1 GPa) and easy to mold.
- Elastomer, conforms to surface over large areas.
- Chemically inert, optically transparent
- Low surface energy, bonds reversibly (or permanent).
- Seals to flat and clean surfaces for micro-fluidic channels
- Durable (reusable), low thermal expansion
- Biocompatible (even used for food additive)



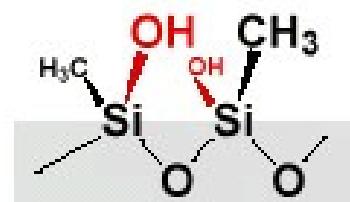
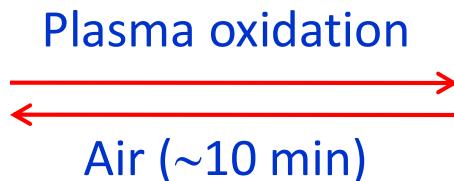
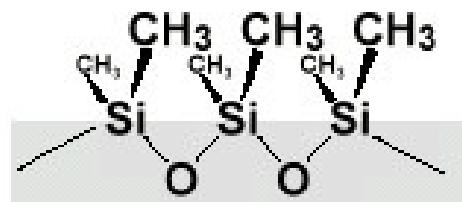
Dow Corning brand



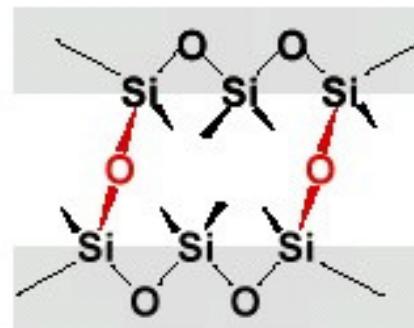
PDMS surface treatment



Upon treatment in oxygen plasma, PDMS seals to itself, glass, silicon, silicon nitride, and some plastic materials.



contact PDMS surfaces



Biggest issue: it becomes hydrophobic quickly, very bad for micro-fluidic applications.
(liquid hard to get into the channels once it becomes hydrophobic)

PMDS is absolutely the most popular material for bio-medical lab-on-chip (microfluidic) applications, but may not be suitable for commercial applications, which need chemically stable surface.

PDMS surface treatment

- PDMS has a low interfacial free energy such that molecules of most polymers won't stick on or react with its surface.
- The interfacial free energy can be manipulated with plasma treatment.
- For nano-imprint or soft lithography mold, plasma can make PMDS surface like SiO_2 , easy for mold release agent coating using silane chemistry.

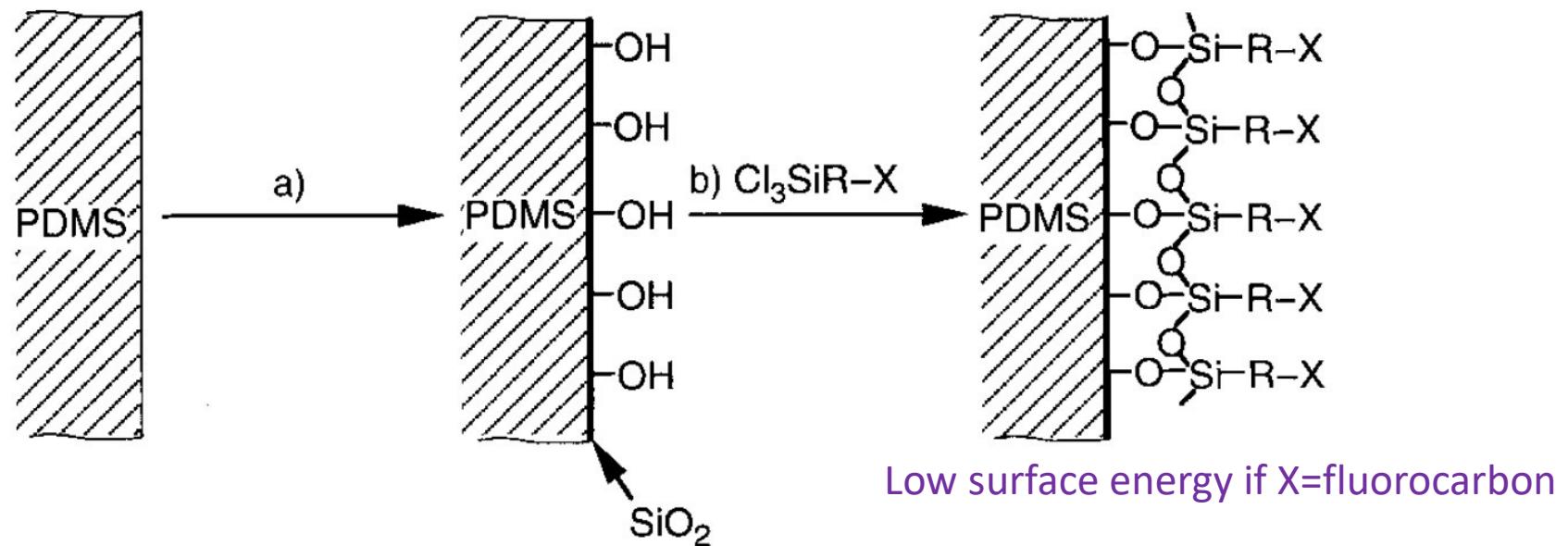


Figure 6. Schematic procedure for the modification of the PDMS surface.
a) Treatment with an O_2 plasma; b) reaction with silyl chloride vapor.
Different terminal groups X of the SAMs give different interfacial properties.^[122]

PDMS is permeable to solvent and gas

Solvent permeability: for example, PDMS can absorb propylene glycol mono ether acetate (PGMEA) up to 27wt.% of its weight and 30wt.% of absorbed PGMEA will diffuse into air in 1 h.

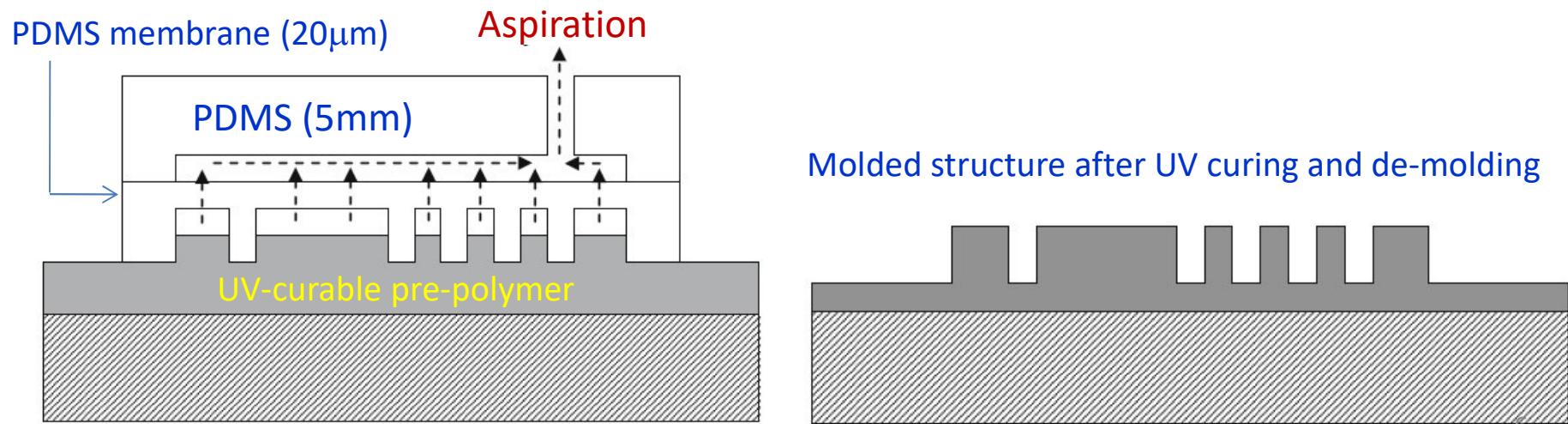
Table 5.1 Gas permeability coefficients of PDMS, PS, and PMMS

Polymers	Permeability coefficient (Barrer)		
	He	N ₂	O ₂
PDMS	590	351	781
Polystyrene (PS)	22.4	0.52	2.9
PMMA	8.4	0.02	0.14

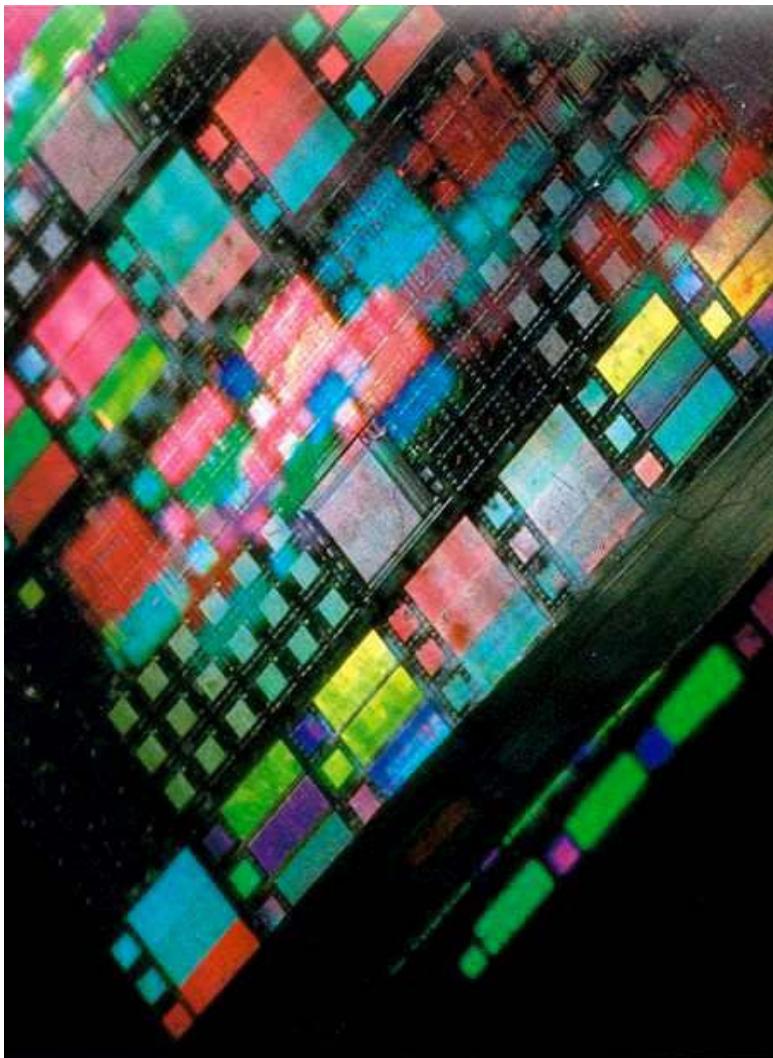
(1 Barrer = $10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm cm}^{-2} \text{ cmHg}^{-1} \text{ s}^{-1}$) [89]

This property is good for cell culture within PDMS channel/cavity, since cell can “breath” the air.

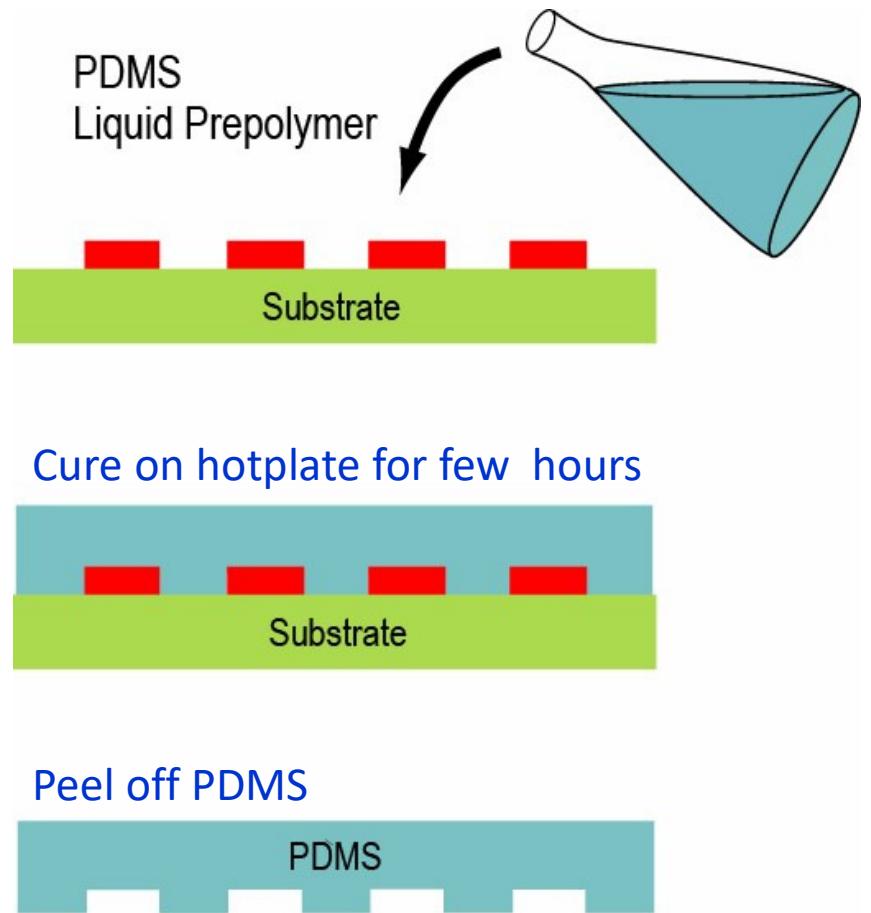
Micro-aspiration assisted lithography (MAAL)



PDMS fabrication



Besides casting, PDMS can also be spin-coated to form thin (many μm) films



Master pattern (red color) can be in:
photoresist (SU-8), silicon, glass...
Silanization of master mold needed to obtain
low surface energy for easy separation.

PDMS problems: soft, low Young's modulus

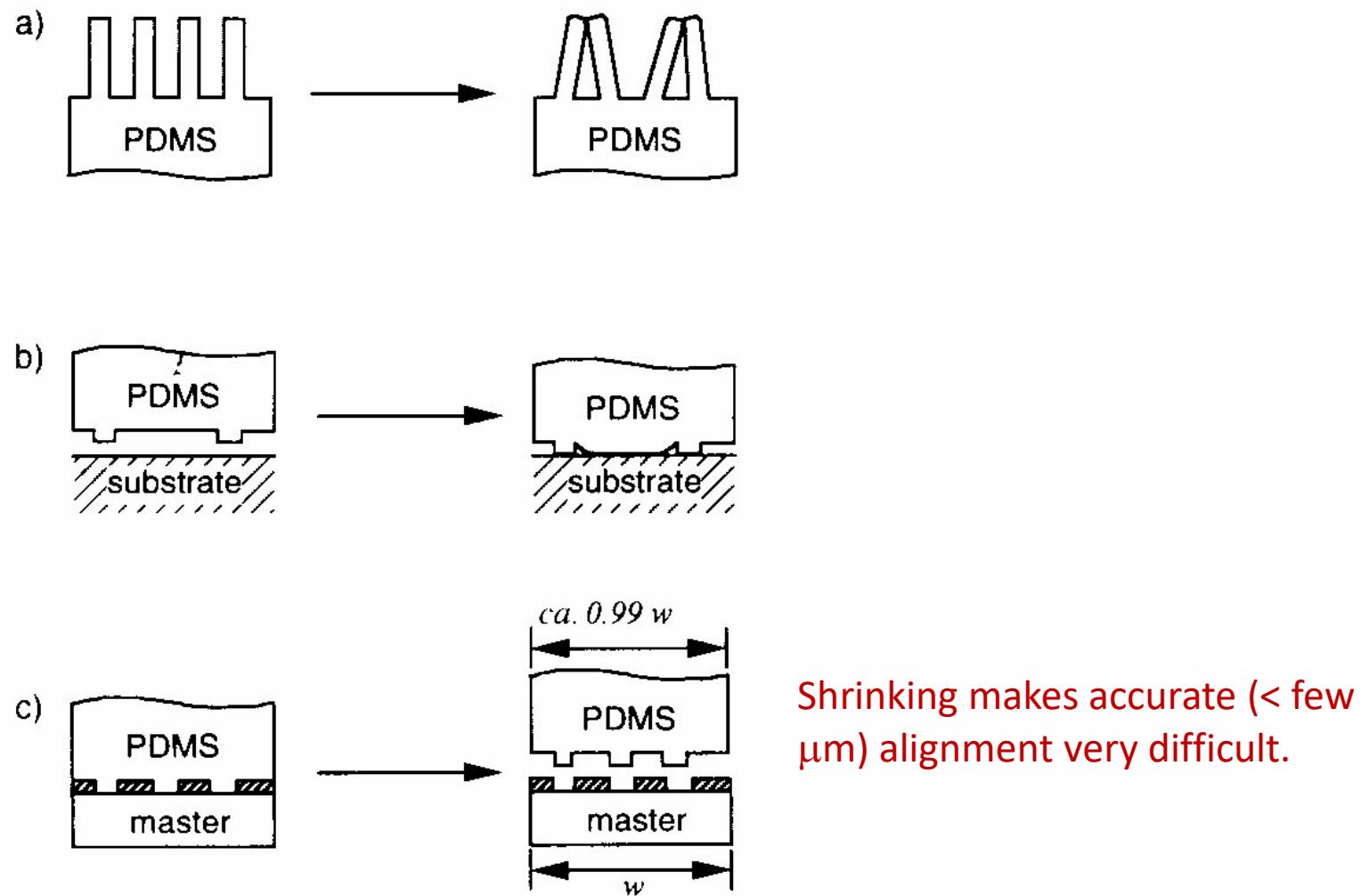
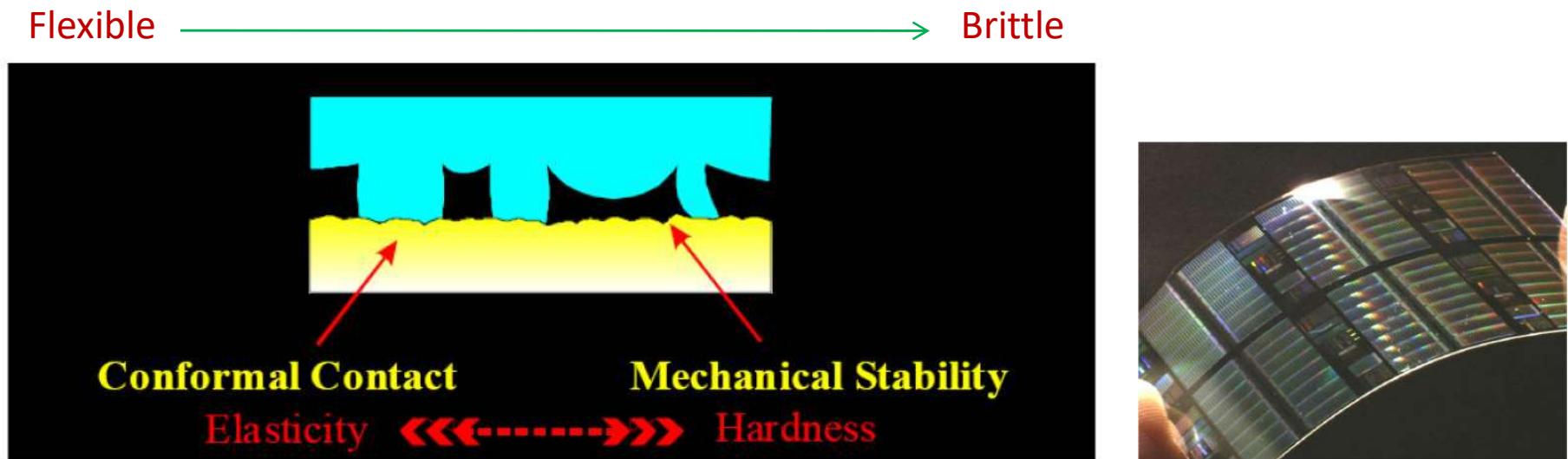


Figure 7. Schematic illustration of possible deformations and distortions of microstructures in the surfaces of elastomers such as PDMS. a) Pairing, b) sagging, c) shrinking.

Hard PDMS (h-PDMS) ("Filler" added for more cross-linking)

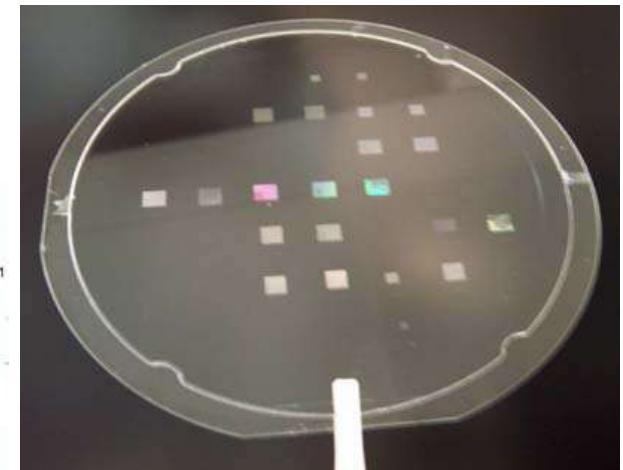
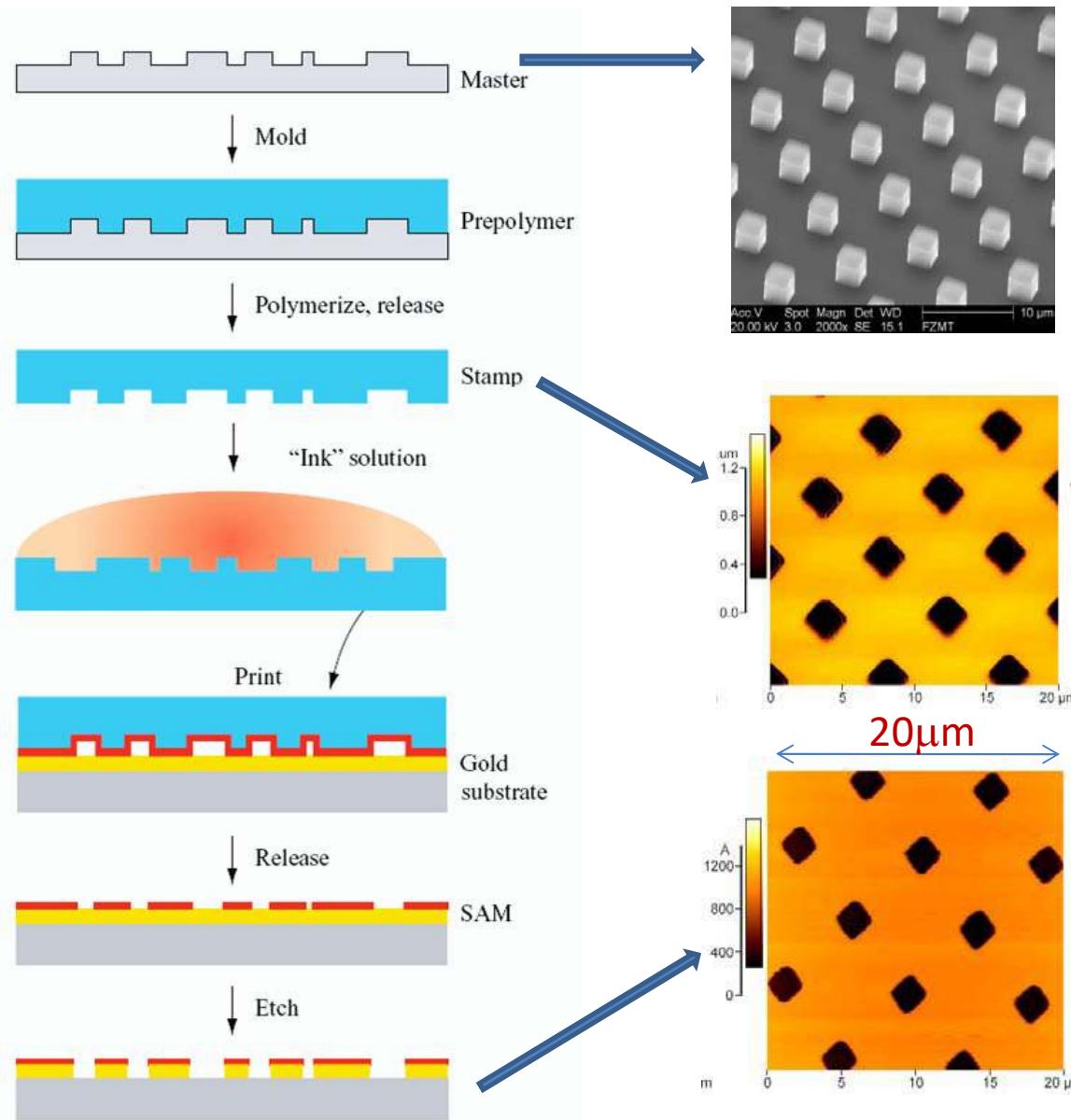
- More cross-linked polymer, so harder.
- Less flexible than regular (soft) PDMS, more brittle.
- Must have a support in order to not crack the stamp, use thick layer PDMS or glass as support.



“Soft” lithography

1. Soft lithography and PDMS.
2. Micro-contact printing.
3. Replica molding.
4. Micro-molding in capillary.
5. Micro-transfer molding/printing.
6. Solvent assisted microcontact molding.

Micro - contact printing (μ CP)



100mm stamp

Self - assembling, classical –SH and Au bonding

- Definition: spontaneous organization of molecules (objects) into stable, well-defined structures by non-covalent forces.
- Driving force: thermodynamic equilibrium.
- Biological 3D self assembly: folding of proteins, formation of DNA helix...



Self assembled monolayer (SAM)

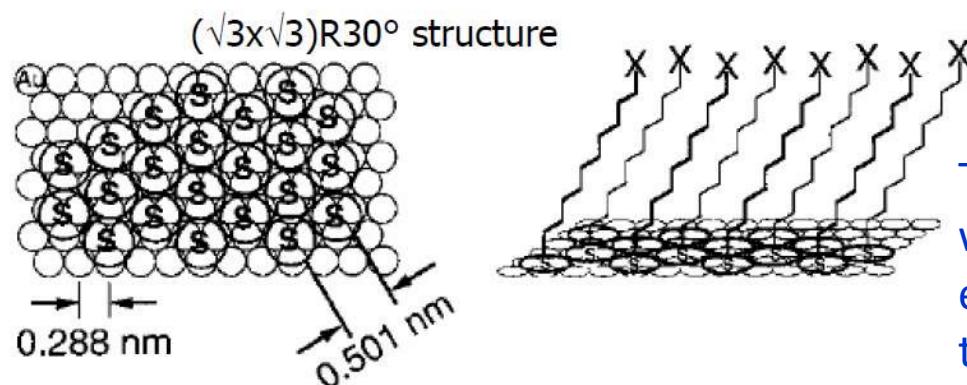
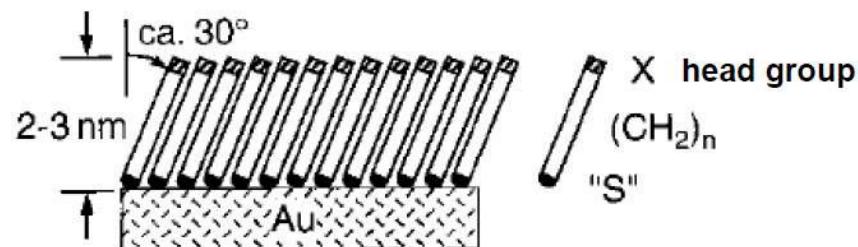


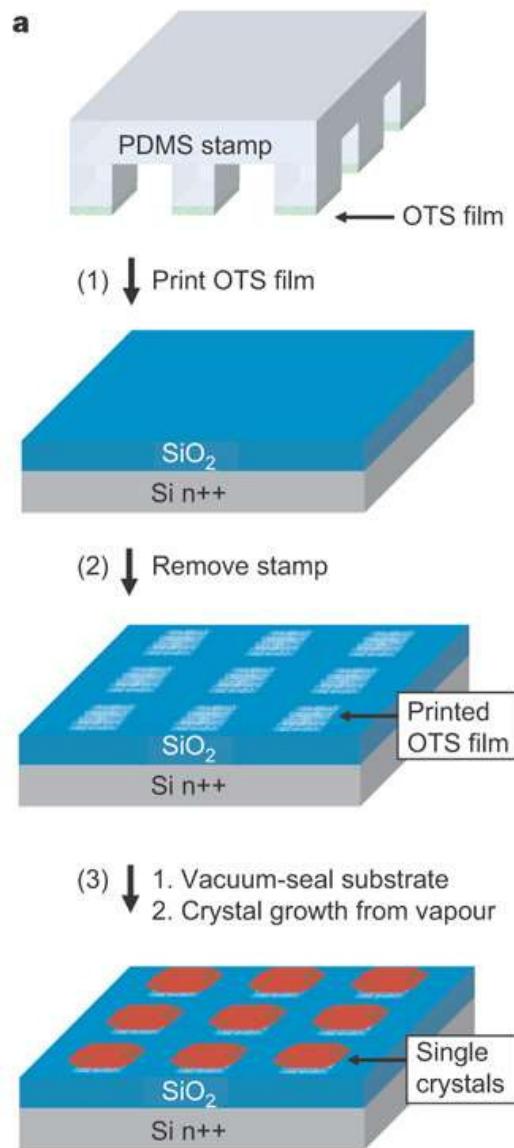
Image of Gold Surface Patterned with Hydrophobic and Hydrophilic SAMs



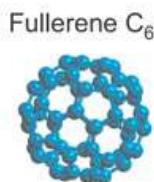
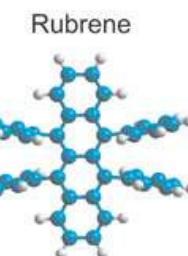
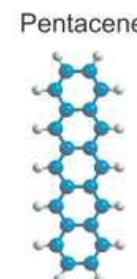
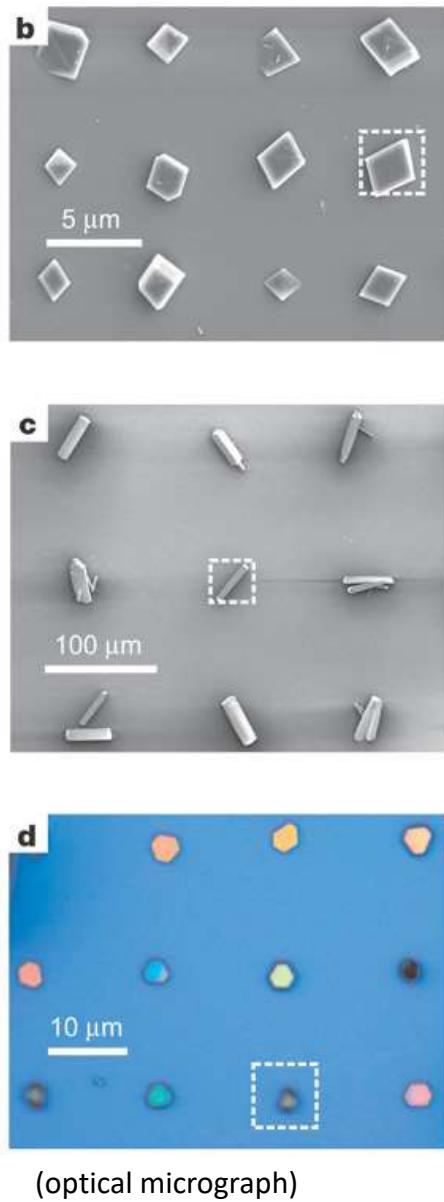
These monolayers allow control over wettability, adhesion, chemical reactivity, electrical conduction, and mass transport to underlying metal

-SH also binds to Ag, but Ag surface not as stable as Au.

Patterning of organic single crystals



OTS: octadecyltrichlorosilane

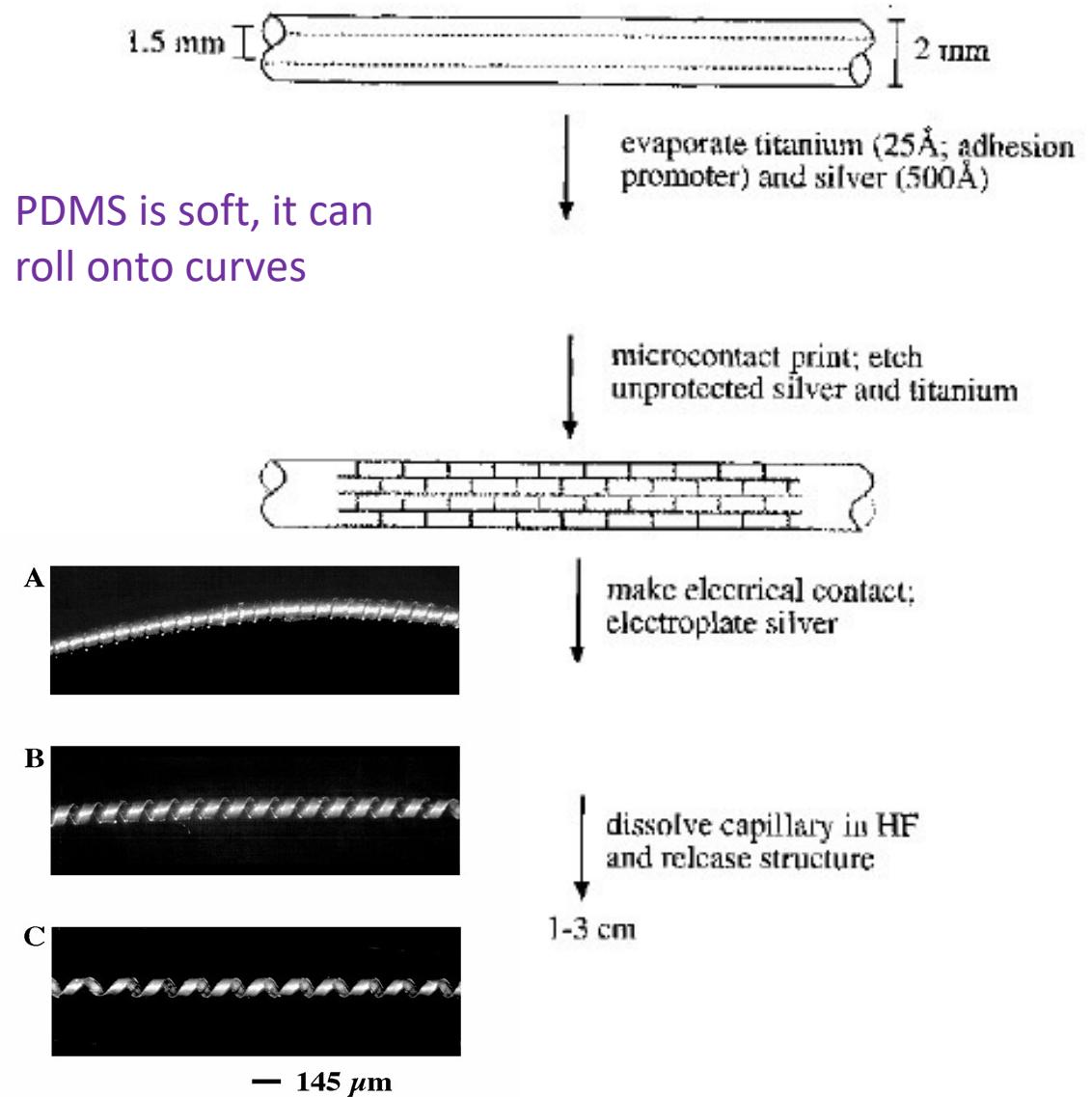
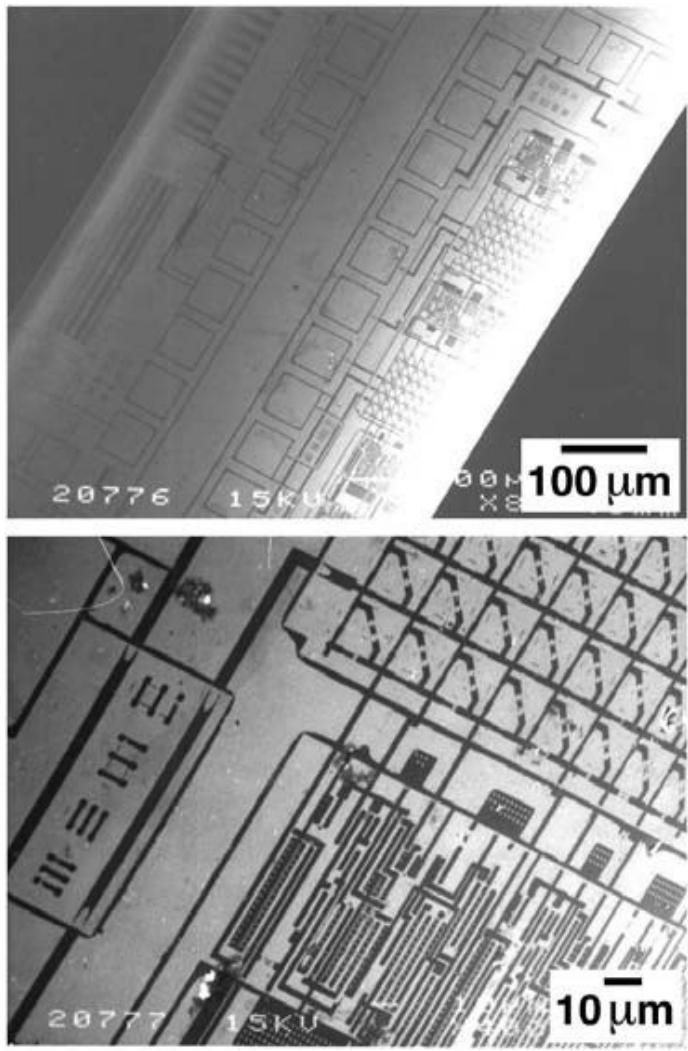


a. Procedure used to grow organic single crystals on substrates that have been patterned by microcontact printing. To grow the patterned single crystals, the patterned substrate is placed in a glass tube with the organic source material, vacuum-sealed (0.38 mmHg), and placed in a temperature gradient furnace tube.

b-d, Patterned single-crystal arrays of different organic semiconductor materials. The dotted square in each image indicates the size and location of one of the OTS-stamped domains, while the molecular structure of the organic material used is shown next to the image of its single-crystal array.

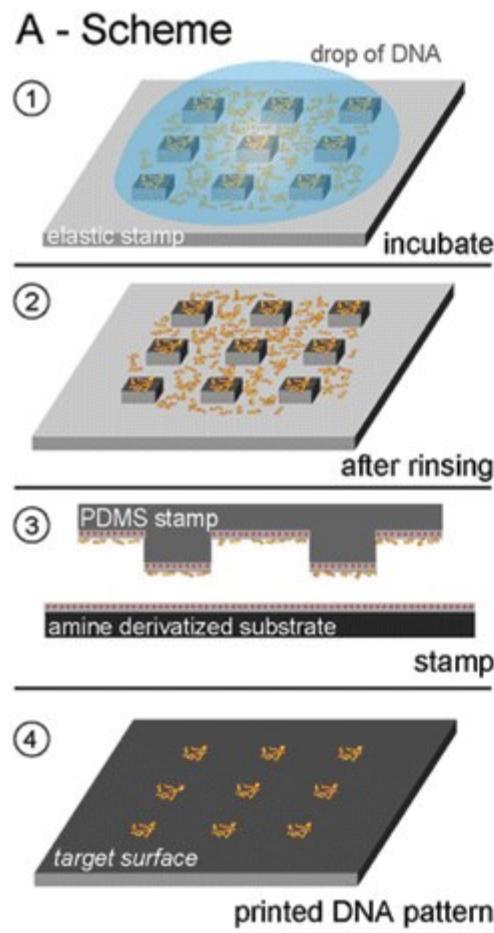
The above three materials are all hydrophobic and they binds/sticks to OTS

Micro-contact printing on curved substrates

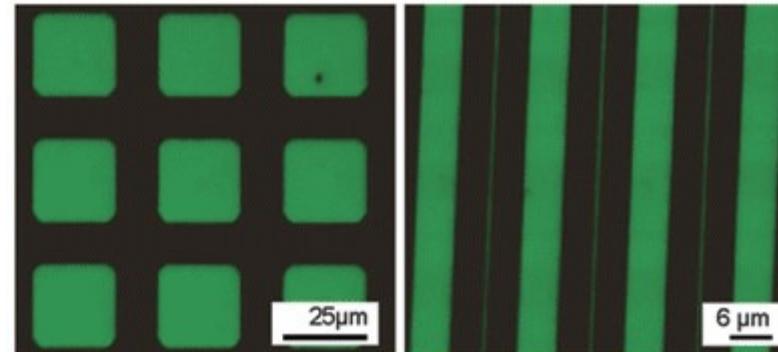


Whitesides, "Fabrication of submicrometer features on curved substrates by microcontact printing", Science, 269, 664 (1995); Rogers and Whitesides, "Microcontact Printing and Electroplating on Curved Substrates: Production of Free-Standing Three-Dimensional Metallic Microstructures", Adv. Mater. 9, 475 (1997).

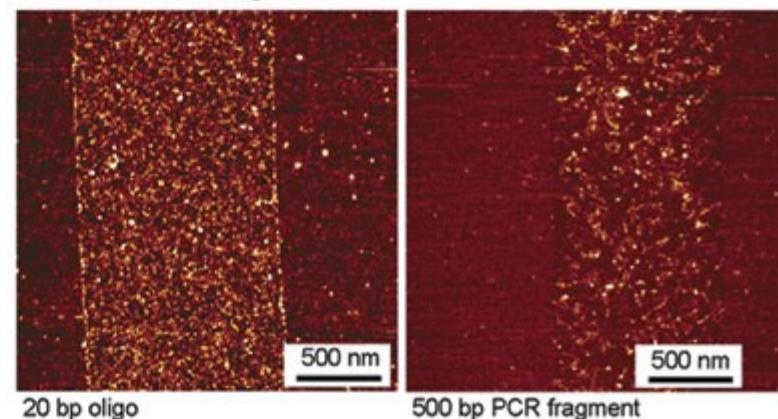
Micro-contact printing of DNA



B - Fluorescence image



C - AFM image



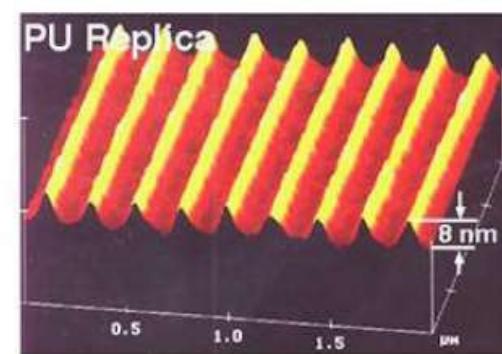
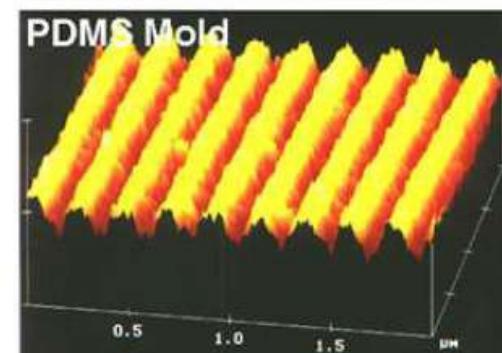
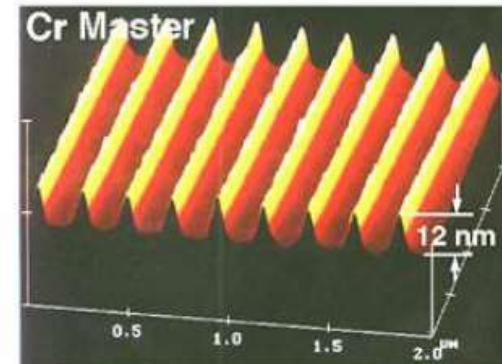
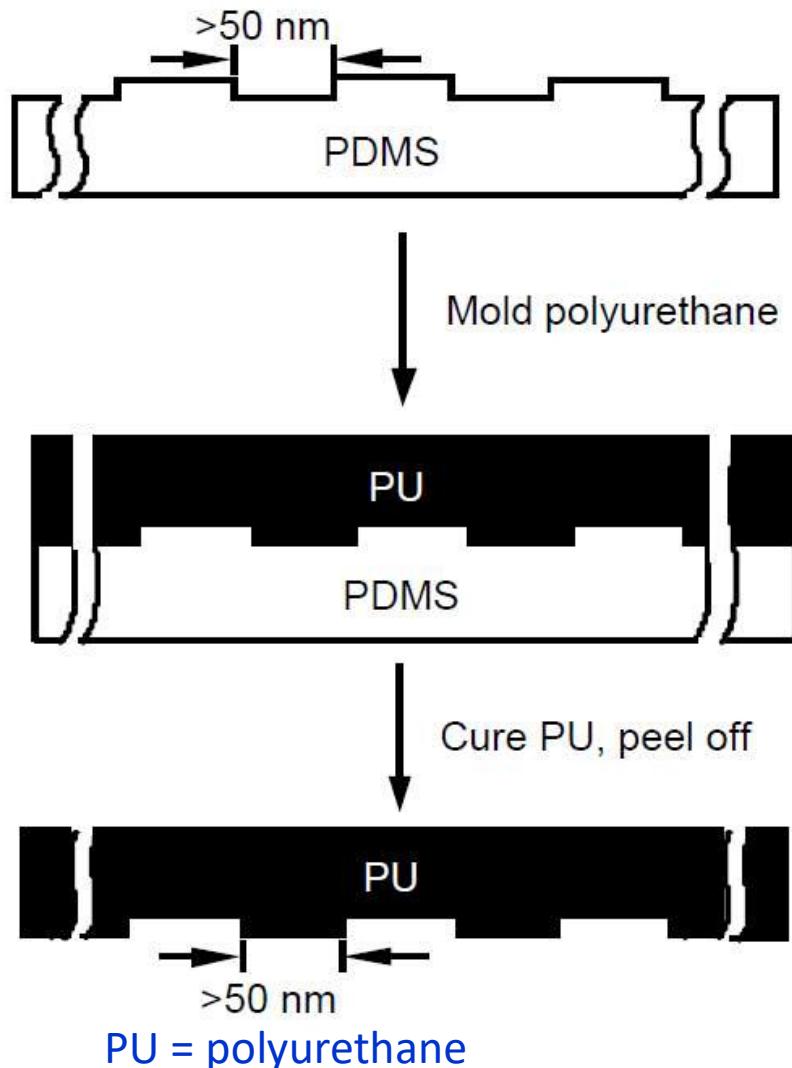
- A. Scheme of DNA printing. The surface of PDMS was modified such that it exposed positive charges on its surface. The stamp was incubated with target DNA molecules in a solution of low pH. The stamp was then rinsed, blown dry, and printed to deliver the DNA to the target surface.
- B. Fluorescence images of patterned FITC-labeled DNA on a glass surface after printing.
- C. AFM images revealing the printed DNA molecules deposited as patterns on mica substrates. AFM images (tapping mode in air) of stamped 1-μm lines of oligonucleotides (left, 20-bp oligos; right, 500-bp PCR fragments).

“Soft” lithography

1. Soft lithography and PDMS.
2. Micro-contact printing.
3. Replica molding.
4. Micro-molding in capillary.
5. Micro-transfer molding/printing.
6. Solvent assisted microcontact molding.

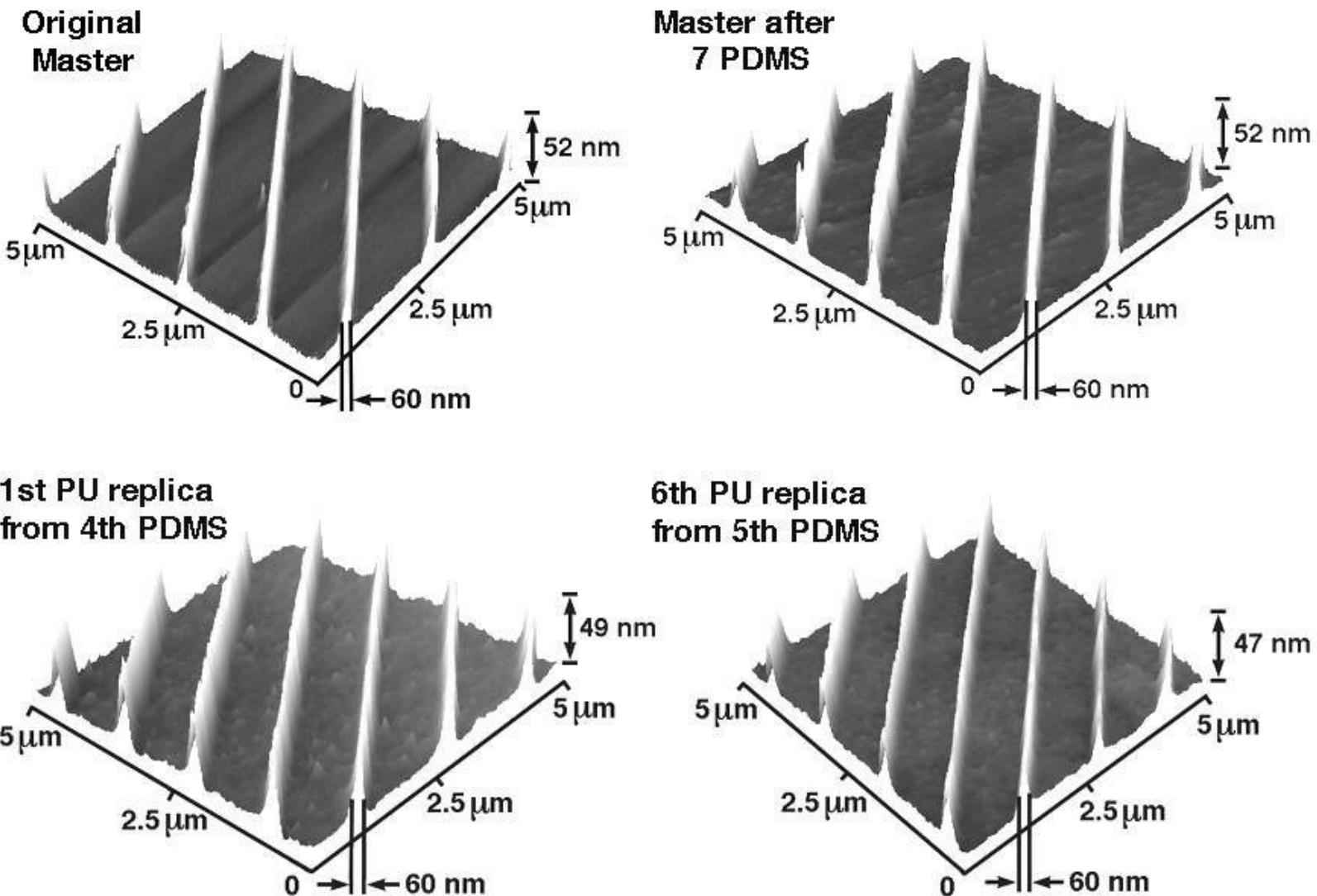
Replica molding (REM)

It is similar to UV-curing nanoimprint lithography
(but UV-NIL uses thin resist, for pattern transfer to substrate/sub-layer)



Replica molding (REM)

The patterning process has high fidelity, with little feature size loss.



Replica molding (REM)

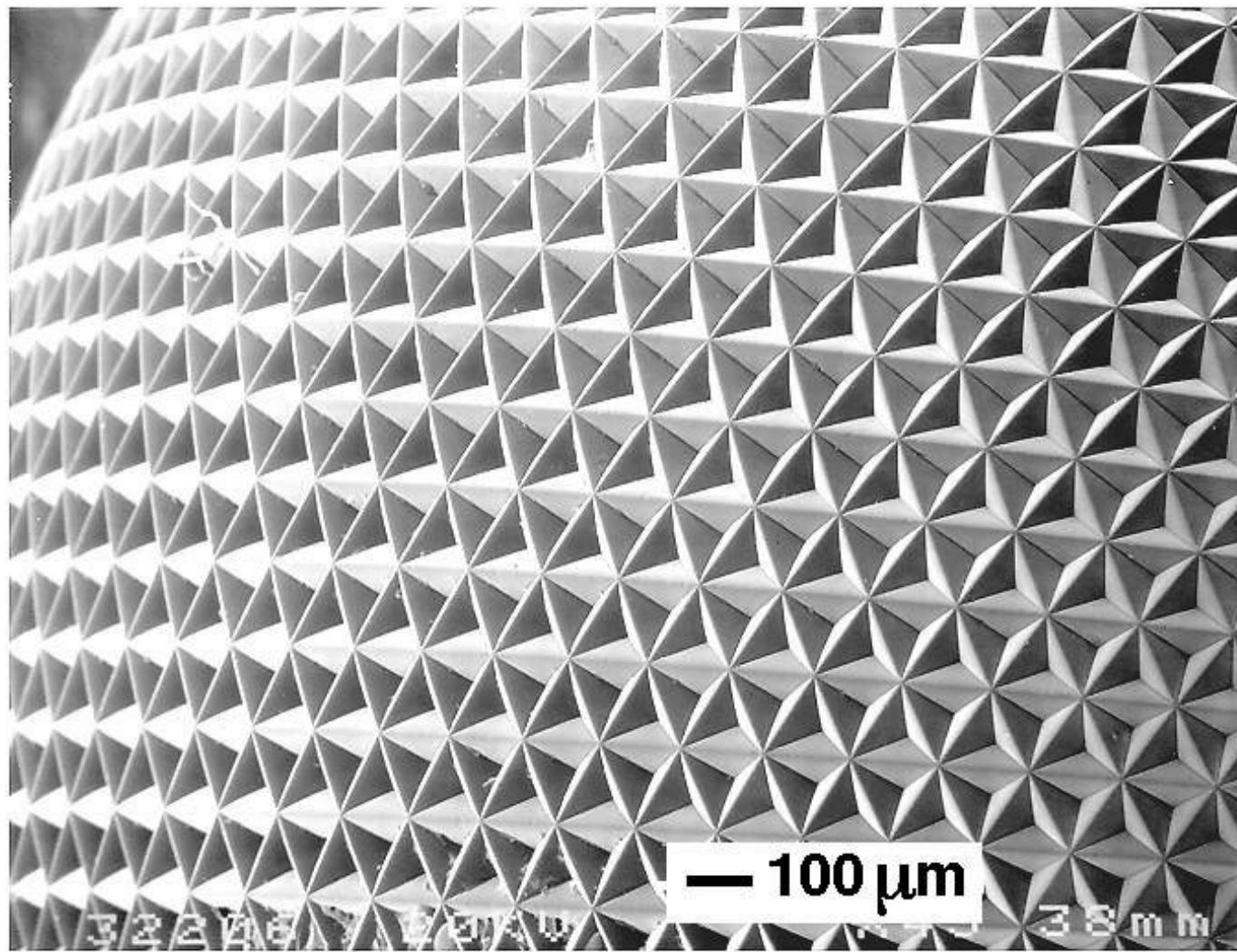
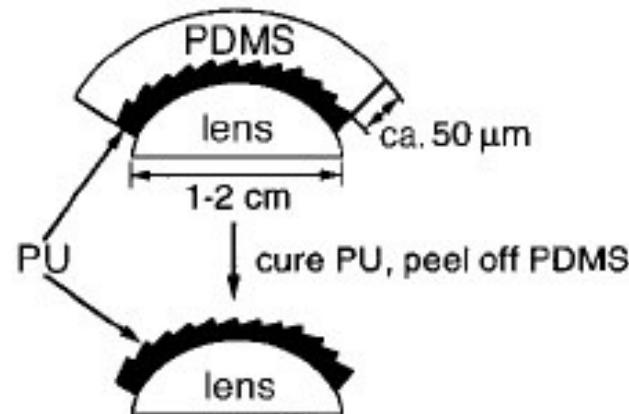
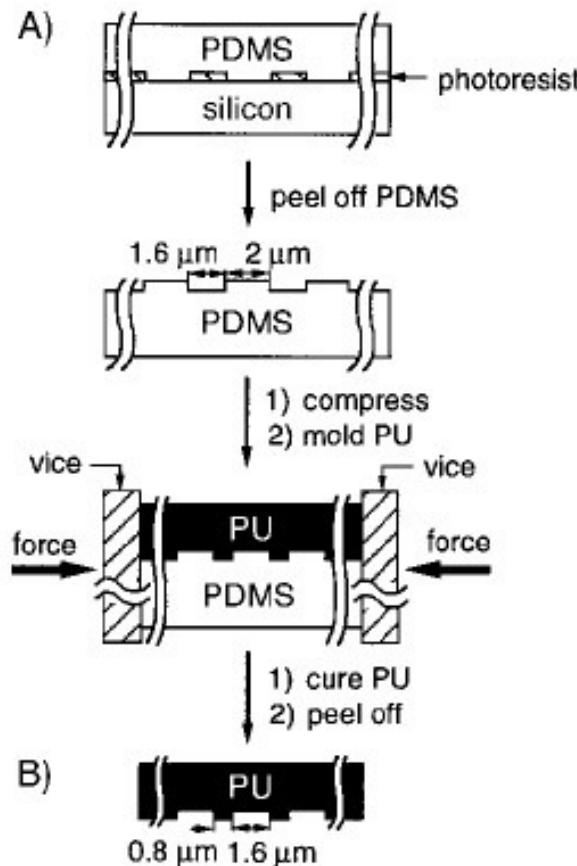
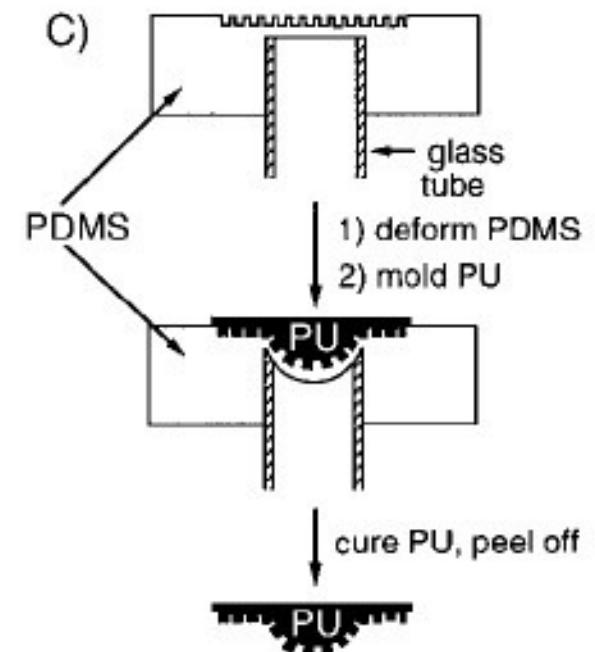


Figure 23. An SEM image of a dome-shaped object in polyurethane with patterned microstructures (corner cubes ca. 100 μm) on its surface that was formed by replica molding against a stretched PDMS mold.^[35]

Using mold elasticity



Molding on curved surface



Creating curved surface

Mechanical compression for feature size reduction

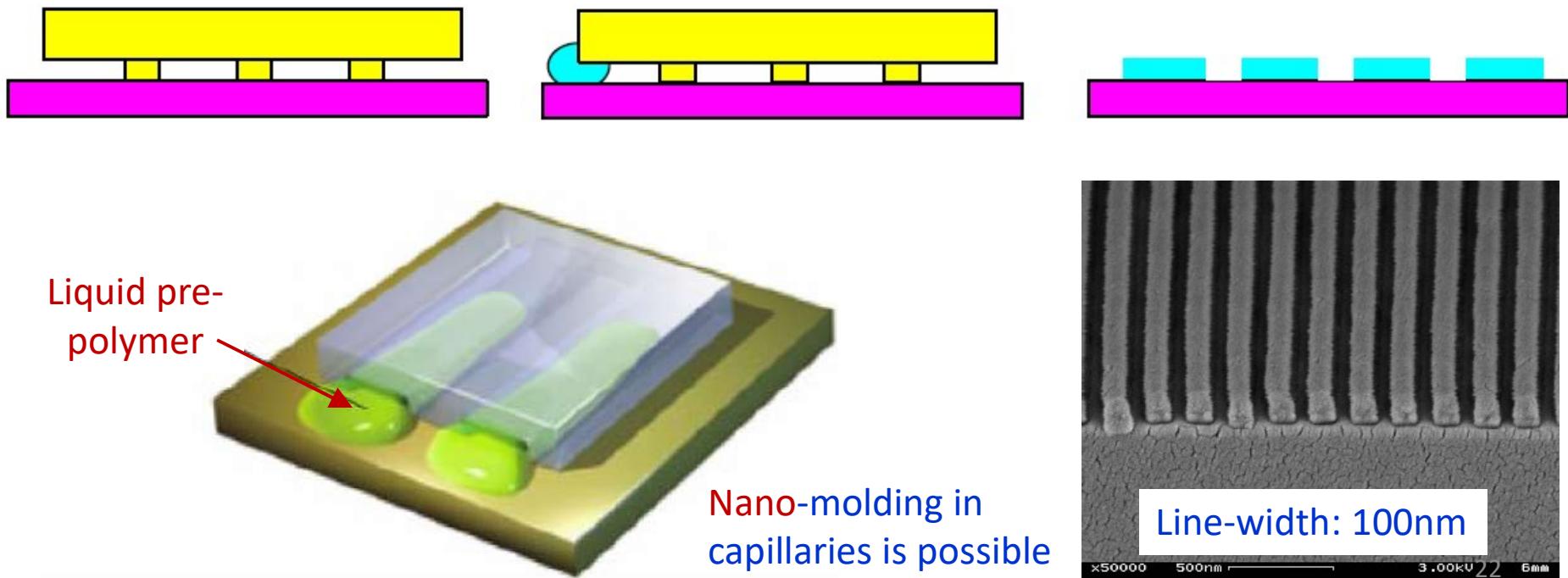
“Soft” lithography

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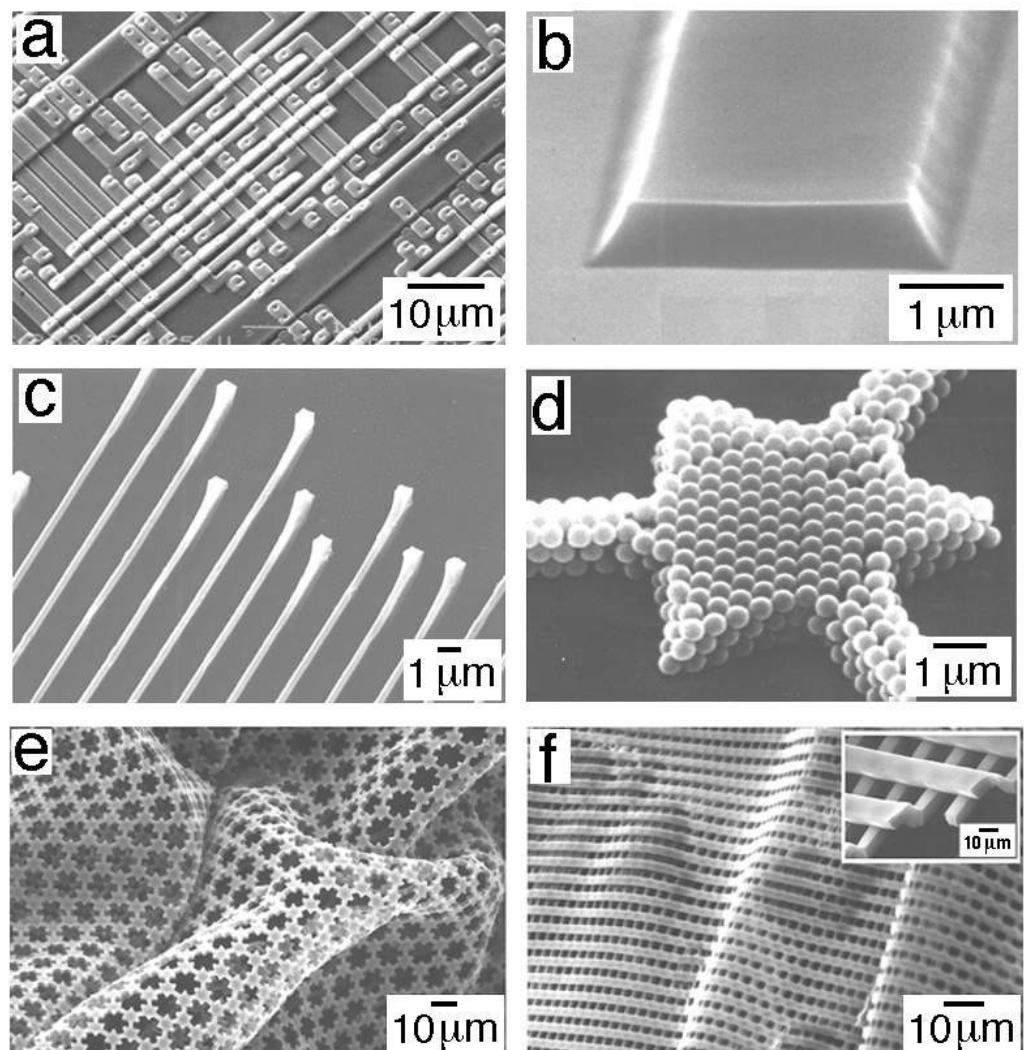
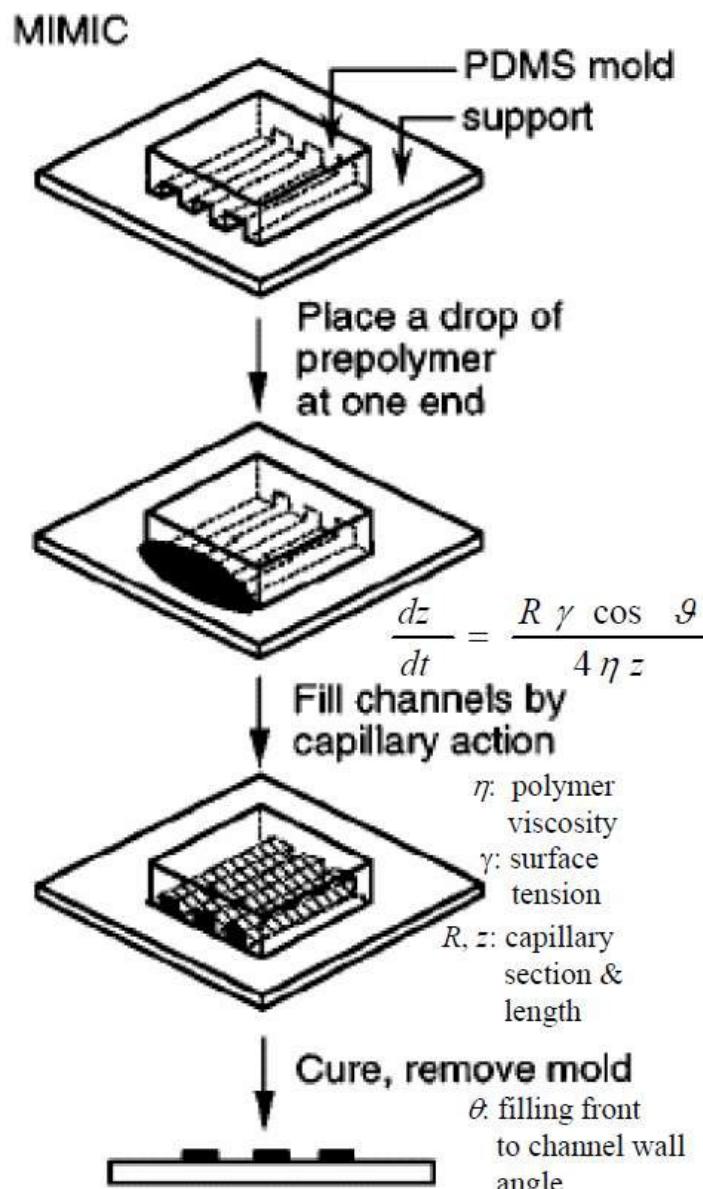
Micro-molding in capillary (MIMIC)

Uses capillary forces to fill the gaps between substrate and PDMS master.

1. The PDMS master is pressed tightly on a planar substrate.
2. Elastic PDMS seals off walls and creates capillary channels.
3. A drop of liquid prepolymer is placed at the ends of these channels and fills them automatically due to capillary force.
4. PDMS can absorb the solvent, which creates a partial vacuum inside the PDMS cavity and helps to draw in liquid polymer.
5. Cure and peel off the PDMS master.



Micro-molding in capillary (MIMIC)

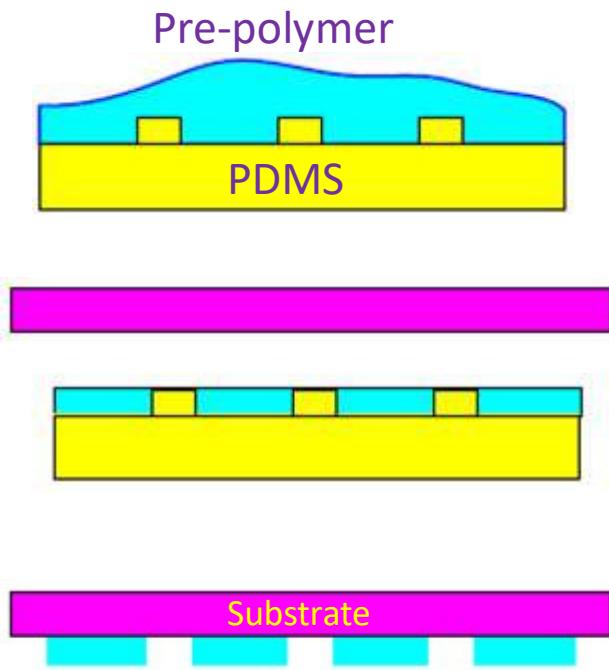


Kim & Whitesides et al, Nature, 1995, 376, 581
Xia, Y.; Whitesides, G. M. Ann. Rev. Mater. Sci 1998, 28, 153.

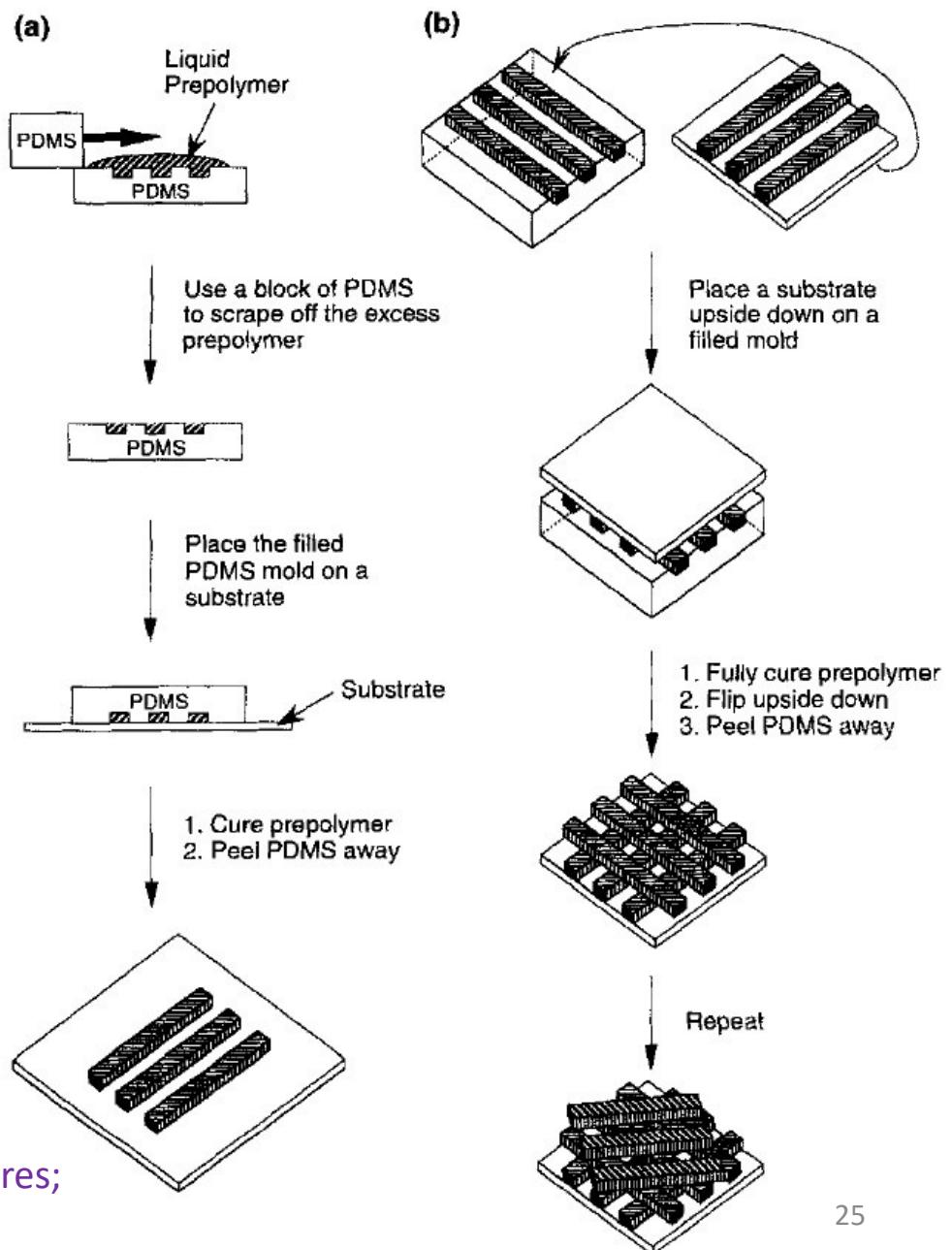
“Soft” lithography

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Micro - transfer molding (μ TM)



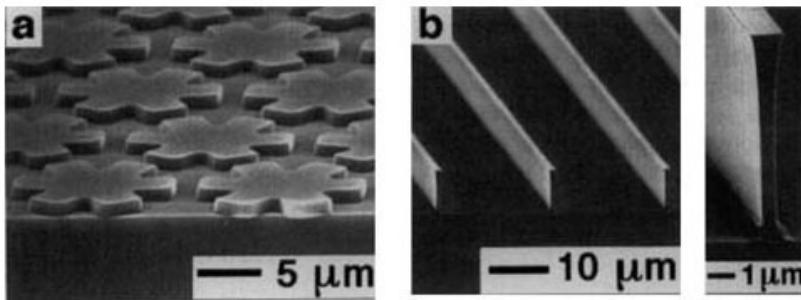
- Apply the liquid prepolymer
- Planarize the prepolymer
- Place the master on a planar substrate
- UV exposure or heating solidifies the prepolymer that sticks to the substrate



μ TM fabrication of a). one-layer microstructures;
b). three-layer polymer microstructures.

Micro - transfer molding (μ TM)

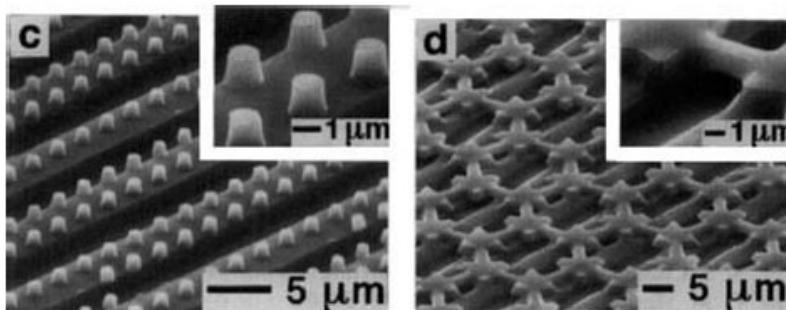
1-layer microstructures



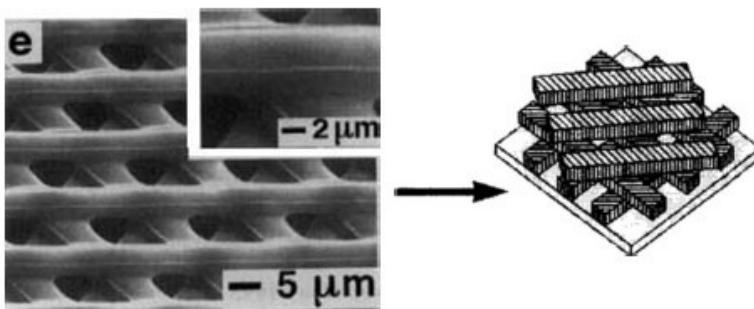
Microstructures fabricated using μ TM.

- An SEM image of a fractured sample showing a pattern of isolated stars of UV-cured polyurethane (NOA 73) on Ag.
- An array of parallel lines of spin-on glass on Si with an aspect ratio (height/width) of ~8.
- A two-layer structure: isolated micro-cylinders (1.5 μ m in diameter) on 5 μ m-wide lines, supported on a glass cover slide.
- A two-layer structure: a continuous web over a layer of 5 μ m-wide lines, supported on a glass cover slide.
- A three-layer structure on a glass cover slide. The layers of 4 μ m-wide lines are oriented at $\sim 60^\circ$ from each other.

2-layer microstructures

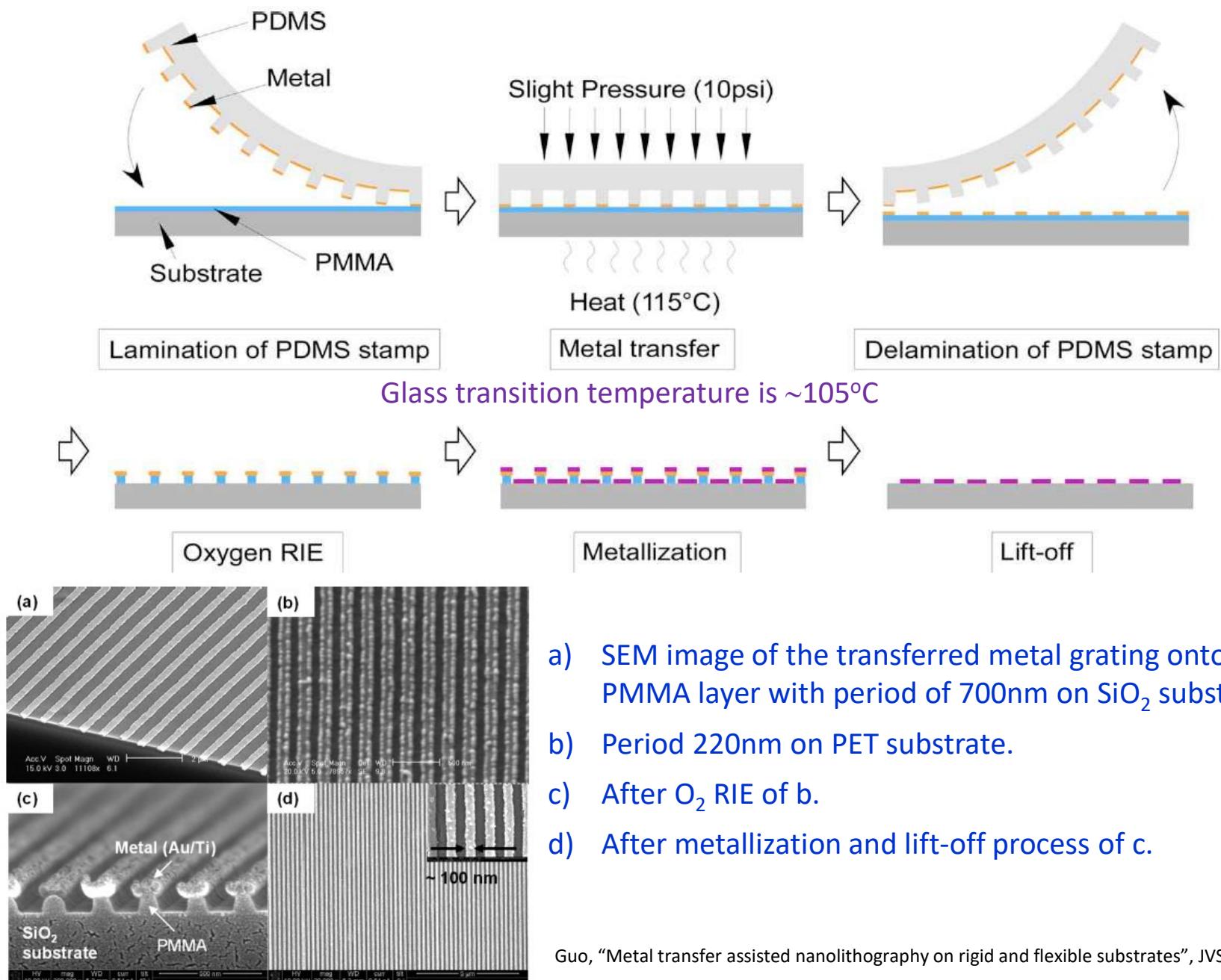


3-layer microstructures



Structures in c-e were made of heat-cured epoxy (F109CLR).

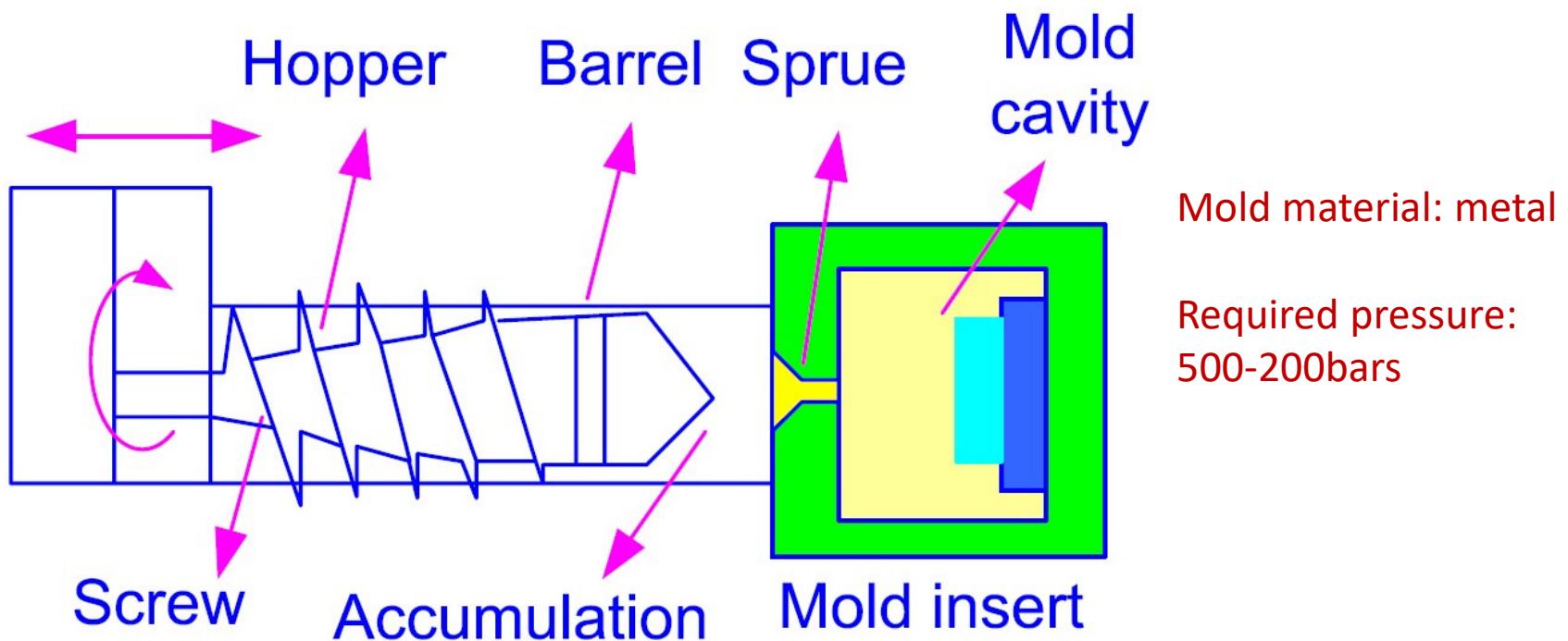
Metal transfer assisted nanolithography



Guo, "Metal transfer assisted nanolithography on rigid and flexible substrates", JVST B, 2008

Injection molding

Very old technology, capable of micro-resolution, much higher throughput than hot embossing, good for microfluidic channel fabrication using thermoplastic polymers. (Thermoplastic polymer is better than PDMS for its “clean, non-sticky” channel wall)



- The mold is heated to the softening temperature of the polymer to prevent the injected polymer material from hardening too early.
- The reciprocating screw shears, melts, and pumps the polymer into the accumulation zones.
- After cooling, the melt solidifies, and can be taken out from the mold.

PDMS elastomer for mold making

Weigh

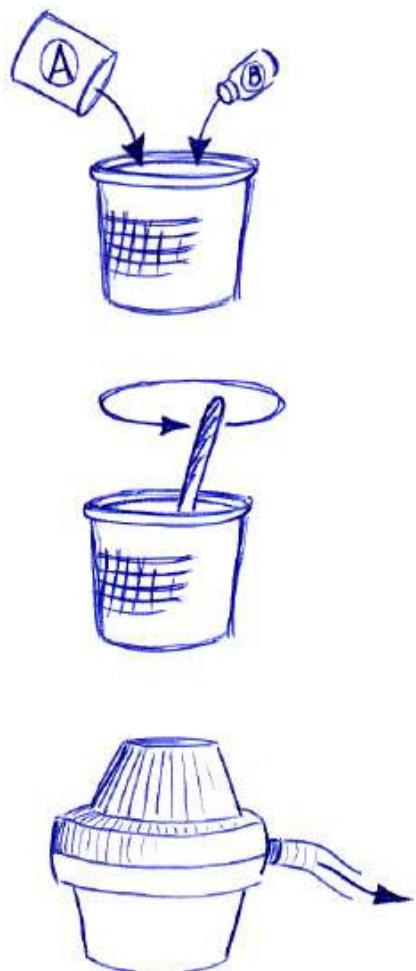
Sylgard 184 is a two-component heat-curing system, i.e. it consists of a base part and a curing agent part. Take a common plastic cup and fill it with *one* part curing agent and *ten* parts of base (by weight). Start with the curing agent, since it is harder to pour the right amount of it! 7-10 g material will be sufficient for covering one template, e.g. 0.7 g curing agent and 7 g base. A small error in the amounts will not effect the final result though.

Mix

Use a plastic spoon to mix the base and the curing agent. Mix it rather carefully for at least a few minutes, depending on the amount of material. When you mix it you will incorporate a lot of air in the solution. Don't worry – it will be removed in the next step. Use a plastic spoon to mix it.

Degas

After the mixing the silicone mixture will be full of air bubbles and needs degassing. This is done in an exsicator using vacuum. During the degassing the silicone expand and start to look like foam, this means that you can only have a small (<5 g) amount in each plastic cup else it will overflow. Also remove the spoon. When the silicone is completely clear and transparent it is finished.



PDMS elastomer for mold making

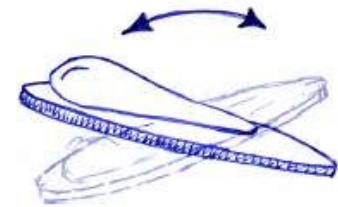
Dispense

Dispensing the silicone on to the template can be a bit tricky, as you do not want to trap air in the process. Sylgard 184 has relatively low viscosity, so the flow is no problem. It is also possible to make the viscosity even lower by mixing in silicone oil or hexane, but this is seldom necessary. Dispensing the material at the center of the template from a low altitude minimizes the risk of trapped air. Keep the template horizontal during dispense.



Spread

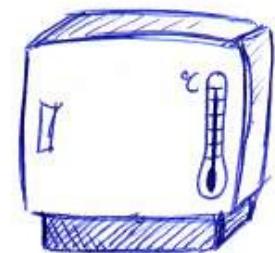
Pick up the template with a pair of flat tweezers and start tilting it at a low angle. The material will now start to spread. By tilting it in different directions it is possible to cover the whole template by silicone. Try to make the shape as circular as possible. When you think it is ok, leave it for a minute in order to get a flatter top surface. Stamps thickness can range from ~0.1 to 5 mm or more.



PDMS elastomer for mold making

Curing

Sylgard 184 is heat curing. It is curable from less than room temperature to over 150°C. Sylgard 184 also has temperature dependant shrinkage as seen below. Curing in 140°C (~15 min) will make the stamp shrink almost exactly 3 %. Take the template and place it in a pre-heated oven. The time is not that critical, it is almost impossible to cure it a too long time.



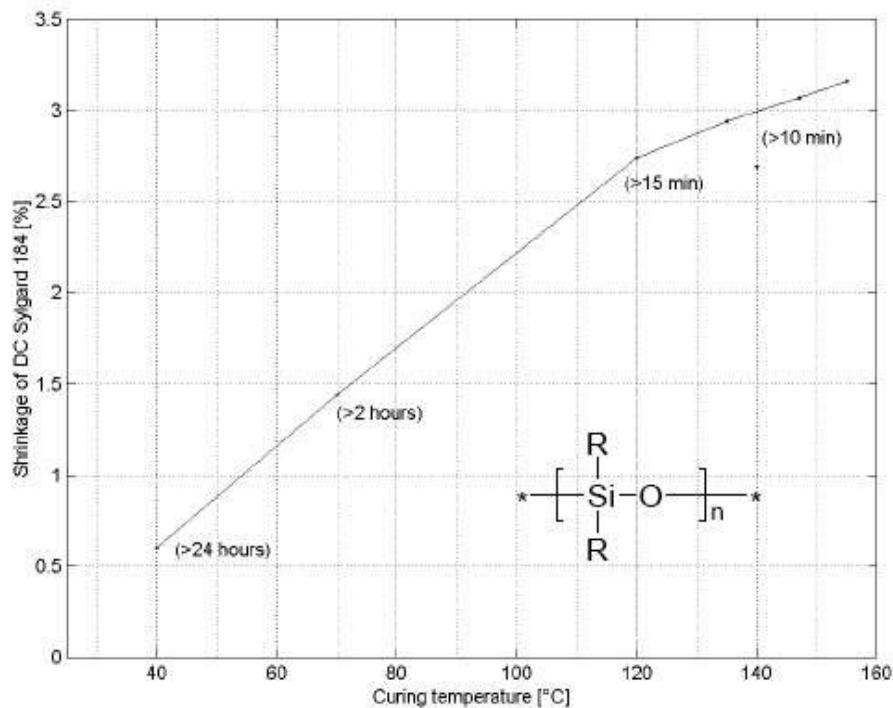
Sylgard 184

As supplied

Mix ratio A:B	10:1
Viscosity (mixed)	3900 centipoise
Specific gravity	1.05
Pot life (25°C)	2 h

As cured

Appearance	Transparent
Durometer hardness	40 Shore A
Tensile strength	6.2 MPa
Elongation	100%
Surface state	Hydrophobic
Water adsorption	0.1%, (7 d immersion)
Refractive index	1.430
Dielectric constant	2.65-2.7



PDMS elastomer for mold making

Peal off

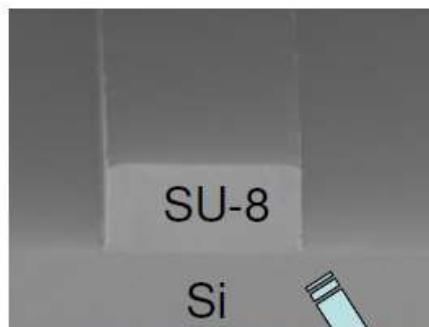
The final step is to peal off the stamp from the template. Use a sharp and curved pair of tweezers to do this. Start by releasing all borders and then continue at a low speed in a direction parallel to most structures and peal off the remaining parts. Store the stamp in a flat plastic container with the pattern facing upwards, i.e. away from the container. Finished!



Making PDMS hydrophilic / Bonding PDMS

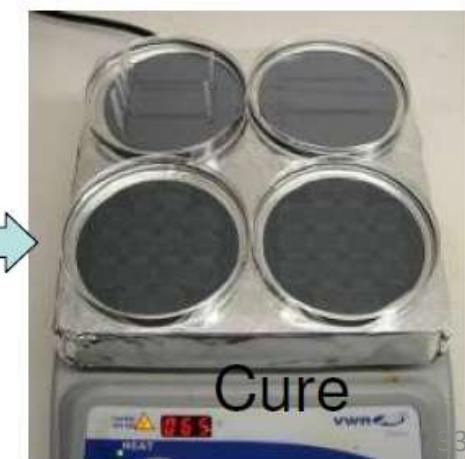
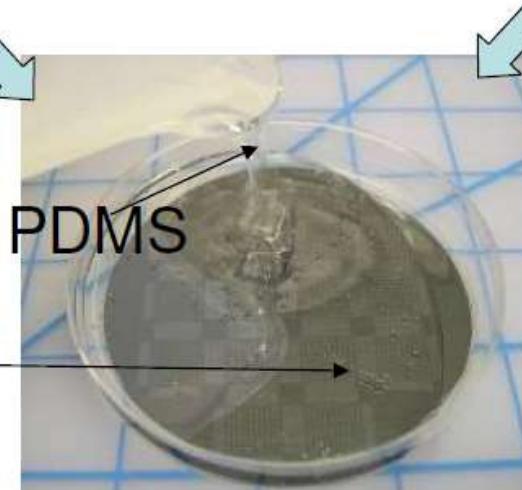
It is simple to make PDMS hydrophilic, simply run it in the plasma preparation chamber for ~15 s. The plasma preparation will incorporate oxygen atoms in the PDMS surface, leaving it hydrophilic. This can also be used to bond PDMS to for instance glass, Si or even another PDMS stamp. What you should do is to plasma prepare *one* of the substrates (*not both!*) and place them in contact for a few days. The bond is very strong and if you try to separate them you most certainly will break the stamp. A tip if you like to remove them again after they have bonded is to place it in water for a while. This will usually break the bond. PDMS can also be made hydrophilic by a mixture of H_2SO_4 and $KMnO_4$. (Note: It works poorly!)

PDMS elastomer for mold making



Silanization of
master mold
(coat mold release agent)

master mold



Scanning probe microscopy (SPM) and lithography

1. Scanning tunneling microscopy.
2. Piezoelectric positioning.
3. Atomic force microscopy (AFM) overview.
4. AFM tip and its fabrication.
5. Tapping mode AFM.
6. Other forms of AFM (LFM, EFM, MFM, SCM...)

“Scanning probe microscopy and spectroscopy” by Roland Wiesendanger is a good comprehensive reference book. It can be found at (read only, no download):

http://books.google.ca/books?id=EXae0pjS2vwC&pg=PA561&lpg=PA561&dq=liquid-metal-covered+tungsten+needle&source=bl&ots=Yy9A2saE3M&sig=KIDbgh_HQLg4LQPA4XIVh7TD3kQ&hl=en&ei=4cdkSsjqMYLWtgOX_ehm&sa=X&oi=book_result&ct=result&resnum=1

NE 353: Nanoprobing and lithography

Instructor: Bo Cui, ECE, University of Waterloo; <http://ece.uwaterloo.ca/~bcui/>

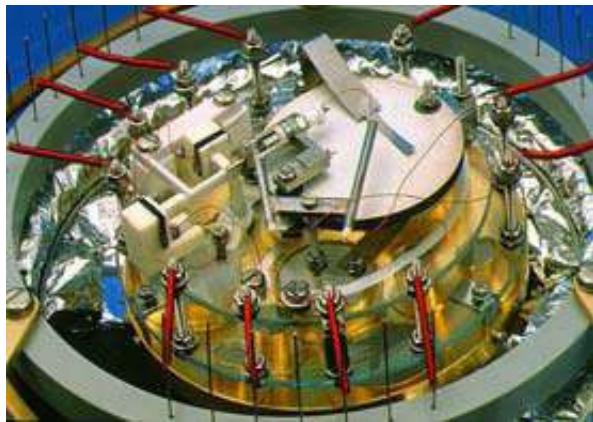
Textbook: Nanofabrication: principles, capabilities and limits, by Zheng Cui

Scanning probe microscopy (SPM) overview

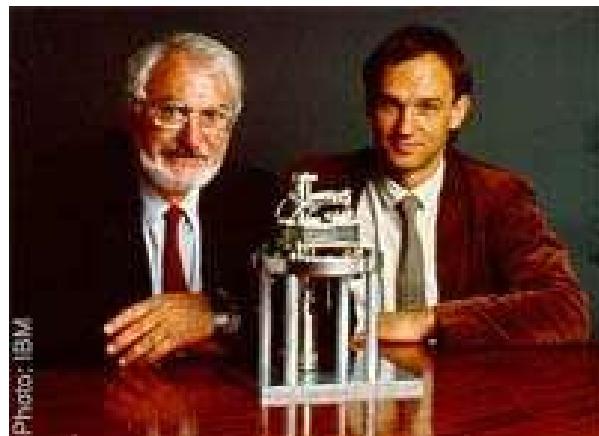
For imaging purpose, compared to SEM:

- Extremely accurate in the z-dimension (<<1Å); whereas for SEM to see the vertical cross-section profile one has to cut the sample and tilt it, and the resolution is much worse than 1nm.
- For lateral (xy-) dimension, SPM is accurate only when the surface is relatively flat, then the resolution is better than SEM (atomic resolution for SPM vs. few nm resolution for SEM).
- AFM generally don't need vacuum and can image any surface (insulator or not) and even inside liquid (very important for bio-imaging).
- AFM is much cheaper than high resolution field emission SEM and is thus more available (>10 AFMs on campus).

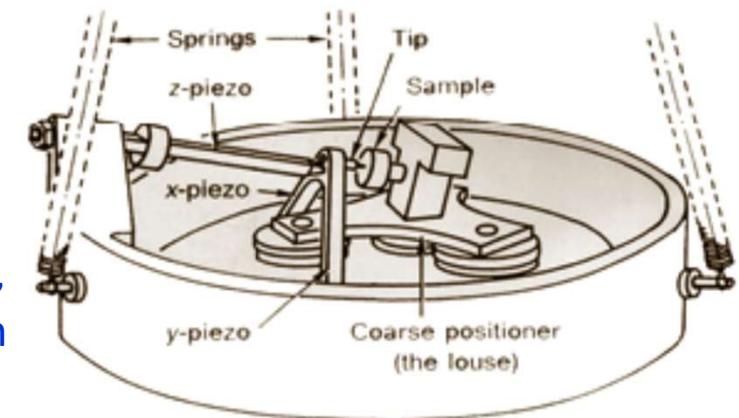
The first STM Instrumentation



Exact copy of first Scanning Tunneling Microscope of Binnig and Rohrer

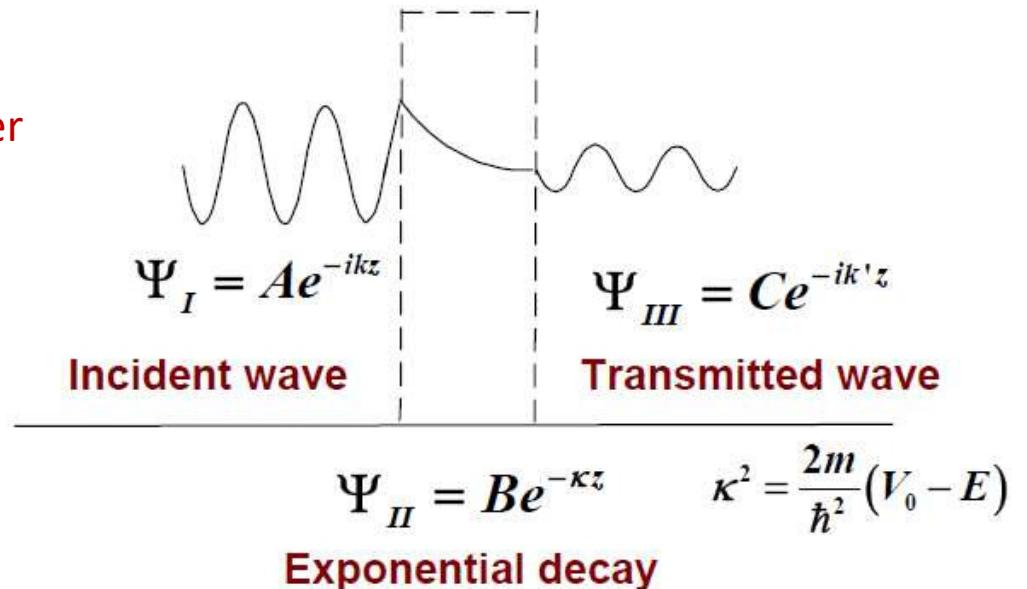


STM inventors Rohrer and Binnig, IBM, Zurich, Nobel Prize in Physics in 1986.



Quantum mechanical tunneling

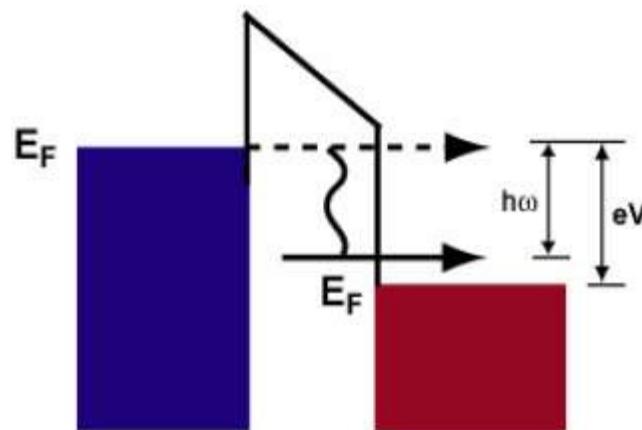
Tunneling through a rectangular barrier



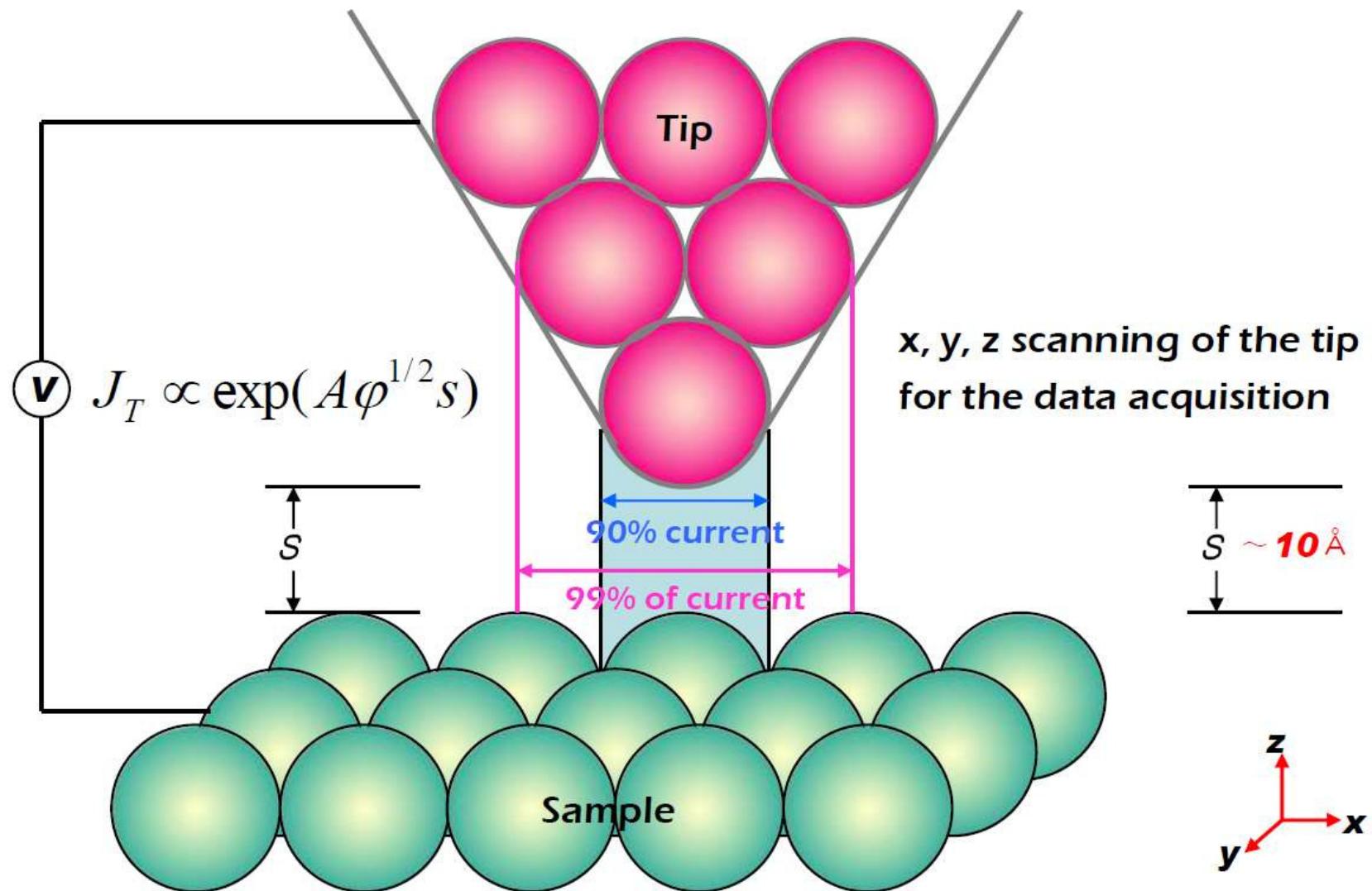
Elastic tunneling vs. inelastic tunneling

Elastic: energy of tunneling electrons conserved.

Inelastic: electron loses a quantum of energy within the tunneling barrier.



Why atomic resolution?



Scanning probe microscopy (SPM) and lithography

1. Scanning tunneling microscopy.
2. Piezoelectric positioning.
3. Atomic force microscopy (AFM) overview.
4. AFM tip and its fabrication.
5. Tapping mode AFM.
6. Other forms of AFM (LFM, EFM, MFM, SCM...)

Probe-sample interaction and detection system

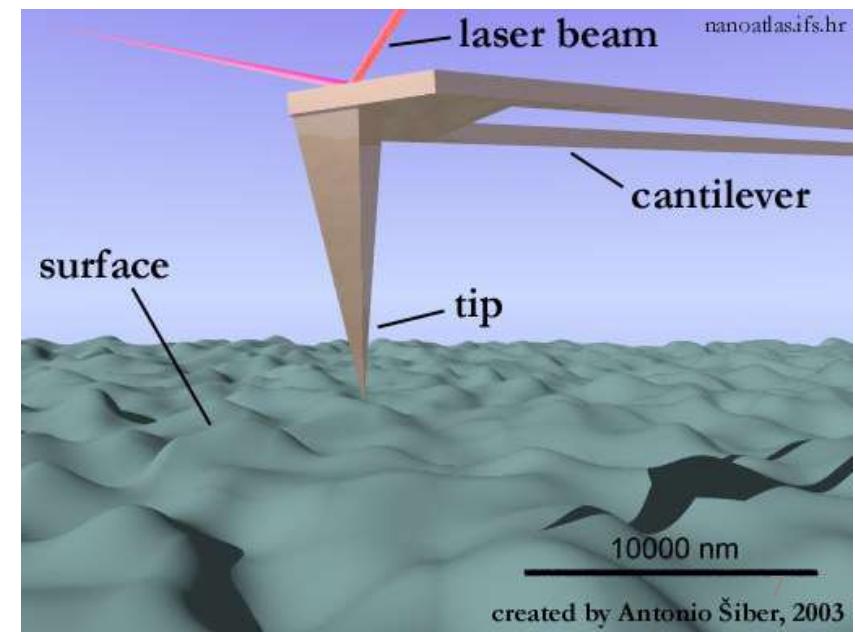
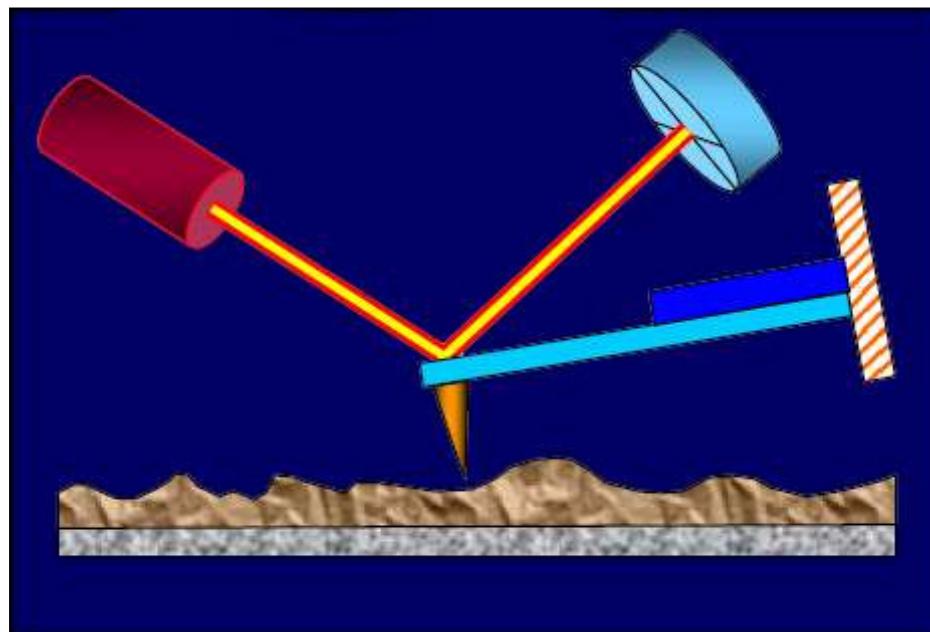
Forces and their range of influence

Long range

- Electrostatic force in air (100 nm)
- Magneto-electrostatic forces (100 nm)
- Double layer electrostatic (fluid) (100 nm)

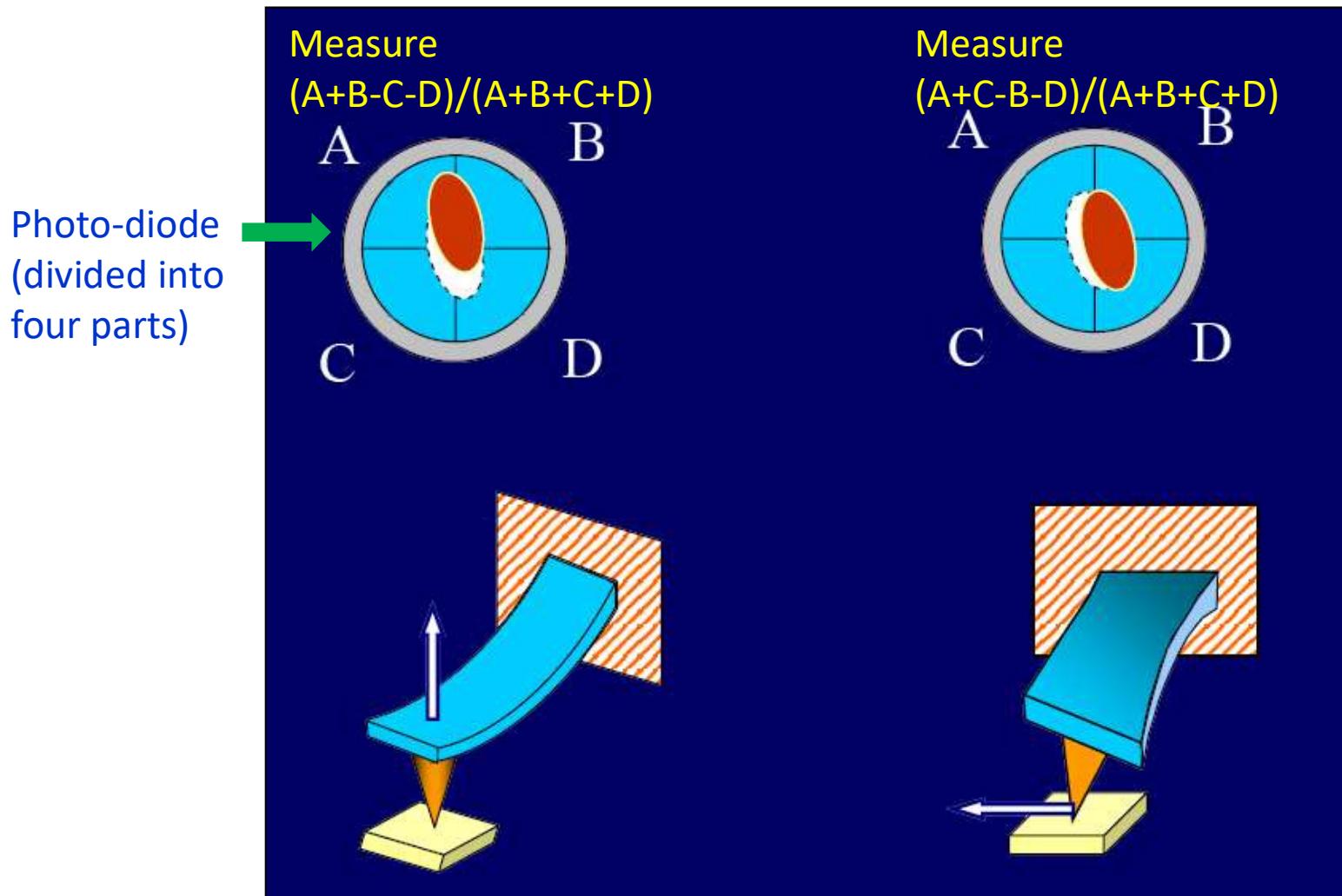
Short range

- Van der Waals (10 nm)
- Surface-induced solvent ordering (5 nm)
- Hydrogen-bonding force (0.2 nm)
- Contact (0.1 nm)



Probe-sample interaction detection system

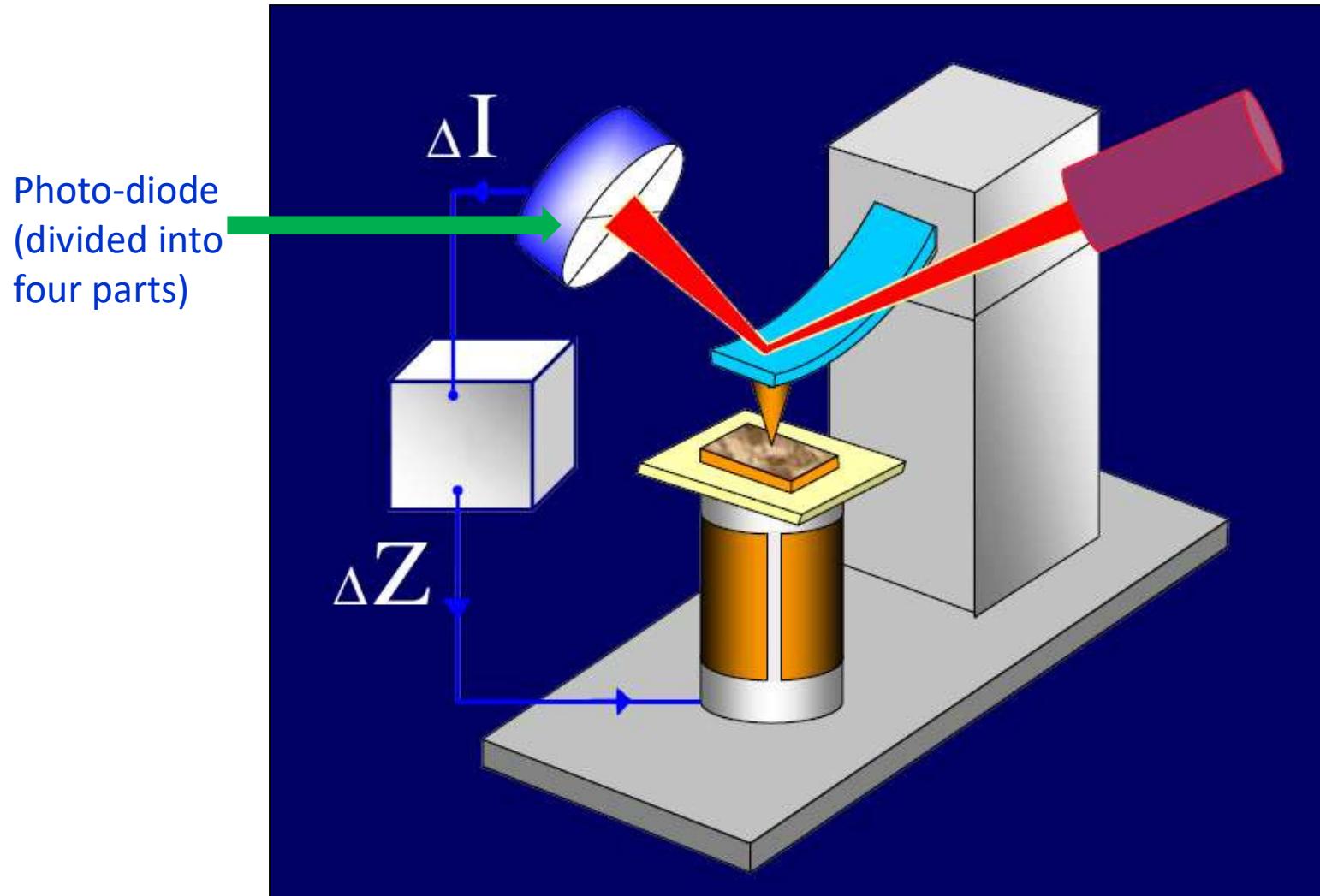
Detect deflection in z-direction
(to maintain constant force for
normal AFM operation)



Detect deflection in the x-y direction,
for lateral force/friction microscopy.

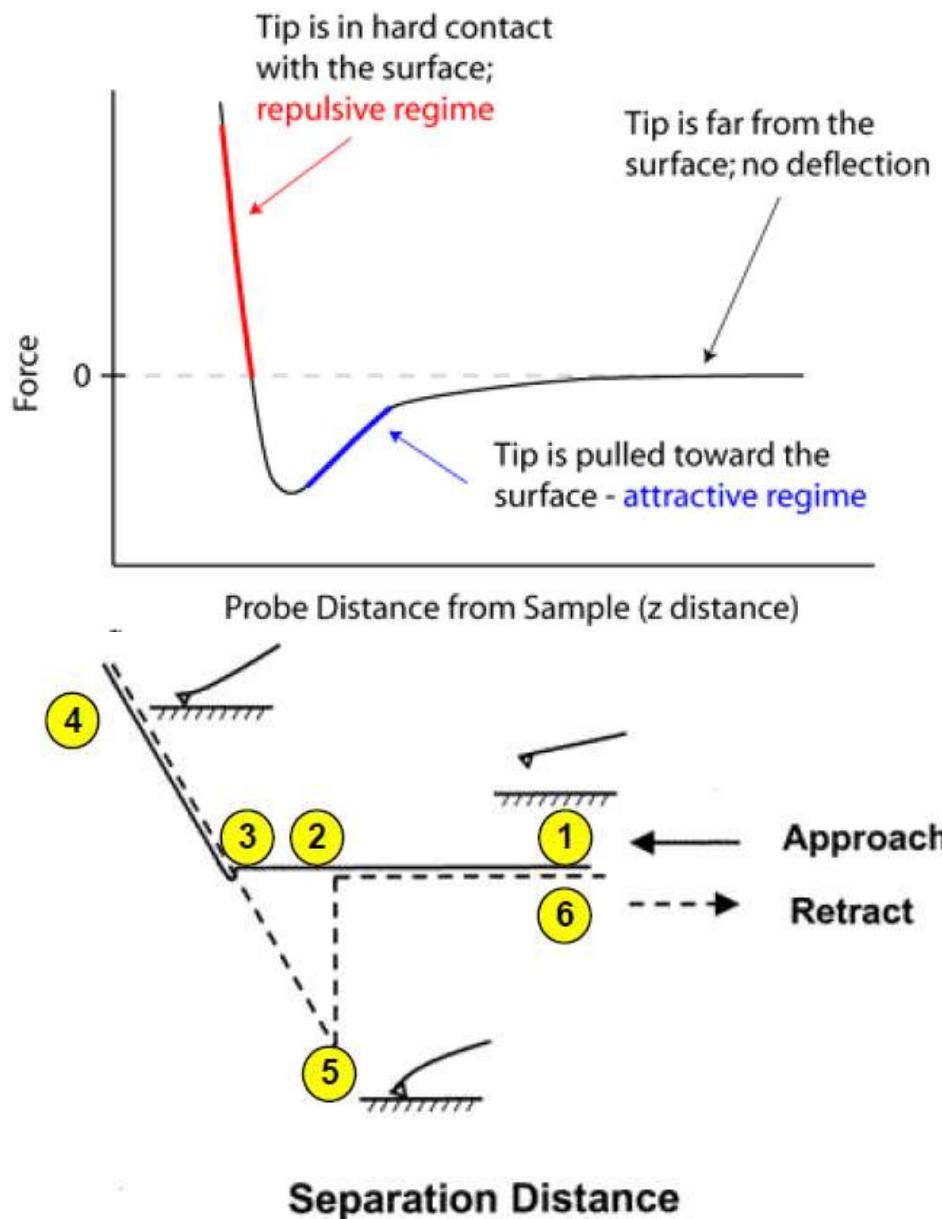
Feedback loop for constant force AFM

ΔZ is equivalent to the topography of the sample



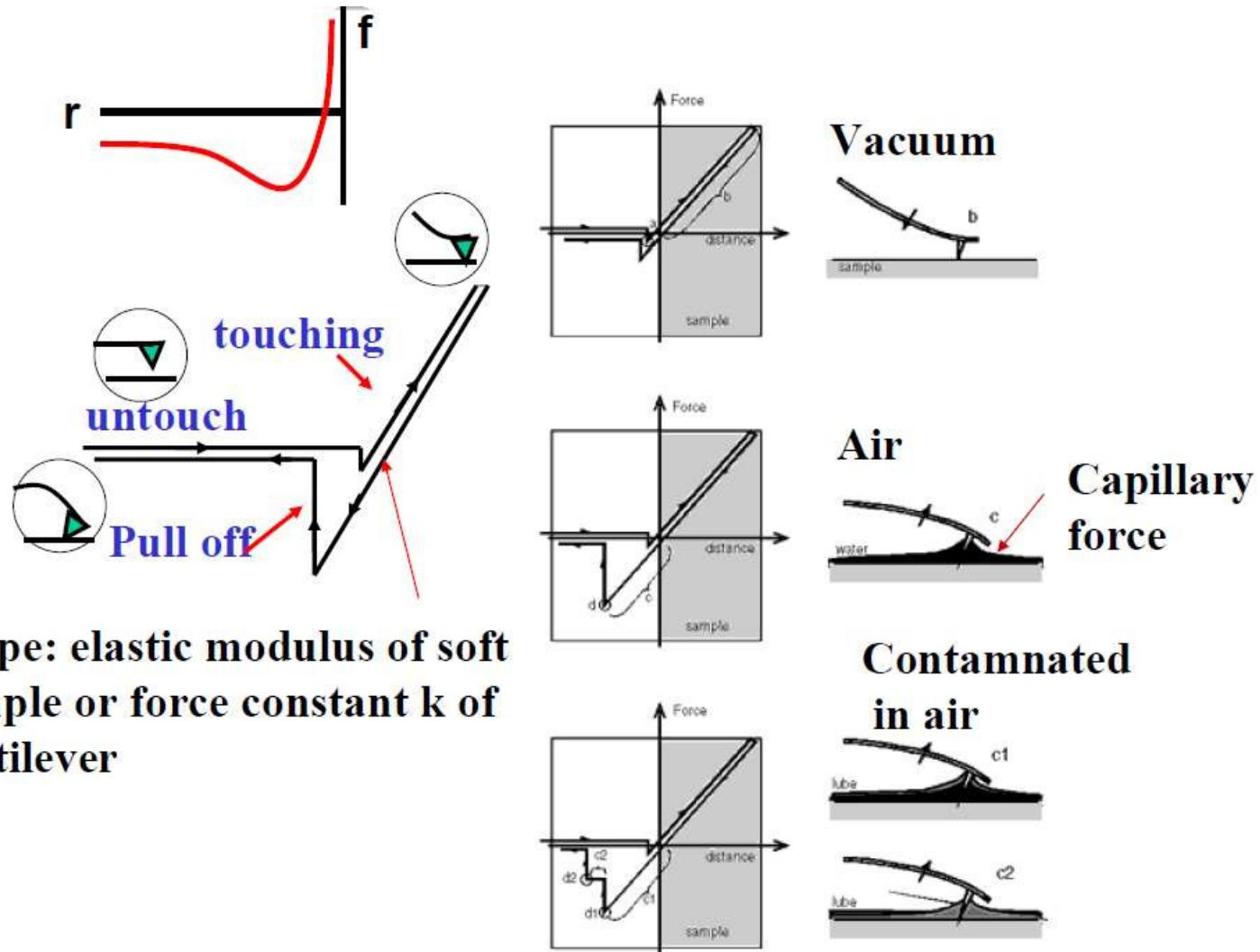
Tiny deflection of cantilever leads to large shift of the beam spot position on the photo-diode, so extremely sensitive for z-dimension detection (sensitivity $\Delta Z \ll 1\text{\AA}$)

AFM tip-sample interaction



- (1) Large tip-sample separations – no detectable interaction force
- (2) Separation distance decreases
- (3) Separation where the gradient of interaction energy exceeds the restoring force of the cantilever – “jump to contact” point
- (4) Tip pushes farther into surface, a positive linear cantilever deflection is observed; tip retracts from surface, a similar cantilever deflection line is traced and the tip and sample remain in contact
- (5) Separation where restoring force exerted by the bending of the cantilever overcomes the adhesive force of the tip-sample – “force of interaction”
- (6) Non-interacting, equilibrium position

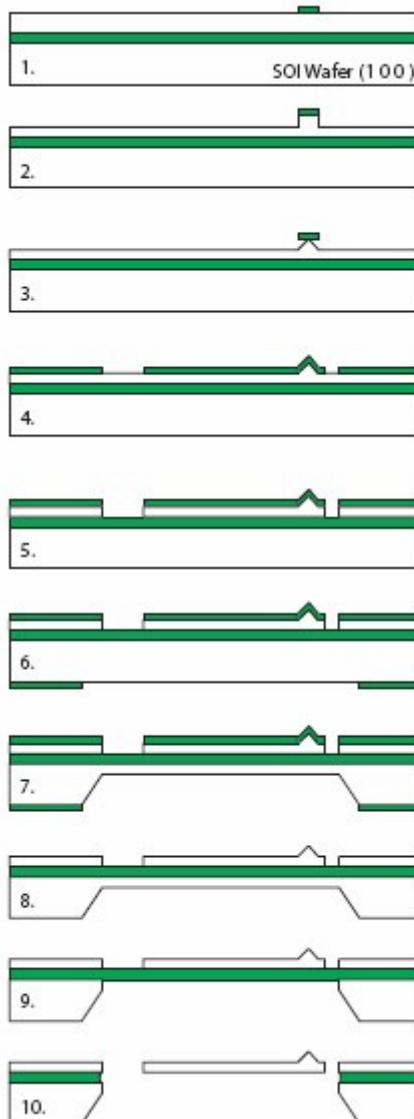
Force vs. distance



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5. Tapping mode AFM.
6. Other forms of AFM (LFM, EFM, MFM, SCM...)

AFM tip fabrication



1. SiO_2 mask

2. RIE Si dry-etch

3. KOH Si wet-etch

4. SiO_2 mask

5. RIE Si dry-etch

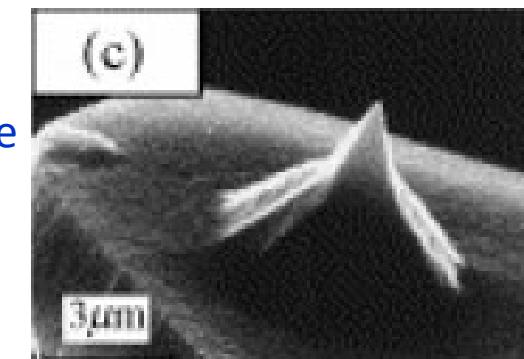
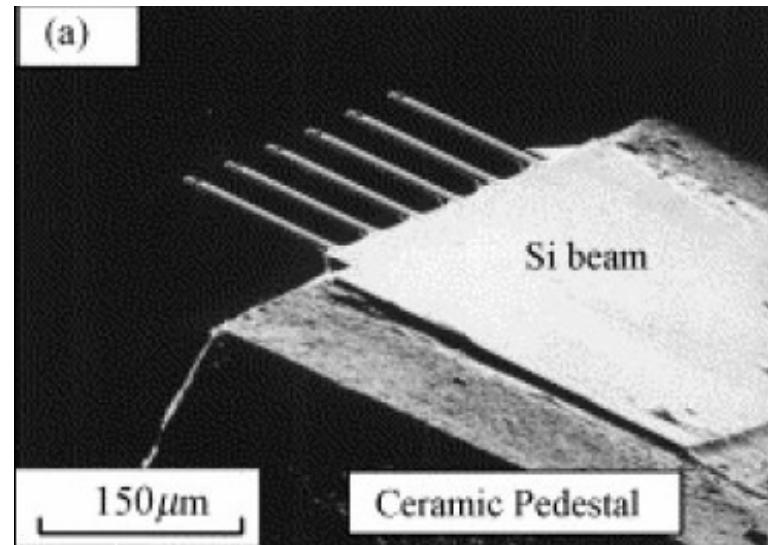
6. SiO_2 mask on backside

7. KOH Si wet-etch, passivation on front-side

8. BHF (buffered HF) SiO_2 wet-etch

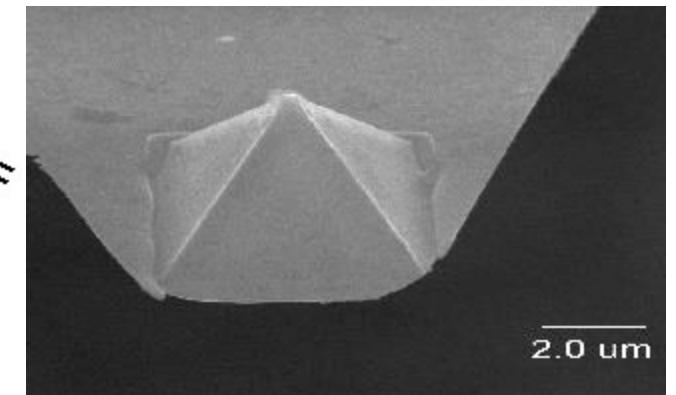
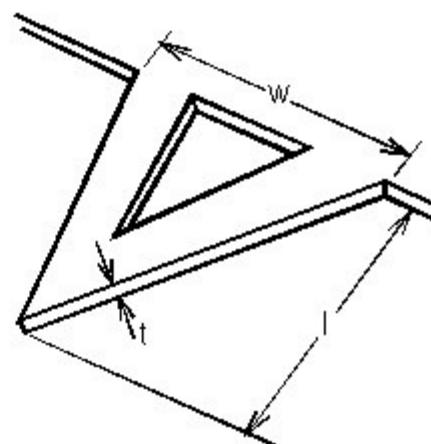
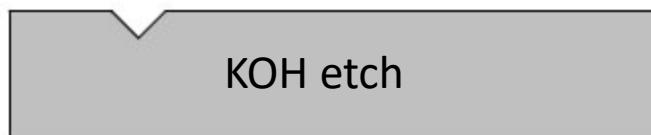
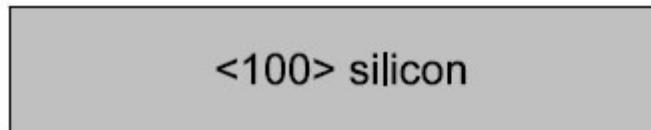
9. RIE Si dry-etch

10. Release of cantilever in BHF

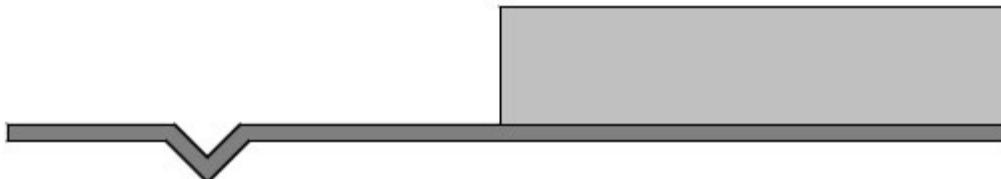
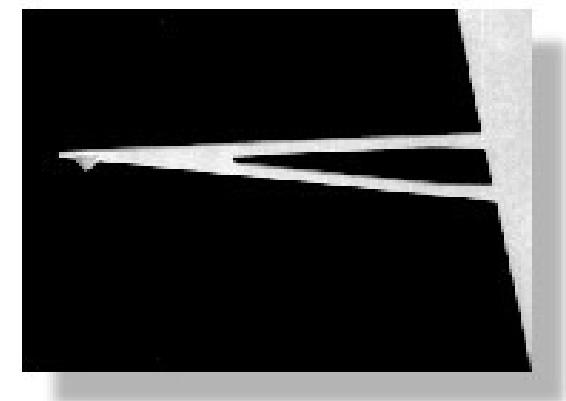


T. Wakayama, T. Kobayashi, N. Iwata, N. Tanifuji, Y. Matsuda, and S. Yamada, *Sensors and Actuators a-Physical*, vol. 126, pp. 159-164, 2006.

Cantilever fabrication – silicon micro-machined probe



Silicon nitride



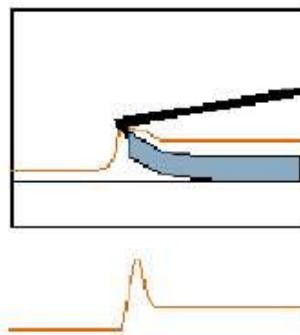
This type of tip is for contact mode AFM.

Scanning probe microscopy (SPM) and lithography

1. Scanning tunneling microscopy.
2. Piezoelectric positioning.
3. Atomic force microscopy (AFM) overview.
4. AFM tip and its fabrication.
5. Tapping mode AFM.
6. Other forms of AFM (LFM, EFM, MFM...)

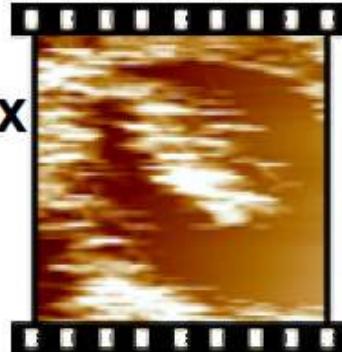
Scanning modes of AFM

Contact

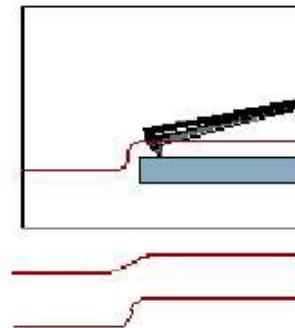


- Cantilever
- Force
- Friction
- Distance
- Damage
- Surface

Polymer latex
particle on
mica



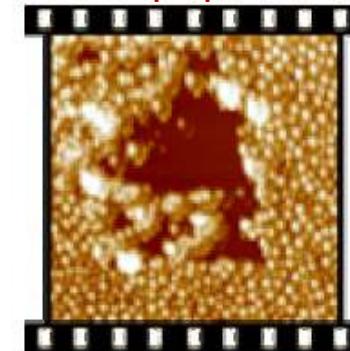
Noncontact



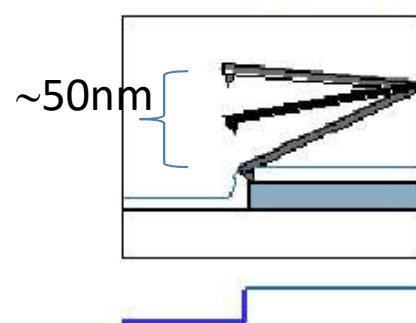
- soft
- 1-10nN
- large
- <0.2nm
- large
- hard surface

- hard
- 0.1-0.01nN
- small
- ~ 1nm
- small
- soft or elastic surface

Not popular

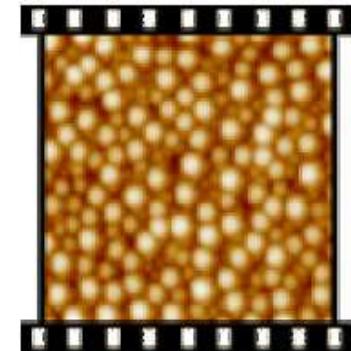


Vibrating (tapping)



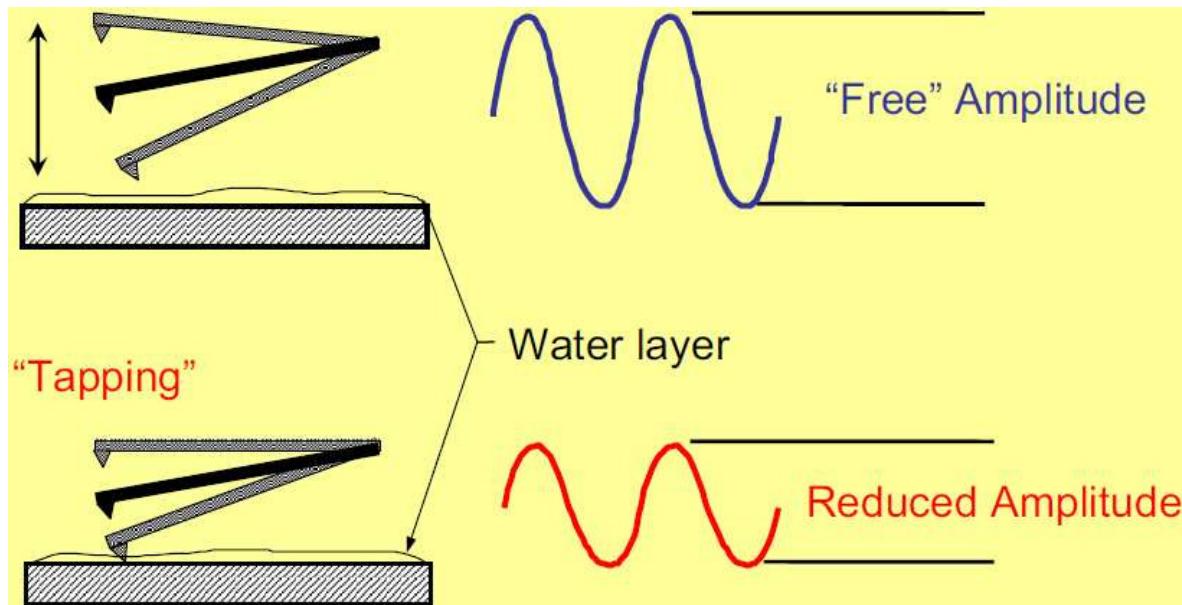
- hard
- small
- >10nm
- small

Vibration 10-100nm



Vibrating cantilever (tapping) mode: most popular

- Vibration of cantilever around its resonance frequency (often hundreds of kHz).
- Cantilever oscillate and is positioned above the surface so that it only taps the surface for a very small fraction of its oscillation period.
- When imaging poorly immobilized or soft samples, tapping mode may be a far better choice than contact mode.

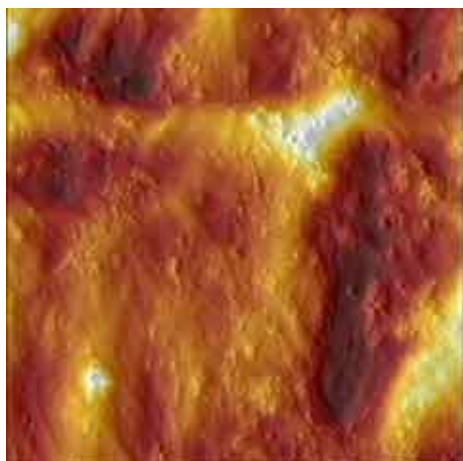


Amplitude imaging (for AFM)
Phase imaging (also for MFM
and EFM)

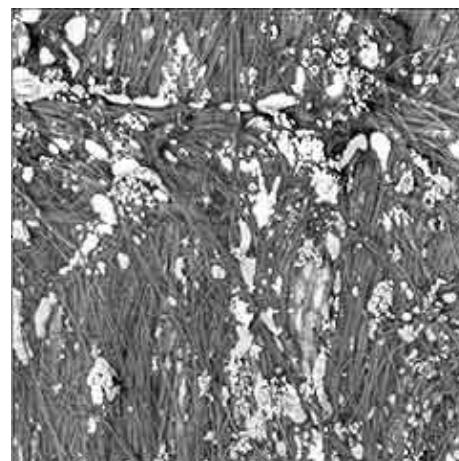
Phase imaging

- Measure the phase lag of the cantilever driving vs. actual oscillation.
- Contrast depends on the physical properties (Young's modulus...) of the material.

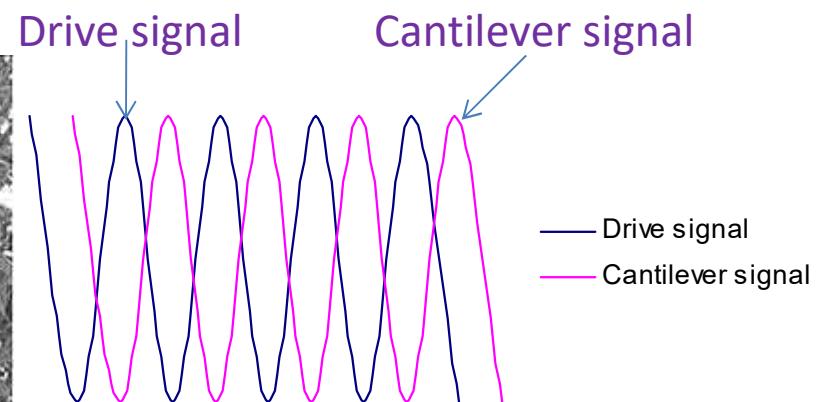
Polymer blend
(Polypropylene & EDPM)



Topography

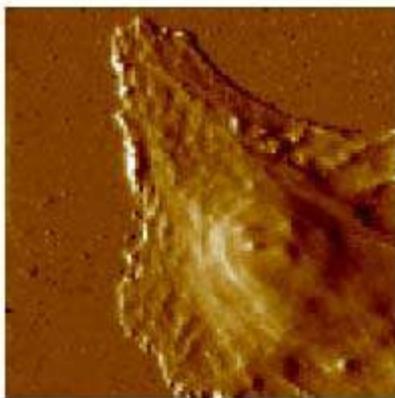


Phase

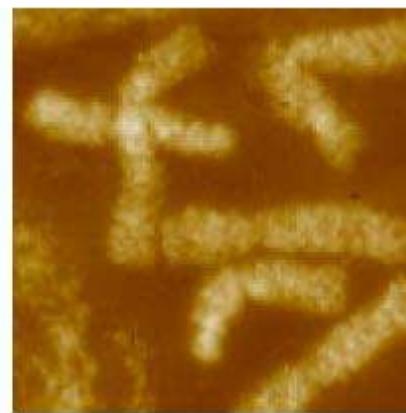


Measure relative elastic properties of complex samples

Applications to biological system

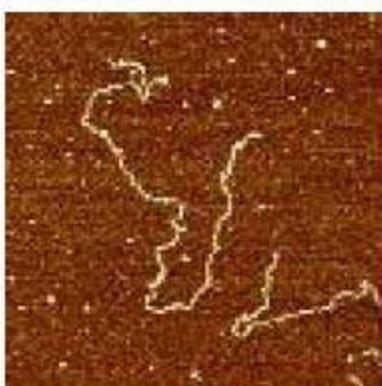


Cell surface imaging
AFM imaging of living
and fixed animal cells

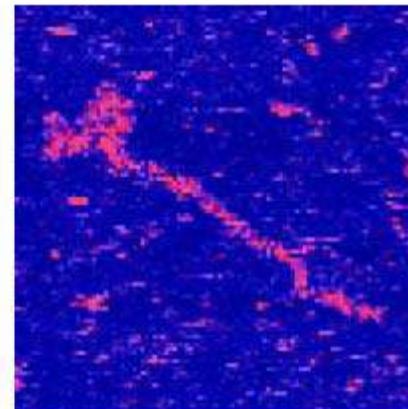


Chromosomes
A large selection of
work on both human
and plant
chromosomes

Scanning Probe Microscope



DNA
AFM images of
double-stranded
DNA and of some
special single-
double-stranded
DNA constructs



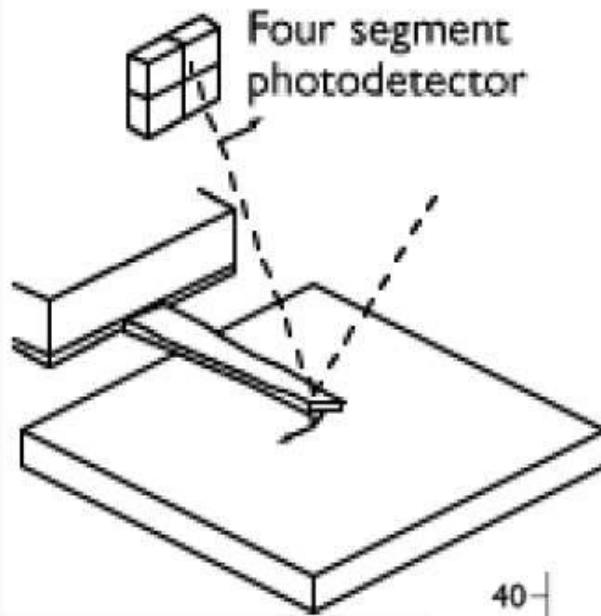
Muscle Proteins
High resolution
AFM images of
myosin and titin

Scanning probe microscopy (SPM) and lithography

1. Scanning tunneling microscopy.
2. Piezoelectric positioning.
3. Atomic force microscopy (AFM) overview.
4. AFM tip and its fabrication.
5. Tapping mode AFM.
6. Other forms of AFM (LFM, EFM, MFM, SCM...)

Lateral (friction) force microscopy

Frictional force microscopy



Possibility to discriminate different materials at the atom level.

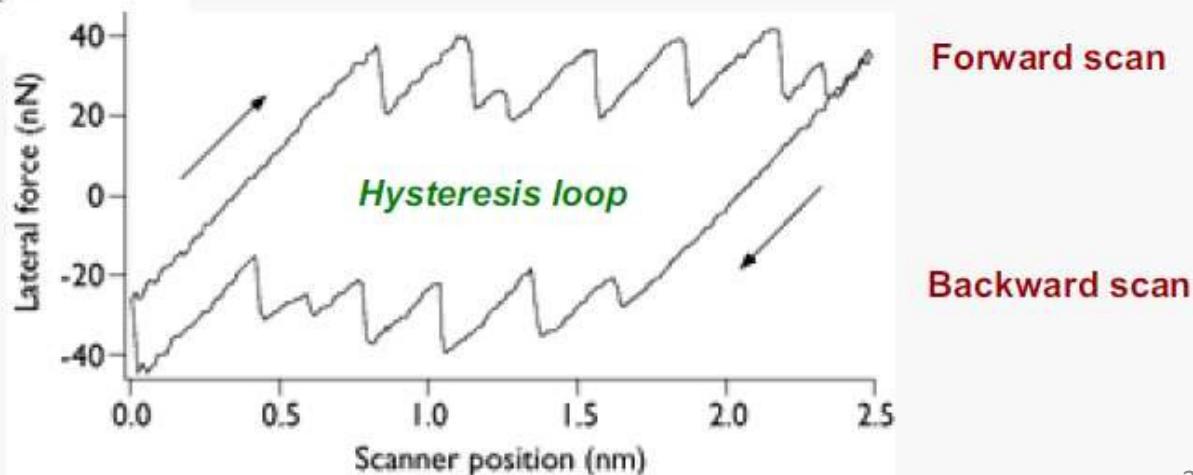
Nano-tribology investigations can be carried out.

During the scan, the tip is continuously displaced with respect to the surface

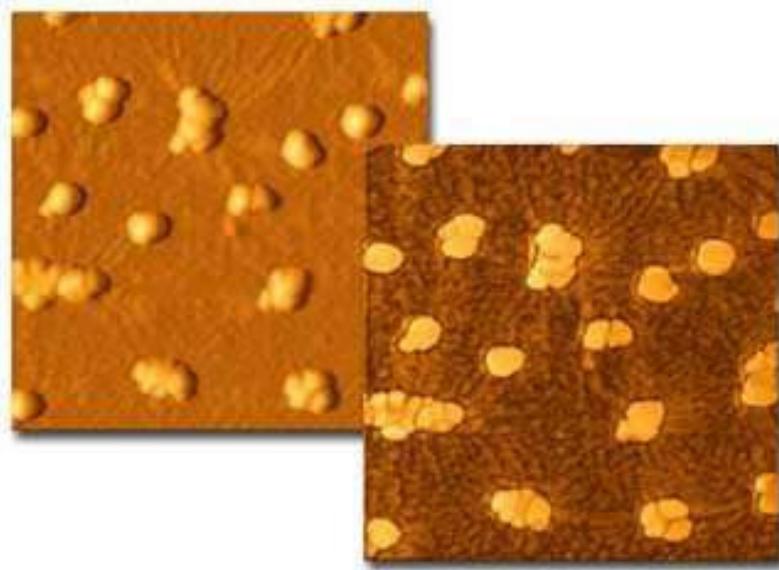
Friction forces occur, resulting in a *twisting* of the cantilever

Cantilever twist can be recorded by a two-dimension position sensitive detector (i.e., a 4-quadrant photodetector)

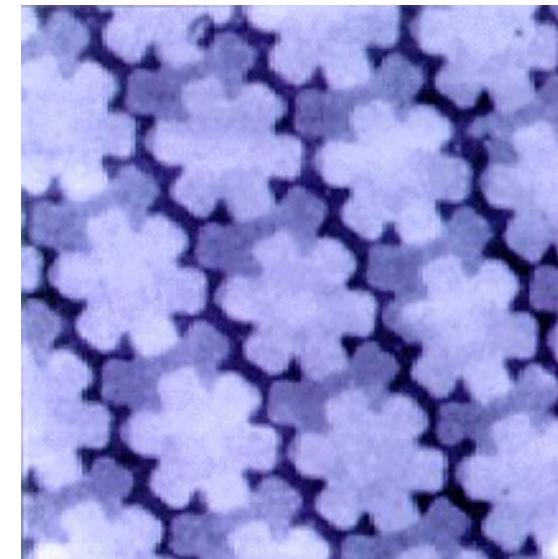
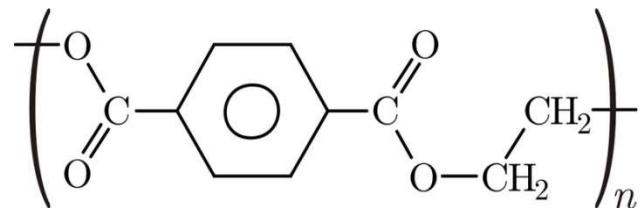
Friction effects can be corrected by the topographical artifacts by comparing forward and backward scans



Lateral force microscopy



High resolution topography (top) and lateral force mode (bottom) images of a commercially available PET film. The silicate fillers show increased friction in the lateral force image.
PET: poly(ethylene terephthalate)

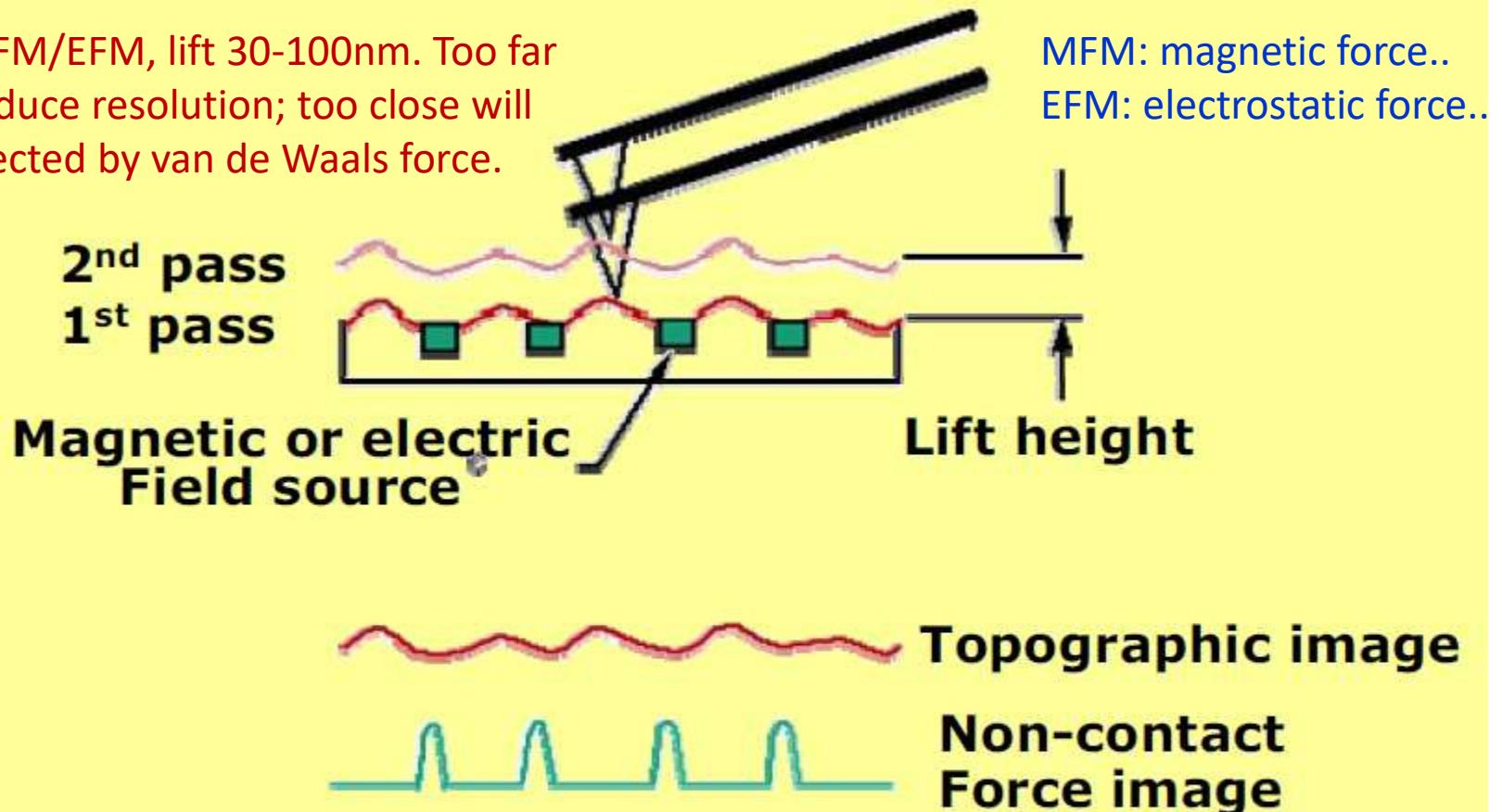


LFM image of patterned SAM (50µm x 50µm, self-assembled monolayer), formed by micro-contact printing of alkane-thiols onto Au surface using an elastomeric stamp

Lift mode AFM

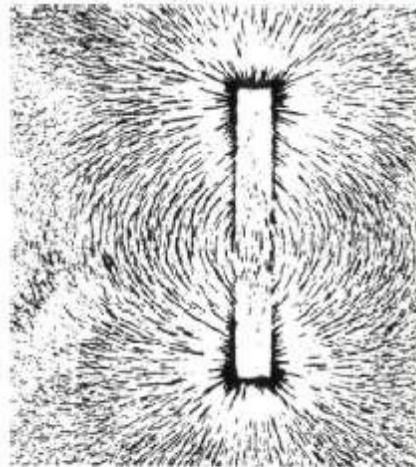
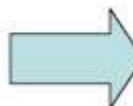
For MFM/EFM, lift 30-100nm. Too far will reduce resolution; too close will be affected by van de Waals force.

MFM: magnetic force..
EFM: electrostatic force..

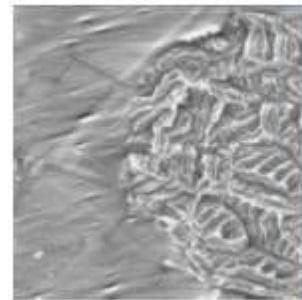
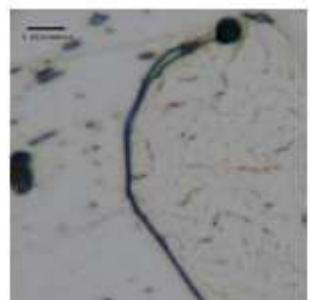
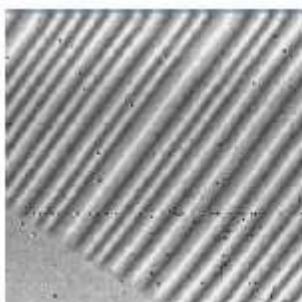
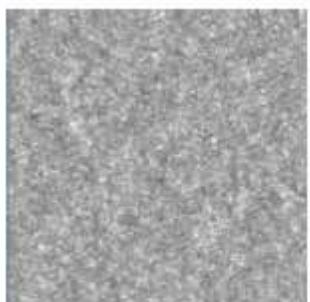


LiftMode is a two-pass technique for measurement of magnetic and electric forces above sample surfaces. On the first pass over each scan, the sample's surface topography is measured and recorded. On the second pass, the tip is lifted a user-selected distance above the recorded surface topography and the force measurement is made.

Magnetic force microscopy (MFM)



How can we visualize magnetic structure of materials?



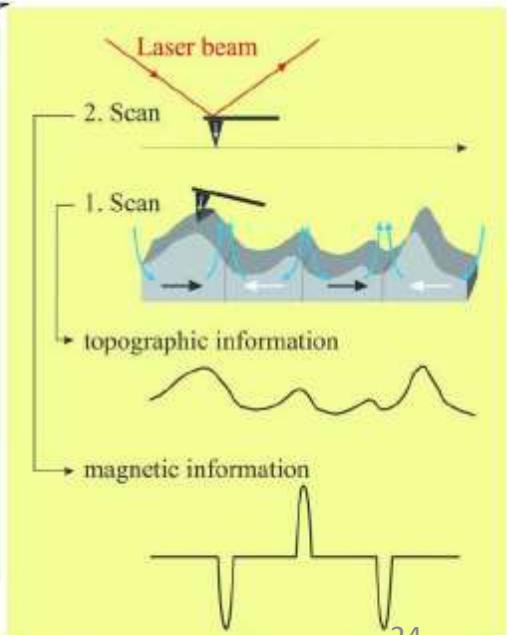
MFM:

- A special type of atomic force microscope with magnetic material coated fine tip
- Sensing the magnetic force gradient
- Better resolution than the Bitter Pattern
- No sample contamination

From: www.europhysicsnews.com
www.materialkemi.lth.se/for_students/courses

- Magnetic fine powders arranging to the magnetic stray fields on the surface (F. Bitter, 1931)
- Pattern indicates the boundaries of the magnetic domains in the material

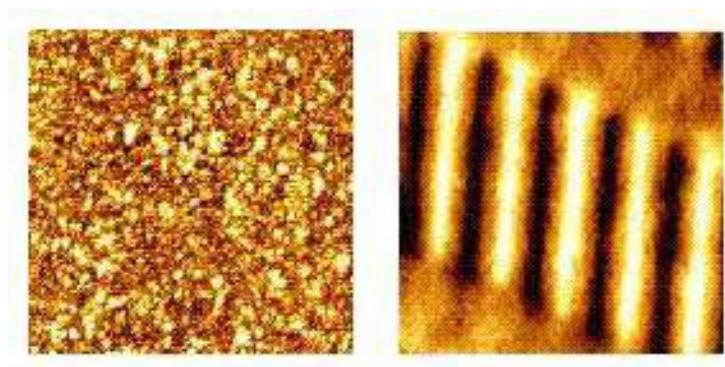
Fine iron powders may help...above certain scale



Magnetic force microscopy (MFM)

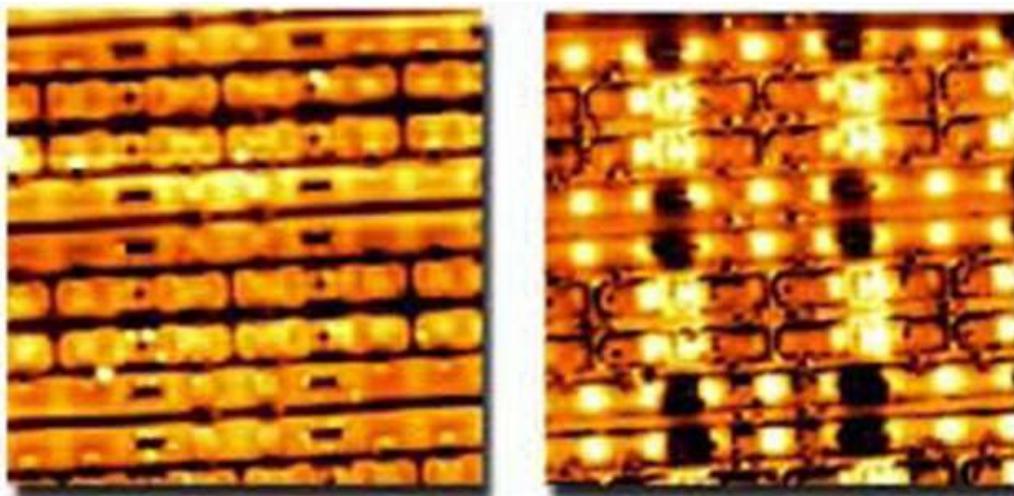
- Ferromagnetic tip: Co, Ni...
 - van de Waals force: short range force (<10nm)
 - Magnetic force: long range force (up to 100nm), small force gradient
 - Close imaging (tapping mode): topography
 - Distant imaging (lift mode): magnetic properties
 - MFM detects changes in the resonant frequency of the cantilever induced by the magnetic field's dependence on tip-to-sample separation.
 - It detects the magnetic field *gradient* (dB/dz , no frequency change for constant magnetic field with zero gradient).
 - Besides frequency change, phase change (correlated to frequency change) is actually often detected to generate MFM image.
- Resonance frequency:
 $k_{\text{eff}} = k_0 - \frac{dF}{dz}$ (F is force)
 $f_{\text{eff}} = (1/2\pi)(k_{\text{eff}} / m)^{1/2}$

(left) AFM image of hard disk drive
(right) MFM image of the same area

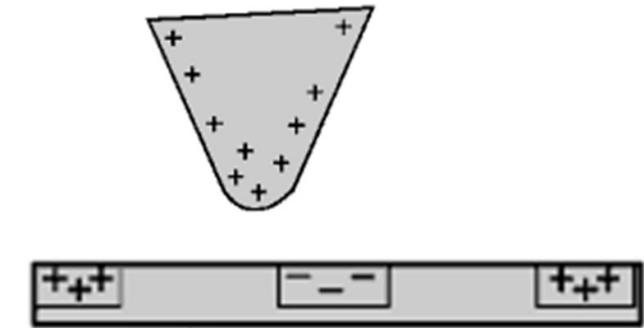


Electrostatic force microscopy (EFM)

- Contrary to MFM, EFM doesn't use ferroelectric material.
- Instead, charge is generated by applied bias voltage on metal tip.
- More difficult to extract the useful information than MFM due to mirror charges (mirror charge from tip to substrate and vice versa).
- So it is not as popular as MFM.



The sub-surface structure of electrical contacts and doping trenches in this SRAM sample can be revealed using EFM



- EFM maps local surface charge distribution on the sample surface, similar to how MFM plots the magnetic domains of the sample surface.
- EFM can also map the electrostatic fields of an electronic circuit as the device is turned on and off.
- This technique is known as "voltage probing" and is a valuable tool for testing live microprocessor chips at the sub-micron scale.

Scanning probe microscopy (SPM) and lithography

1. Atom and particle manipulation by STM and AFM.
2. AFM oxidation of Si or metals.
3. Dip-pen nanolithography (DPN).
4. Resist exposure by STM field emitted electrons.
5. Indentation, scratching, thermal-mechanical patterning.
6. Field evaporation, STM CVD, electrochemical deposition/etching.
7. Scanning near field optical microscope (SNOM) overview.
8. Nanofabrication using SNOM

Pushing/pulling atoms using STM

STM Lithography:

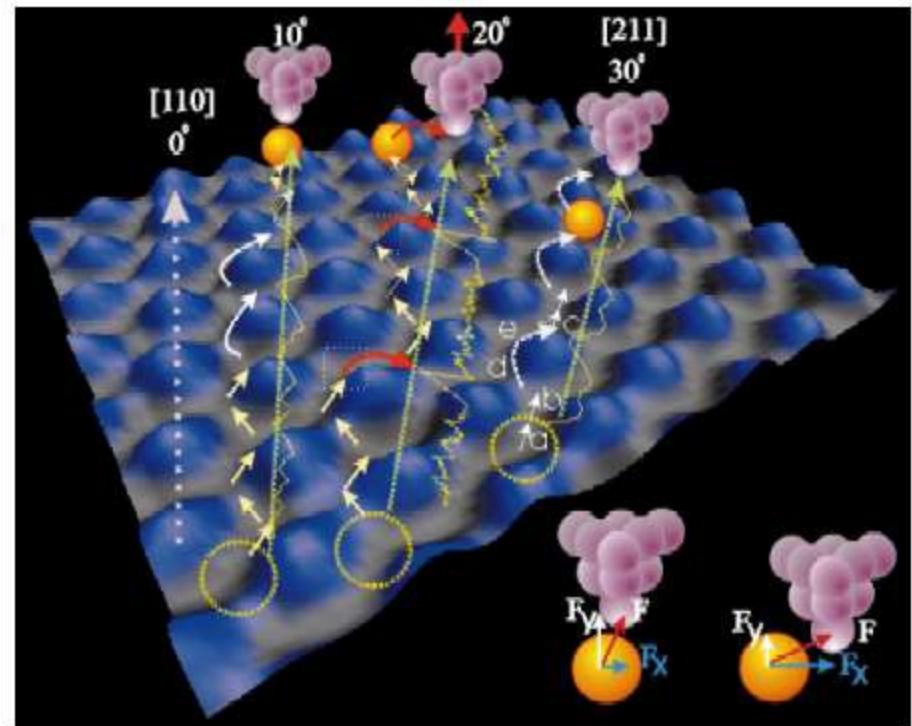
- Atomic scale patterning technique
- Manipulation of both single atoms or molecules
- Can be used, for example, quantum data storage with extremely high storage density (one atom per bit).

Atom movement mechanism:

When lateral force F_x exceeds the hopping barrier, the atom jumps to the adjacent row.

High electric field polarizes the molecule and may make it jump from the surface to the tip or tip to the surface.

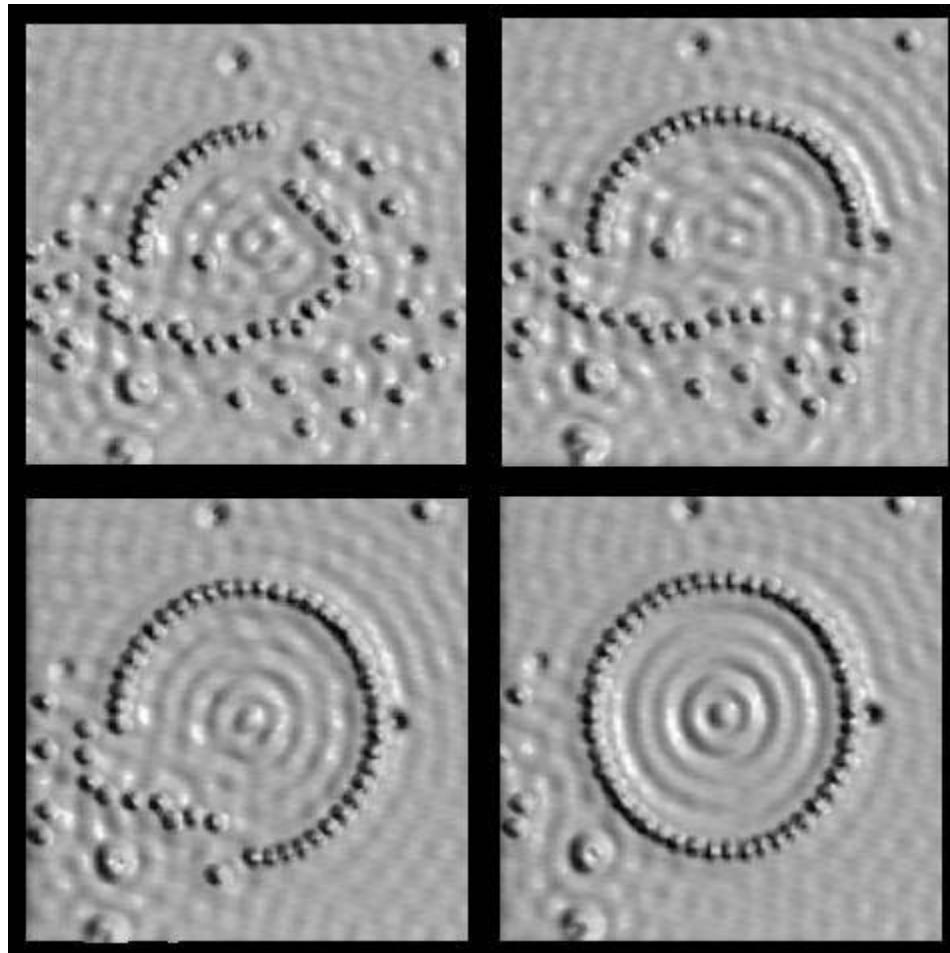
However, this might not be well controllable, then one should avoid too high electric field (so atom remains close to substrate surface all the time) and use attractive van der Waals force to pull the atoms.



Atomic manipulation by STM

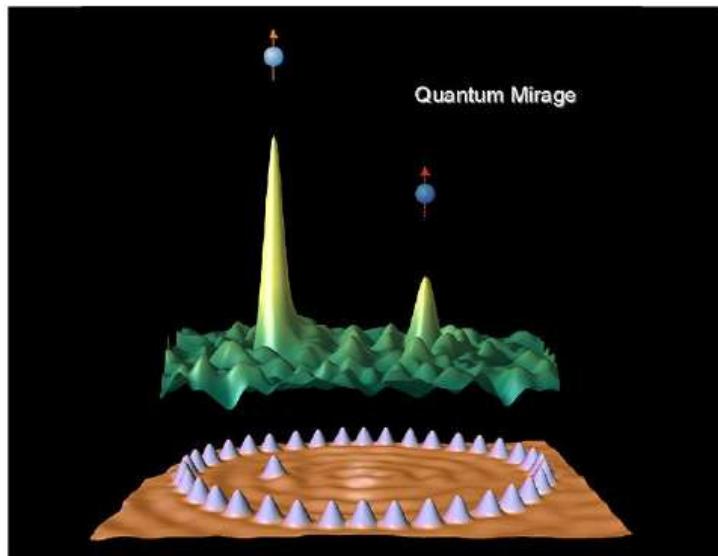
Circular corral (radius 71.3Å),
48 Fe atoms on copper (111).

Quantum-mechanical
interference patterns



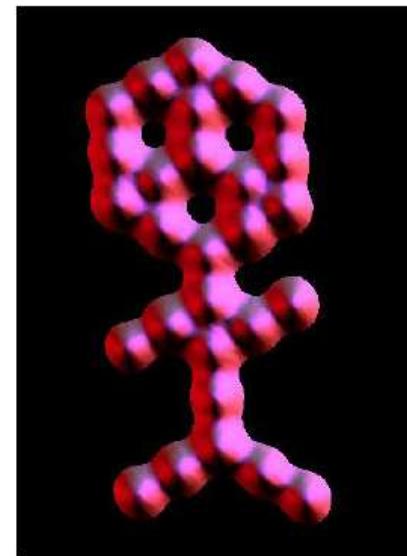
STM nano-patterning at IBM

Quantum Corral



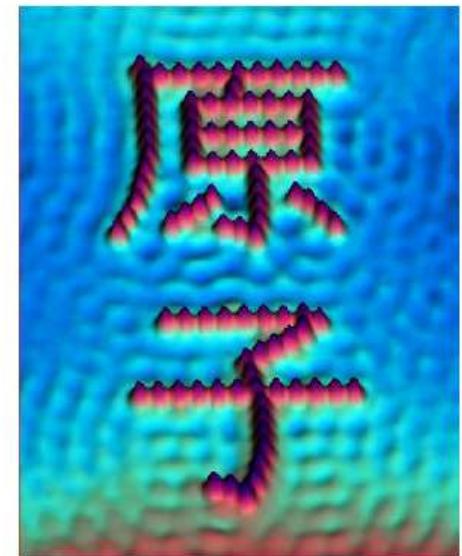
Cobalt on Copper (111)

Carbon Monoxide Man



Carbon Monoxide
on Platinum (111)

The Kanji for "atom."

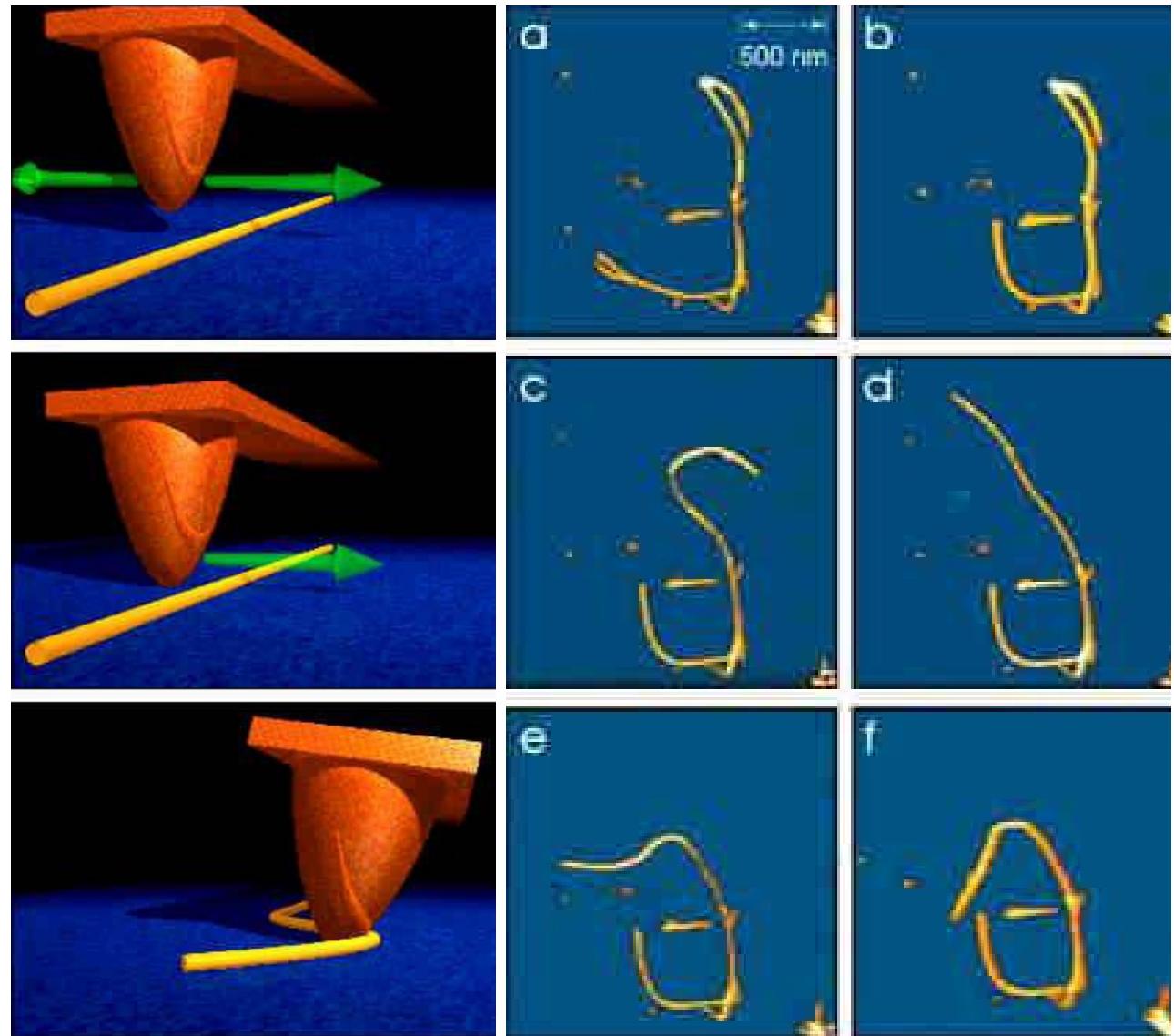
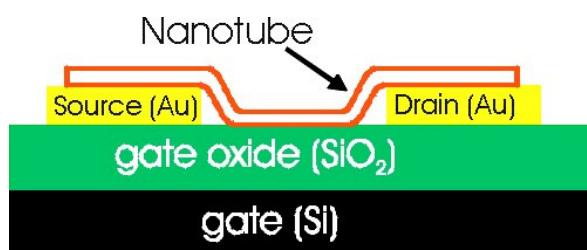
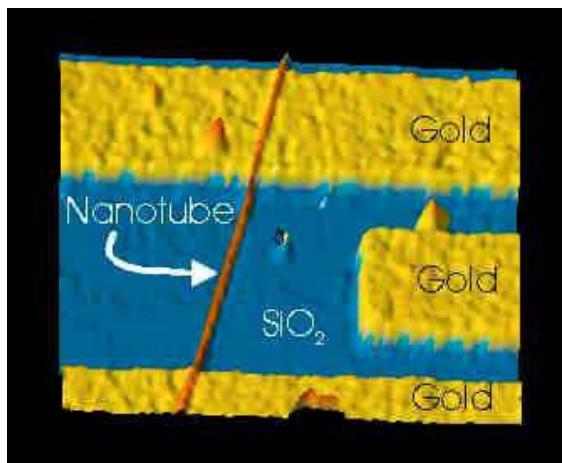


Iron on Copper
(111)

M.F. Crommie, C.P. Lutz, D.M. Eigler, Science 262, 218-220 (1993).
M.F. Crommie, C.P. Lutz, D.M. Eigler, Nature 363, 524-527 (1993).⁴

AFM manipulation of carbon nanotube

IBM nanotube
manipulation for position
nanotube on transistors.

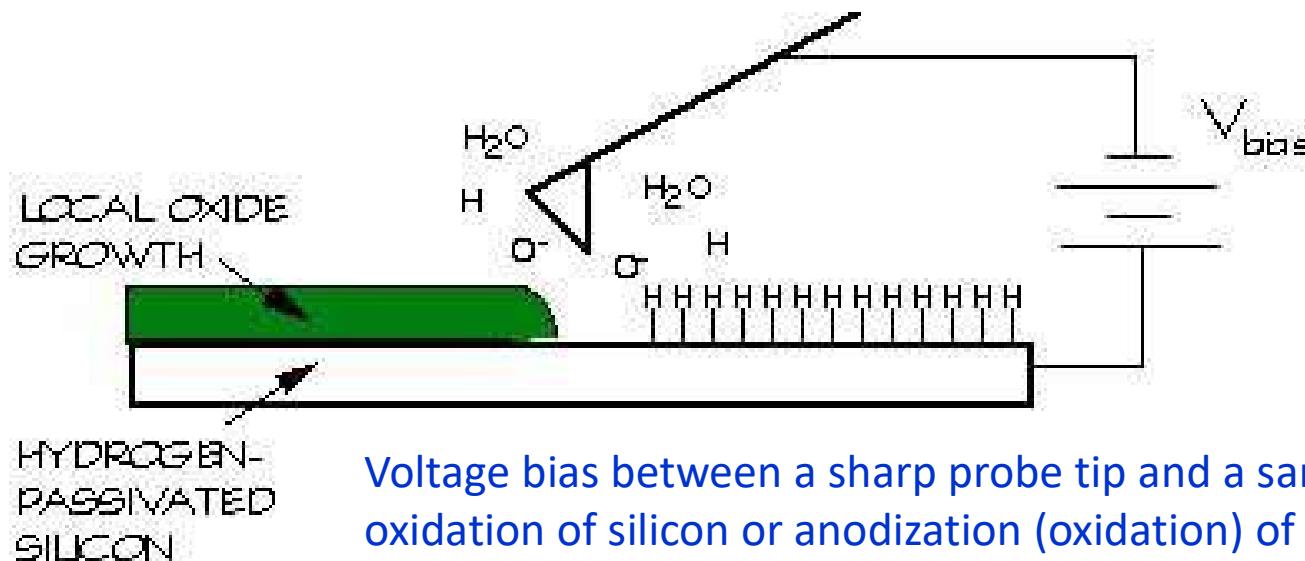
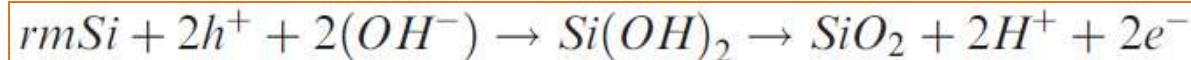


Scanning probe microscopy (SPM) and lithography

1. Atom and particle manipulation by STM and AFM.
2. AFM oxidation of Si or metals.
3. Dip-pen nanolithography.

AFM oxidation (STM also works)

- This is an electrochemical process, even though it is not done in bulk liquid (but actually there is always liquid when operated in air).
- The high field desorbs the hydrogen on the silicon surface and enables exposed silicon to oxidize in air.
- Since the oxidation process requires an electrical current, both the tip and substrate must have some conductivity.



Voltage bias between a sharp probe tip and a sample leads to oxidation of silicon or anodization (oxidation) of metals.

AFM oxidation results

- Resulting oxide affected by experimental parameters
 - Voltage (typically from 5-10V)
 - Tip Scan Speed (stationary to tens of $\mu\text{m/s}$)
 - Humidity (20% to 80%)
- Detected current can be used for process control

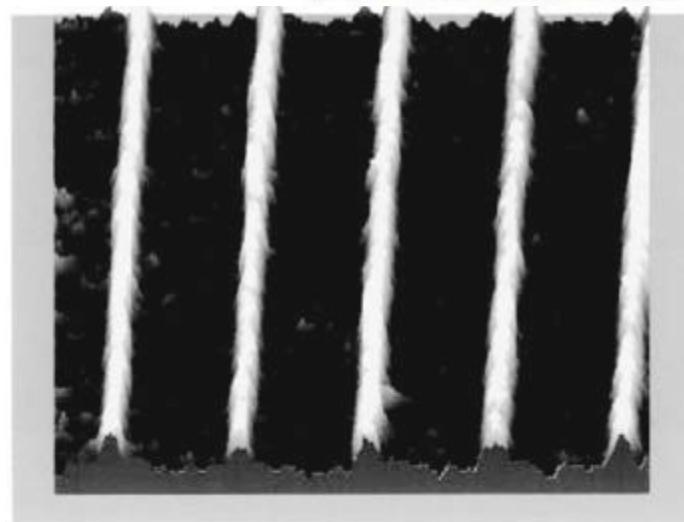
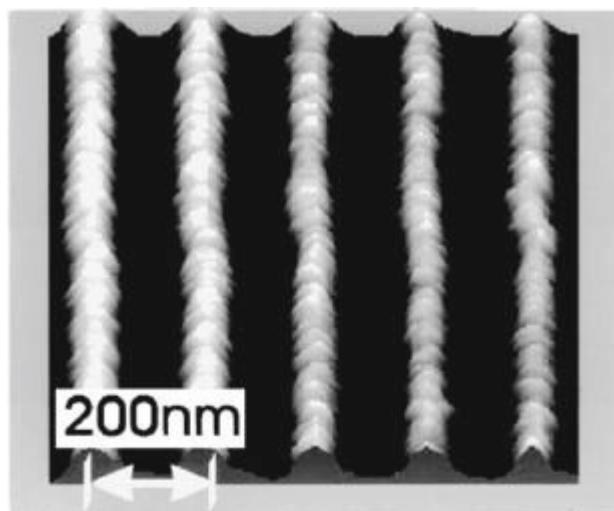
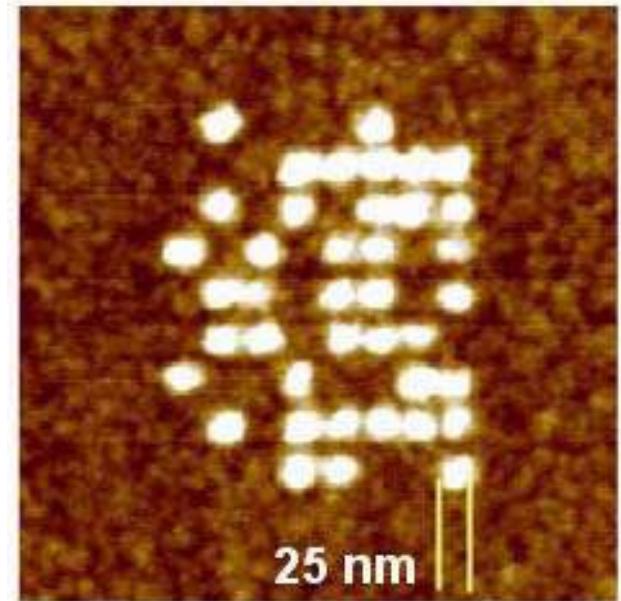


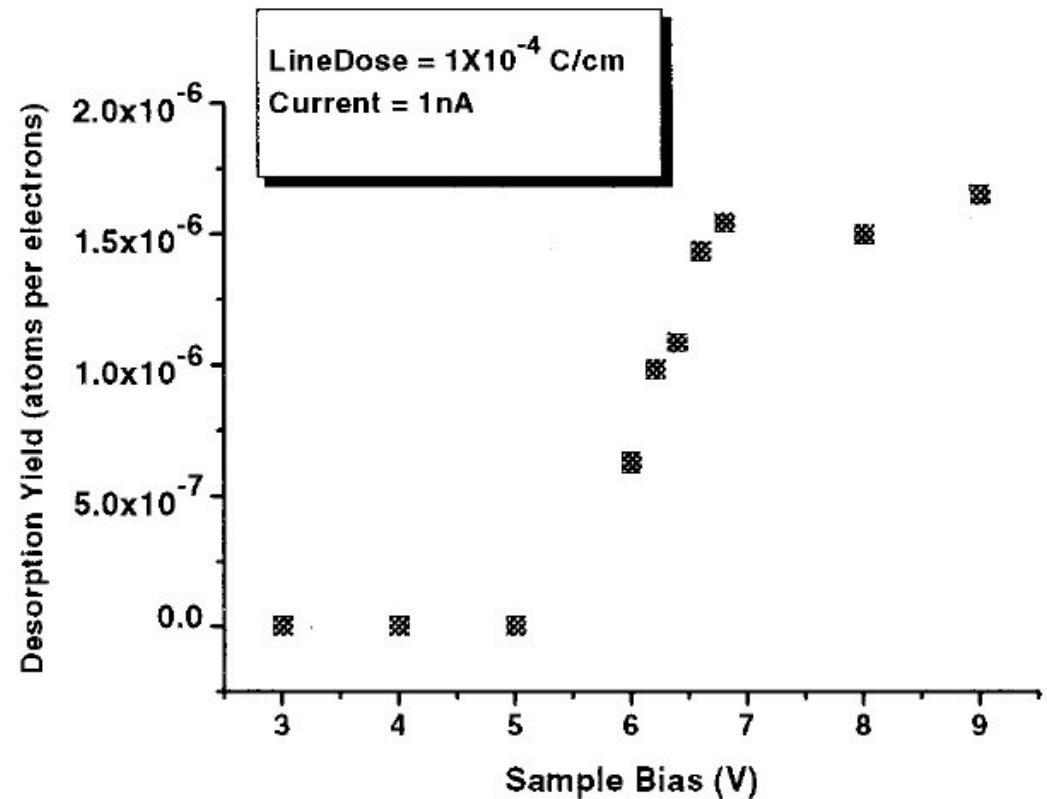
Fig. 4.12 AFM images of oxide lines produced at (left) 61% of humidity (line 91nm wide); and (right) 14% humidity (22nm wide).

De-passivation of Si:H by STM

H- terminated Si resulted from HF etch of Si whose top surface (~2nm) is usually oxidized in air.



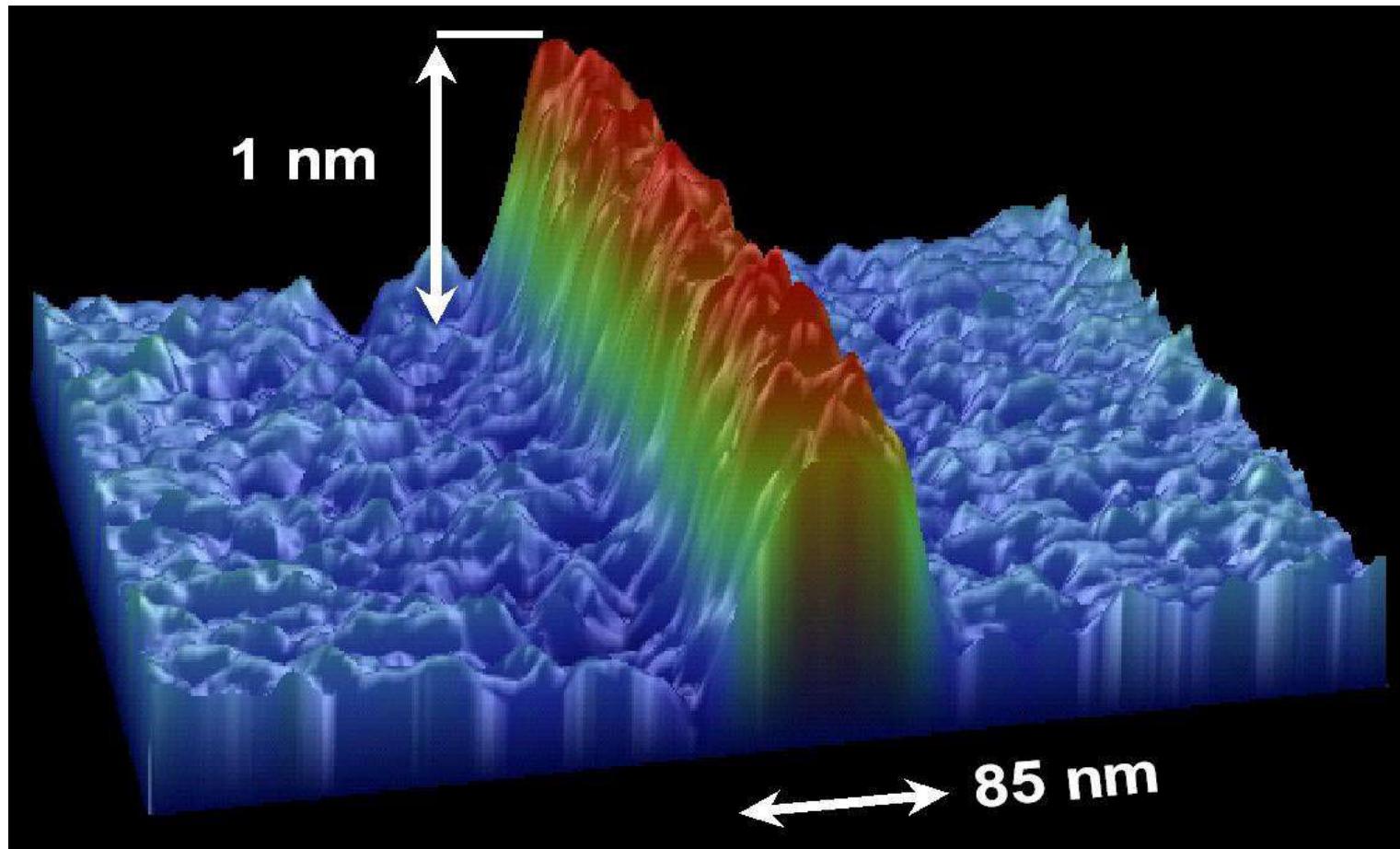
STM image of a Si(100)-2×1-H surface. M corresponds to a STM induced hydrogen desorption obtained with a constant current of 2nA, an electron dose of 4×10^{-4} C/cm, and a sample bias voltage of 6V.



Hydrogen desorption yield as a function of the sample bias voltage.

Silicon dioxide line on silicon written by AFM oxidation

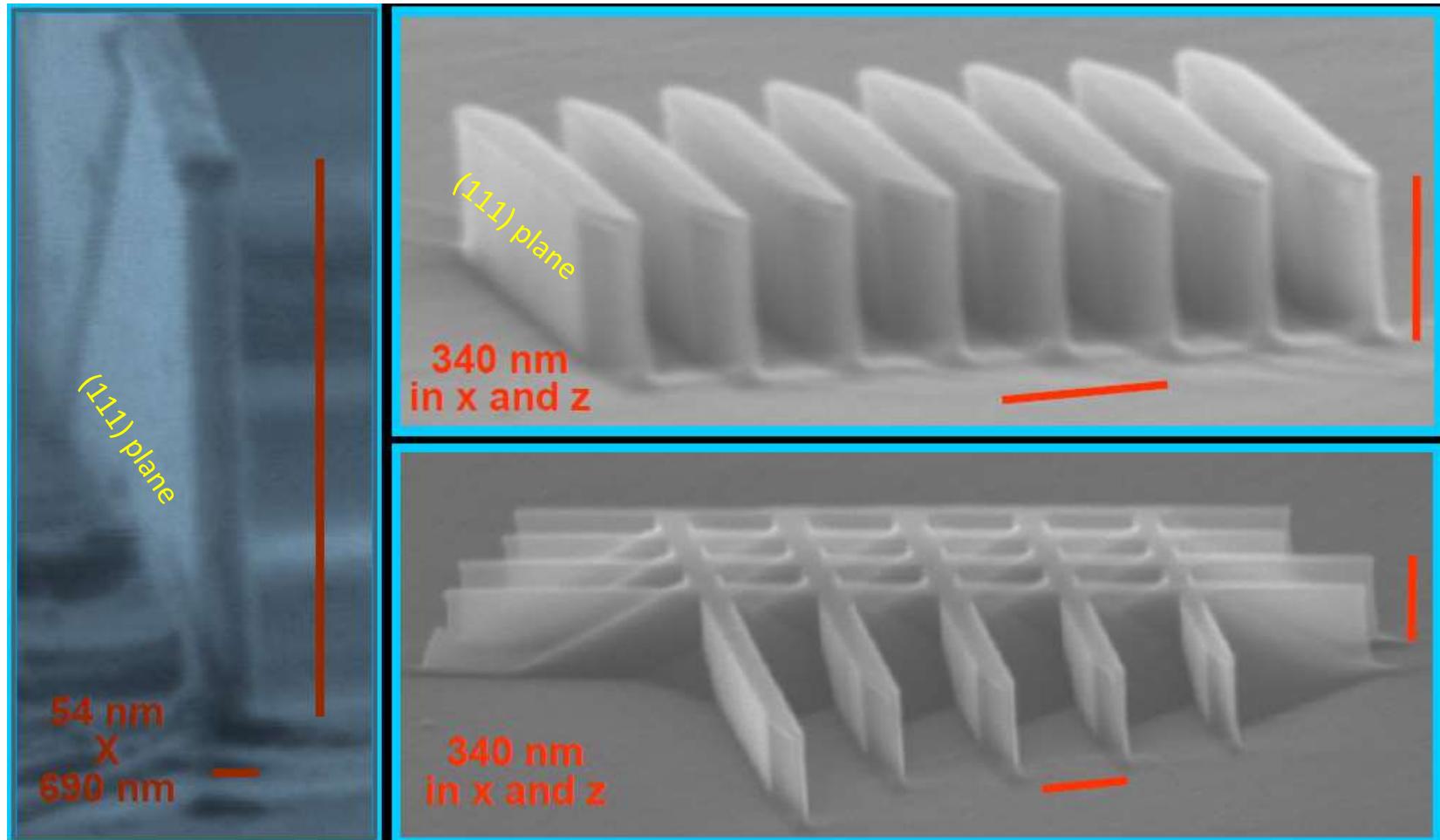
Though the height is only $\sim 1\text{nm}$, it is enough to etch deep into Si using hot KOH solution with etching selectivity (Si:SiO₂) $\sim 1000:1$.



Silicon dioxide line on silicon written & profiled by AFM

Etching into Si by KOH using SiO_2 as mask

Produced by chemical etching of AFM written lines



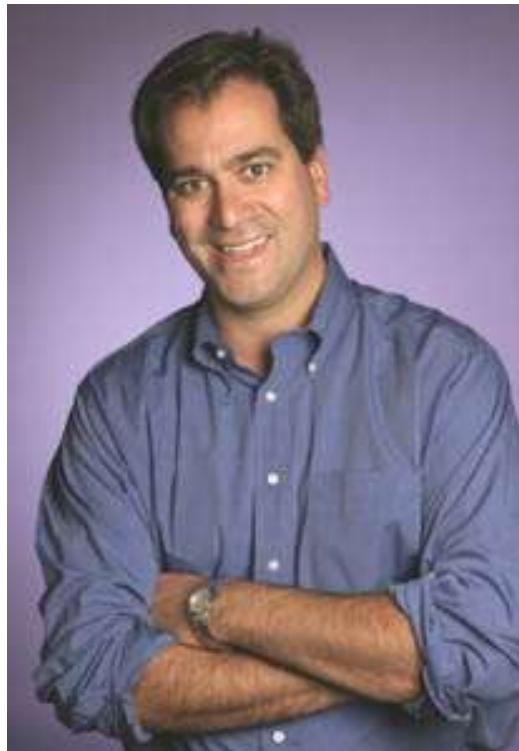
However, such high aspect ratio anisotropic vertical etching can only be achieved along certain directions ((111) plane) on (110) Si wafer.

Scanning probe microscopy (SPM) and lithography

1. Atom and particle manipulation by STM and AFM.
2. AFM oxidation of Si or metals.
3. Dip-pen nanolithography.

Dip pen nanolithography (DPN)

- Revolutionary science developed at Northwestern University.
- Allows for deposition of inks, including DNA and other biomaterials, at nm resolution.
- For ultra-high-density gene chips with direct write of DNA onto substrate....
- It resembles micro-contact printing, yet it creates pattern (rather than duplicating pattern), and is very slow.



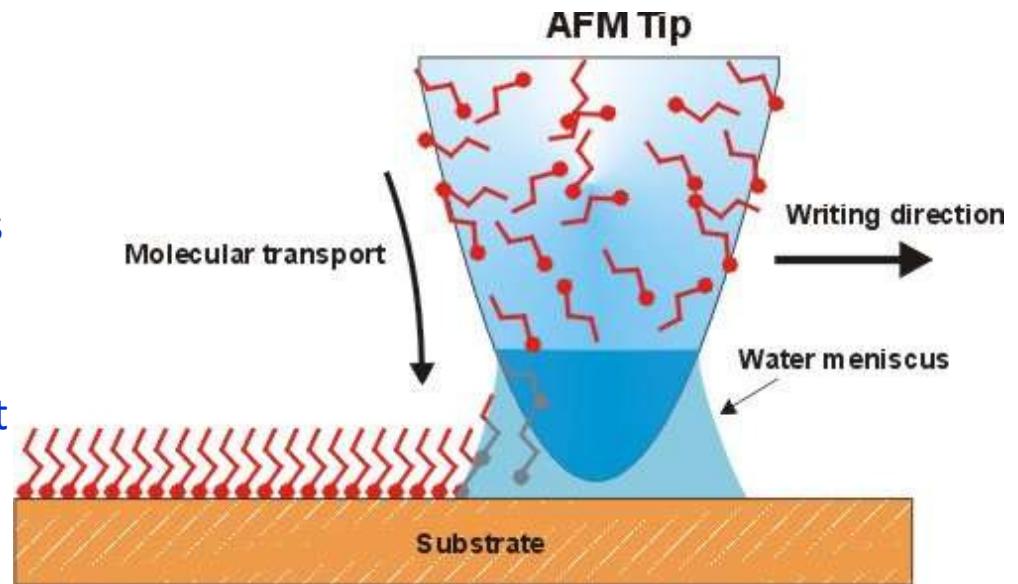
Chad Mirkin (Northwestern)



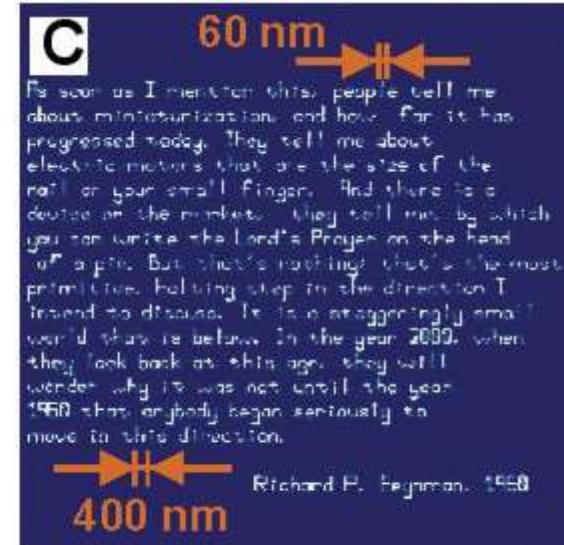
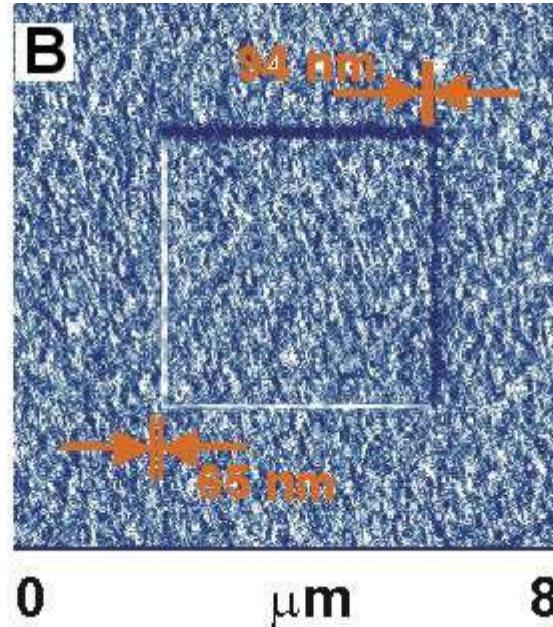
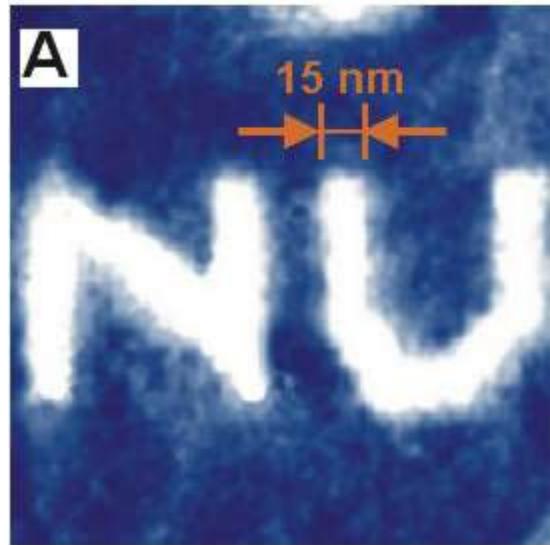
DPN is commercialized by Nanolink,
founded by Mirkin who invented DPN.

Dip-pen nanolithography (DPN)

- Tip is dipped in chemical “ink” and transfers nanoparticles, biomolecules, etc. to substrate through contact “writing”.
 - In a high-humidity atmosphere, a nanoscale water droplet condenses between the AFM tip and the substrate.
 - The drop of water acts as a bridge over which the ink molecules migrate from the tip to the substrate surface where they are deposited.
 - Demonstrated resolution: 15nm.
-
- By far DPN is the most widely used SPM-based patterning techniques, because other methods (e-beam lithography, FIB, photolithography...) cannot handle liquids important for chemical and bio-applications.
 - The competing technique is micro-contact printing (faster, though lower resolution).
 - It is still used for research, not for production.

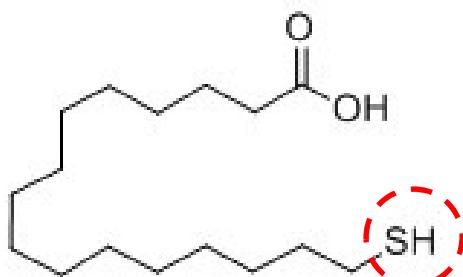


Dip pen nanolithography patterns

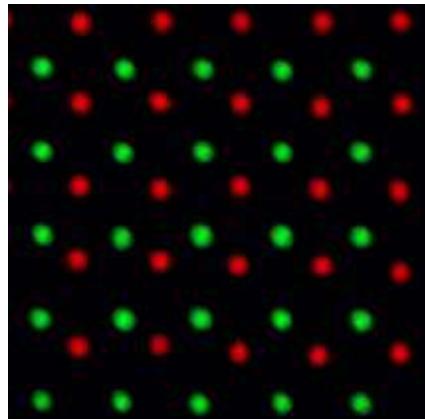


0 nm 180 nm

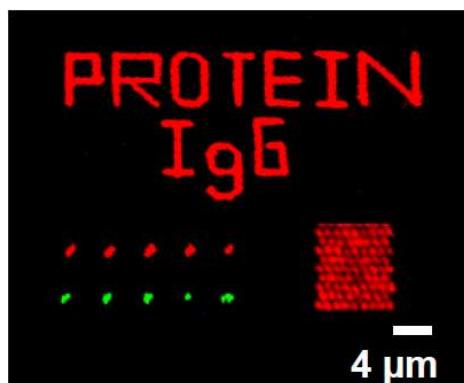
0 μm 8 μm



- A) Ultra-high resolution pattern of mercaptohexadecanoic acid on atomically-flat gold surface.
- B) DPN generated multicomponent nanostructure with two aligned alkanethiol patterns.
- C) Richard Feynman's historic speech written using the DPN nanoplotter.

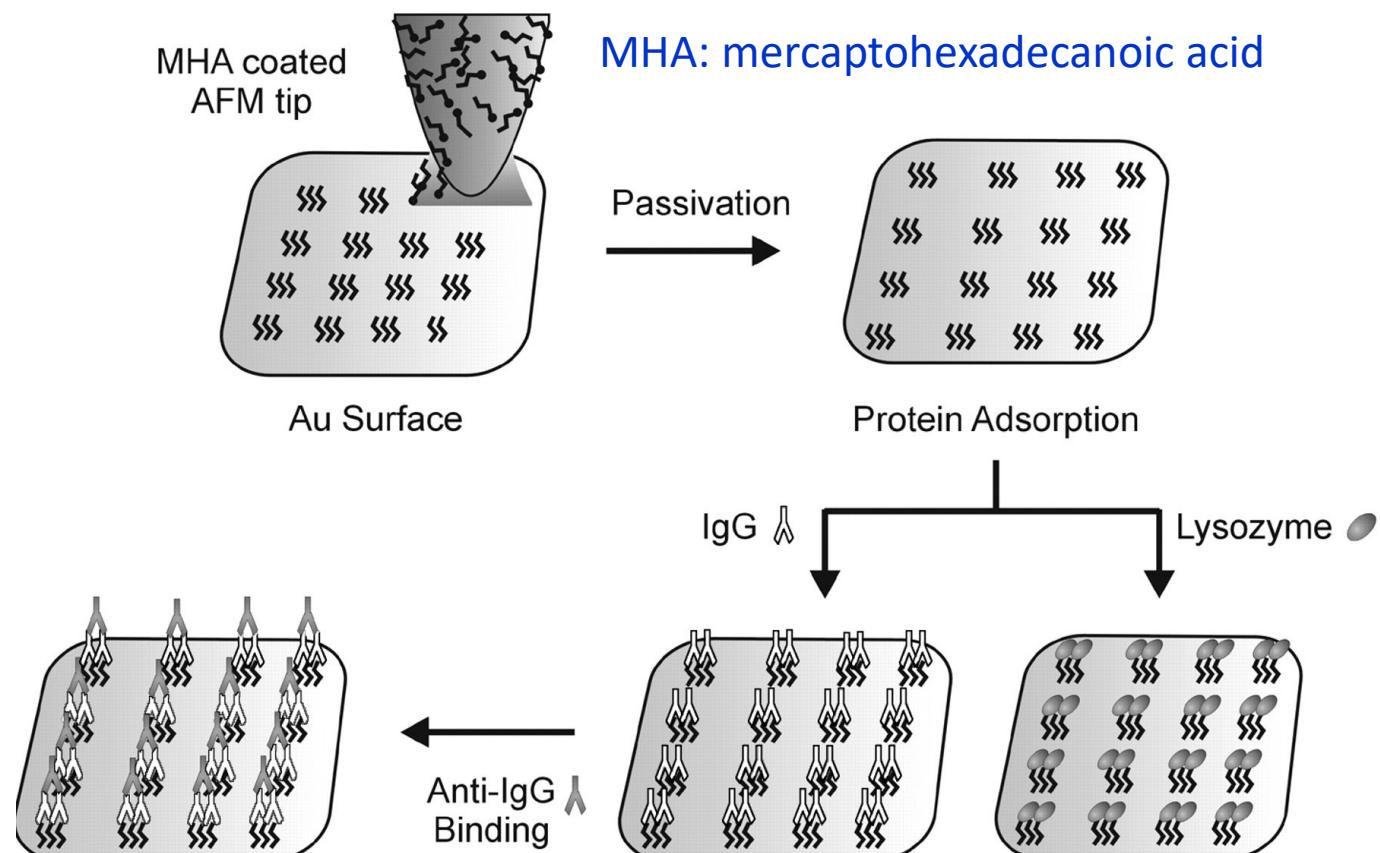


Ultrahigh density DNA arrays
fluorescent image



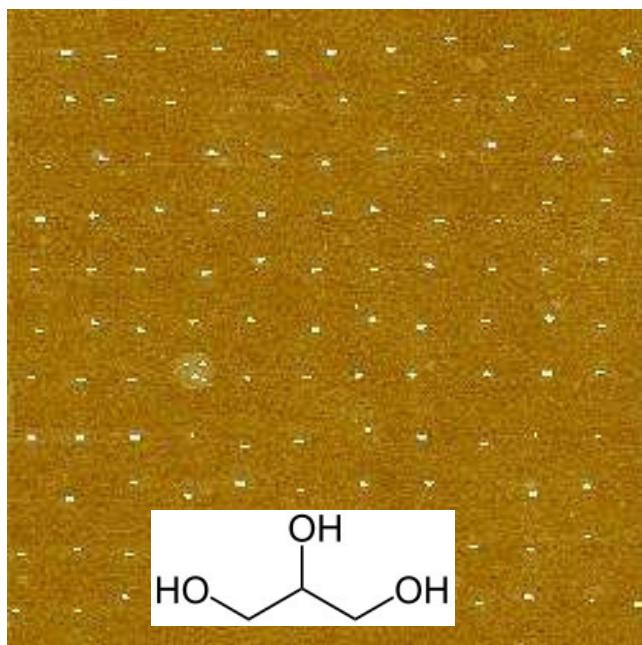
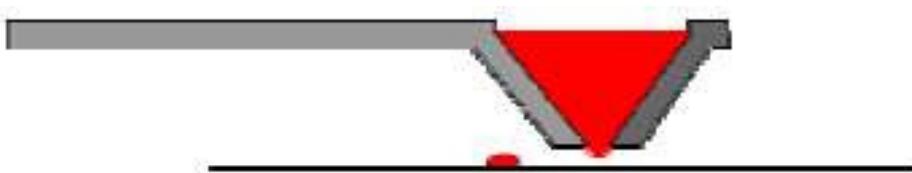
Virus nano-arrays

Bio-matter patterning by DPN

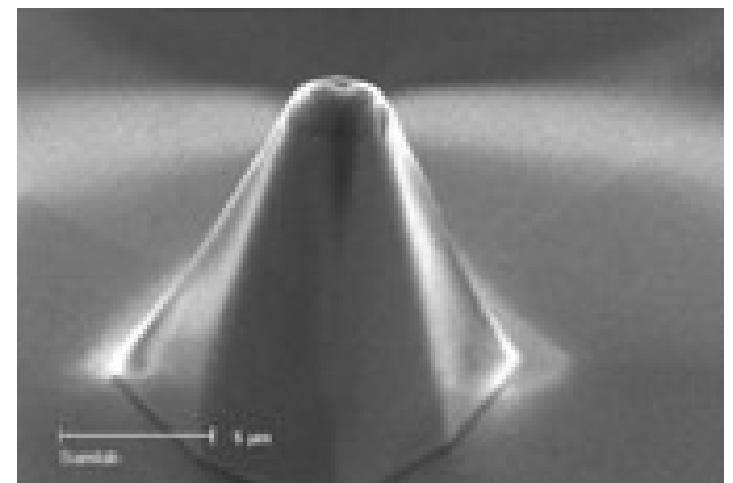
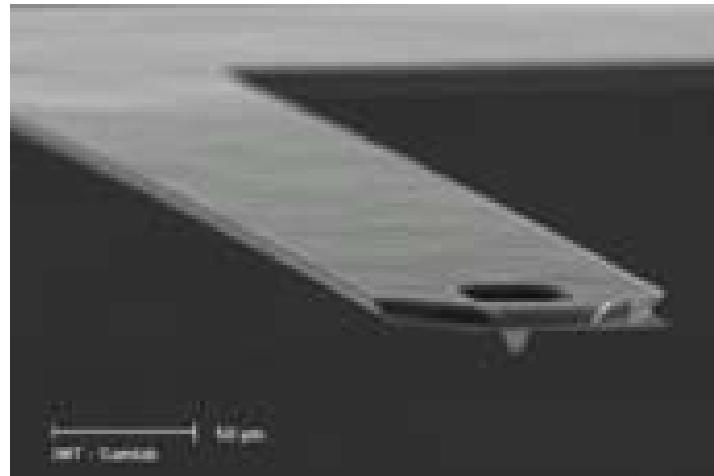


Nanoscale dispensing

- Pattern liquids, e.g. biomolecules, suspensions, by surface chemistry.
- Parallel probes for multi-material deposition.

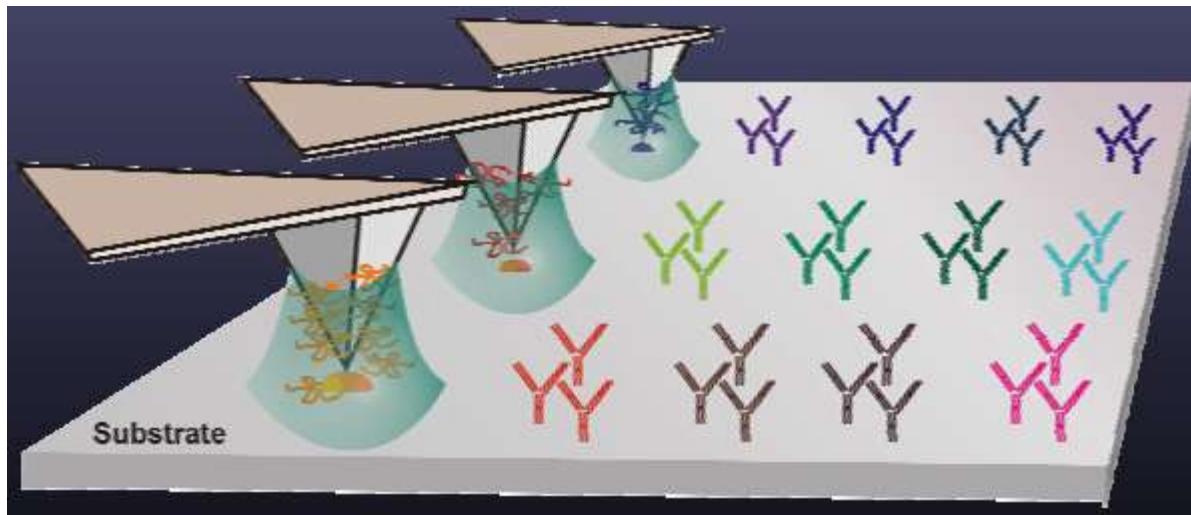


Glycerol on SiO_2 , image size $10\mu\text{m} \times 10\mu\text{m}$
dots size 50–100nm



Tip can be fabricated by FIB milling

One application: cancer diagnosis using tumor markers

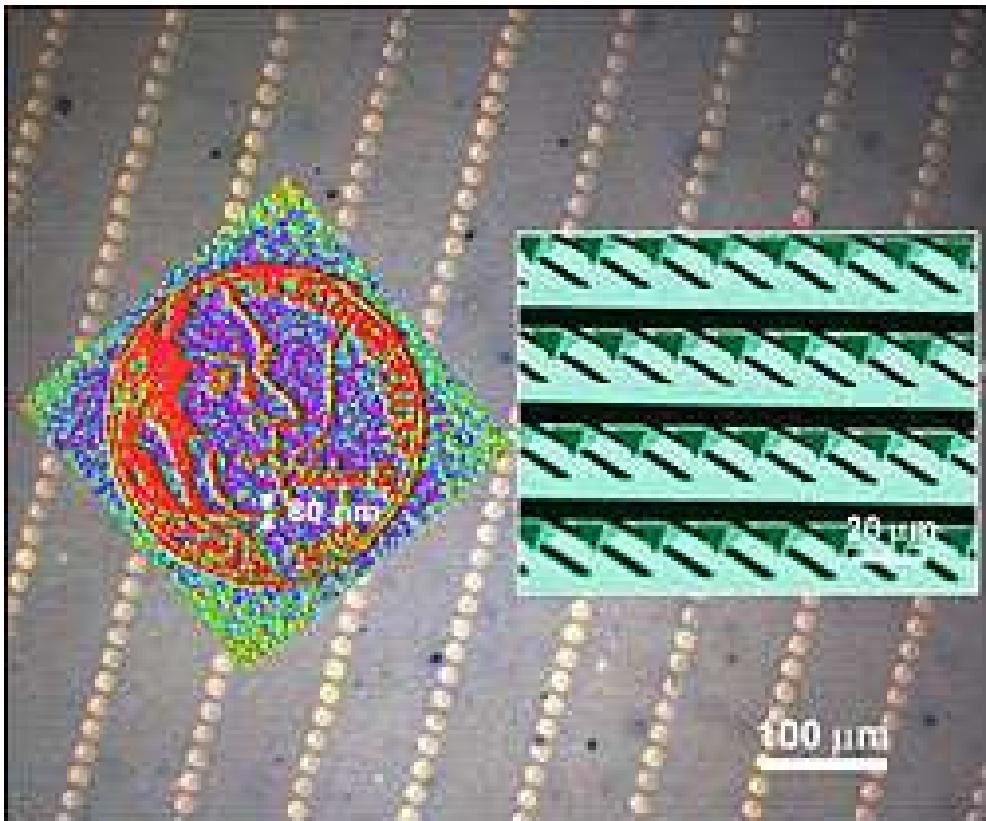


Antibody/antigen array that binds specifically to tumor marker antigen/antibody.

Tumor marker:

- Found in the blood, other body fluids, or tissues.
- High level of tumor marker may mean that a certain type of cancer is in the body.
- Currently, the main use of tumor markers is to assess a cancer's response to treatment and to check for recurrence.
- Scientists continue to study these uses of tumor markers as well as their potential role in the early detection and diagnosis of cancer.

Parallel dip-pen nanolithography



The background shows some of the 55,000 miniature images of a 2005 US nickel made with dip-pen lithography. Each nickel image with Thomas Jefferson's profile (in red) is made of a series of 80nm dots. The inset (right) is a SEM image of a portion of the 55,000-pen array.

A dip-pen nanolithography that has an array of 55,000 pens that can create 55,000 identical patterns.

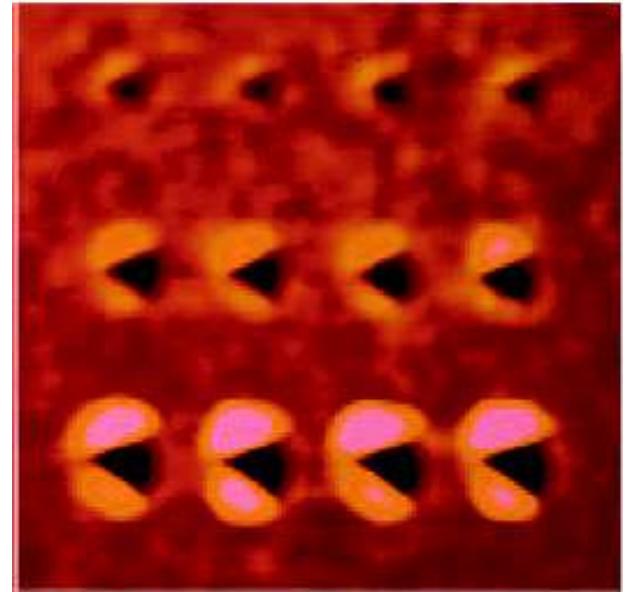
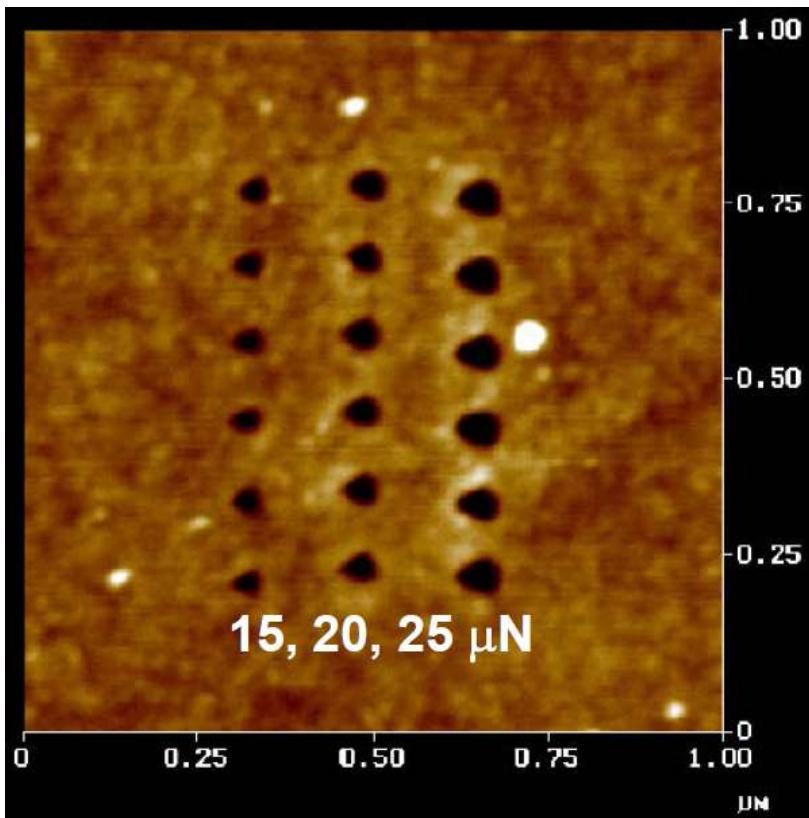
However, here each pen is not individually and independently addressed/controlled, which is not necessary when writing identical arrays (though some tips may hit the surface and get damaged due to lack of feedback).

Scanning probe microscopy (SPM) and lithography

1. Atom and particle manipulation by STM and AFM.
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3. Dip-pen nanolithography (DPN).
4. Resist exposure by STM field emitted electrons.
5. Indentation, scratching, thermal-mechanical patterning.
6. Field evaporation, STM CVD, electrochemical deposition/etching.
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AFM-based nanofabrication: nanoindentation

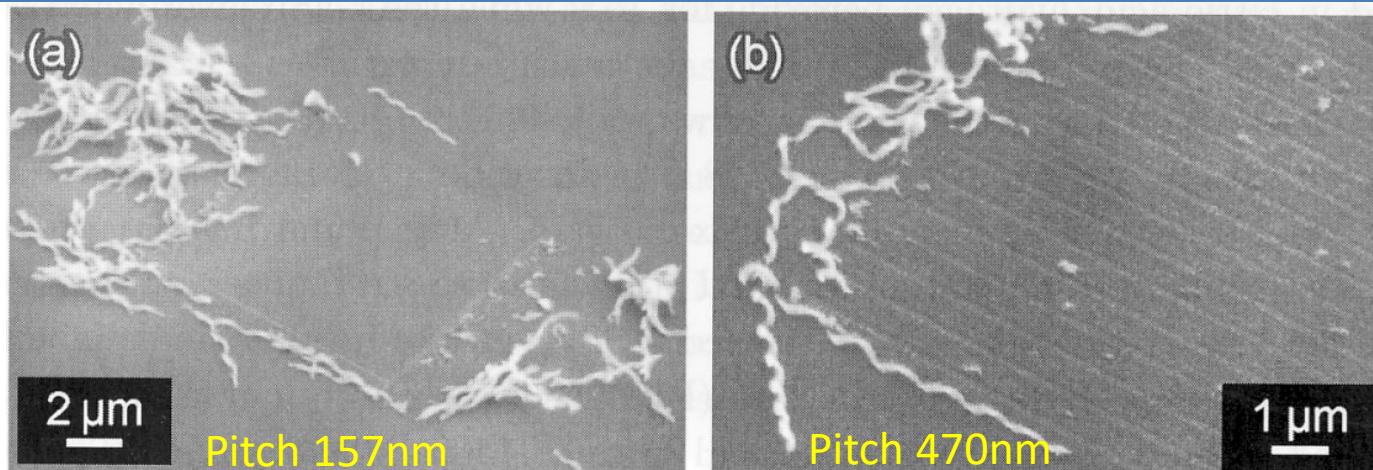
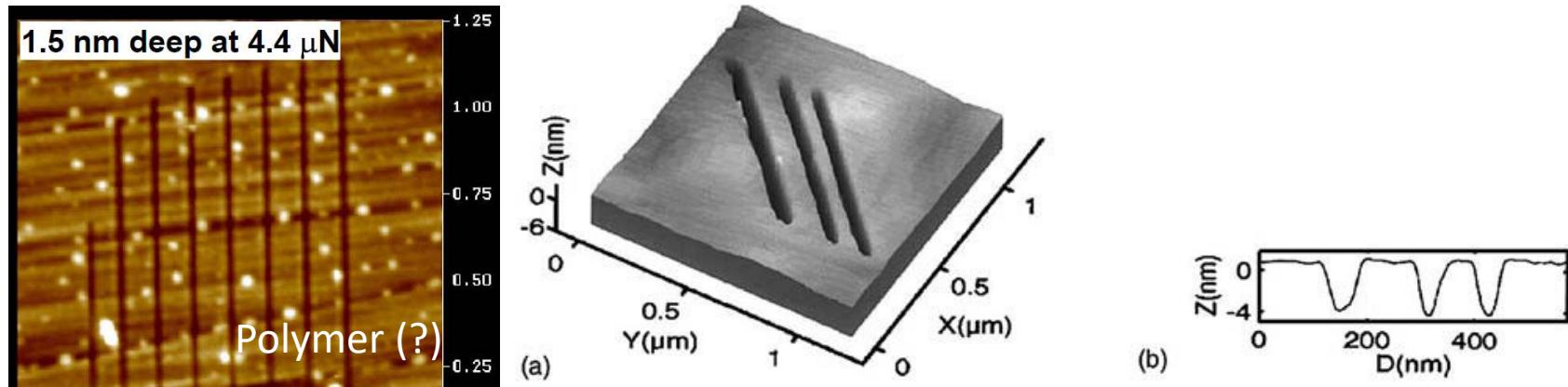
- Popular early examples of nanofabrication using an AFM probe, since it is so simple.
- This approach allows site-specific nanoindentation, and straightforward imaging of the resulting indents immediately after indentation.



Nano-indentations made with an AFM on a diamond-like carbon thin film.

AFM lithography: scratching

- Material is removed by AFM tip scratching.
- SAM (self-assembled mono-layer) can also be removed by tip scratching, which is the inverse process of dip-pen nanolithography.
- As a nanofabrication method this is fairly limited due to the tip wear and debris produced on the surface.
- It can also be used to characterize micro-wear process of materials.

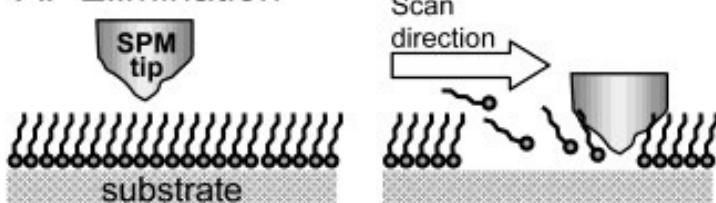


Here silicon was machined using a stiff diamond tip cantilever at a normal load of $2403\mu\text{N}$. One grain of diamond attached to Si AFM tip.

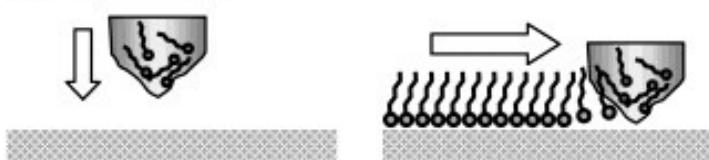
Fabrication using self-assembled mono-layers (SAM)

Schematic diagram illustrating the principles of elimination, addition, and substitution lithographies with a scanning probe

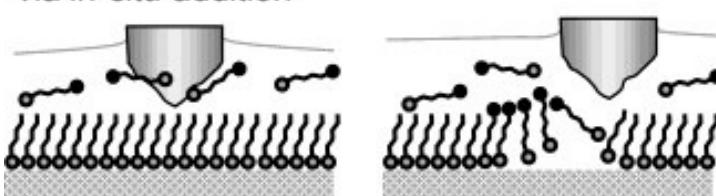
A. Elimination



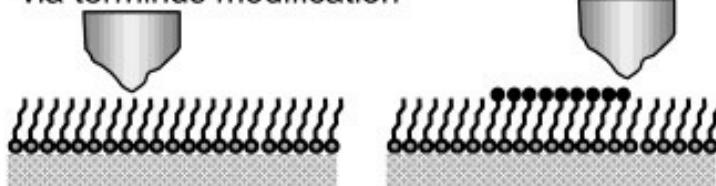
B. Addition



C. Substitution via *in-situ* addition



D. Substitution via terminus modification

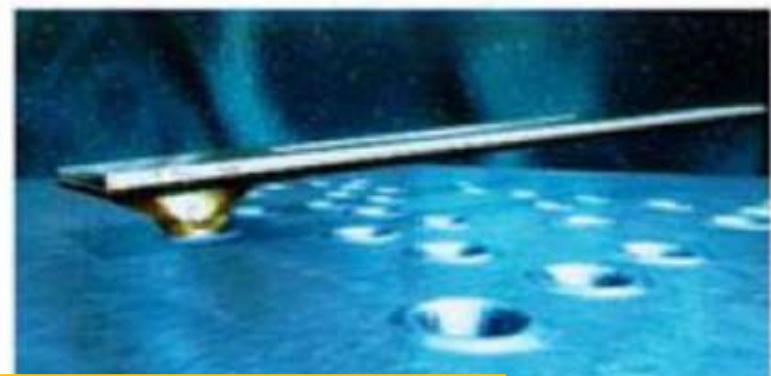
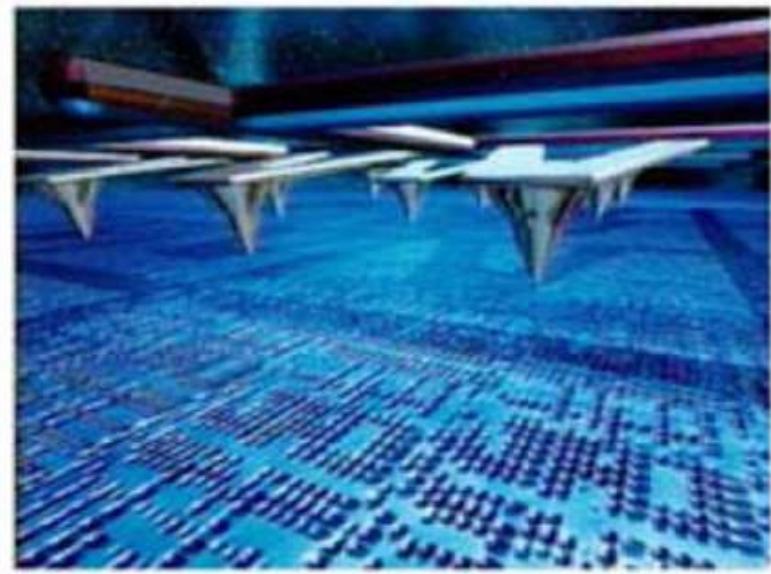


In general, the probe images the surface first with non-destructive imaging parameters, to find an area suitable for patterning.

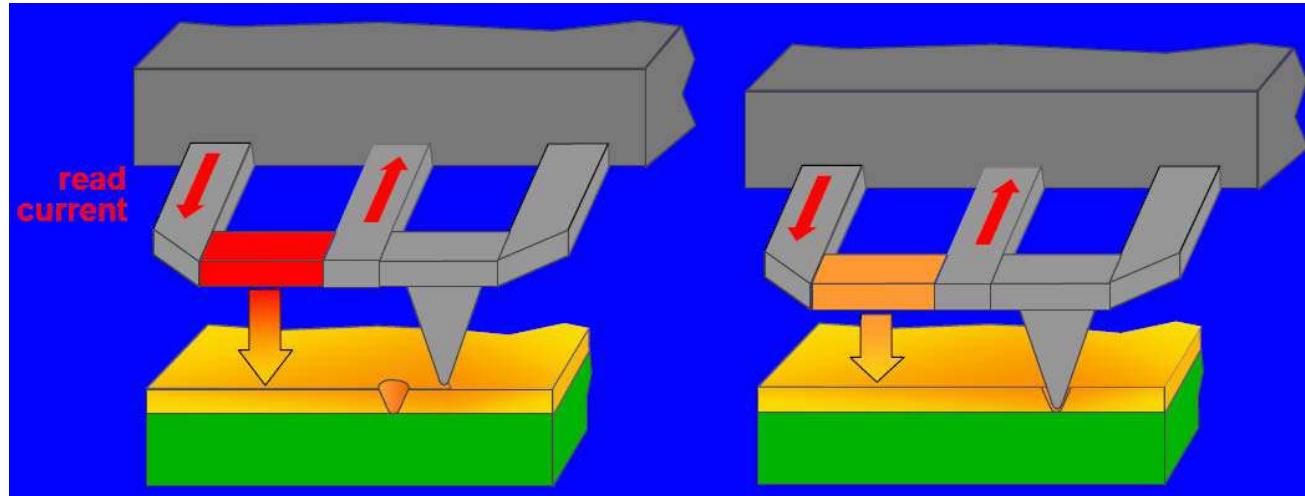
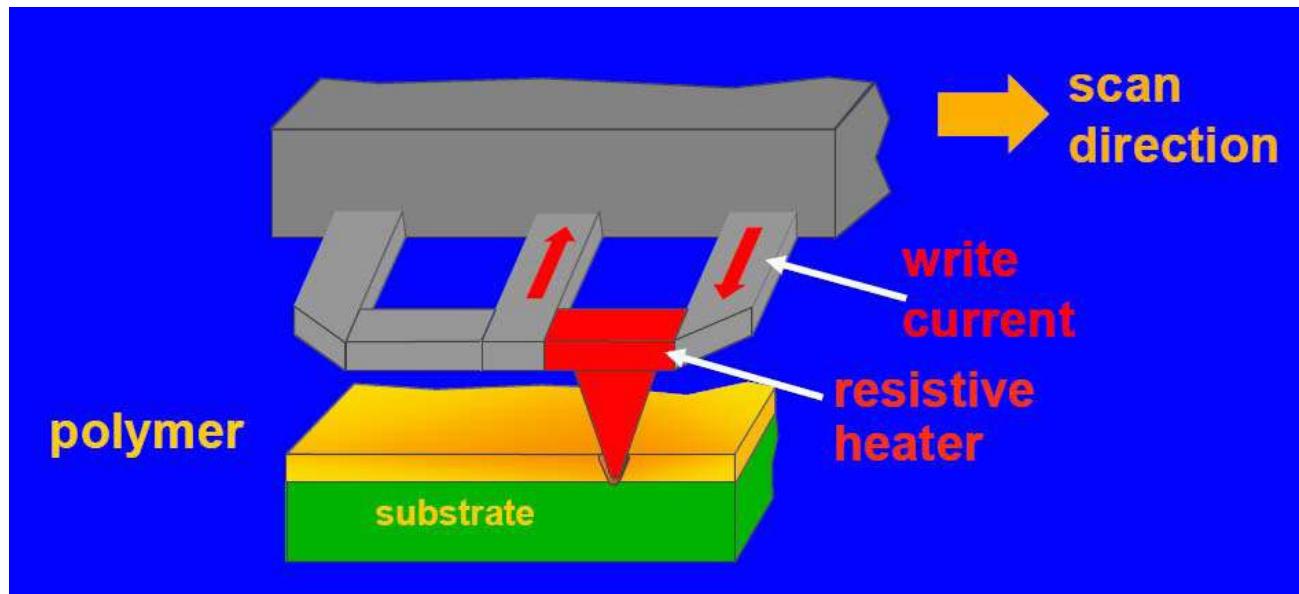
- A. Elimination was achieved by the removal of the SAM in proximity of the probe by mechanical or electrical means.
- B. A probe coated with a molecular "ink" was brought into contact with a nominally "bare" substrate. The ink transferred from the probe to the surface (dip-pen nanolithography).
- C. In the first substitution pathway, the tip removed the SAM while scanning, and an *in-situ* addition of a different molecule into the bare region occurred (substitution via elimination and *in-situ* addition).
- D. The alternative substitution via SAM terminus modification occurred by the probe modifying the head groups of the SAM through electrochemical or catalytic interaction.

Millipede: thermal-mechanical data storage on a polymer

- Tips are brought into contact with a thin polymer film. Each tip is independently controlled.
- Bits are written by heating a resistor built into the cantilever to a temperature of ~400°C. The hot tip softens the polymer and briefly sinks into it, generating an indentation.
- For reading, the resistor is operated at lower temperature, ~300°C. When the tip drops into an indentation, the resistor is cooled by the resulting better heat transport, and a measurable change in resistance occurs.
- The 1024-tip experiment achieved an areal density of 200Gbit/in².
- Very ambitious idea, totally different from previous data storage technologies.
- This project was finally not successful commercially, partly due to too much power needed (too much heat need to be dissipated).

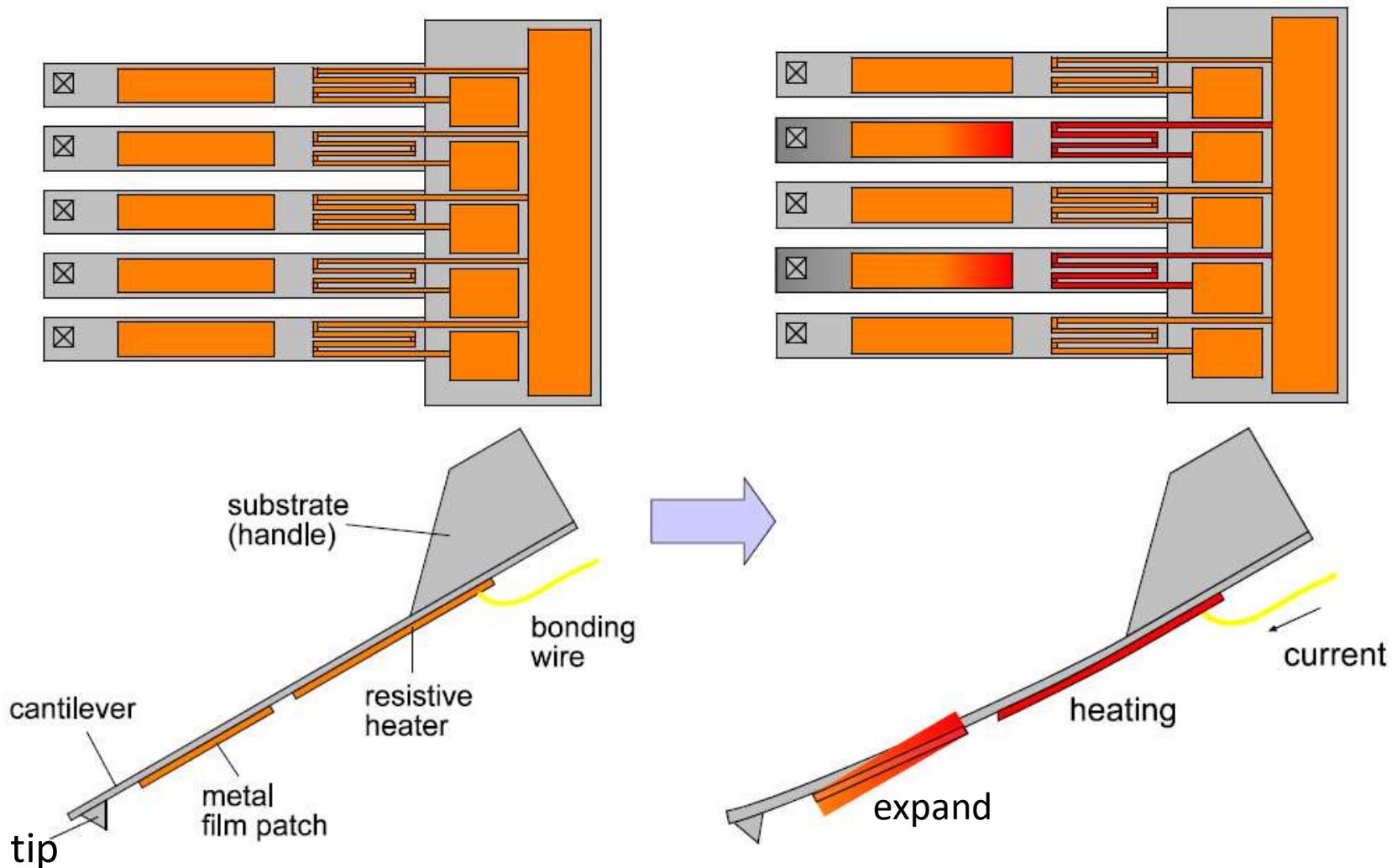


IBM Millipede – write and read



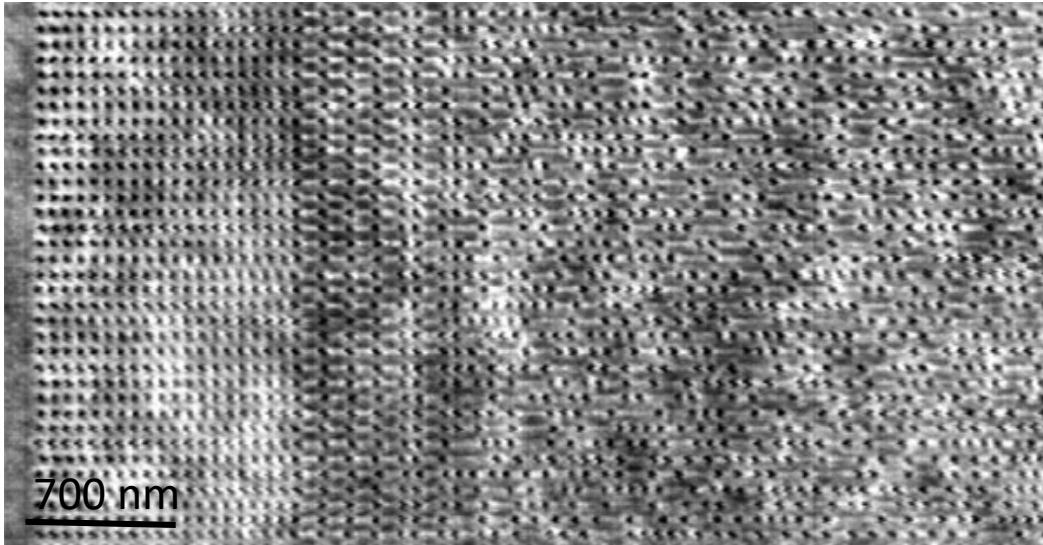
Resistance change:
 $\Delta R/R \approx 10^{-4}/\text{nm}$

Thermal bimetallic actuation



Bi-metal means two metal films one on top of another, here with different thermal expansion.
Go to http://en.wikipedia.org/wiki/Bi-metallic_strip for a nice video.

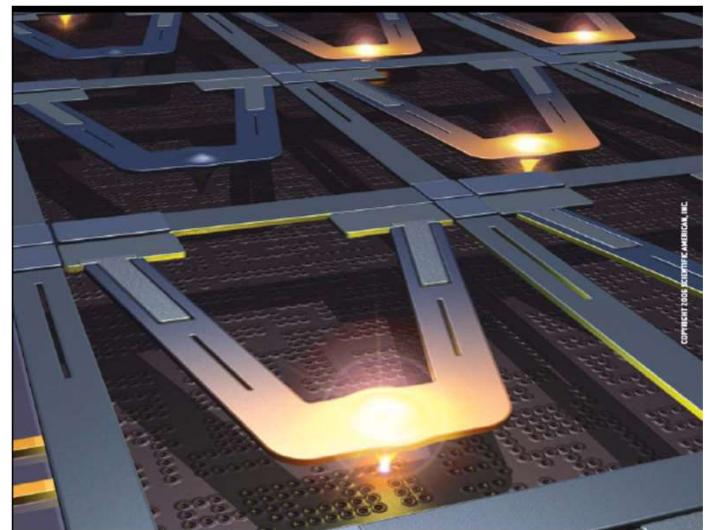
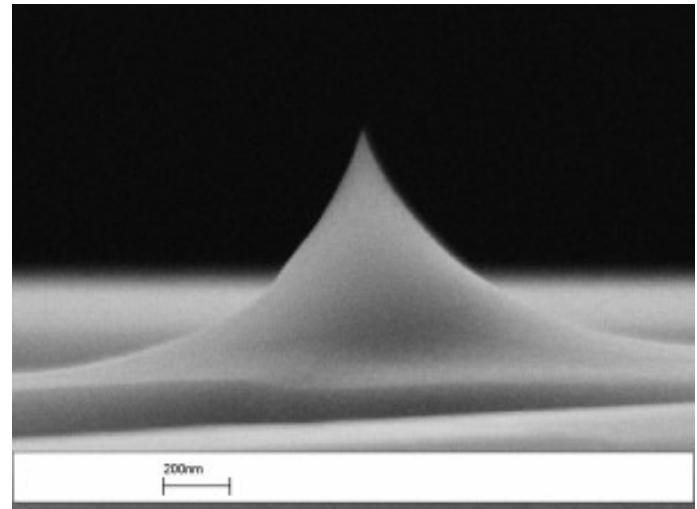
The Millipede data storage



All the nanoscale pits in the array were written simultaneously by the millipede cantilever array. Storage density > 1TBit/in², ϕ of indentations \approx 15 nm, pitch \approx 25 nm.

This is the most successful demonstration of *large scale* nano-patterning using SPM tip-based nanofabrication.

Read/write tip, radius at tip apex a few nm, tip-height 500 - 700 nm

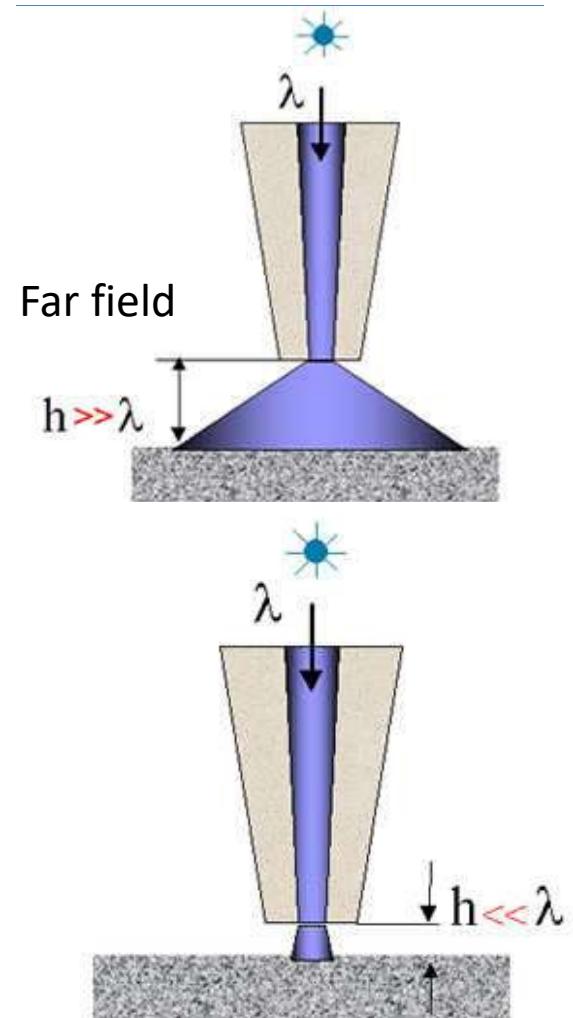


Scanning probe microscopy (SPM) and lithography

1. Atom and particle manipulation by STM and AFM.
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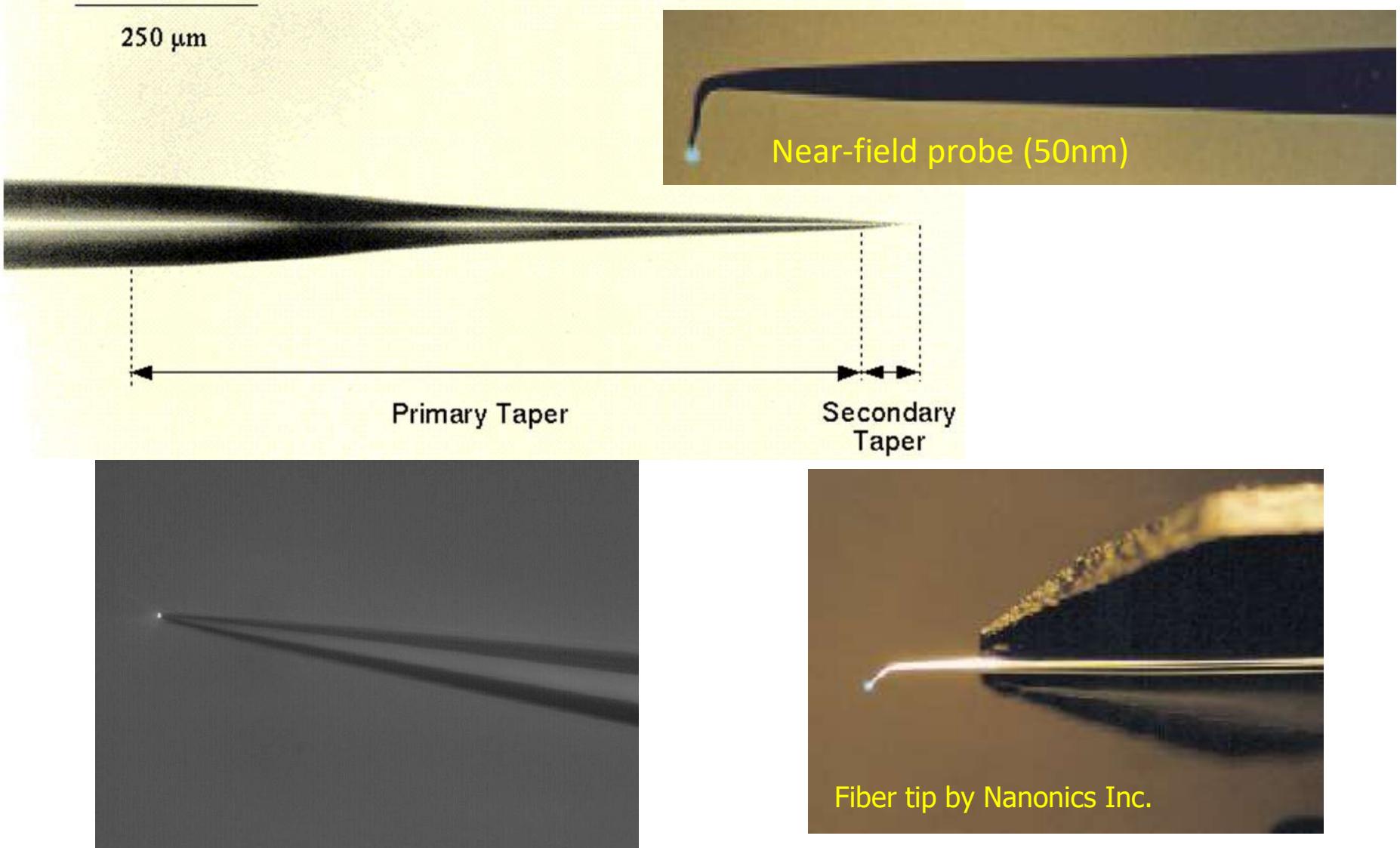
Near field scanning optical microscope (NSOM) or Scanning near field optical microscope (SNOM)

- NSOM is a scanning optical microscopy technique that enables users to work with standard optical tools beyond the diffraction limit.
- It works by exciting the sample with light passing through an aperture formed at the end of a single-mode drawn optical fiber, whose diameter is only tens of nanometers.
- Broadly speaking, if the aperture-specimen separation is kept roughly less than half the diameter of the aperture, the source does not have the opportunity to diffract before it interacts with the sample, and the resolution of the system is determined by the aperture diameter as oppose to the wavelength of light used.
- An image is built up by raster-scanning the aperture across the sample (or fix the aperture while scanning the sample) and recording the optical response of the specimen through a conventional far-field microscope objective.



Nearfield imaging

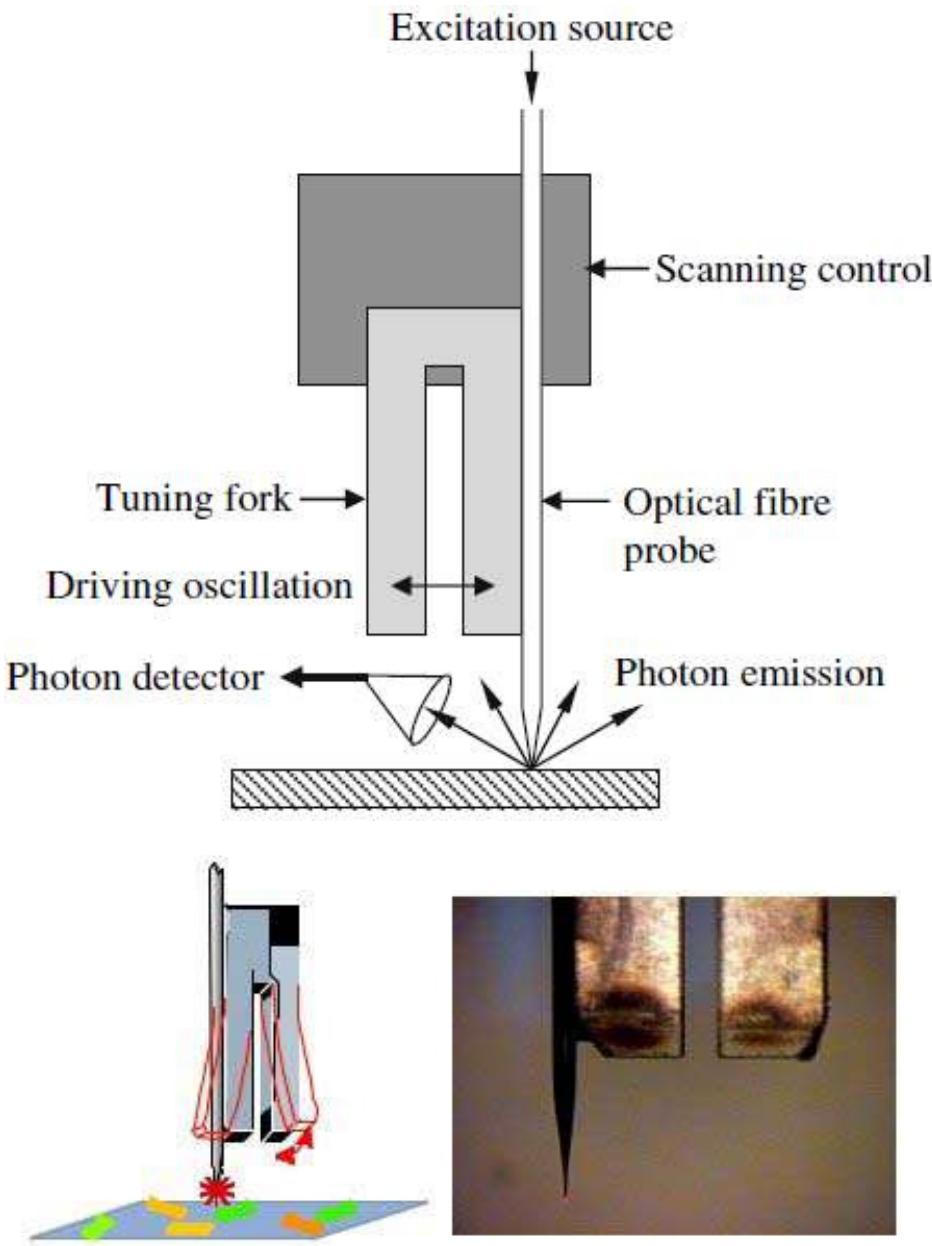
Melt-drawn straight NSOM tip



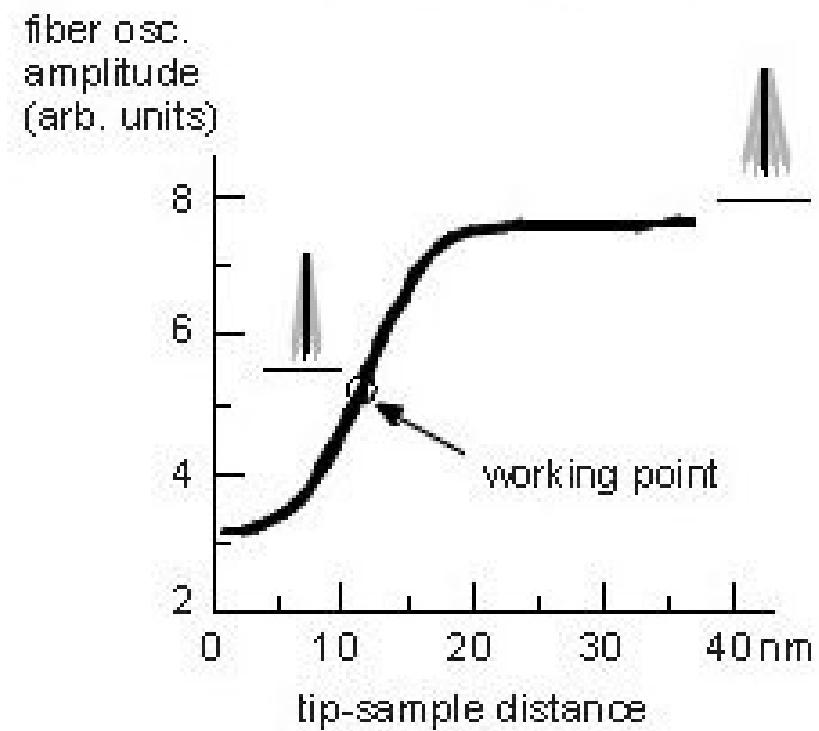
Melt drawn from a single optical fiber with the core material already removed.

Review paper: Tseng, "Recent developments in nanofabrication using scanning near-field optical microscope lithography", Optics & Laser Technology, 39, 514-526 (2007).

Tuning fork based shear-force detection

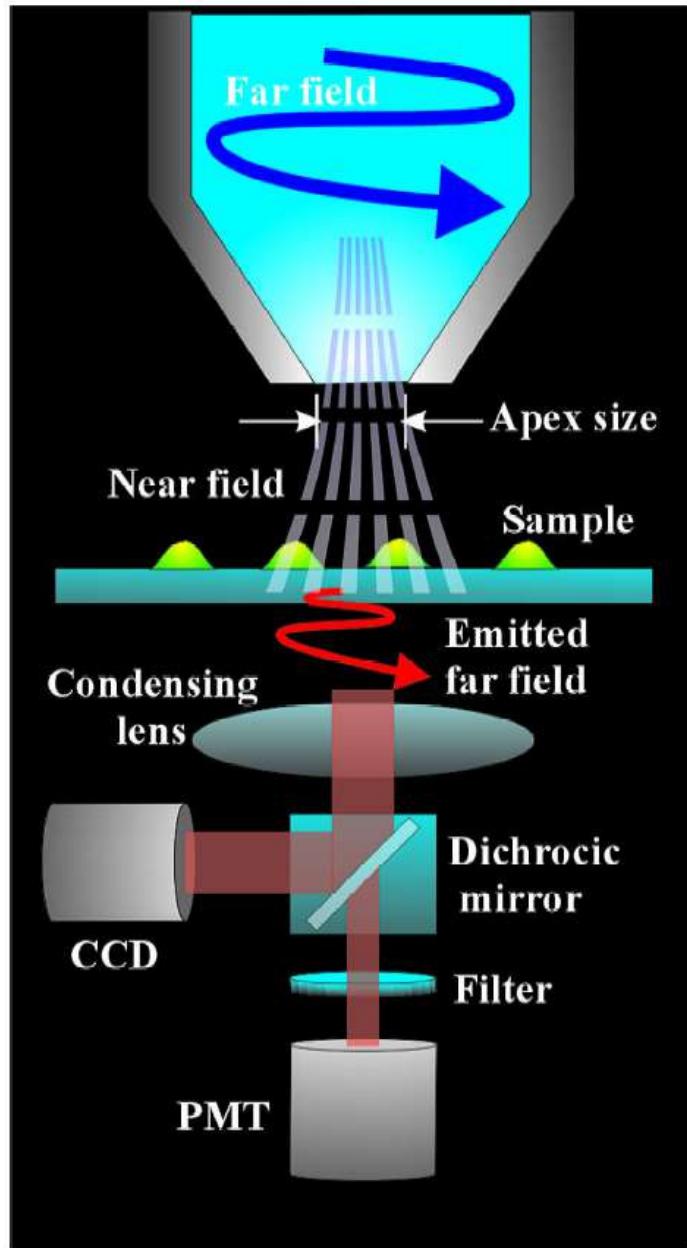


tip approach curve

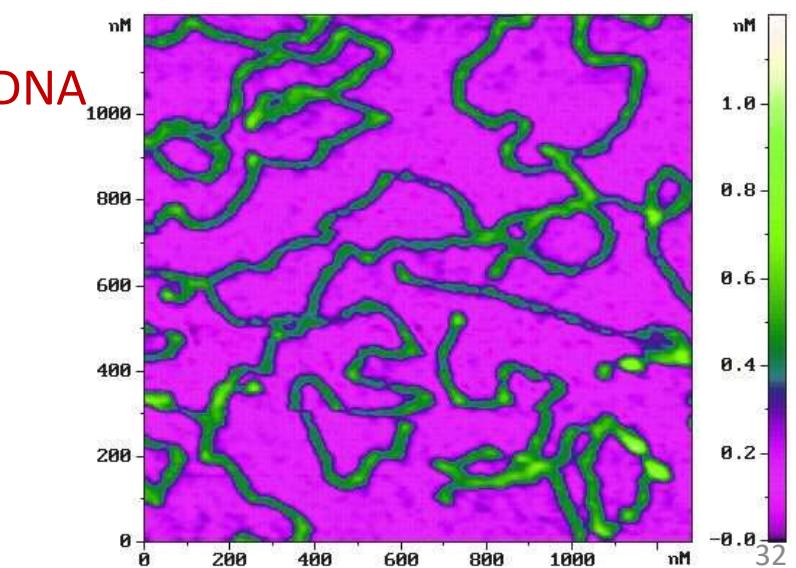
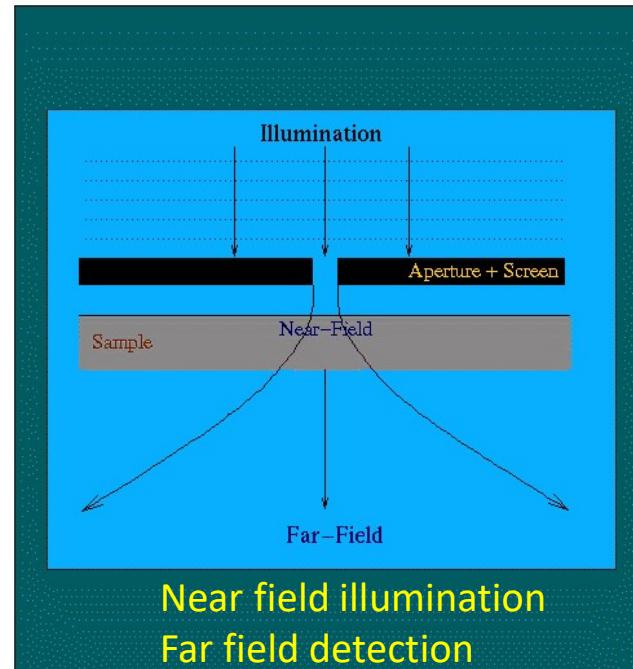


The farther away from sample surface,
the less damped vibration.
Control system keeps the optical probe at
constant distance from the sample.

Near-field microscope (for imaging)



Near field illumination, far field detection



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Near-field lithography: direct serial writing



Tapping mold image of a lithography test pattern. The Aurora-3 used nanolithography software to write into S1805 photoresist. Scan size 25μm.

Serial writing/exposure of a photo-resist using fiber tip, like photolithography, but with high resolution and is very slow.

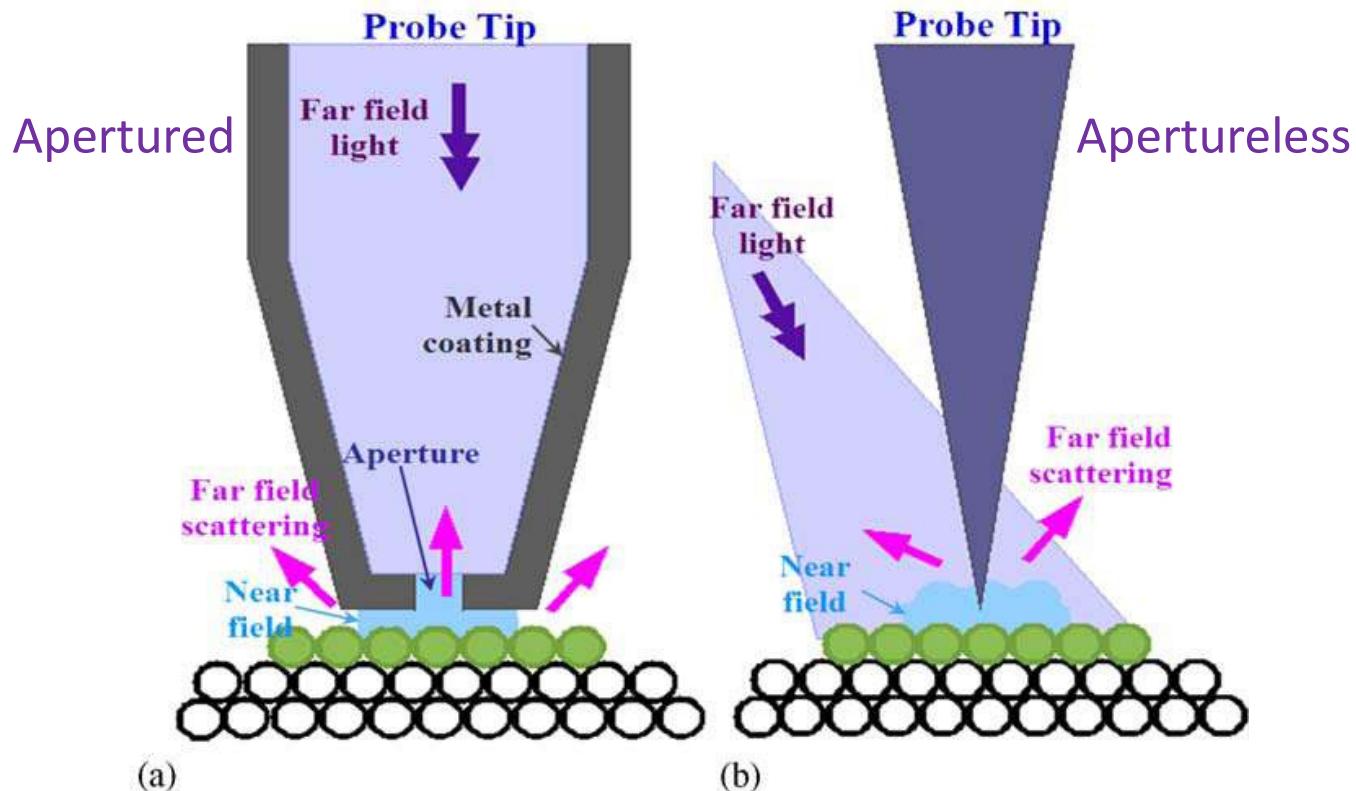
Comparison of apertured and apertureless SNOM

Apertured: low light intensity, slow writing, tip very difficult to make small and flat at the end.

For typical wavelengths, if the aperture is 100nm, less than third orders of magnitude of light can pass through; when it reaches 50nm, only $1/10^7$ light makes it through.

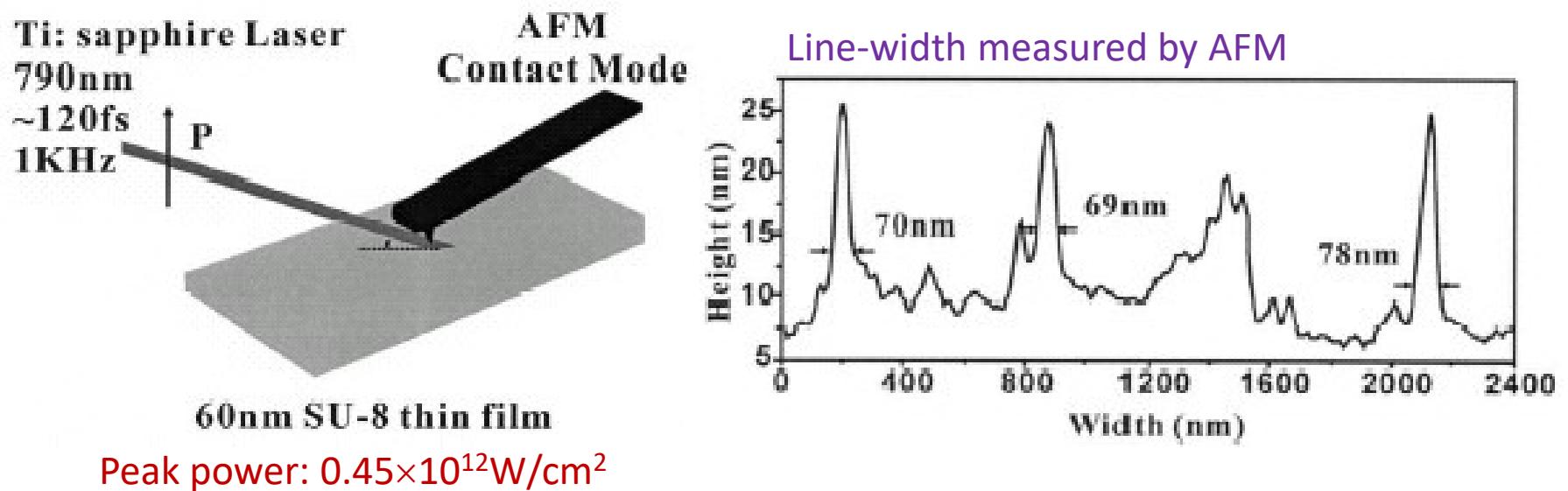
Apertureless: metal tip easy to make tiny, so demonstrated higher resolution (40nm). Light is greatly enhanced at the metal tip due to “lightning rod” (surface plasmon resonance) effect. However, stray light everywhere that may expose resist nearby.

Both: good only for thin resist (sub-50nm) since it is near (evanescent) field.



Two photon near-field optical lithography

790nm cannot expose SU-8, but $790/2=395\text{nm}$ can.



- Achieve $\sim\lambda/10$ resolution by focusing femto-second laser beam onto Au coated AFM tip in close proximity to SU-8.
- Two-photon polymerization occurs in SU-8 over confined regions due to local enhancement of electromagnetic field by surface plasmon on metal AFM tip.
- Different from two-photon lithography in that here the field is “focused” (enhanced) by the tip, not by a focusing lens.

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

Those are the three most important self-assembly techniques, widely used for nanofabrication, with numerous publications each year.

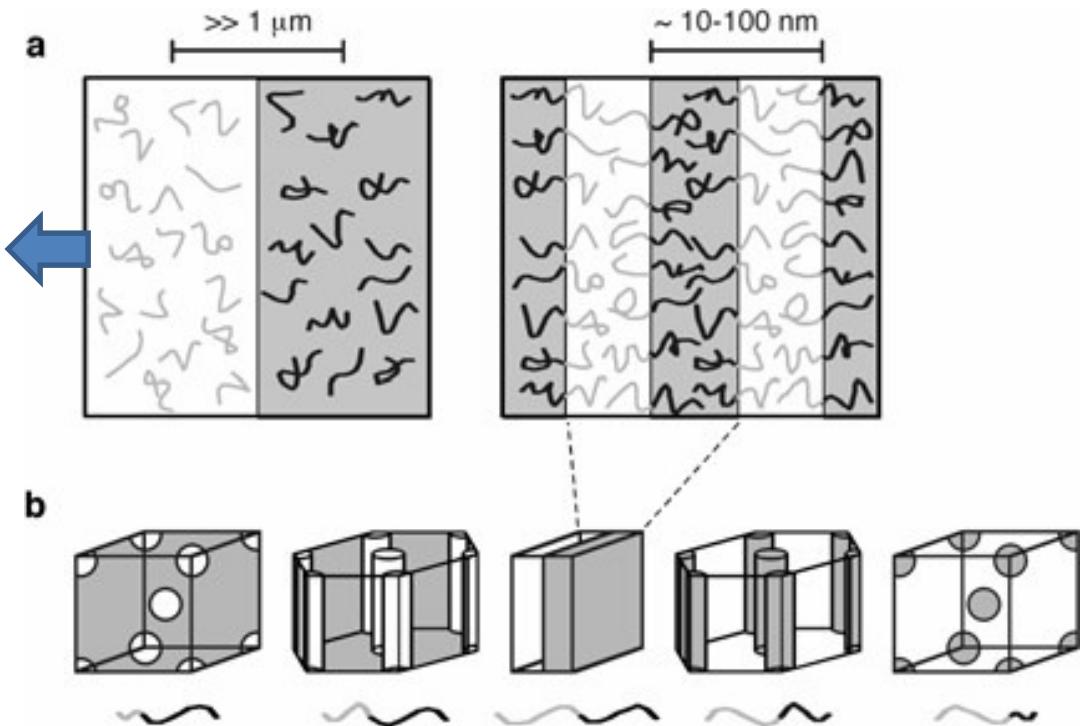
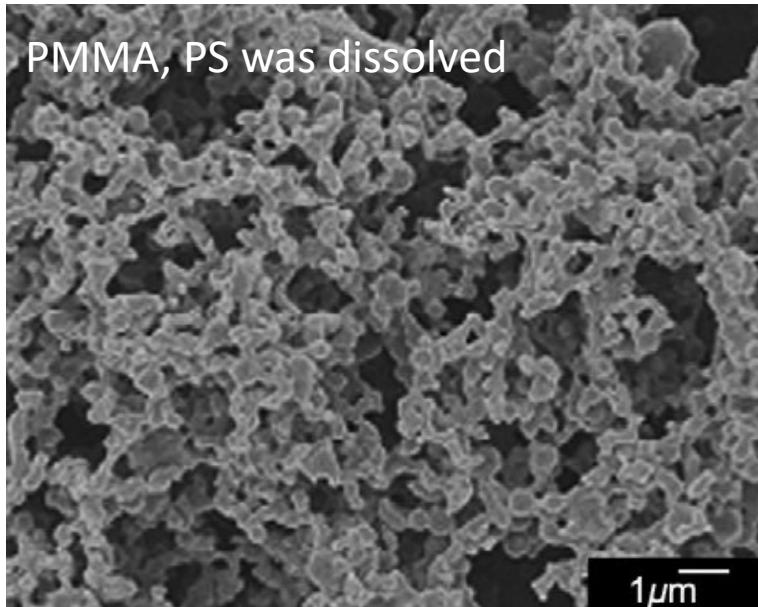
Basically, for those who don't have access or don't like too much EBL, FIB or imprint, they can often use self-assembly fabrication to demonstrate their idea.

The most significant advantage of self-assembly is low cost.

The biggest limit: only periodic pattern can be created, usually without long range ordering.

Phase separation of block copolymers

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

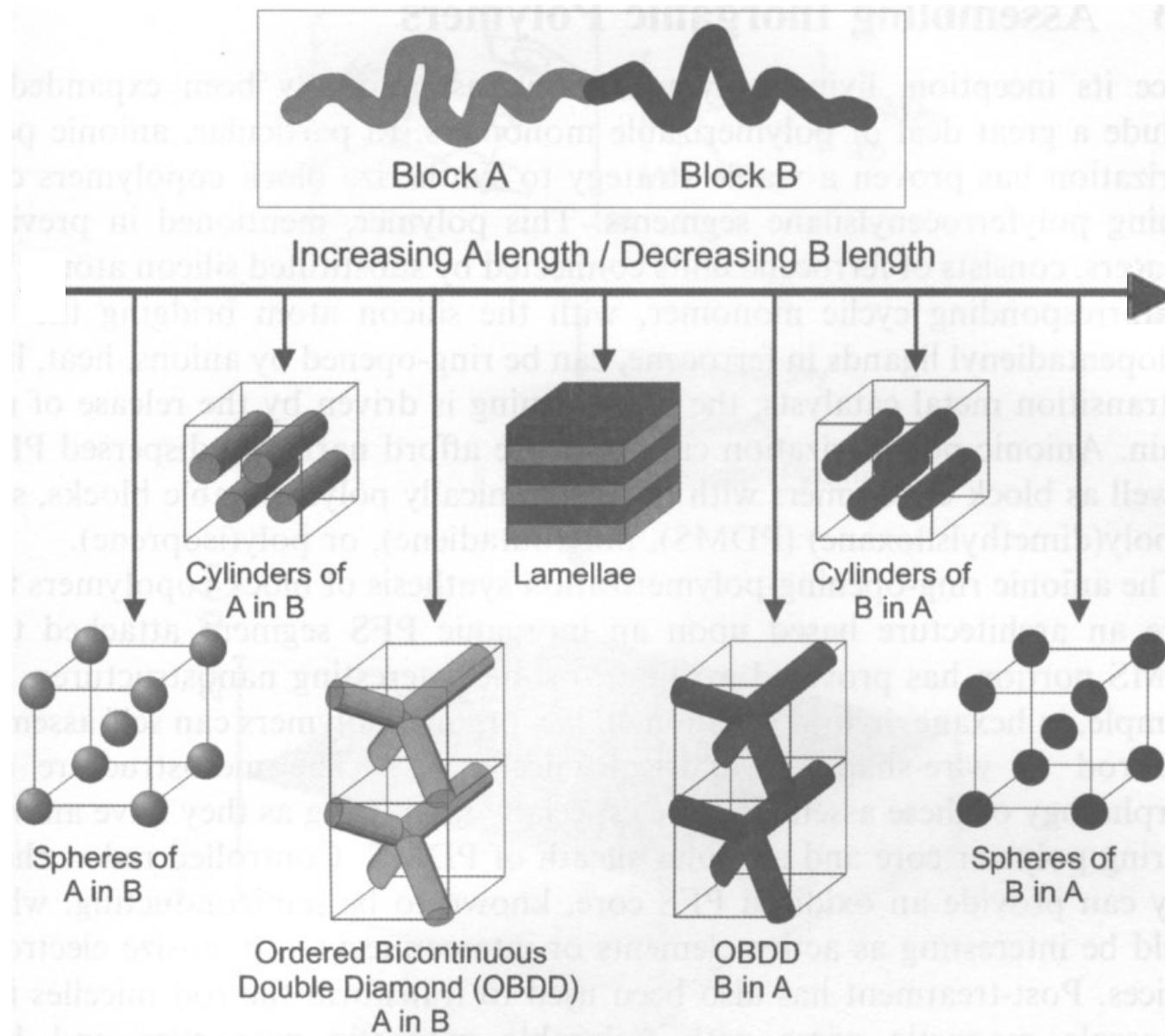


1. A mixture of PMMA ($M_w=93.9 \text{ kg/mol}$) and polystyrene (PS, $M_w=194.9 \text{ kg/mol}$) (PS/PMMA=70/30, w/w) was dissolved in tetrahydrofuran (THF) to form a 5 wt% solution.
2. Polymer film was made by spin-cast the solution on glass slide.
3. Exposure to cyclohexane at 70°C to dissolve PS.

- A 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).
- Basic morphologies obtained by different block copolymer compositions.

Ma, "Fabrication of super-hydrophobic film from PMMA with intrinsic water contact angle below 90°", Polymer, 48, 7455-7460 (2007).

Typical self assembly behavior for linear block copolymers



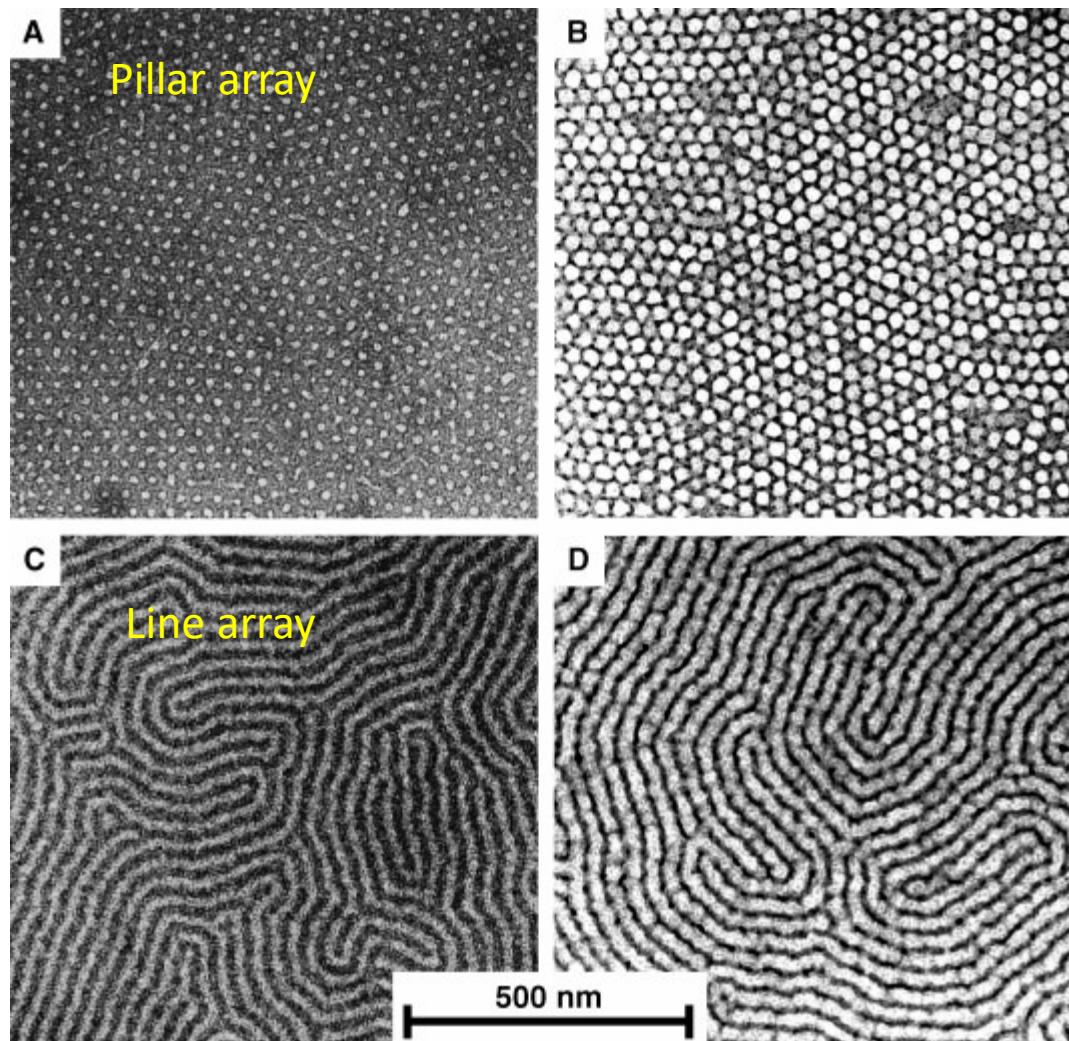
Typical self assembly behavior for linear block copolymers

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

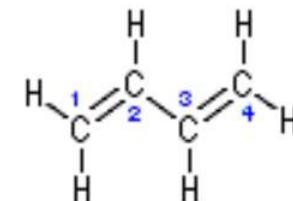
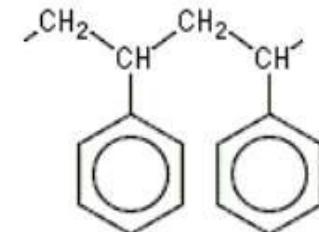
Block copolymer self-assembly study is started in the bulk phase, as shown above; whereas thin film is desired for nanofabrication and device application.

When film thickness is well controlled, hole/pillar array or line array pattern can be created.

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



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.

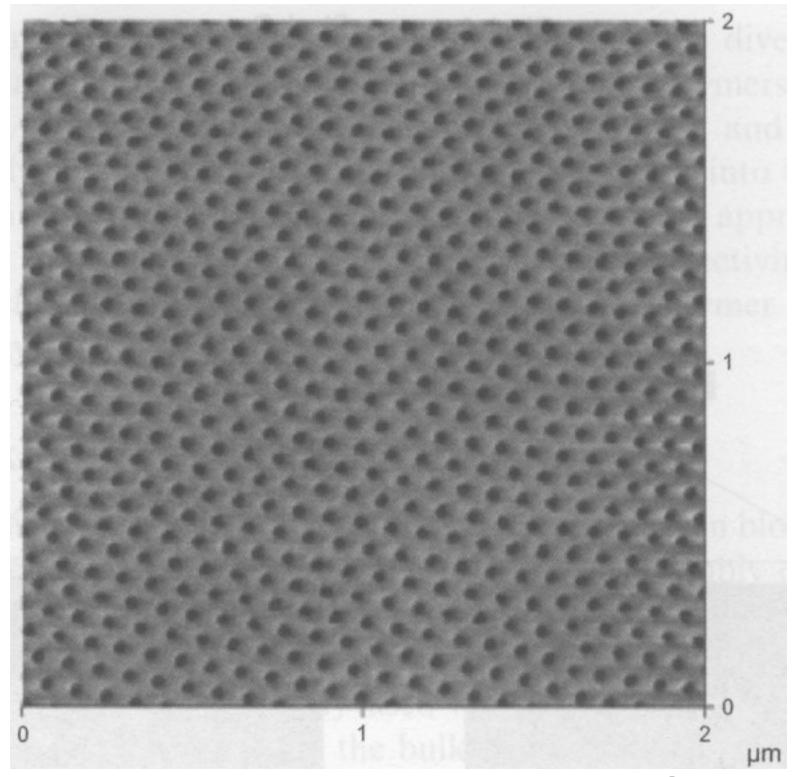
TEM images of PS-PB diblock copolymer film masks (a,c) and lithographically patterned silicon nitride (b,d).

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 at 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.



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

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Review papers:

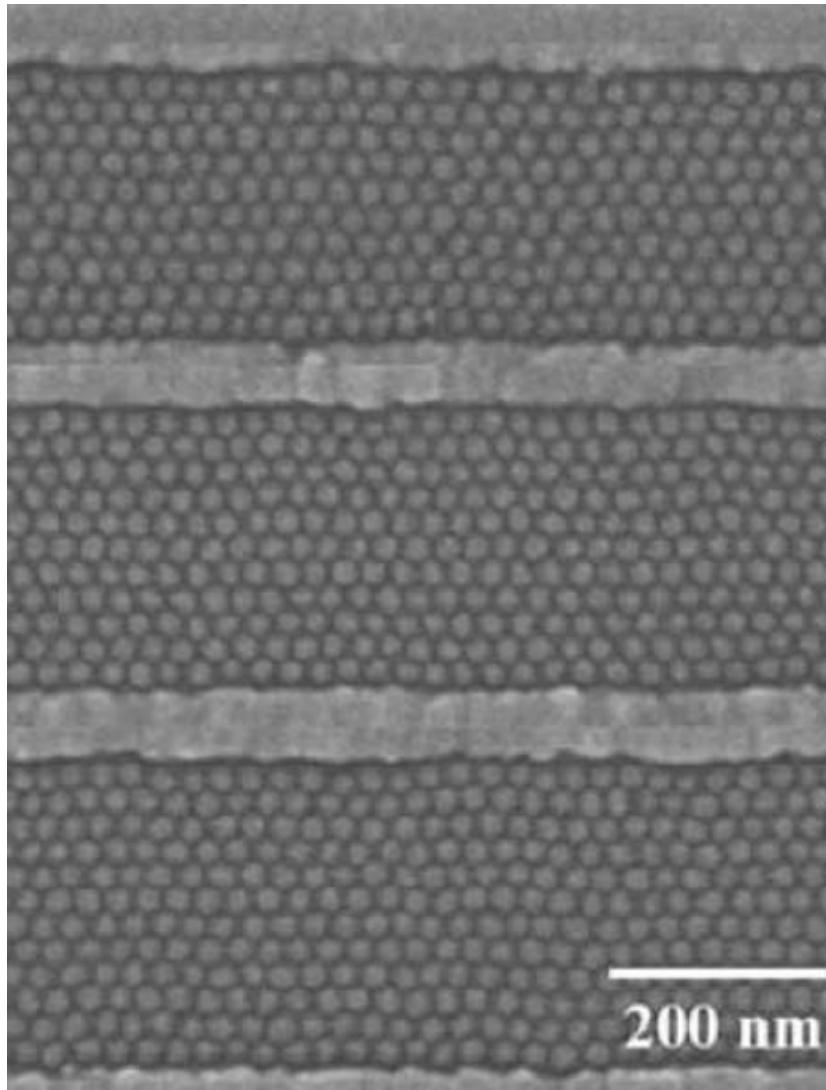
- R. A. Segalman, "Patterning with block copolymer thin films", Materials Science and Engineering R, 48, 191-226 (2005).
- Y. Tseng and S. B. Darling, "Block copolymer nanostructures for technology", Polymers, 2, 470-489 (2).
- M. Luo and T. H. Epps III, "Directed copolymer thin film self-assembly: emerging trends in nanopattern fabrication", Macromolecules, 46, 7567-7579 (2013).
- S. J. Jeong, J. Y. Kim, B. H. Kim, H. S. Moon and S. O. Kim, "Directed self assembly of block copolymers for next generation nanolithography", Materials Today, 16, 468-476 (2013).
- X. Gu, I. Gunkel and T. P. Russel, "Pattern transfer using block copolymers", Phil. Trans. R. Soc. A, 371, 20120306 (2012).
- H. C. Kim, S. M. Park and W. D. Hinsberg, "Block copolymer based nanostructure: materials, processes, and applications to electronics", Chem. Rev., 110, 146–177 (2010).

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

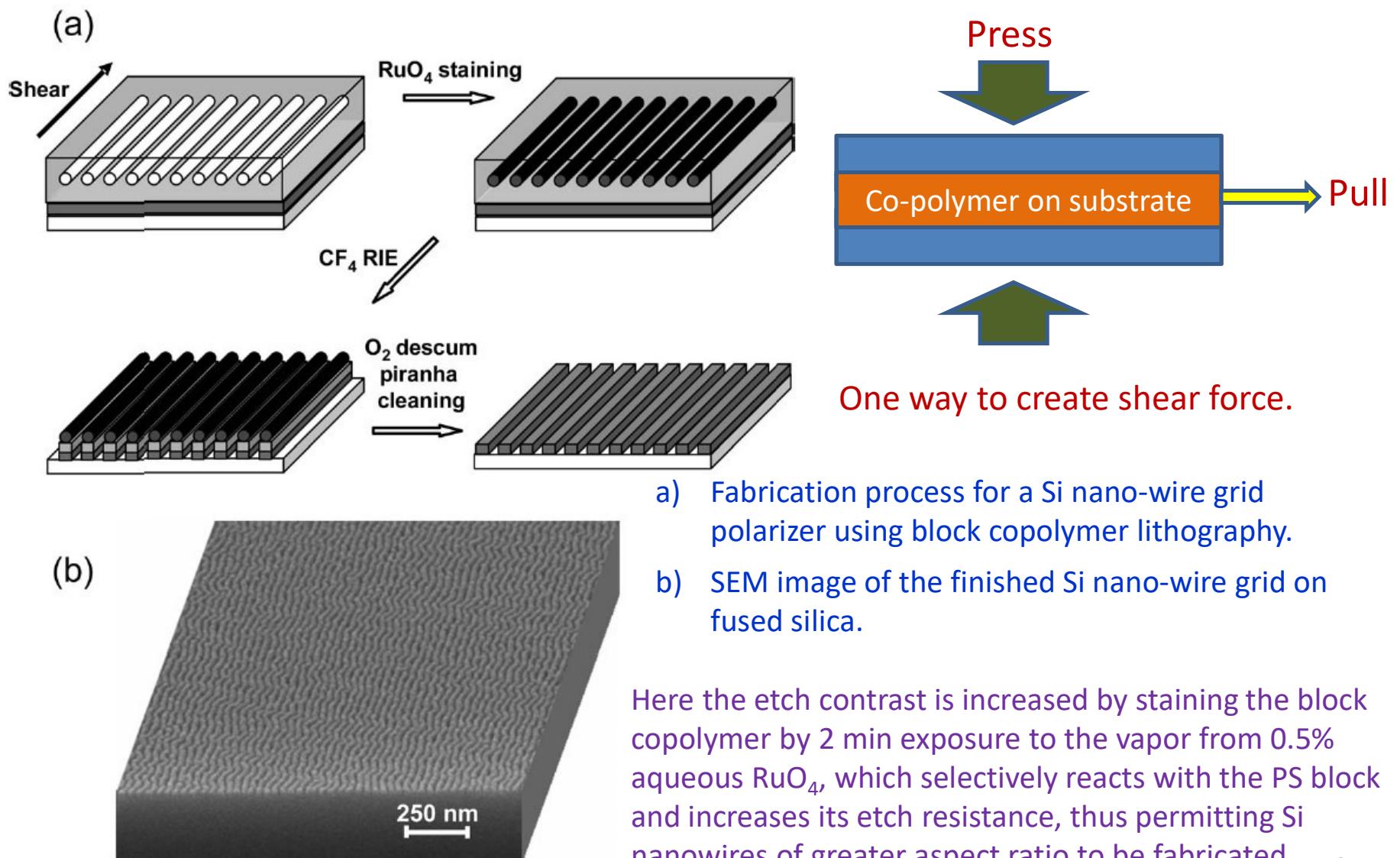
Alignment by pre-patterning the substrate



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

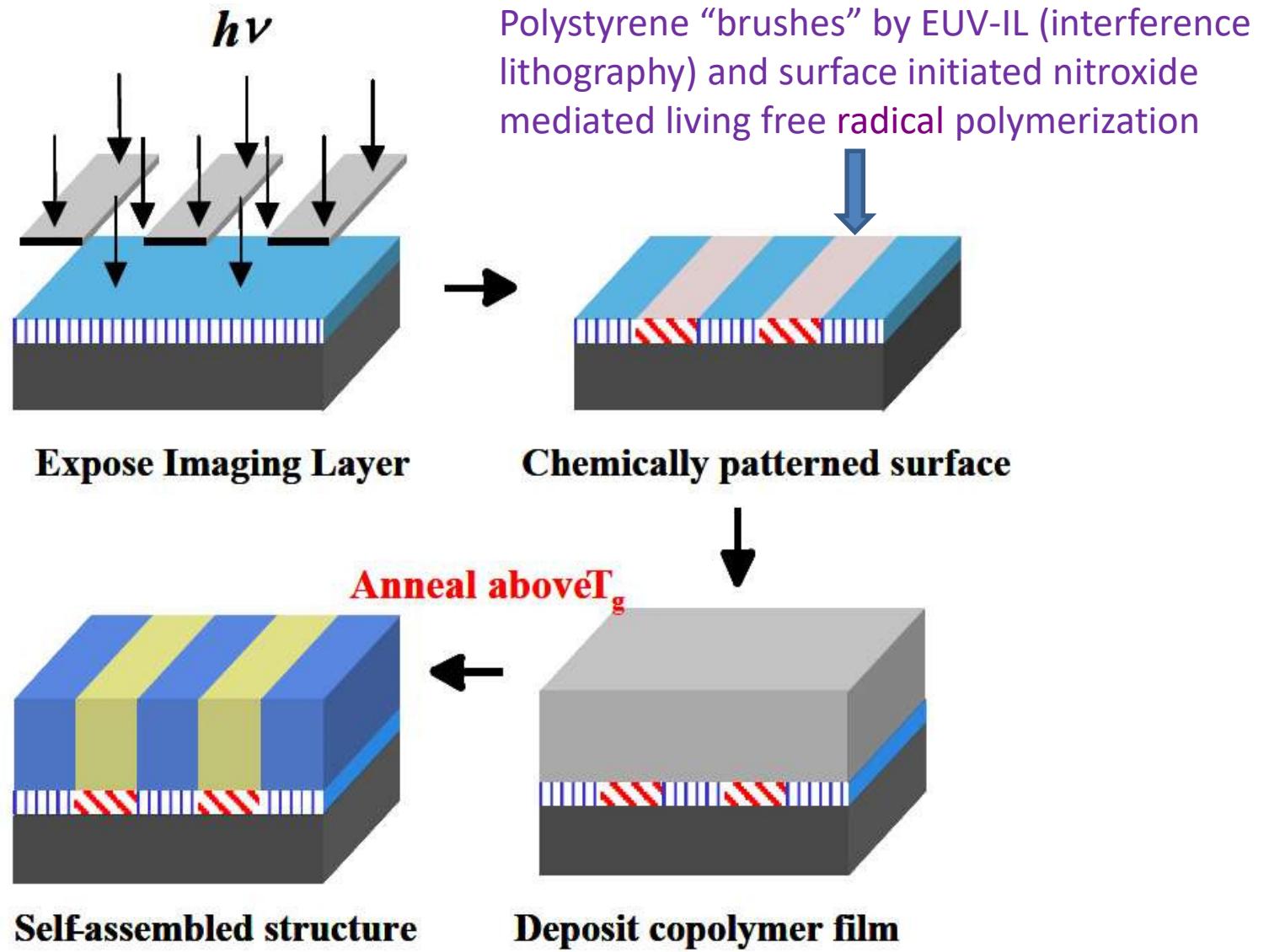
The 1.5 wt.% PS-PFS block copolymer in toluene solution was spin-coated onto the grooved substrate and then annealed at 140°C for 48h to obtain a monolayer of spherical PFS domains in a PS matrix within the substrate grooves.

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

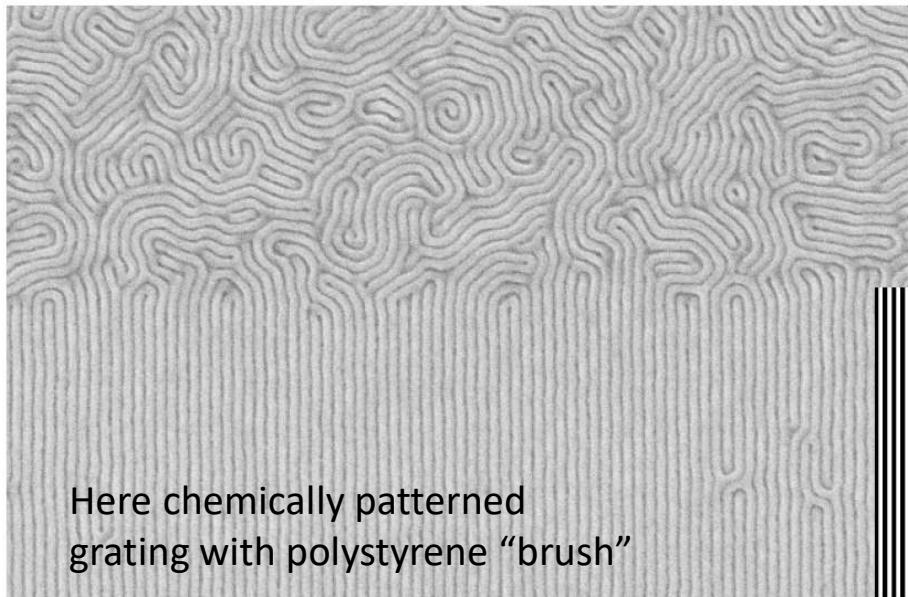


Here the etch contrast is increased by staining the block copolymer by 2 min exposure to the vapor from 0.5% aqueous RuO₄, which selectively reacts with the PS block and increases its etch resistance, thus permitting Si nanowires of greater aspect ratio to be fabricated. 10

Templated self-assembly of block copolymers



Polymerization of block-copolymers on chemically pre-patterned substrates



unpatterned
substrate area

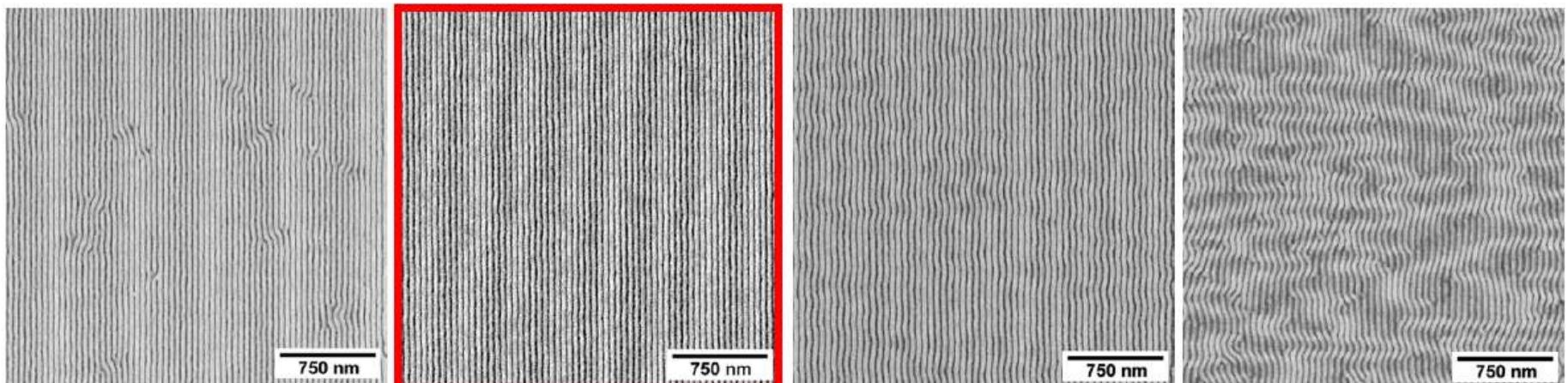
Polystyrene-block-methyl meth acrylate (PS-b-PMMA), $L_o = 48\text{nm}$



patterned
substr. area

Thermodynamics dominates interface widths and domain sizes.

When $L_s=47.5\text{nm} \approx L_o=48\text{nm}$, block copolymer is almost defect free.



$L_s = 45\text{ nm}$

$L_s = 47.5\text{ nm}$

$L_s = 50\text{ nm}$

$L_s = 52.5\text{ nm}$

12

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

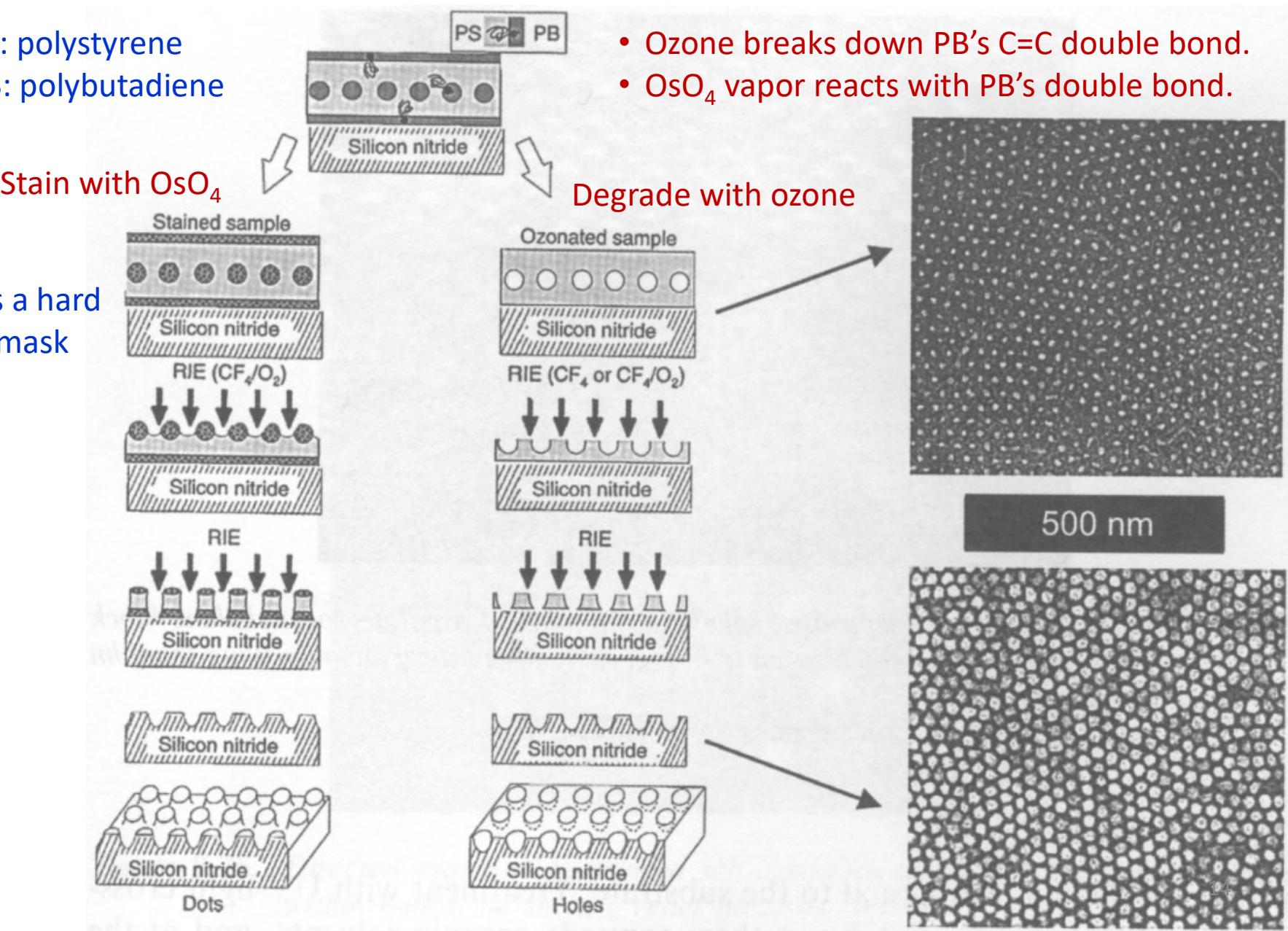
1. Di-block copolymer self assembly overview.
2. Guided (directed, aligned) self assembly.
3. Block copolymer lithography.
4. Anodized aluminum oxide (AAO) overview.
5. Nanofabricating using AAO template

Block copolymer lithography (add pattern transfer)

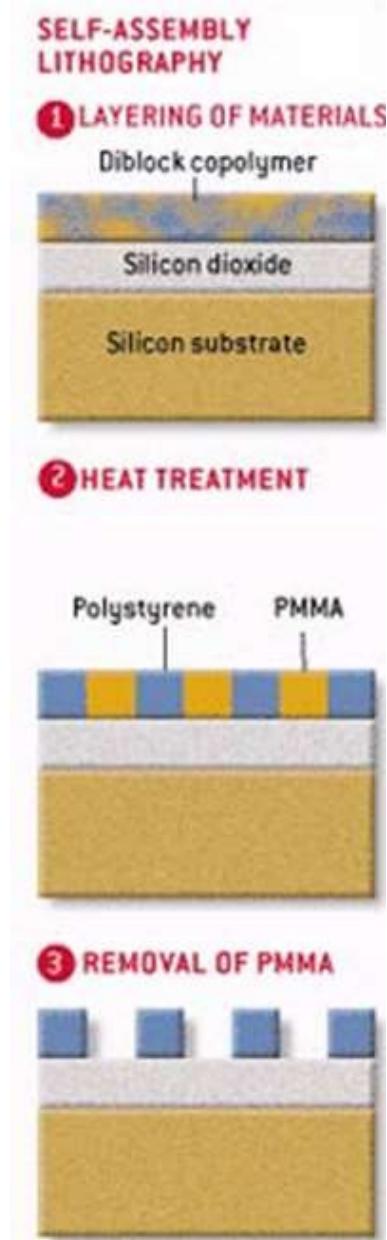
PS: polystyrene

PB: polybutadiene

O_s is a hard
RIE mask

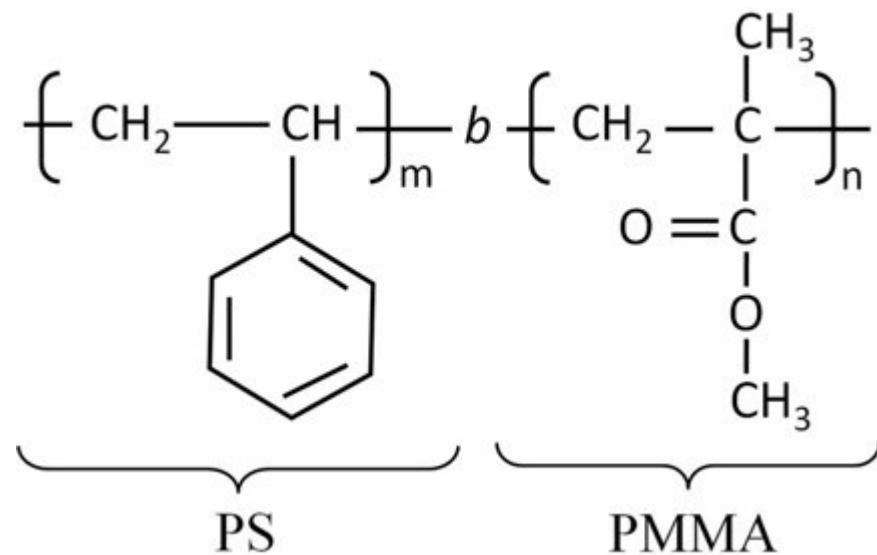


Block copolymer lithography using PMMA-PS

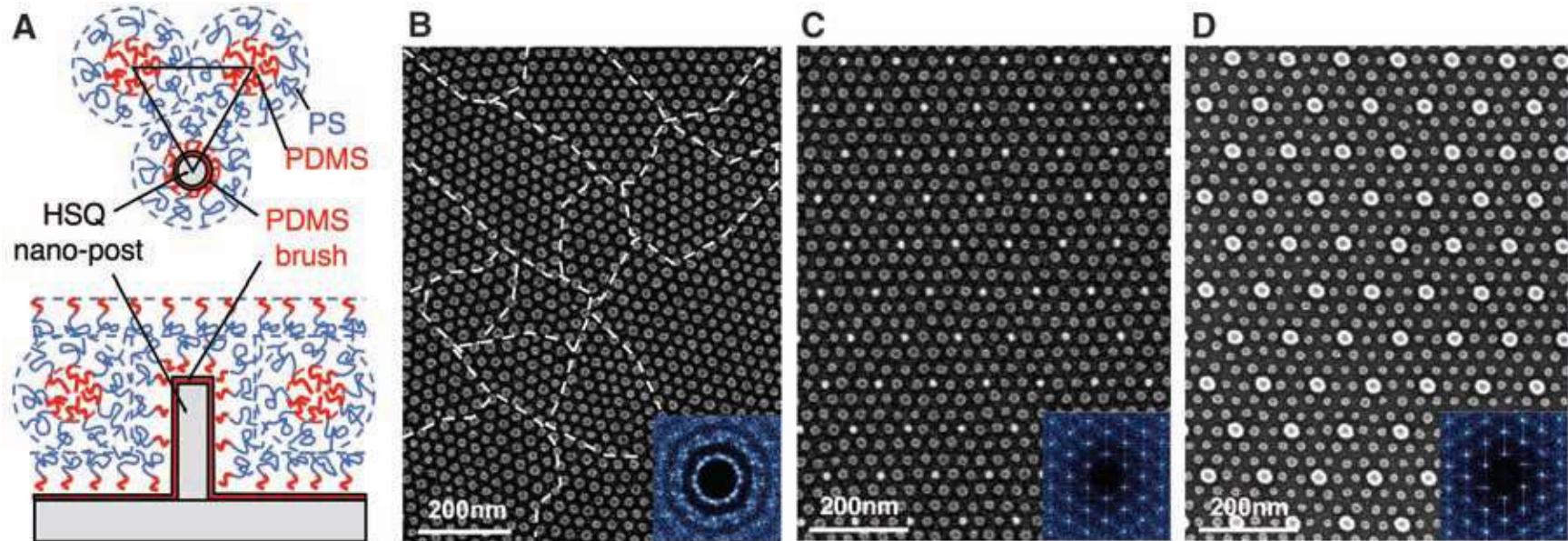


- After deep UV-exposure, polymer chain of PMMA is cut (PMMA is a positive deep UV lithography resist), making it more soluble in solvent.
- Whereas the polystyrene (PS) chain is cross-linked, making it hard to dissolve by solvent.
- Therefore, PMMA can be selectively removed by solvents like acetic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

(PMMA chain can also be broken by UV light at $\lambda=365\text{nm}$, but need very long time exposure, $\sim 1 \text{ h}$ at 40mW/cm^2 intensity)



Density multiplication (here by 9x) 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

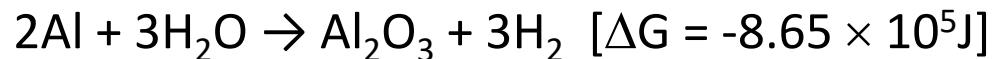
For the moment, this is considered as the most promising route for bit-patterned magnetic recording media fabrication (make the mold for nanoimprint lithography), up to 10Tbits/in² for pitch ~8nm.

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

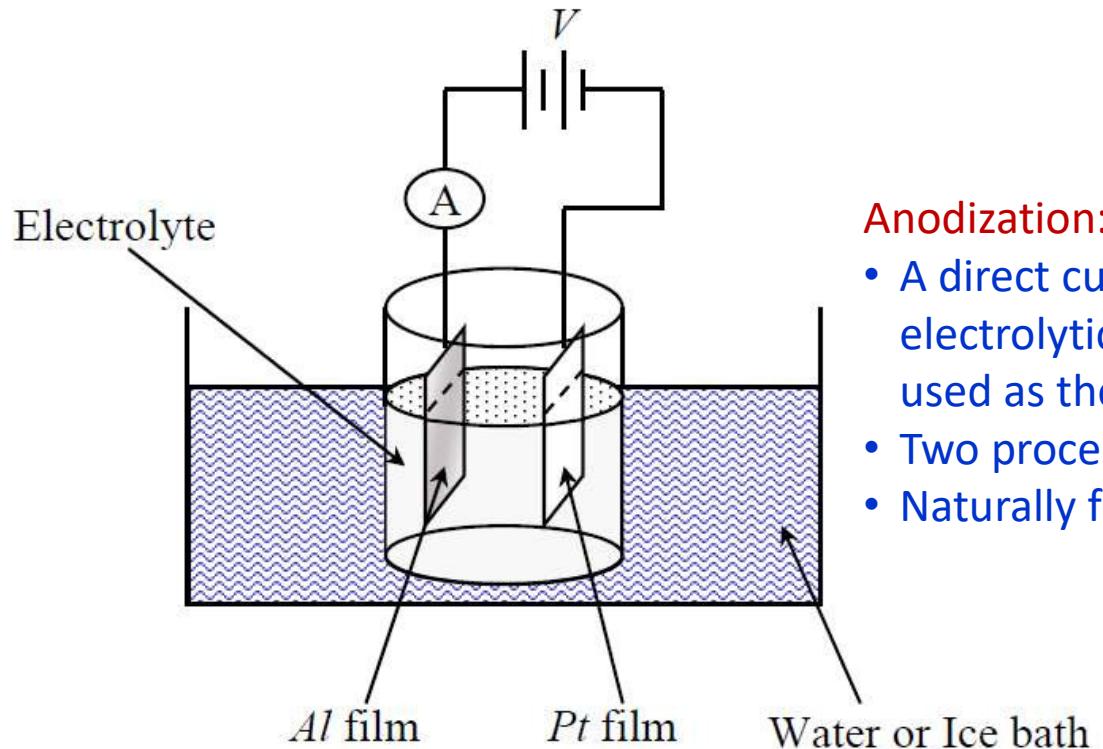
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Aluminum anodization setup

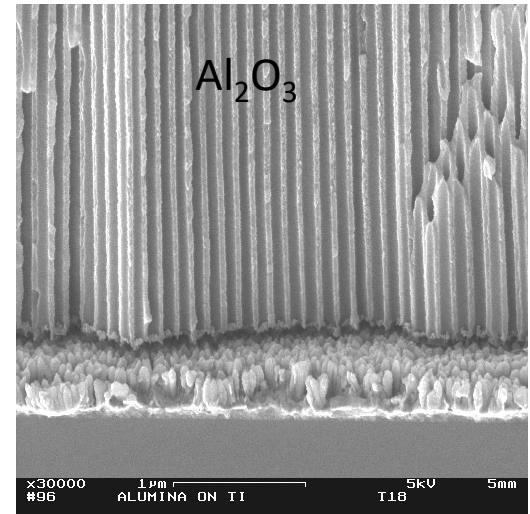
Anodization Reaction :



Experiment Setup :



Porous anodized aluminum



Anodization:

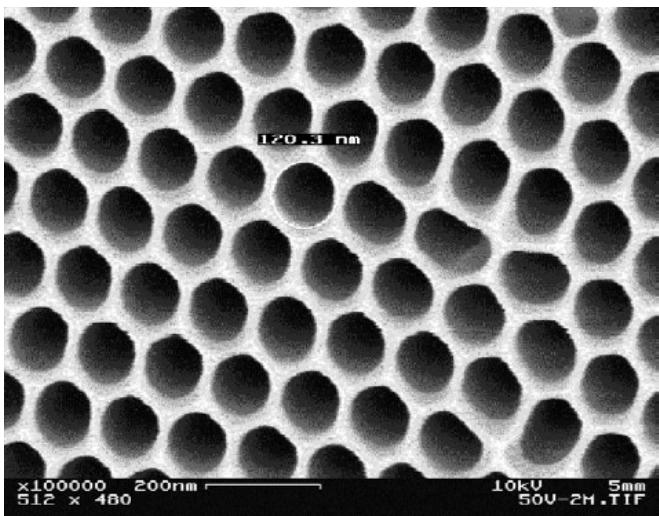
- A direct current is passed through an electrolytic solution where the Al sheet is used as the anode.
- Two processes: dissolving and oxidation
- Naturally formed triangular pore arrays

Electrolyte:

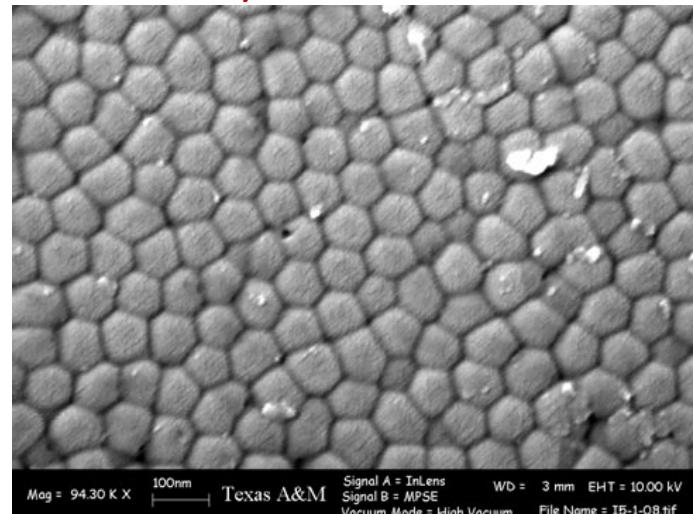
Oxalic acid, phosphoric acid,
sulfuric acid ...

Porous Al₂O₃ membranes

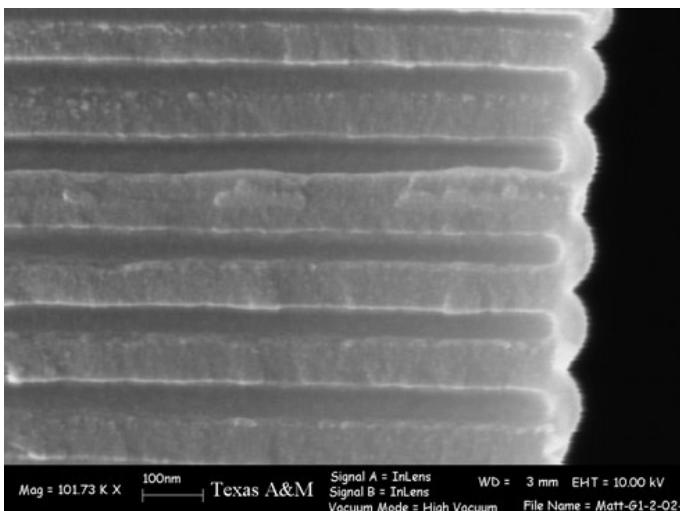
Top surface of the AAO



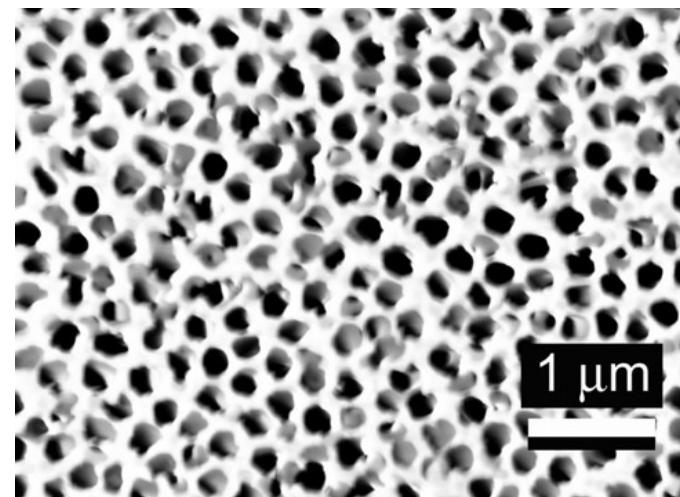
Bottom surface of the AAO showing the barrier layer



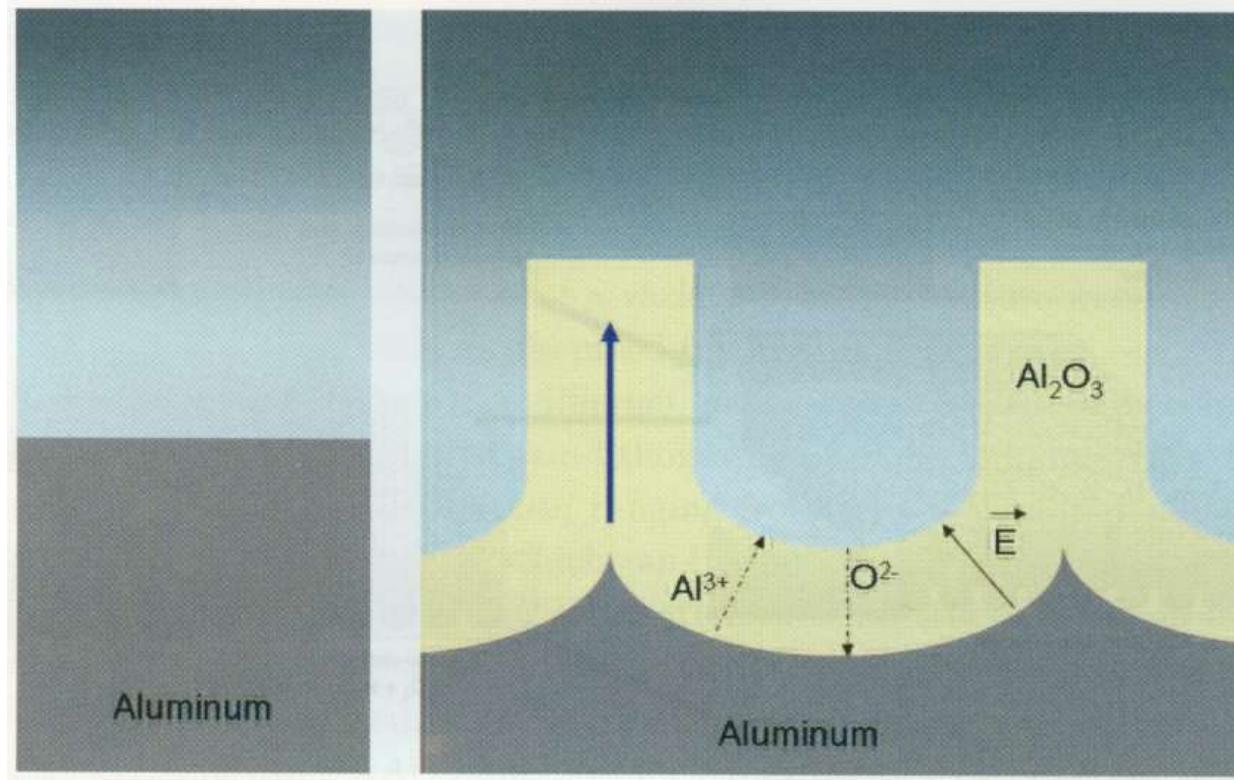
Cross section of the AAO



AAO filter from Whatman Inc.

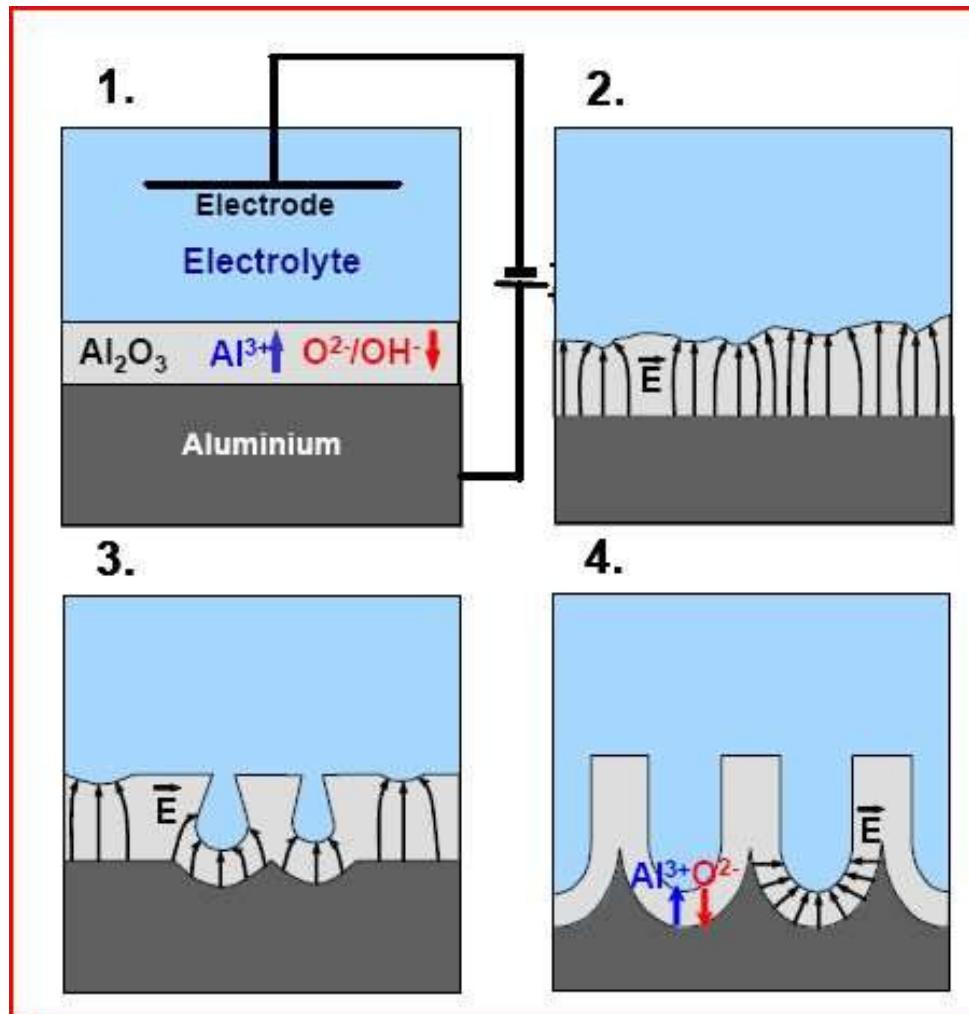


Nano-pore formation mechanism



- 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 interact 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.

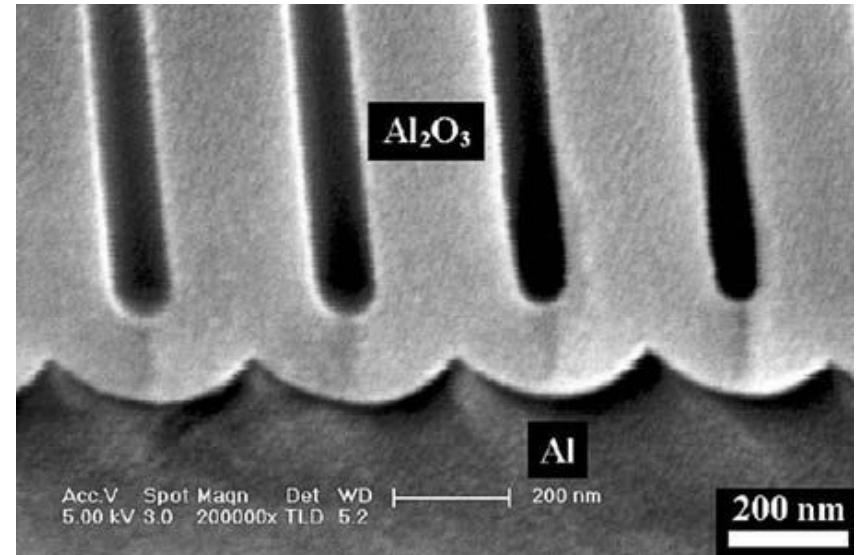
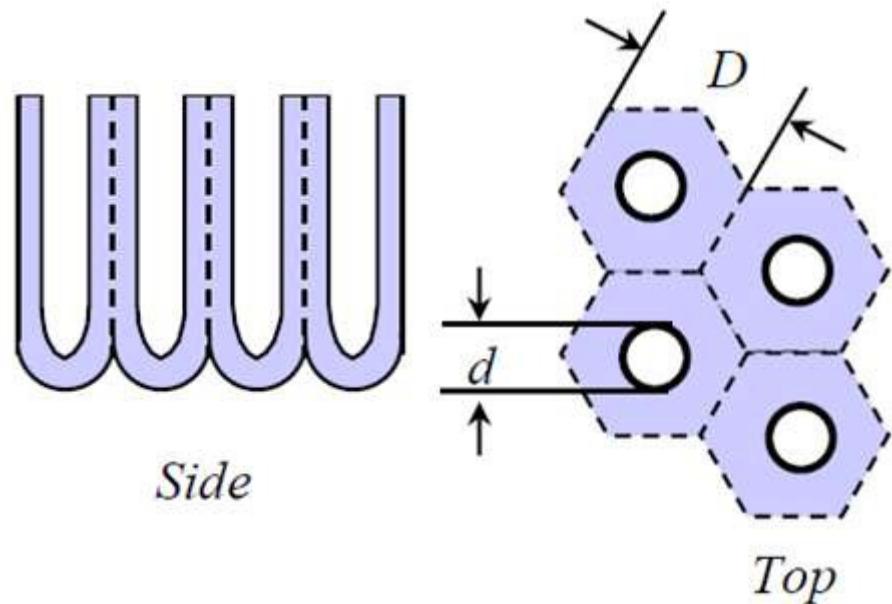
Nano-pore formation mechanism



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.

Pore dimensions



Controlling parameters: voltage, electrolyte, temperature and time.

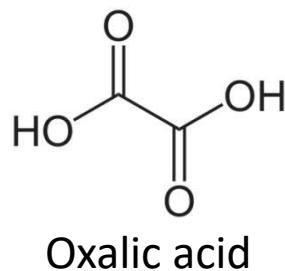
Cell size $D \sim 2.5 \times V$ (nm), V is voltage with a unit volt.

Pore size $d \sim V$ (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.

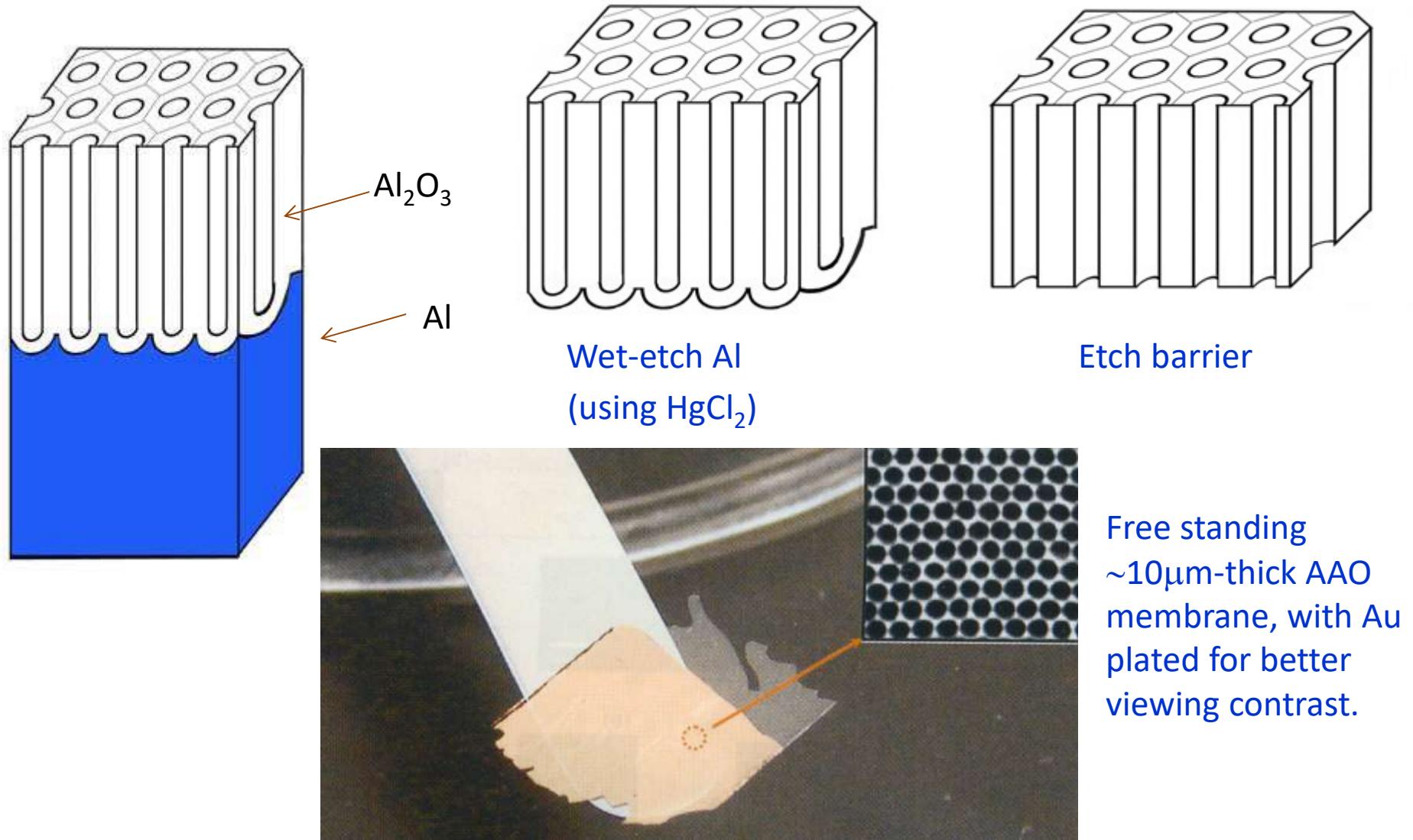
Electrolyte	Interpore Distance, D_{int}	Inner Wall Thickness, D_{inner}	Pore Diameter, D_p	Porosity
H_2SO_4 25 V 0.3 M	66.3 nm	7.2 nm	24 nm	12%
$(COOH)_2$ 40 V 0.3 M	105 nm	9.1 nm	31 nm	8%
H_3PO_4 195 V 0.1 M	501 nm	54 nm	458.4 nm	9%



Wrong number

Sulfuric acid generally gives smallest pore diameter and largest pore density.
Standard deviation of pore diameter usually is within 10%.
Other voltages also work, but only those three conditions give good ordering.

AAO membrane production

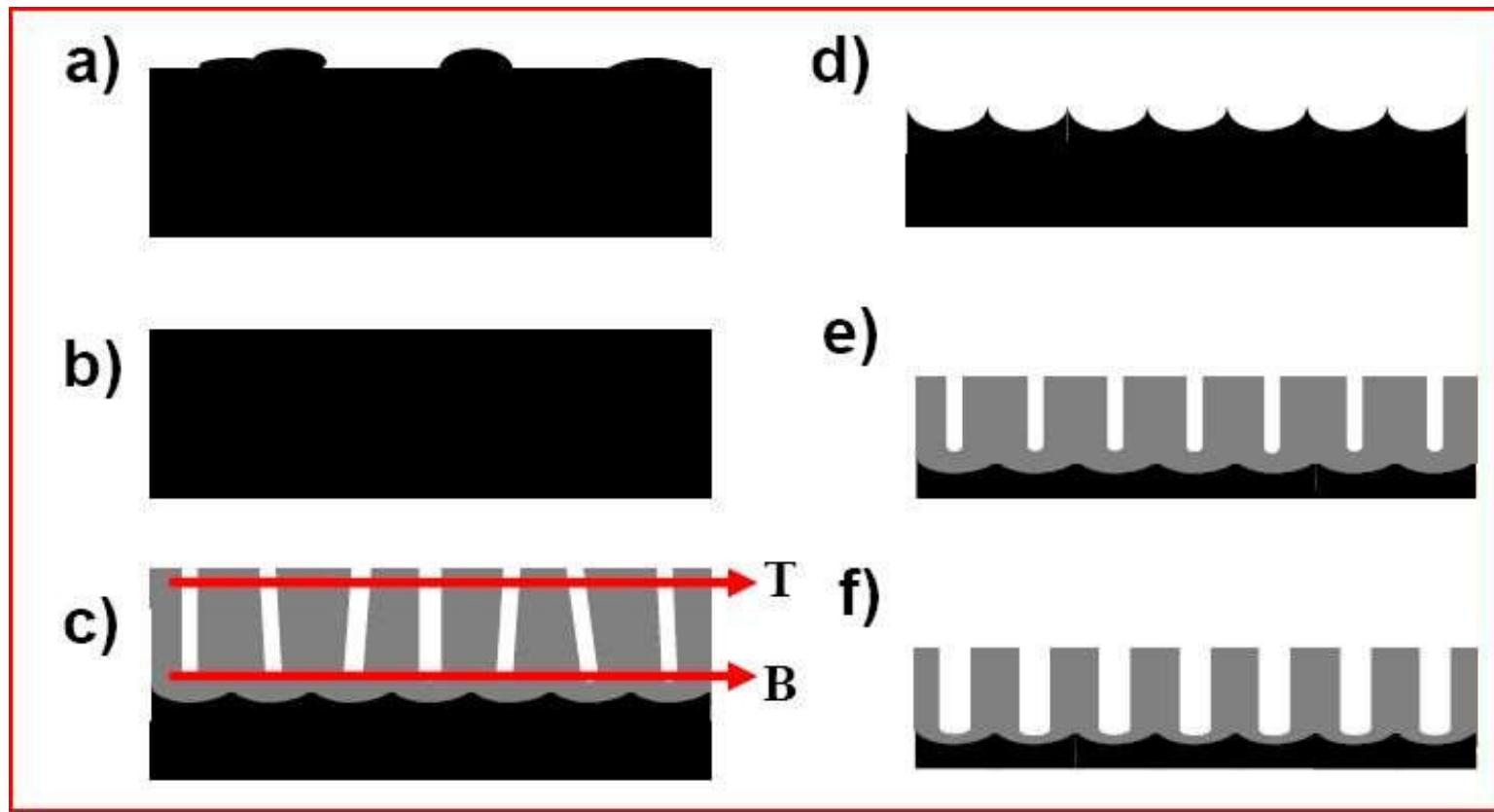


Commercial membrane: thickness ~ $60\mu m$, pore size down to 20nm (one side only!)
Application: filter, as template for nano-wire production.

Chemistry involved in nanofabrication using AAO

- Removing Al without attacking AAO: saturated HgCl₂
$$\text{Al} + \text{HgCl}_2 \rightarrow \text{Al}^{3+} + \text{Hg}$$
, room temperature
- Removing AAO without attacking Al: It is not easy for Al to dissolve in H₂CrO₄ aqueous.
6%H₃PO₄ + 1.8%H₂CrO₄, 60°C, 2h
- Removing the barrier layer at the bottom without attacking too much the AAO pores.
5%H₃PO₄, 30°C, 30min

Two-step anodization process to improve periodicity



Stages of the formation of self-ordered alumina: **a)** Annealing at 500°C for 3h to increase grain size; **b)** electro-polishing in a solution of $\frac{1}{4}$ HClO_4 + $\frac{3}{4}$ $\text{C}_2\text{H}_5\text{OH}$ 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°C to widen the pores.

Pre-pattern Al surface can also improves periodicity

Al is pre-patterned by FIB

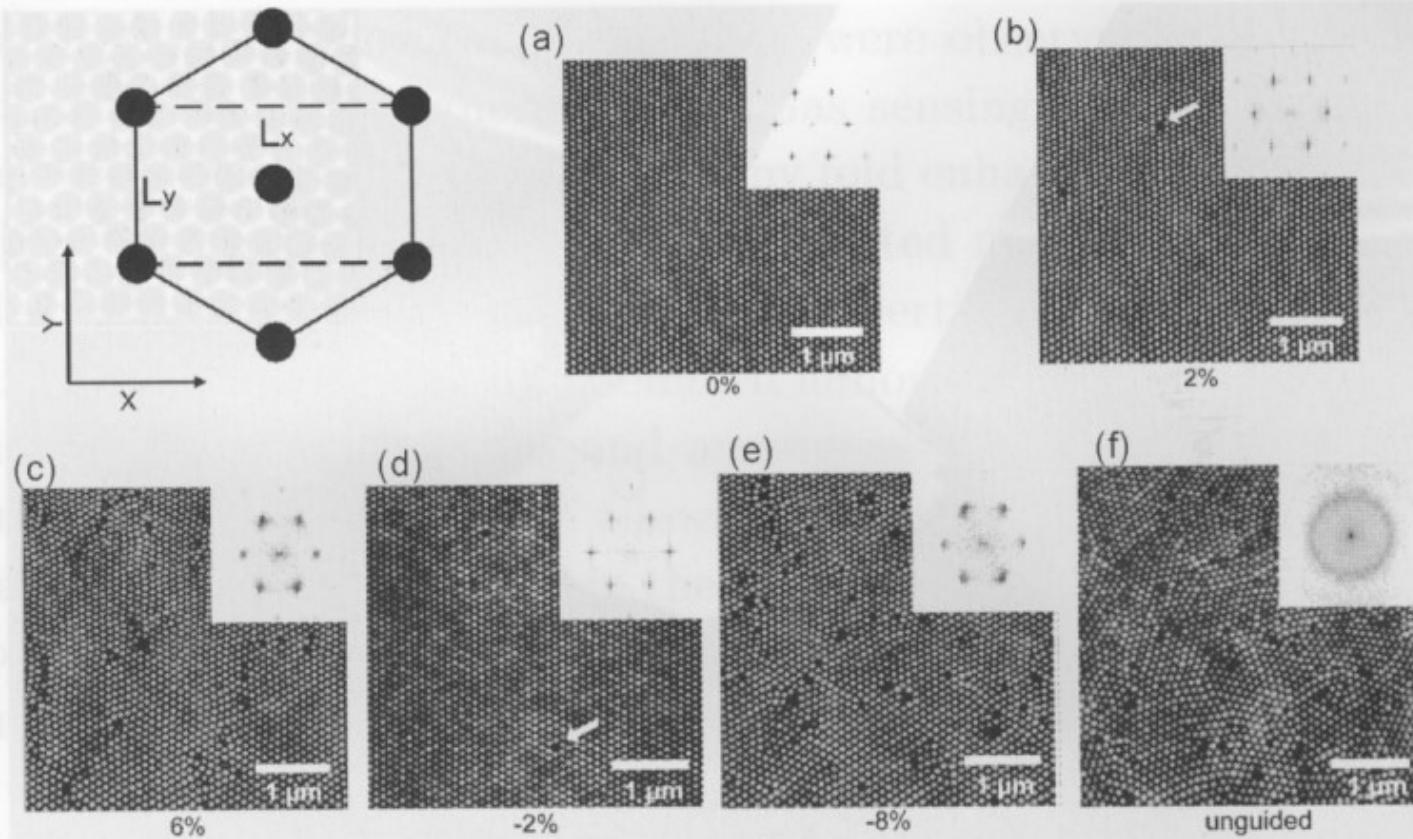
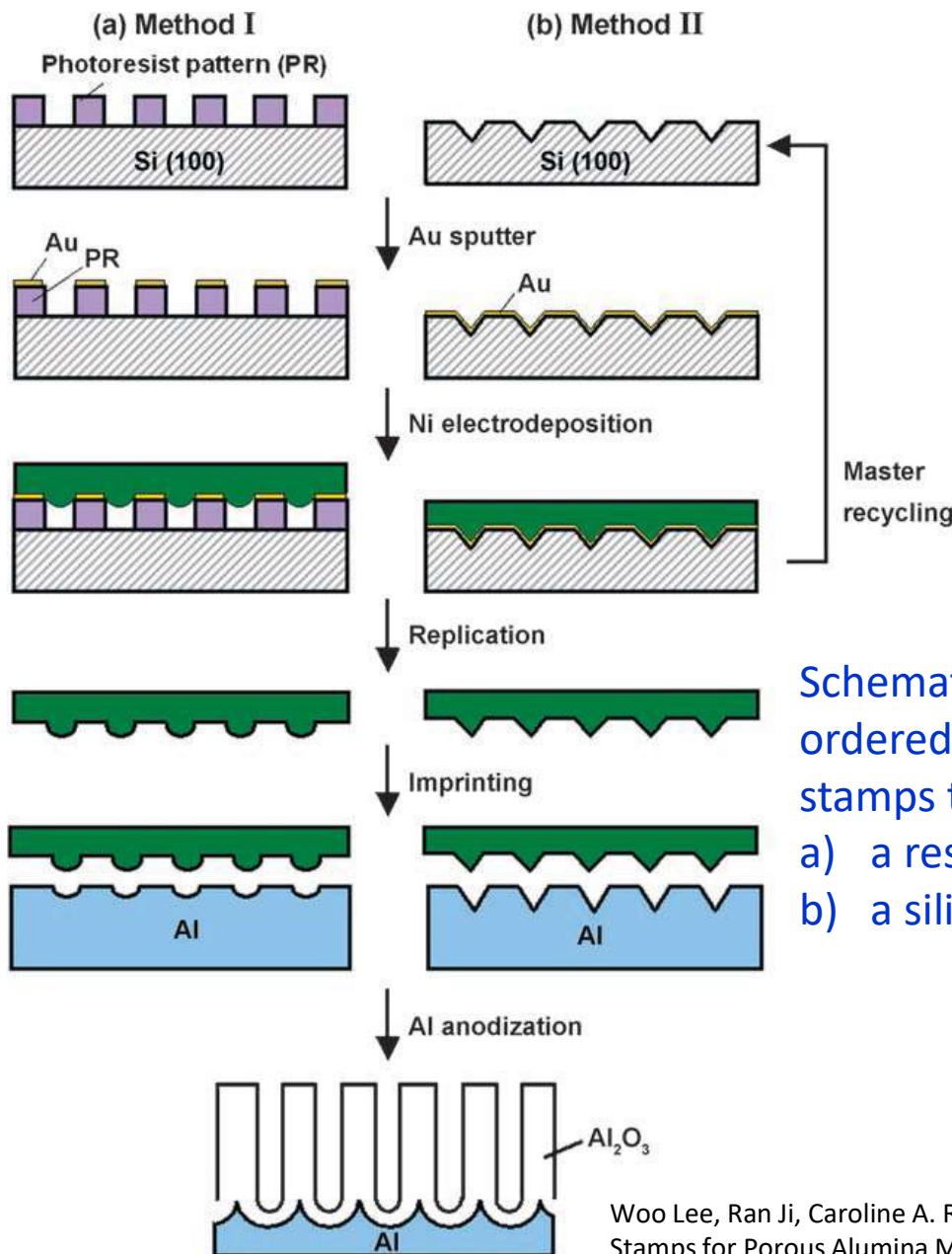


Figure 3. Diagram of an unit cell of the lattice followed by AFM images of the barrier with lattice mismatch = (a) 0%, (b) 2%, (c) 6%, (d) -2%, (e) -8% and (f) a self organized structure with insets showing the 2D power spectra of the corresponding regions of the 10 micron AAO films. White arrows in (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. 27

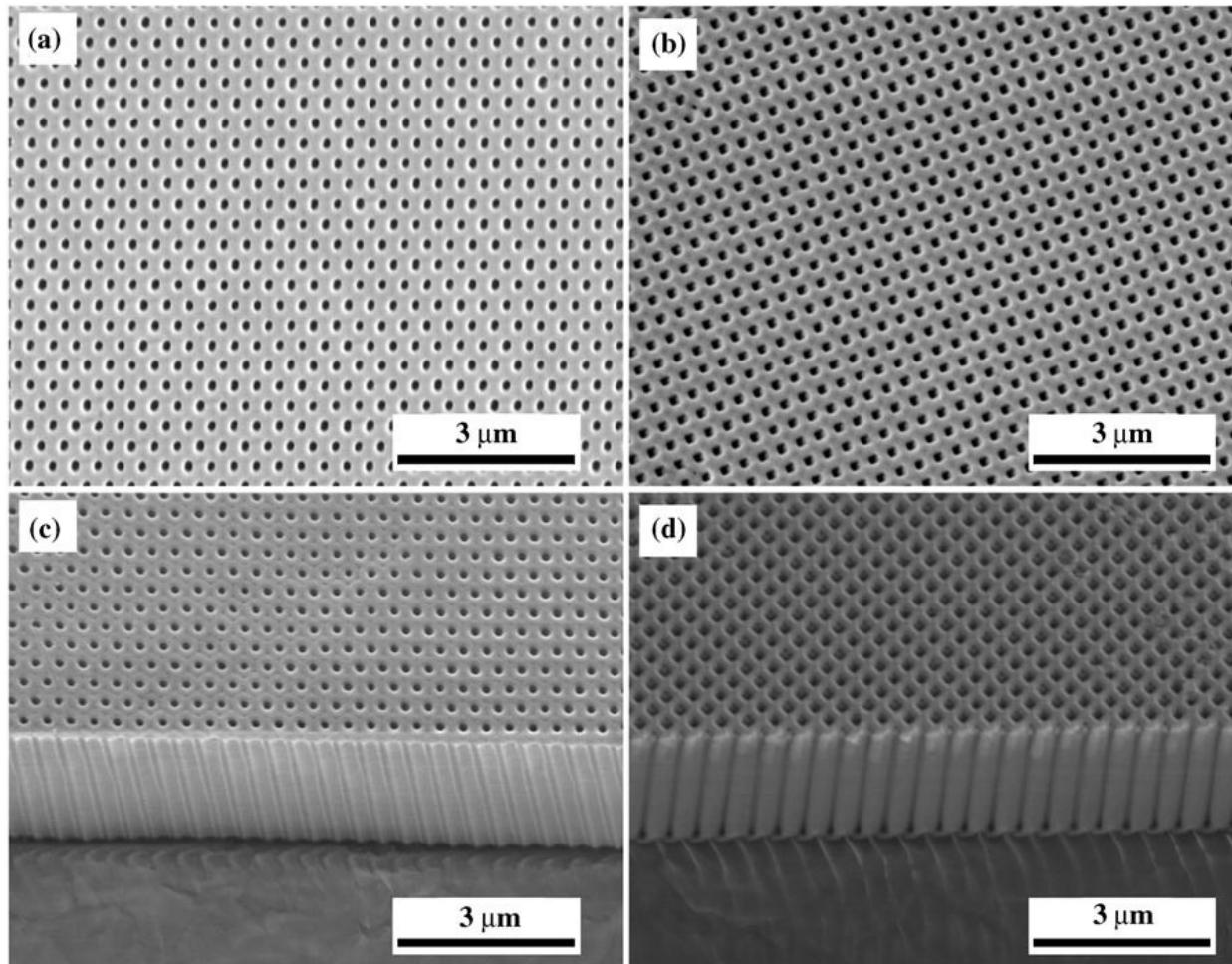
Pre-pattern Al surface using imprint with a Ni mold



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

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

Ideally ordered AAO by imprint pre-patterning 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.

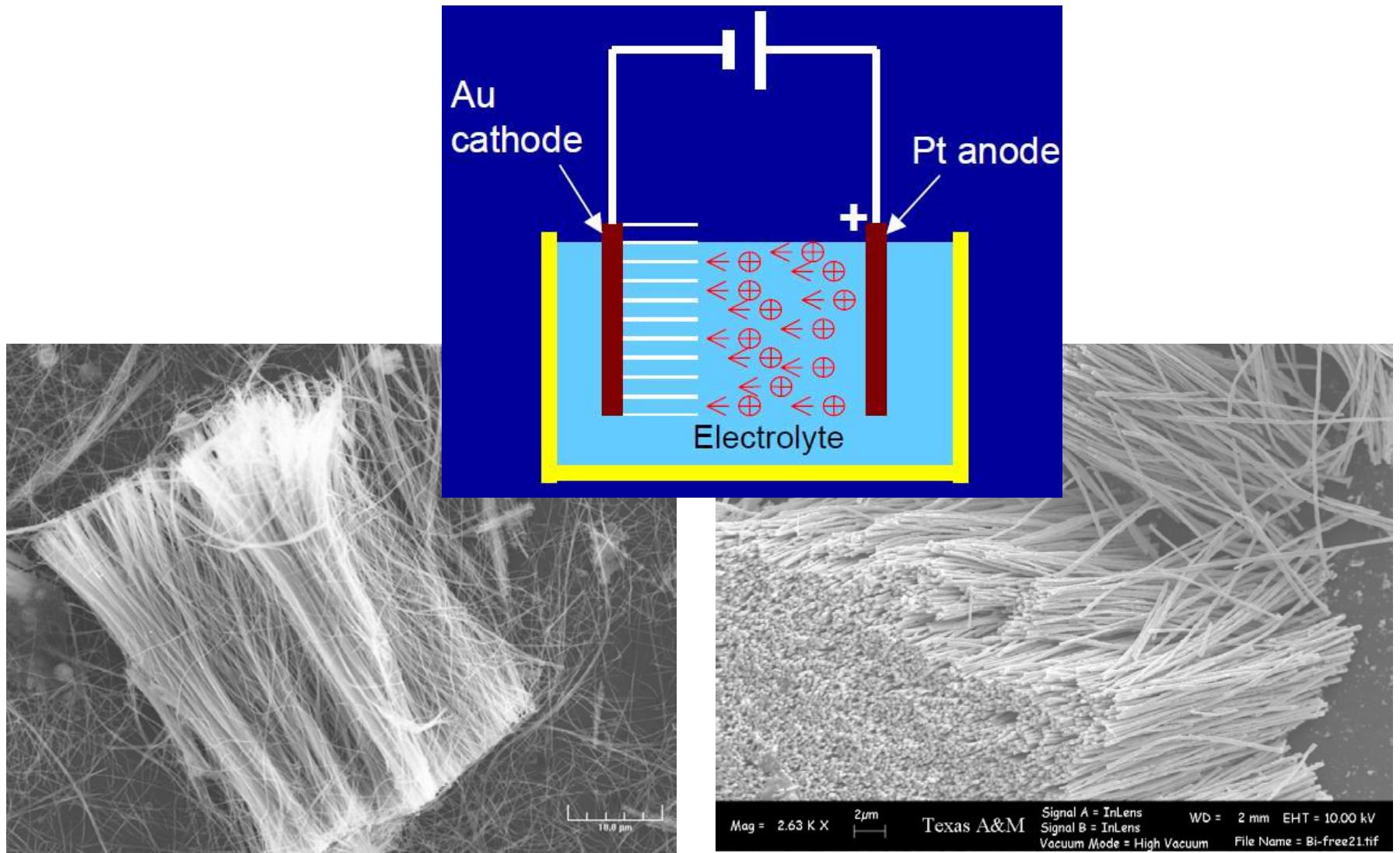
No other way can get such a high aspect ratio periodic pattern.²⁹



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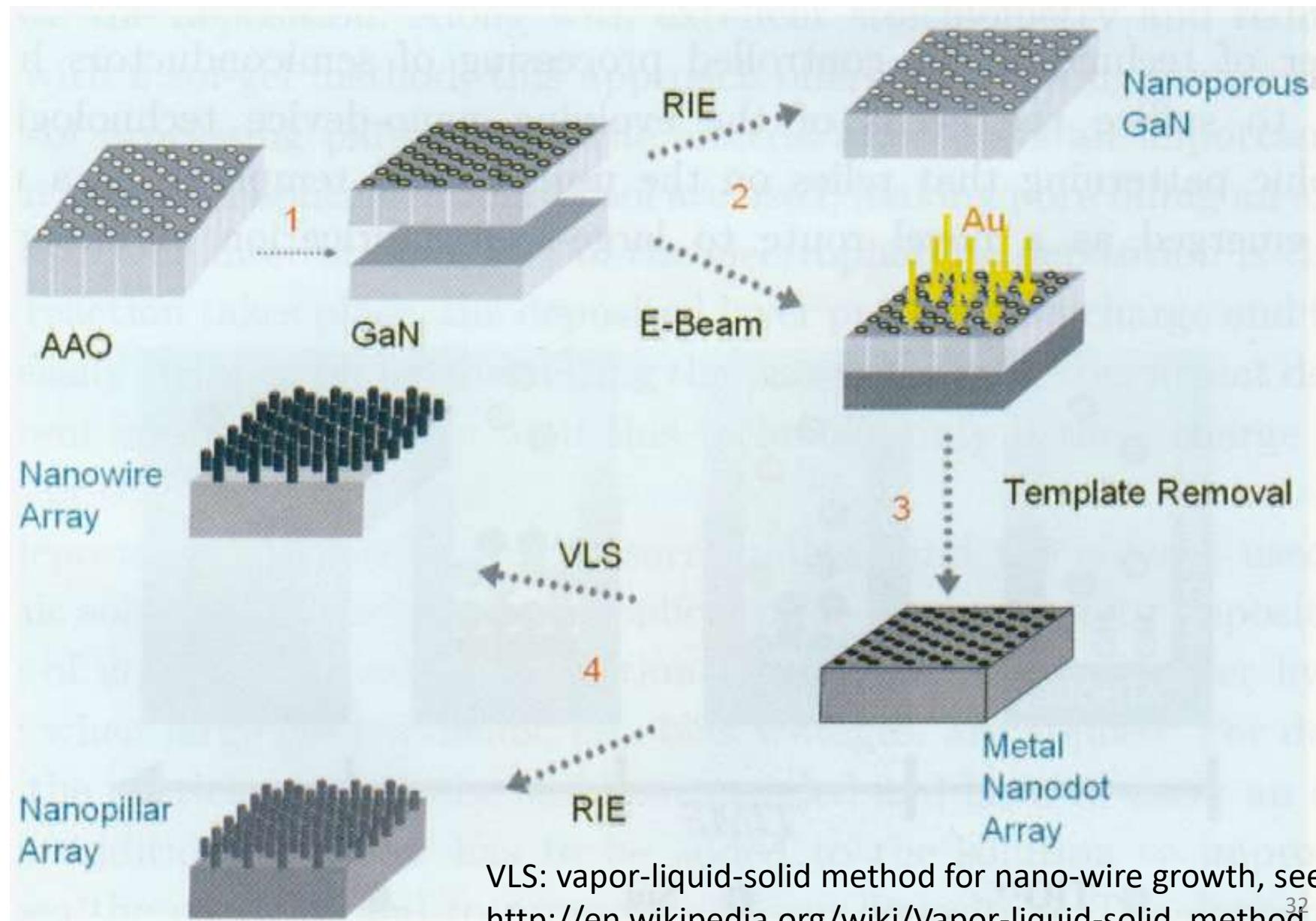
Electroplating of nanowires



Aspect ratio: $50\mu\text{m}/60\text{nm} \sim 800$

This extremely high aspect ratio is hard to achieve by lithography plus etching

Other nanofabrication routes using AAO



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

Grow carbon nanotube into AAO pores

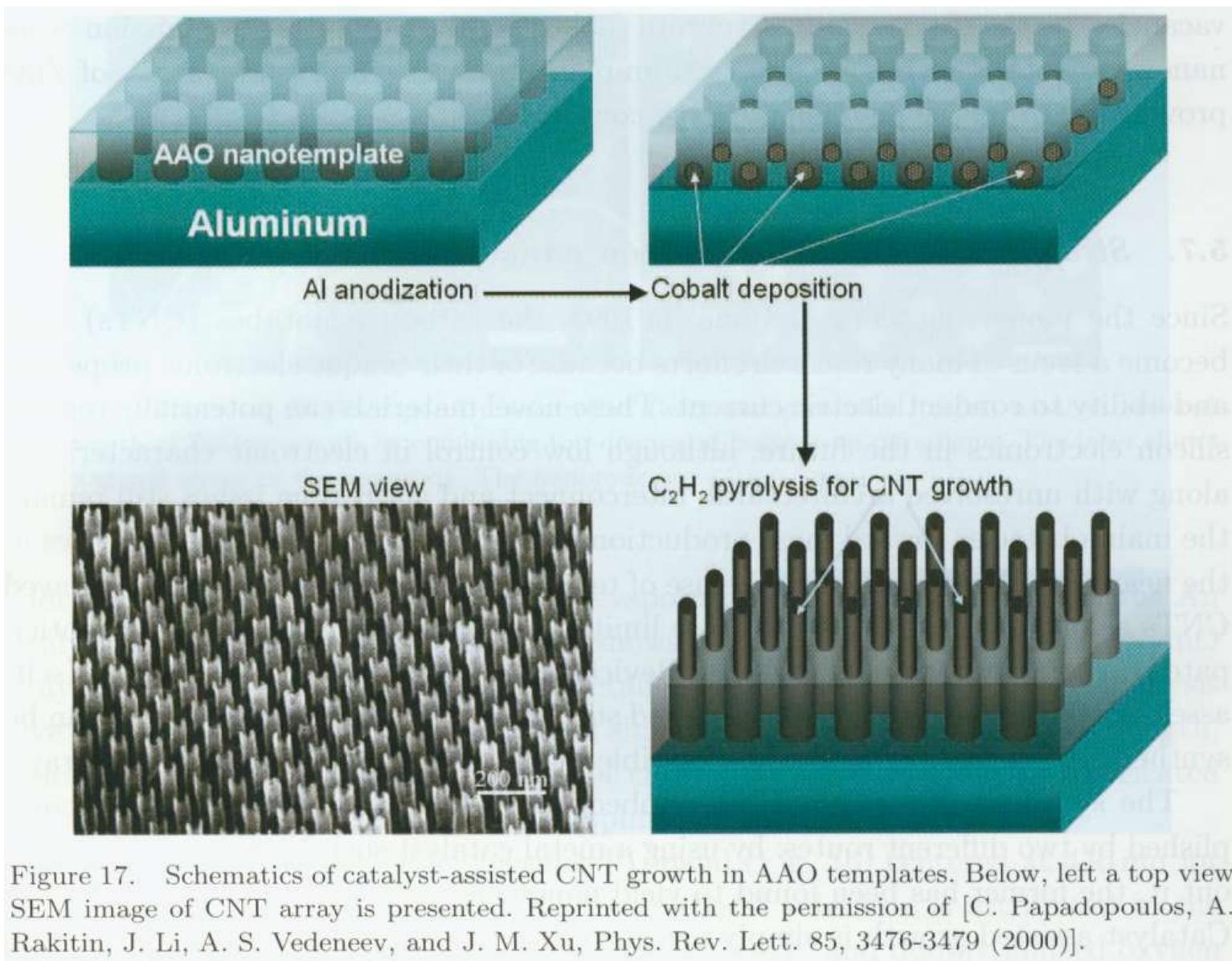
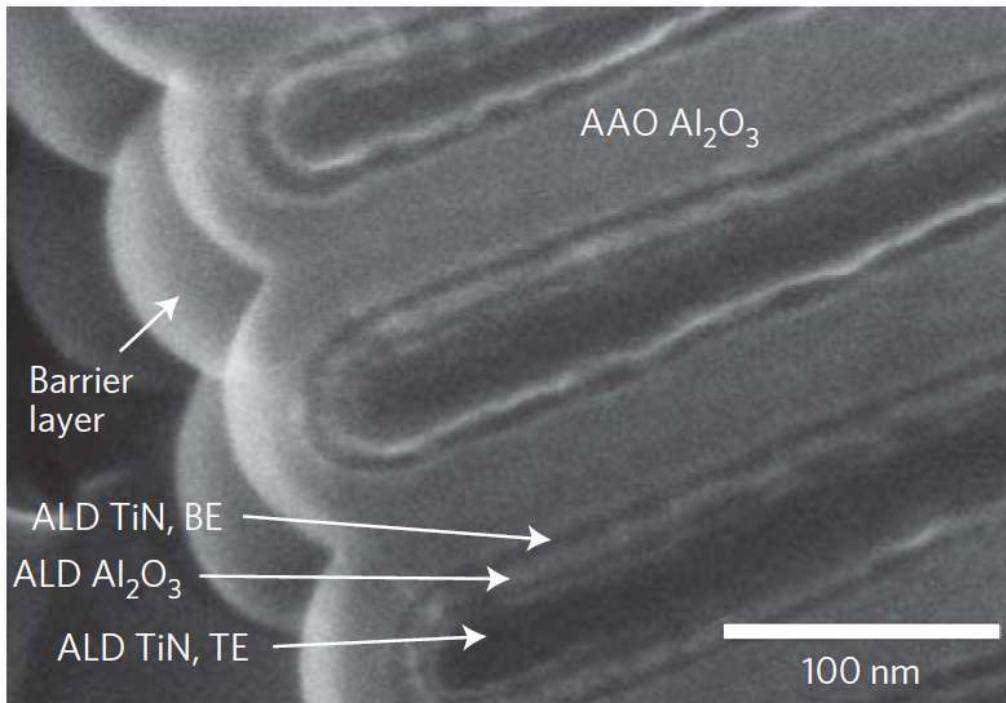
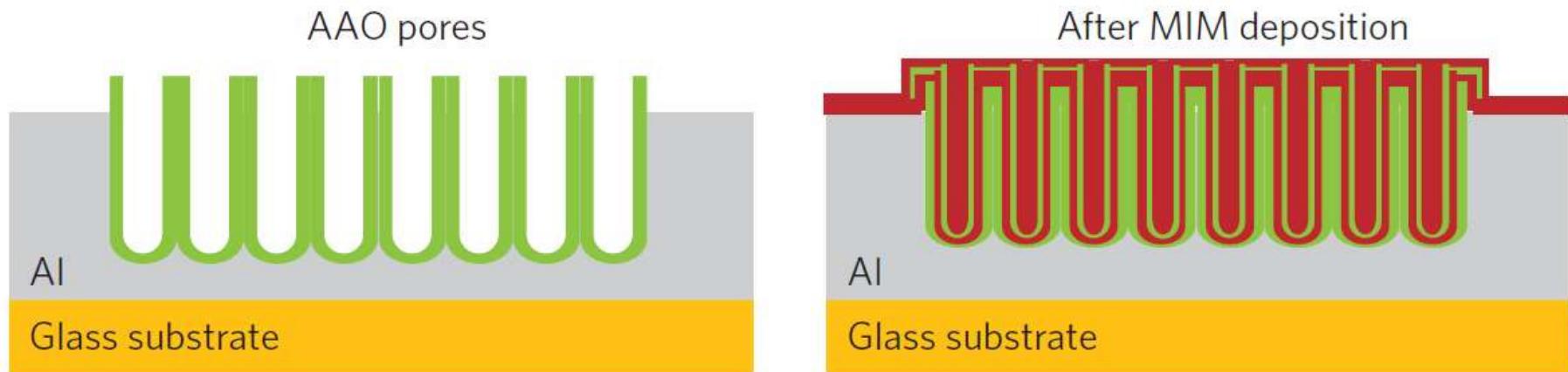


Figure 17. Schematics of catalyst-assisted CNT growth in AAO templates. Below, left a top view SEM image of CNT array is presented. Reprinted with the permission of [C. Papadopoulos, A. Rakitin, J. Li, A. S. Vedeneev, and J. M. Xu, Phys. Rev. Lett. 85, 3476-3479 (2000)].

Nanotubular super-capacitor for energy storage



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 .

$$\text{Energy stored} = \frac{1}{2} CV^2 \propto C.$$

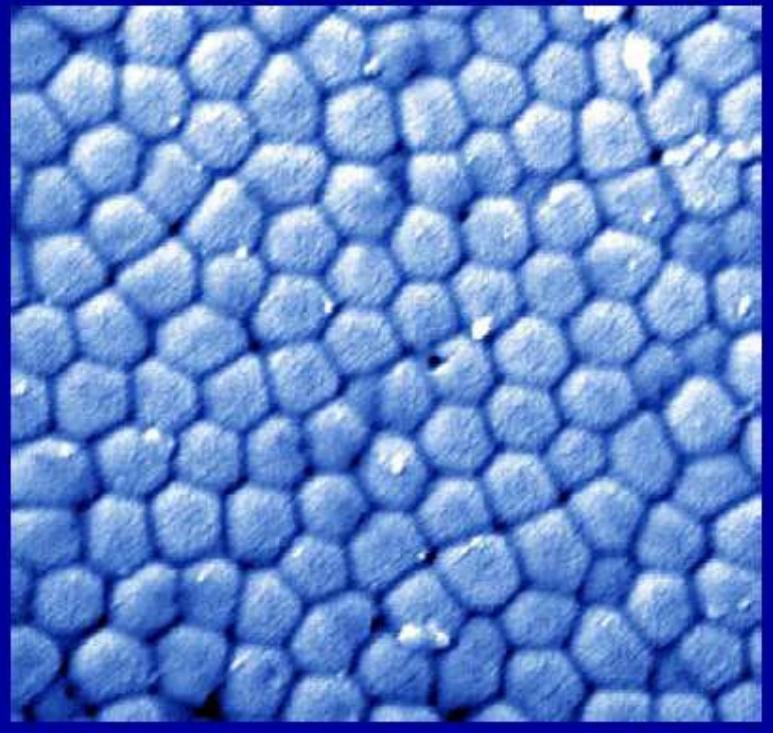
“Nanotubular metal–insulator–metal capacitor arrays
for energy storage”, Nature Nanotechnology, 2009.
³⁴

Water-cube in Beijing

The aquatics center for 2008
Beijing Olympics



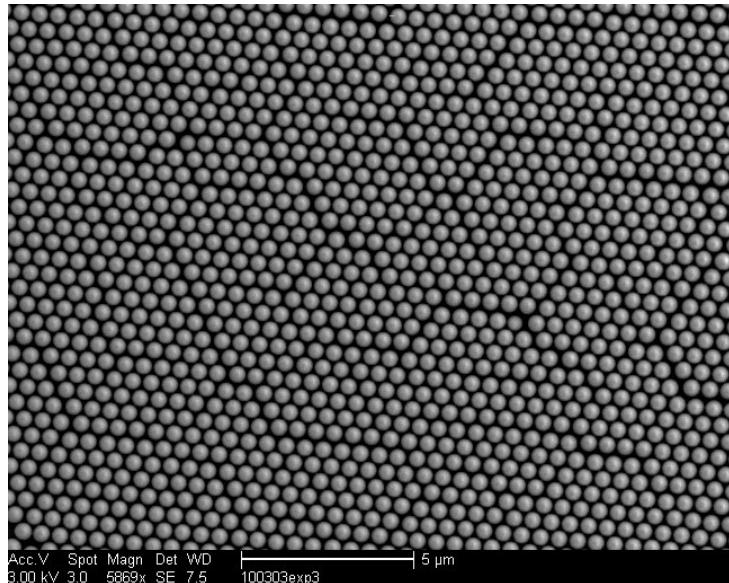
<http://news.wenxuecity.com/messages/200808/news-gb2312-689529.html>



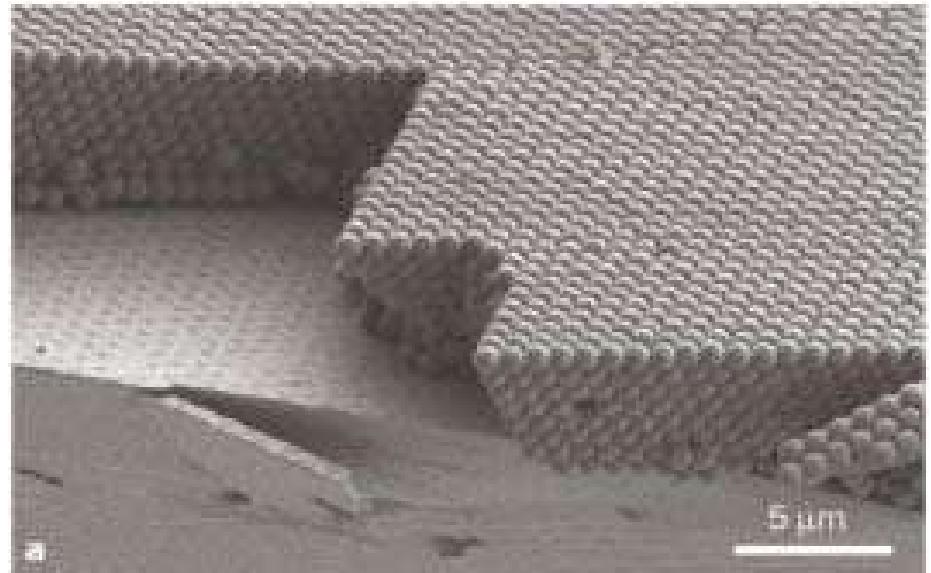
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5. Nanofabricating using AAO template.
6. **Nanoparticle self assembly (nanosphere lithography) overview.**
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8. Guided nanoparticle self assembly.
9. Applications of nanosphere lithography

Self assembly of colloidal particles



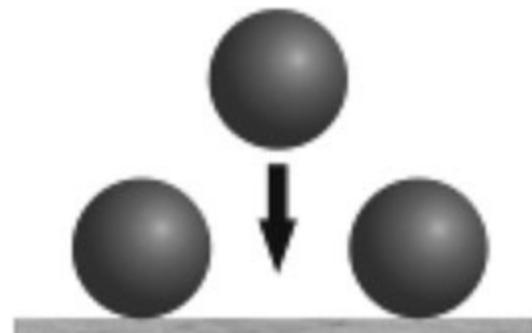
2D self assembly (mono-layer)



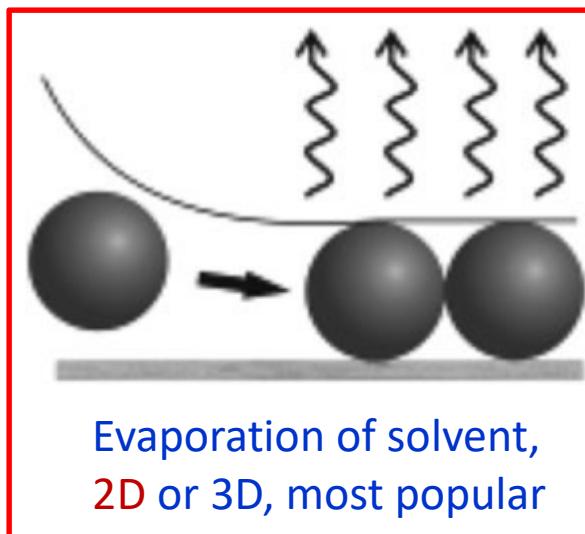
3D self assembly

Typical particle size 100-1000nm, larger is easier to assemble into more regular arrays.
It is a lot easier and cheaper than block copolymer self assembly and anodized alumina.

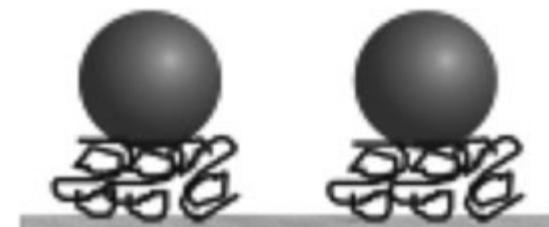
Common techniques for colloidal particles self assembly



Sedimentation from bulk liquid, 3D, low cost



Evaporation of solvent,
2D or 3D, most popular



Adsorption, 2D or
3D (layer by layer)



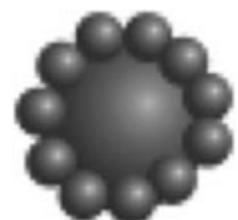
External force field
(electric, magnetic),
1D 2D or 3D, not
scalable to large area



Bio-specific, 1D 2D or 3D,
high cost



Templated on surfaces,
1D 2D or 3D

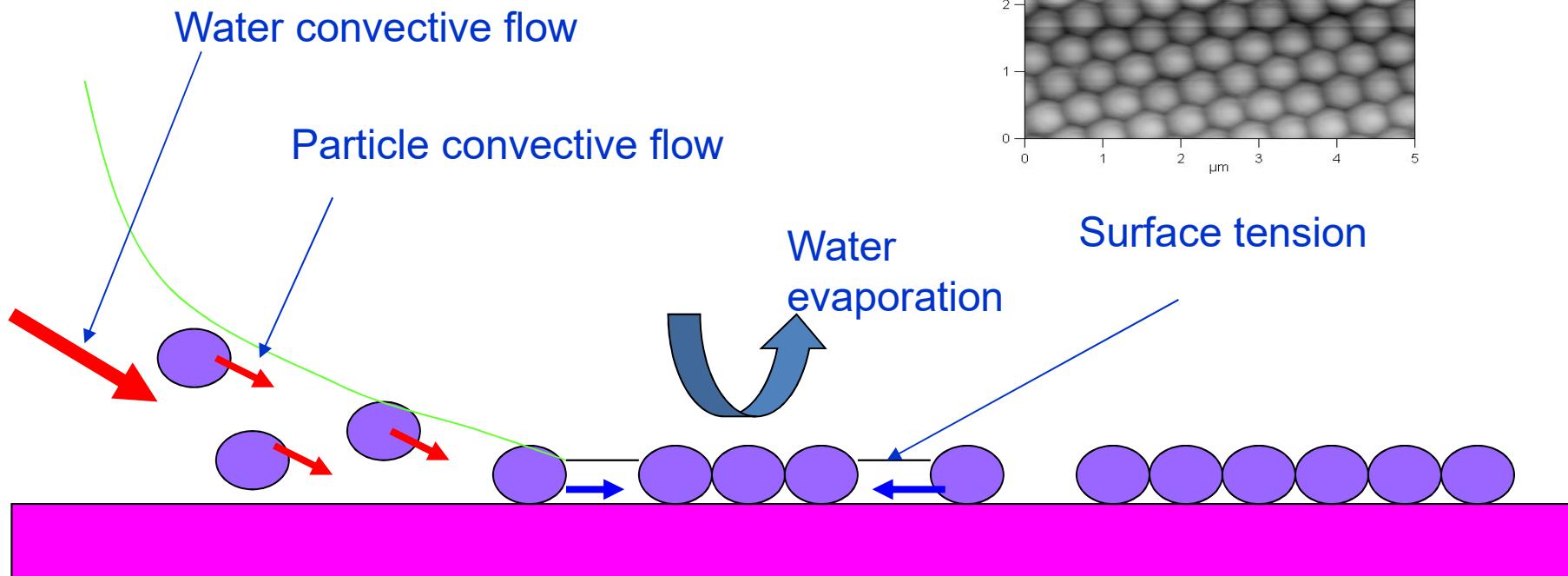


Templated on
droplets

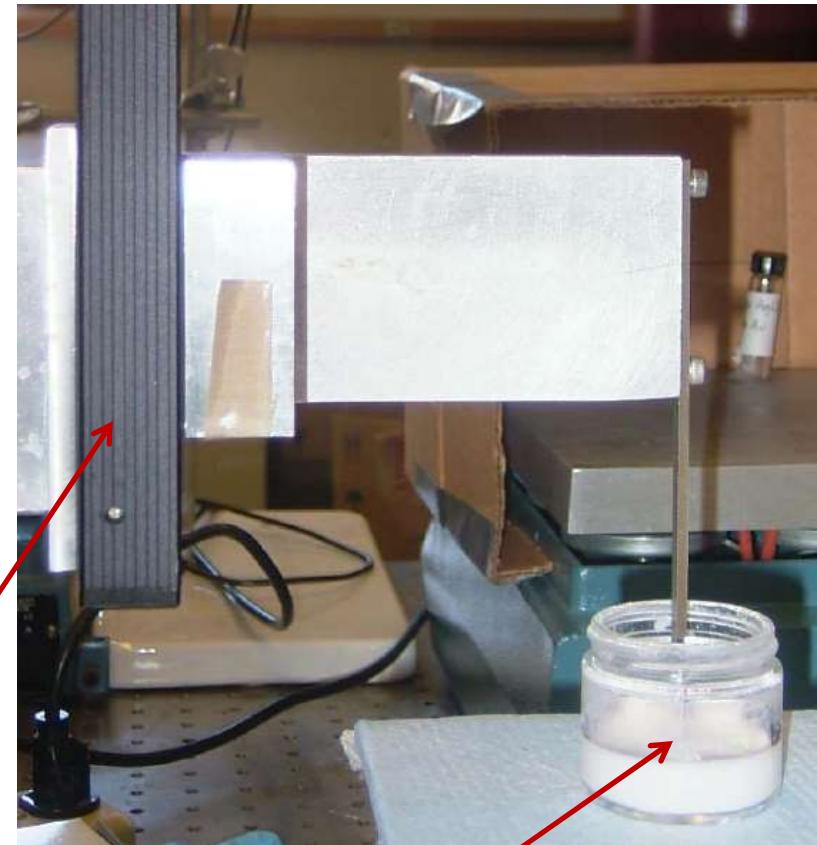
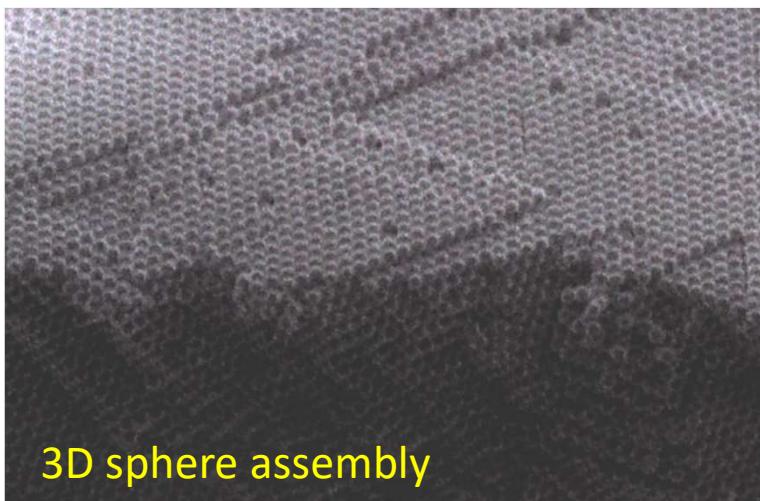
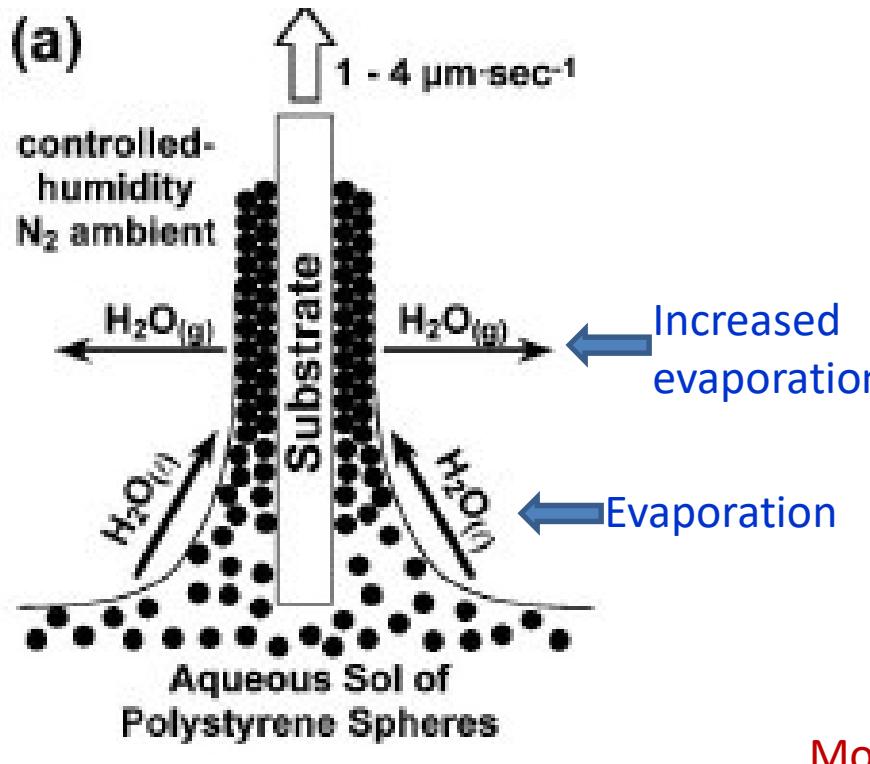
"Materials Fabricated by Micro- and Nanoparticle Assembly – The Challenging Path from Science to Engineering", Advanced Materials, 2009

2D and 3D assembly by solvent evaporation

- Capillary force (surface tension) due to meniscus formation, most important.
- Convective flow due to water evaporation.
- Forces that hold the particle together: Van der Walls force, hydrogen bond, ionic interaction force (they are all attractive forces)...



Slow vertical withdrawal method



Continuous convective assembly using a stepper motor.

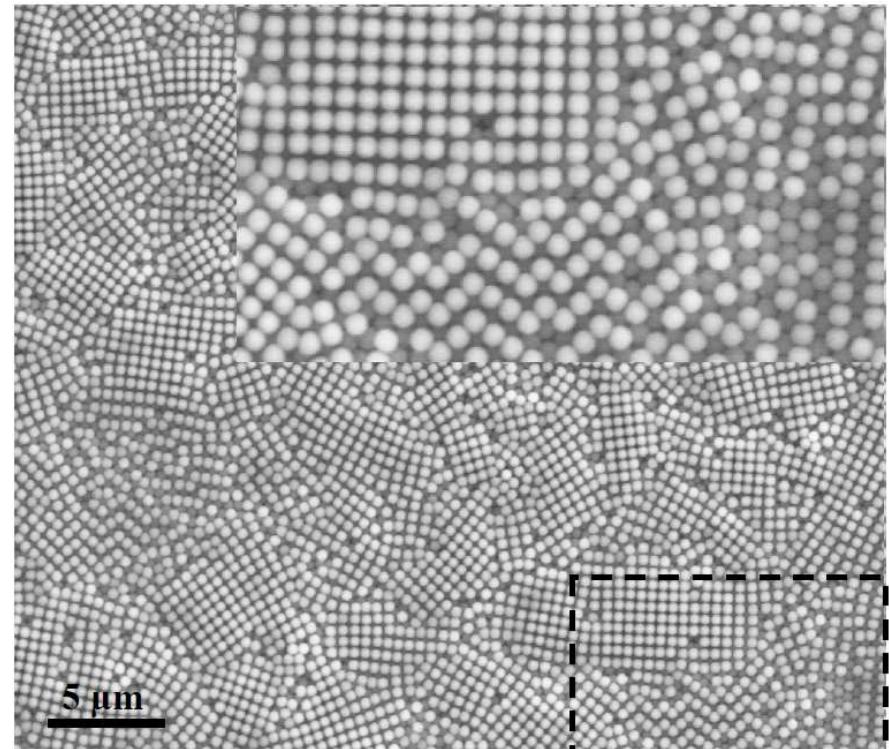
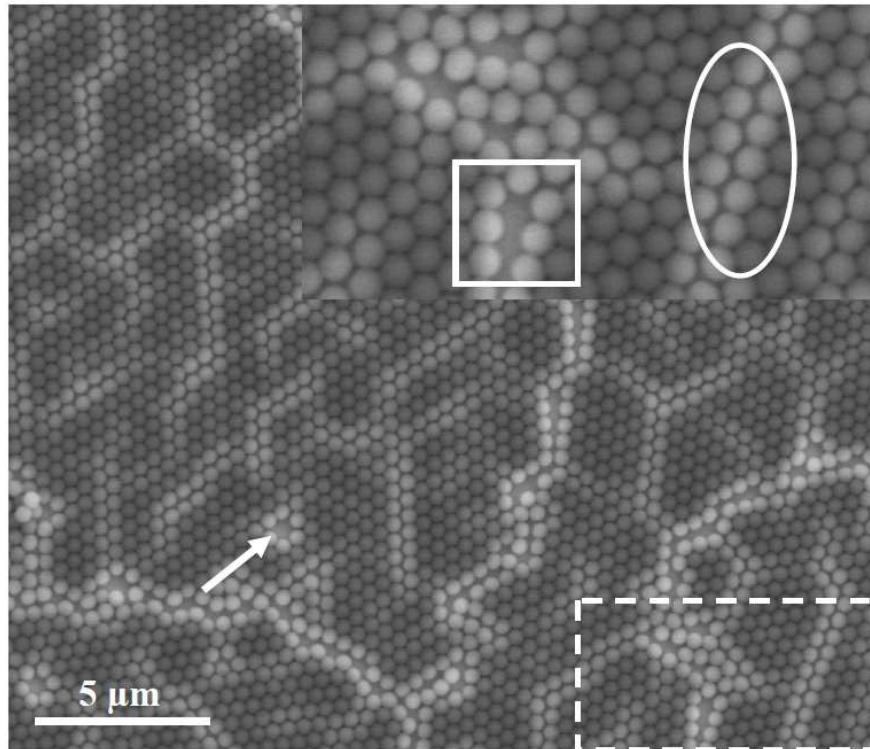
Slide is withdrawn out of the solution at a particular rate (slow: $\sim 60\mu\text{m}/\text{min}$; fast: $180\mu\text{m}/\text{min}$)

Spin-coating method: mono- and bi-layer

Spin coating or drop coating using polystyrene or silica sphere is the most popular form of nanosphere lithography.

Spinner is very available, relatively easy to get mono-layer, as needed for nanofabrication (i.e. pattern transfer to substrate).

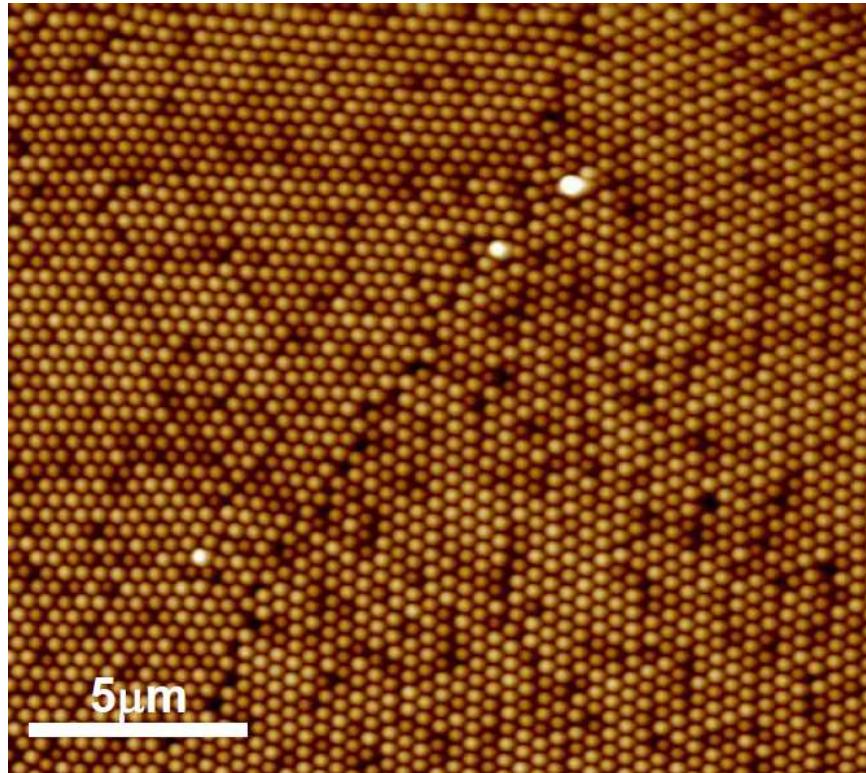
Polystyrene (PS) sphere 500nm



Substrate cleaning is important

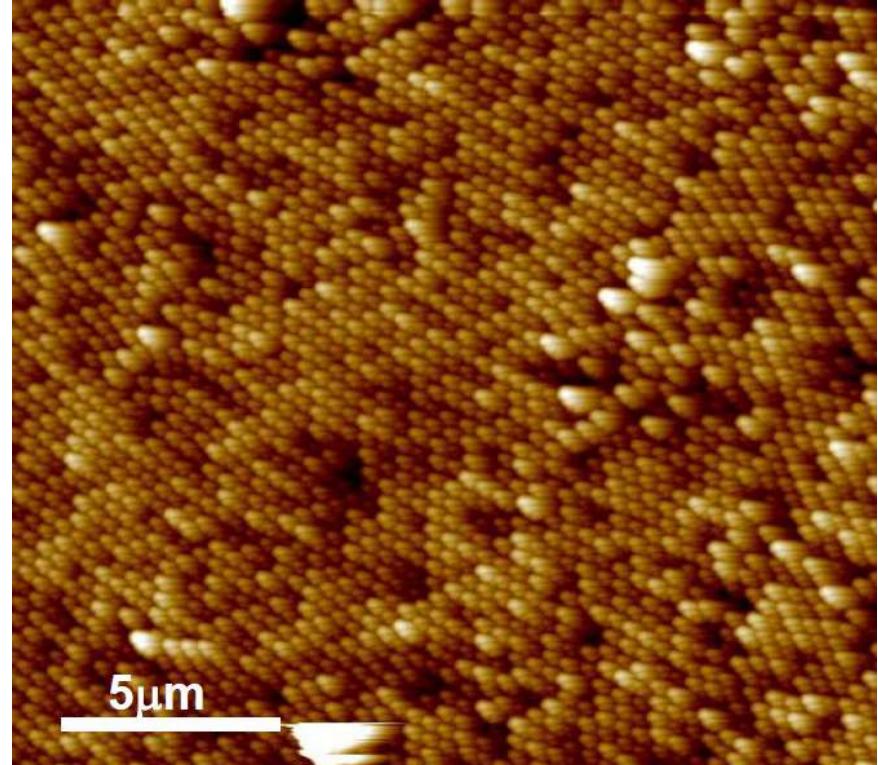
Surface needs to be very clean, with low (ideally <20°) contact angle for the sphere solution.

900nm spheres



Piranha/RCA

Piranha: concentrated sulfuric acid and 30% hydrogen peroxide, usually 3:1
RCA #1: H₂O/NH₄OH/H₂O₂=5:1:1, 80°C



Chromic/sulfuric acid bath

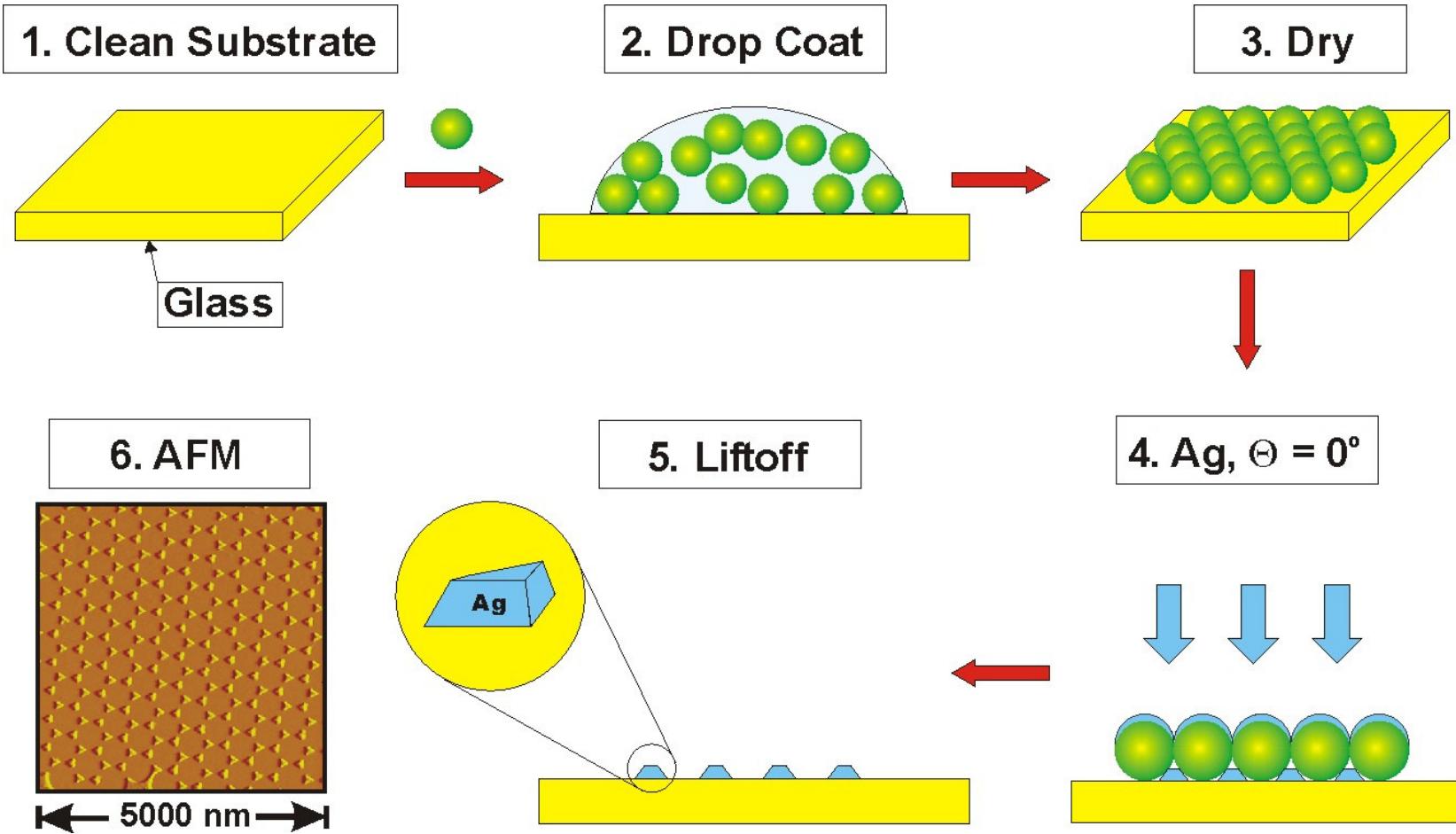
Chromium trioxide in concentrated sulfuric acid

http://en.wikipedia.org/wiki/Piranha_solution
http://en.wikipedia.org/wiki/RCA_clean

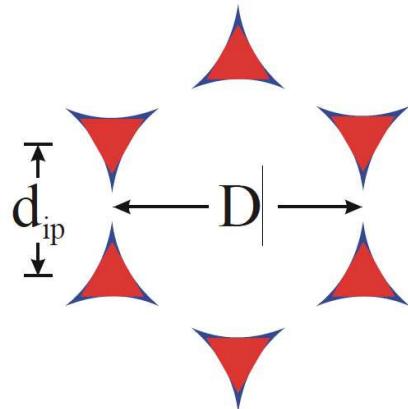
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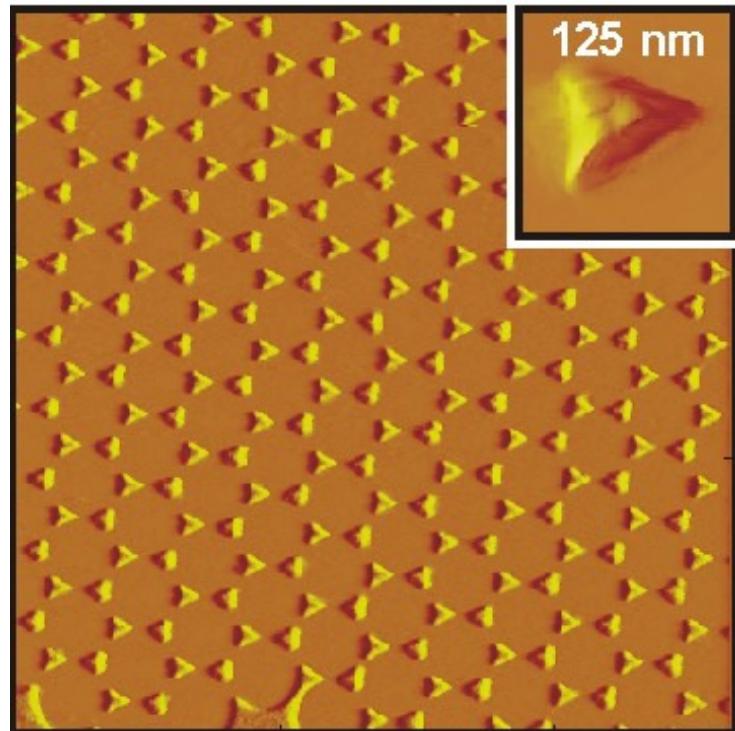
Nanosphere lithography



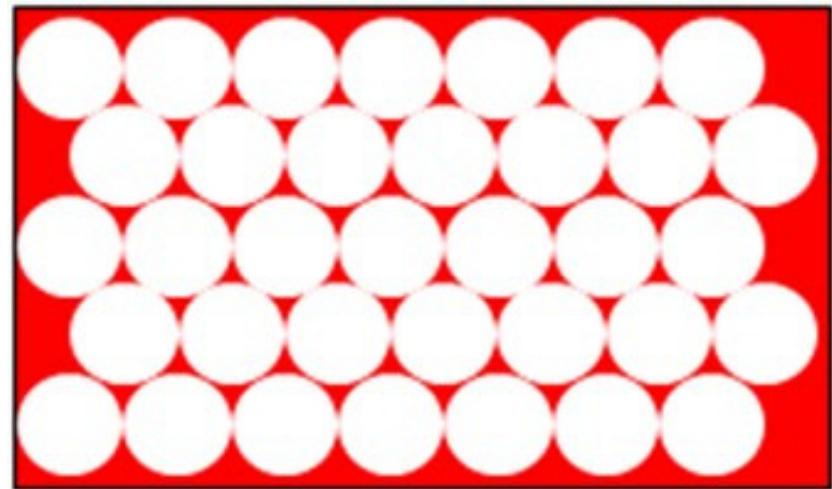
Size and spacing control



$$d_{ip} = \left(1/\sqrt{3}\right)D = 0.577 D$$



$$\begin{aligned} a &= \frac{3}{2} \left(\sqrt{3} - 1 - \frac{1}{\sqrt{3}} \right) D \\ &= 0.233 D \end{aligned}$$

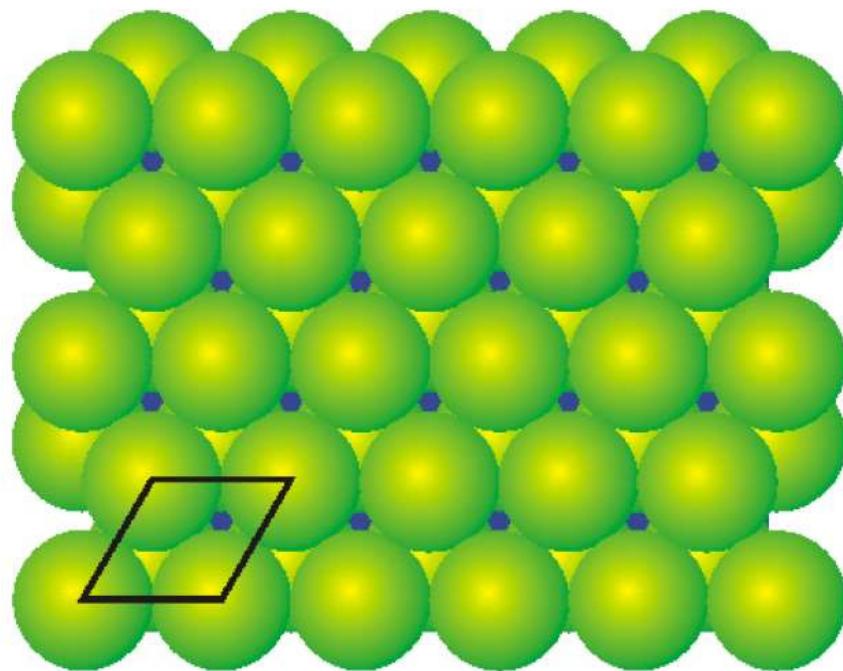


$$D = 542 \text{ nm}$$

$$a = 126 \text{ nm}; d_{ip} = 313 \text{ nm}$$

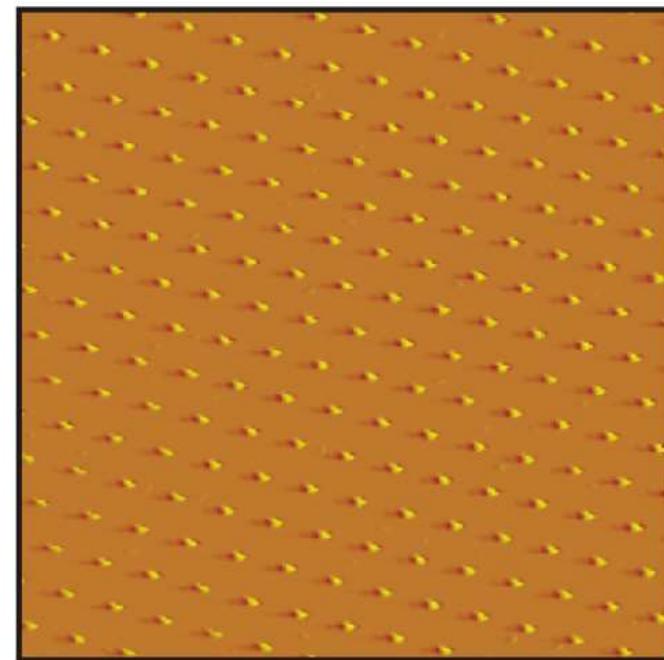
Nanosphere lithography: double layer mask

Colloidal Crystal Mask



$D = 400 \text{ nm}$; $d_m = 30 \text{ nm}$

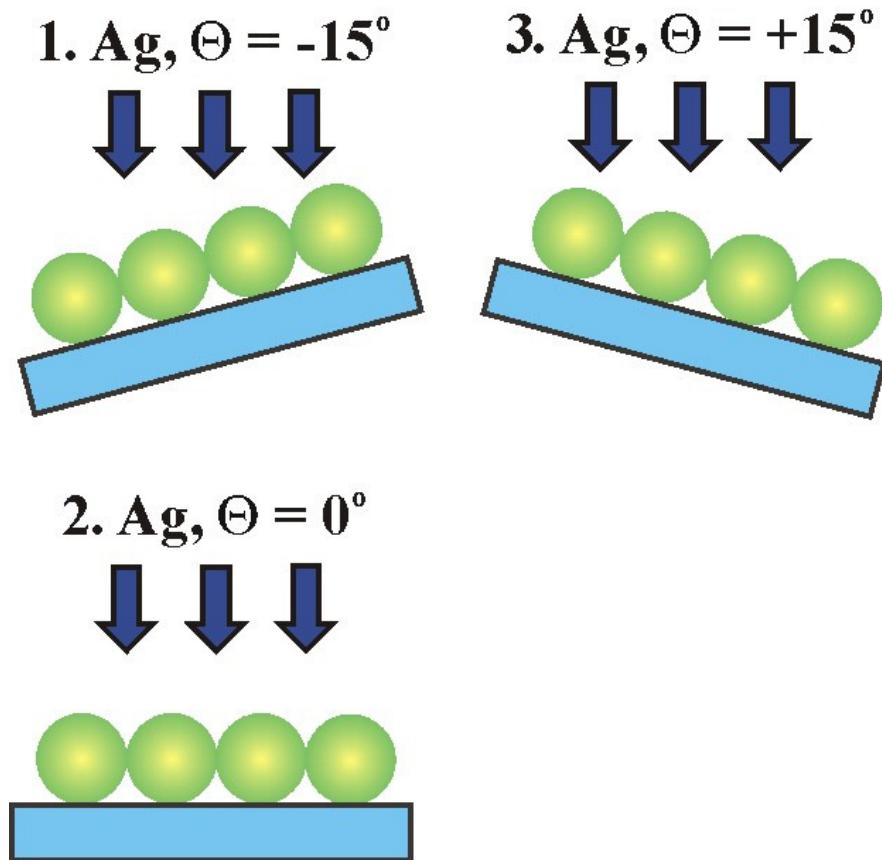
Ag Nanoparticles



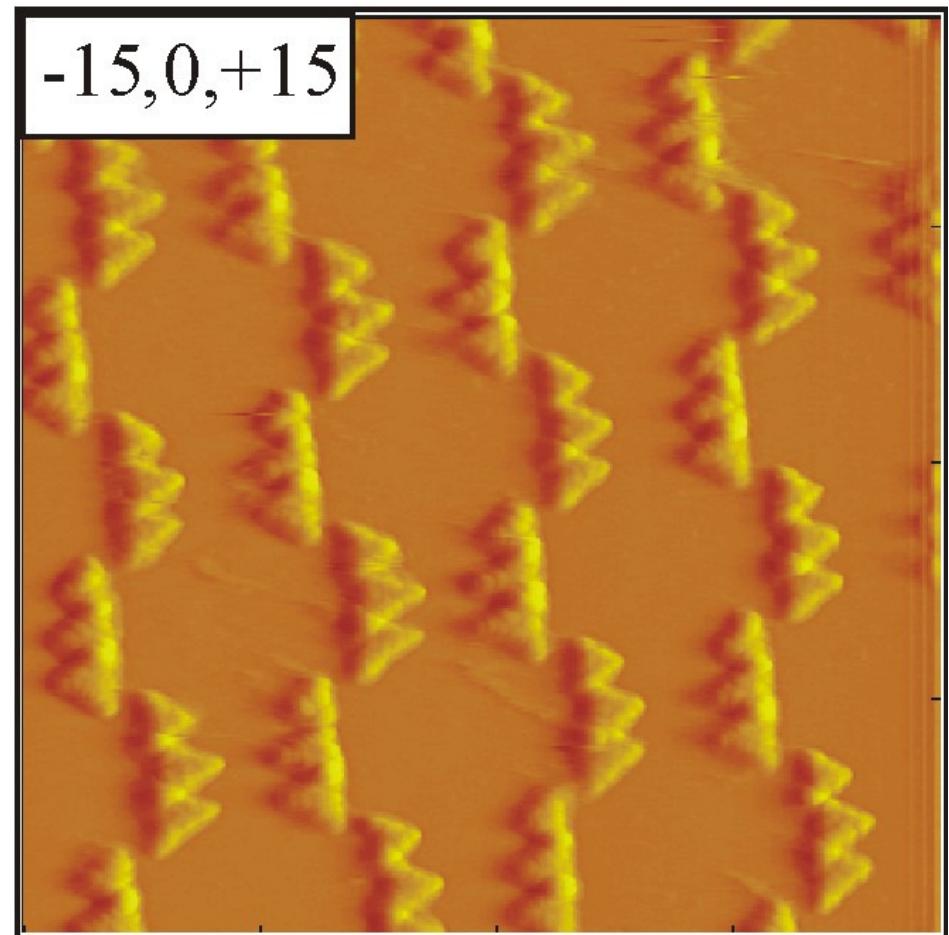
← 5000 nm →

Angle resolved nanosphere lithography

Angle-Tuned Mask



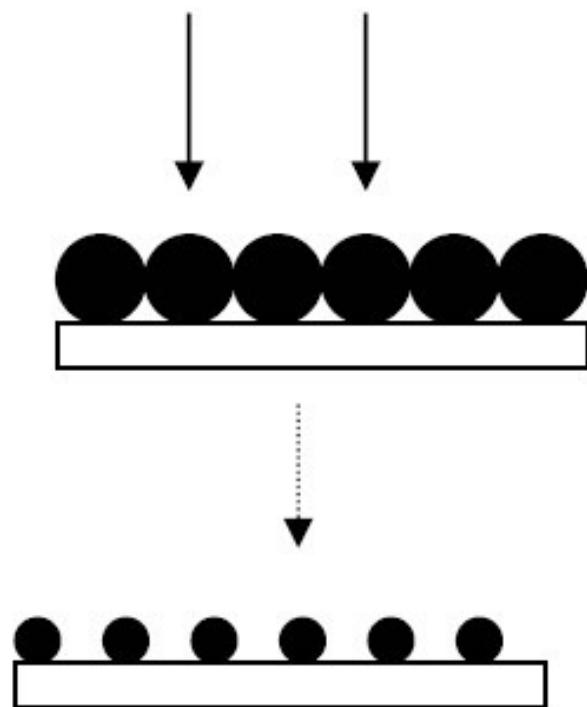
Ag Nanochains



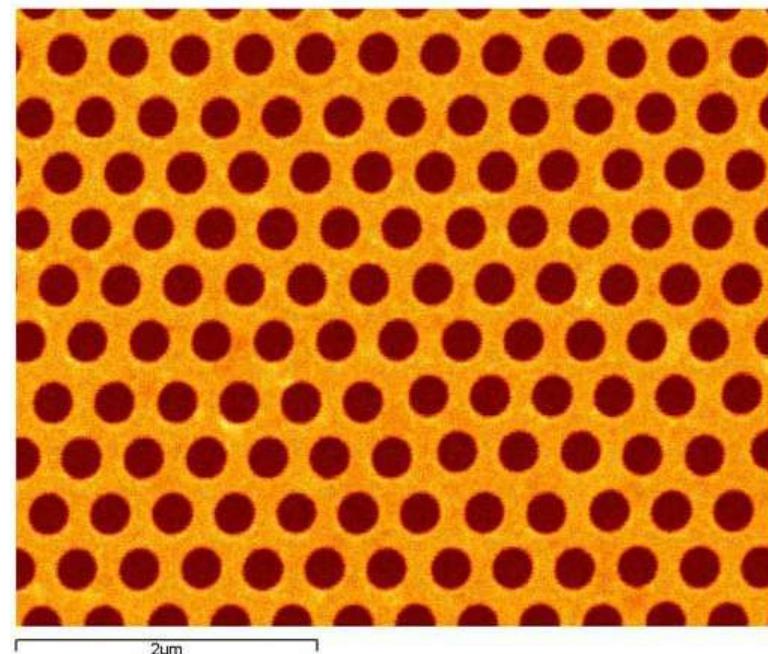
C. L. Haynes, R. P. Van Duyne, J. Phys. Chem. B, 105, 5599 (2001).

Sphere shrinkage for nano-hole array fabrication

PLASMA

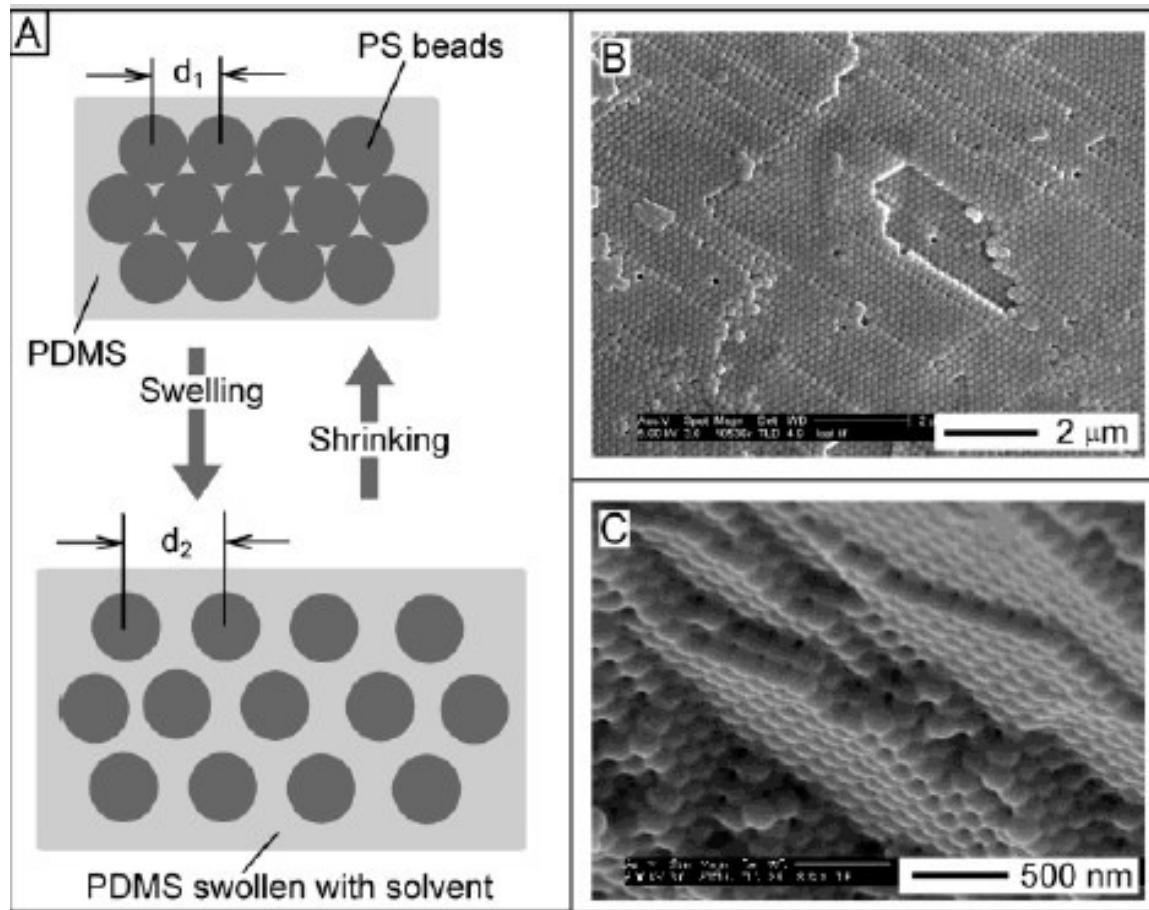


Etch nanosphere array in an oxygen plasma



Evaporate metal and remove nano-spheres, leaving hexagonal array of holes in a metal film.

Colloidal crystals with tunable colors for photonic papers



Printing colorful patterns without using conventional pigments.

Here the sphere array is like a grating filter, whose transmission or reflection spectrum (color) depends on its period

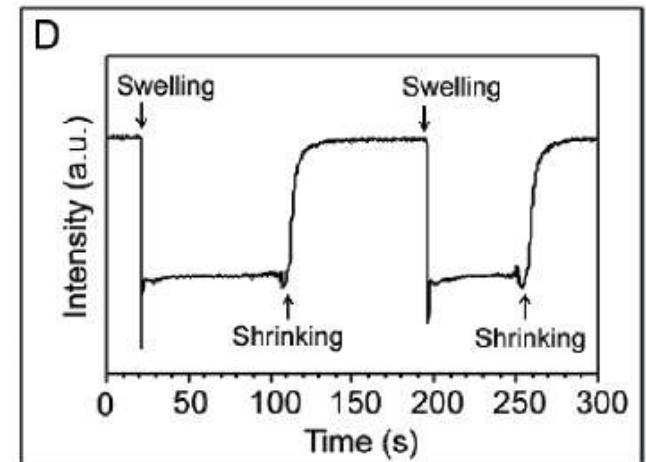
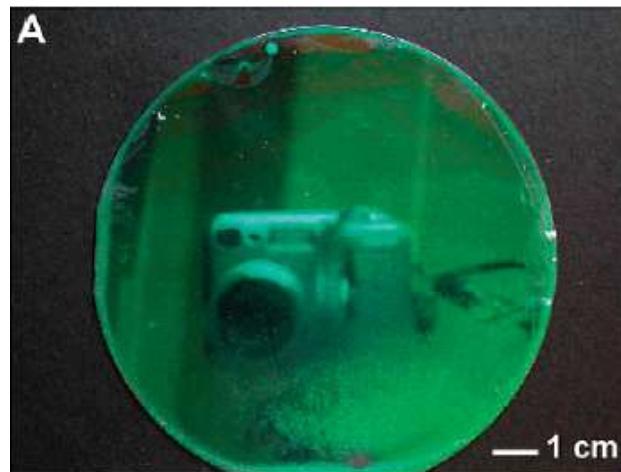
(and on refractive indexes of the sphere and matrix, and viewing angle).

- Basically the “paper” is a colloidal crystal of polymer beads embedded in PDMS elastomer matrix, whereas the “ink” is a liquid capable of swelling PDMS. (PDMS can be swelled easily by many solvents, which property is usually very undesirable for nanofabrication)
- As the elastomer is swollen by ink molecules, lattice constant is changed, so is the color.

Colloidal crystals with tunable colors and their use as photonic papers

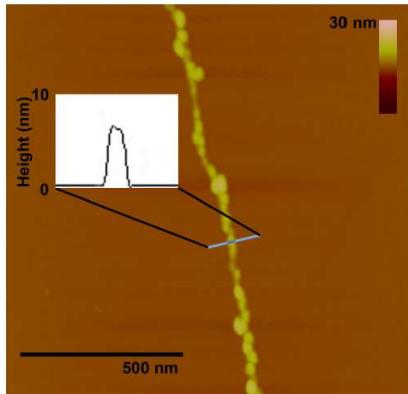
If the colors of these states are sufficiently different to be distinguished by the naked eye, the contrast can be exploited to write and display color letters and patterns with certain spatial resolutions.

As the ink molecules are evaporating, the PDMS matrix will gradually shrink back to its originated state and the color patterns will be automatically erased.



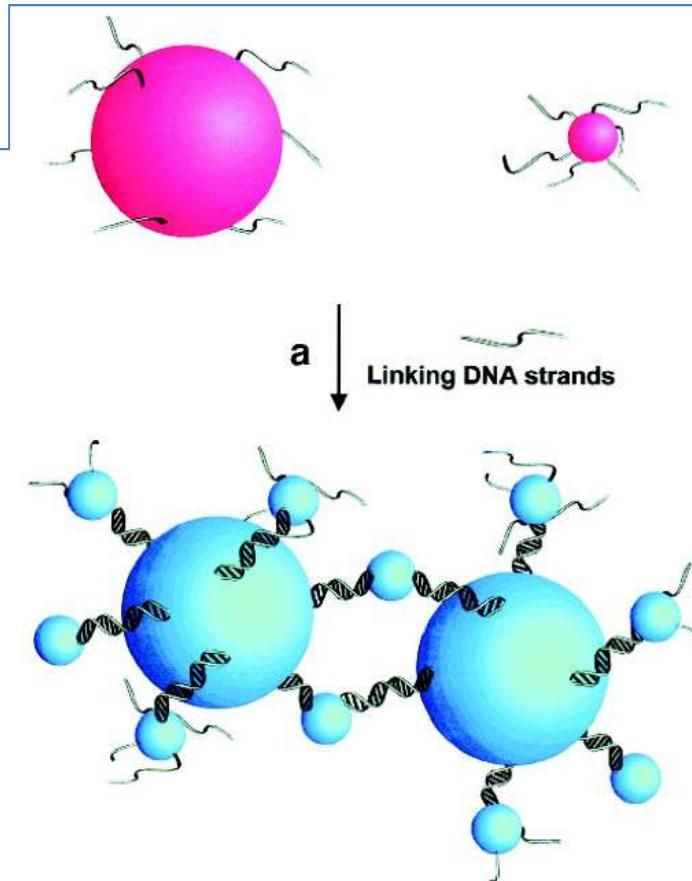
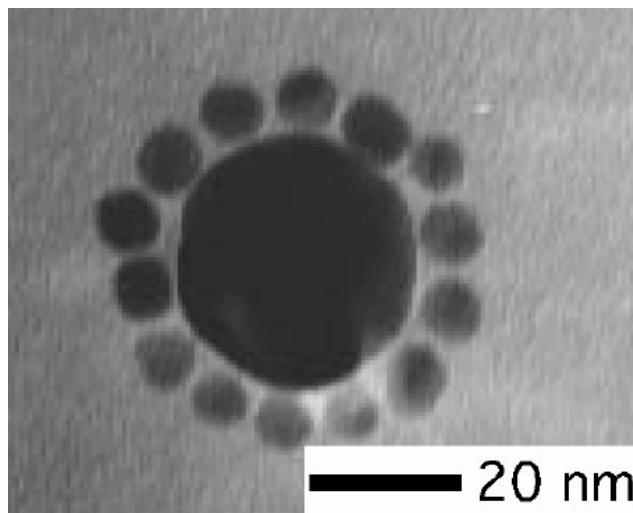
DNA templated self assembly

(NOT nano-sphere lithography!!)



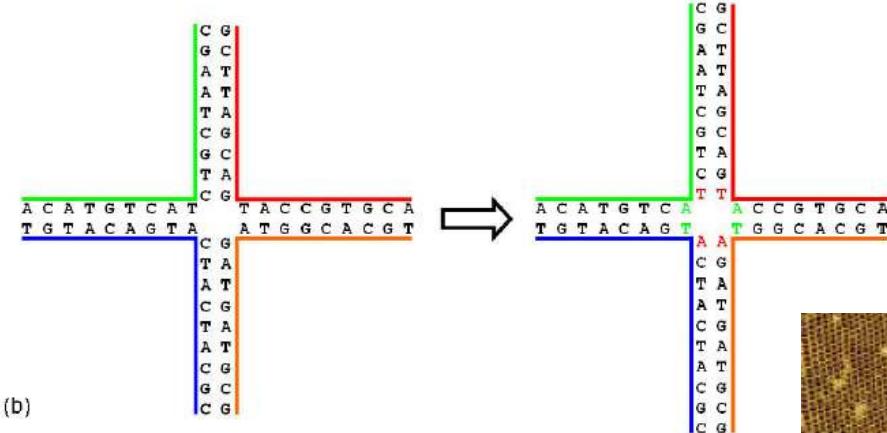
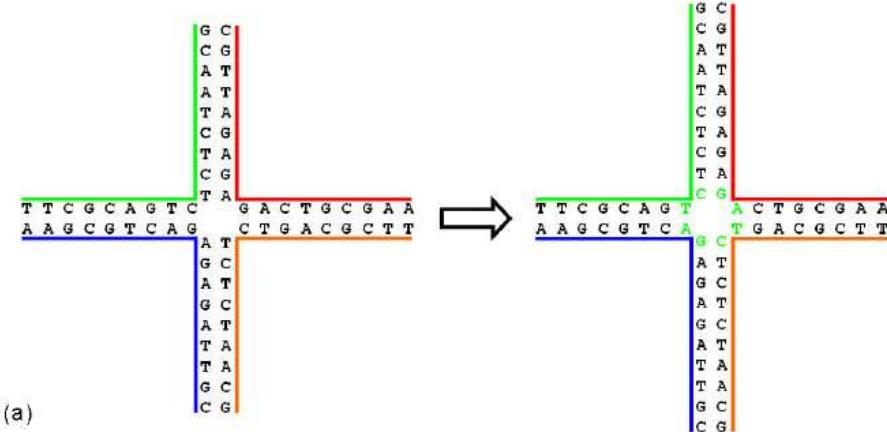
DNA is negatively charged in solution, onto which positive metal ions can be reduced to form metal structures.

AFM image of a DNA molecule stretched on a surface and metallized with a layer of palladium.



The particles can be released by heating to “detach” the two DNAs from each other.

DNA templated self assembly



Two-dimensional array of *three-arm* DNA stars forming hexagonal patterns. Insets show the Fourier transform of each image.

