

Overview of the main nano-lithography techniques

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Zaragoza



Outline

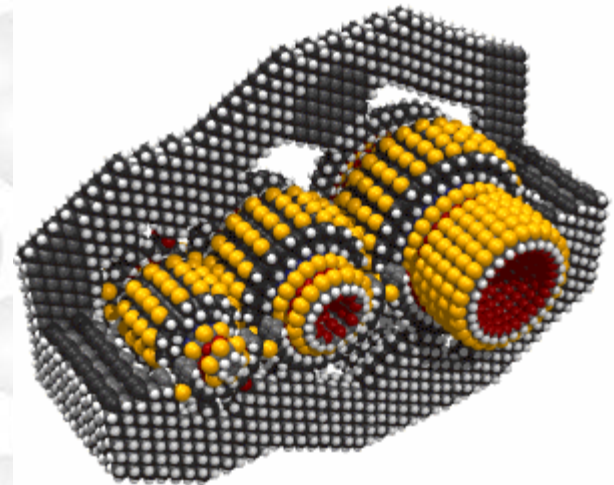
- Introduction: Nanotechnology.
- Nano-lithography techniques:
 - Masked lithography techniques:
 - ✓ Photolithography.
 - ✓ X-ray lithography.
 - ✓ Nanoimprint lithography.
 - Maskless lithography techniques:
 - ✓ Electron beam lithography.
 - ✓ Ion beam lithography.
 - ✓ Scanning probed based lithographies.
- Summary.



Introduction: Nanotechnology

What is Nanotechnology?

- The study of the controlling of matter on an [atomic](#) and [molecular](#) scale.
- Generally nanotechnology deals with structures sized between 1 to 100 [nanometer](#) in at least one dimension.
- Nanotechnology involves developing or modifying materials or devices within that size.



With 15,342 atoms, this gear is one of the largest nanomechanical devices ever modeled in atomic detail.

<http://www.crnano.org/whatis.htm>



Introduction: Nanotechnology

Some key dates in Nanotechnology:



1857

- 1857: Michael Faraday discovered “ruby” gold colloid.



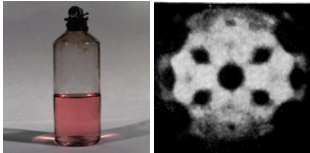
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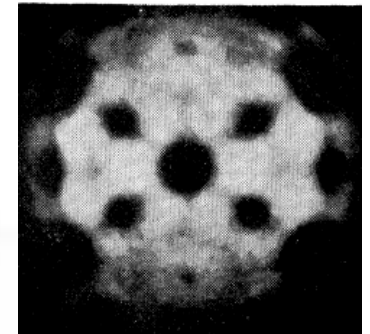
Introduction: Nanotechnology

Some key dates in Nanotechnology:



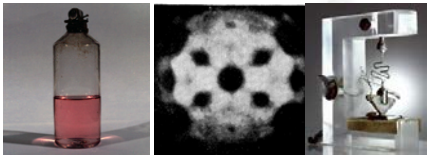
1857 1936

- 1936: Erwin Müller invented the field emission microscope.



Introduction: Nanotechnology

Some key dates in Nanotechnology:



- 1947: Bardeen, Shockley and Brattain discovered the semiconductor transistor.

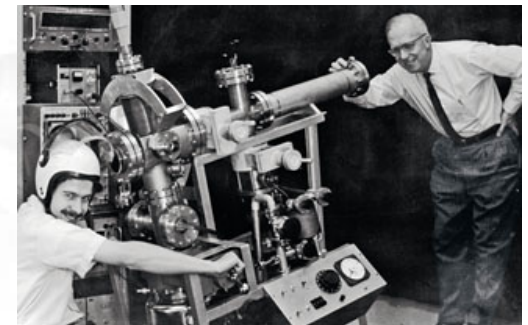


Introduction: Nanotechnology

Some key dates in Nanotechnology:

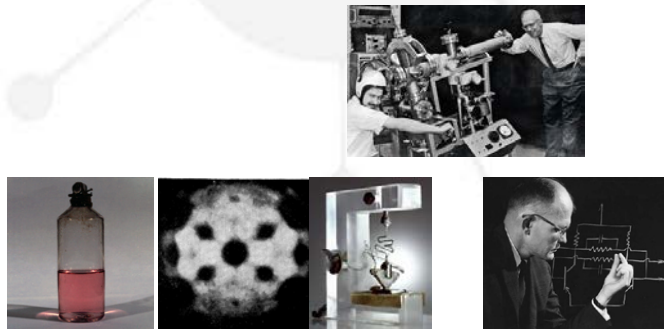


- 1951: Erwin Müller pioneered the field ion microscope.

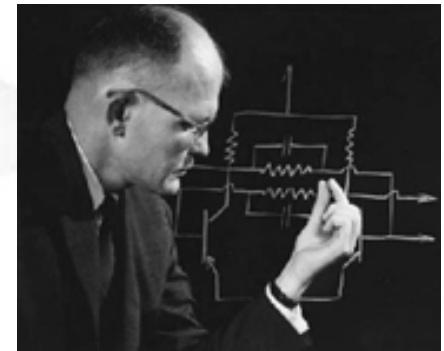


Introduction: Nanotechnology

Some key dates in Nanotechnology:



- 1958: Jack Kilby built the first integrated circuit.



Introduction: Nanotechnology

Some key dates in Nanotechnology:



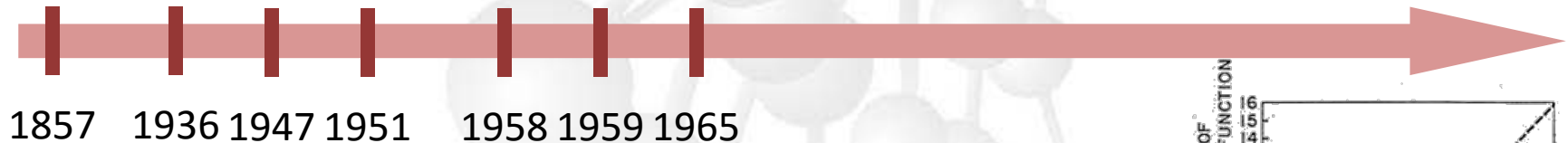
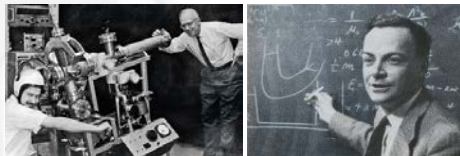
- 1959: Richard Feynman gave the first lecture on technology and engineering at the atomic scale.

<http://calteches.library.caltech.edu/1976/1/1960Bottom.pdf>



Introduction: Nanotechnology

Some key dates in Nanotechnology:



- 1965: Gordon Moore described a trend in electronics known as “Moore’s law”.

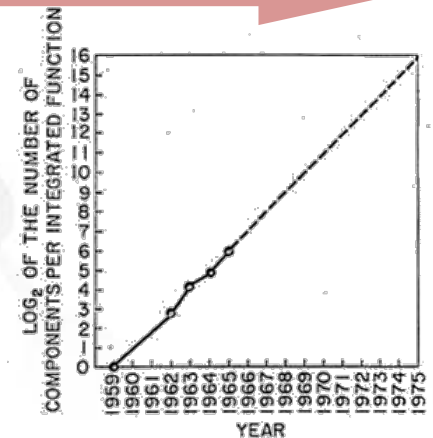
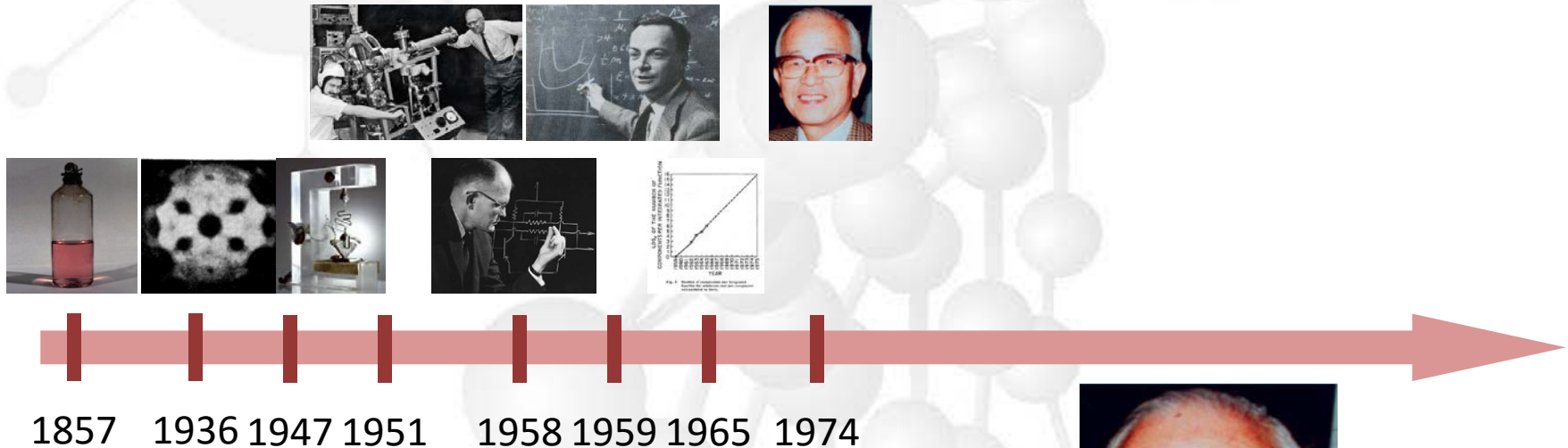


Fig. 2: Number of components per integrated function for minimum cost per component extrapolated vs time.



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Some key dates in Nanotechnology:

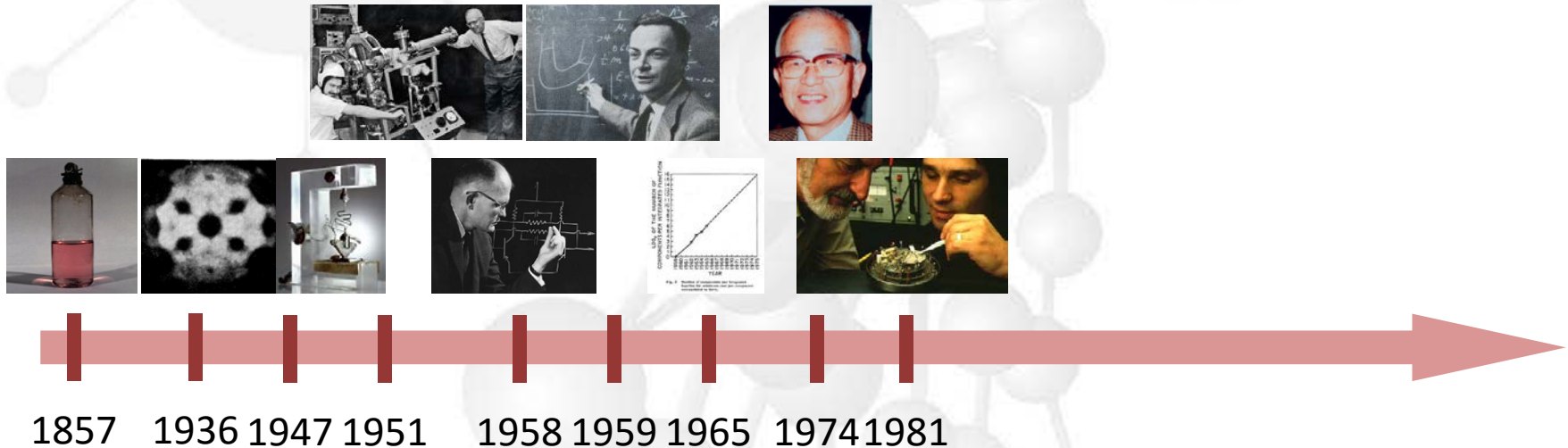


- 1974: Norio Taniguchi coined the term Nanotechnology.



Introduction: Nanotechnology

Some key dates in Nanotechnology:

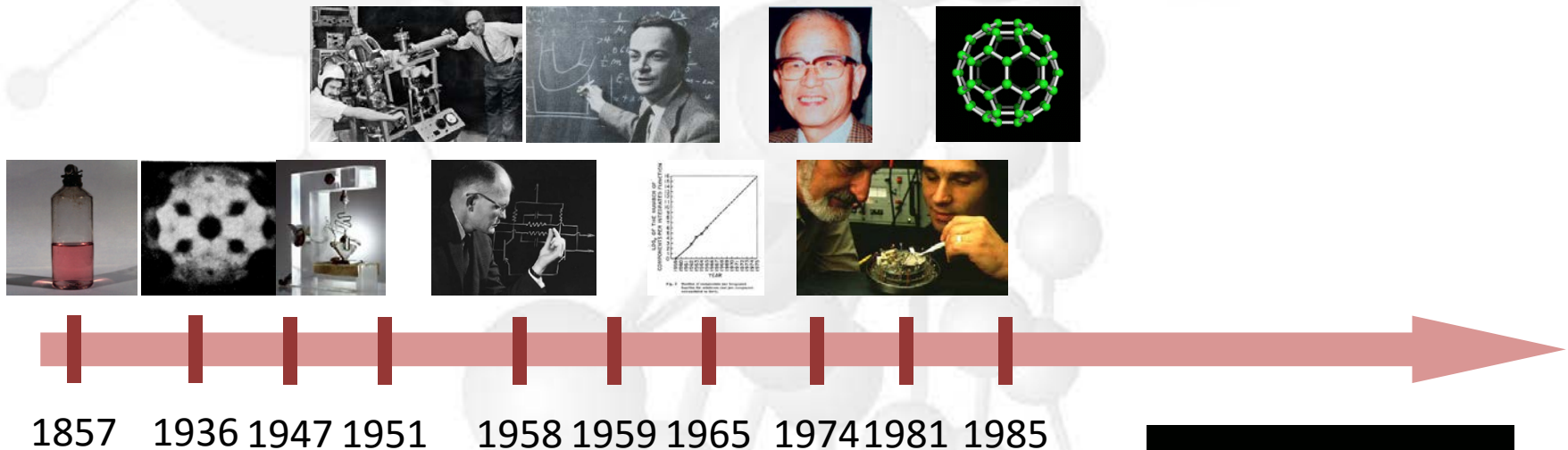


- 1981: Binnig and Rohrer invented the scanning tunneling microscope.

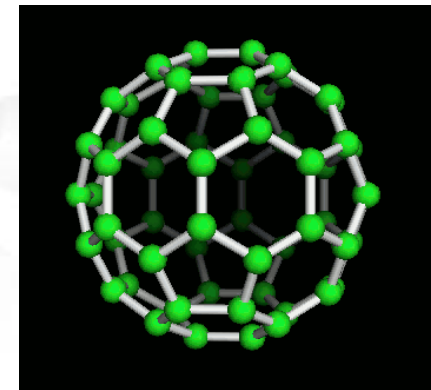


Introduction: Nanotechnology

Some key dates in Nanotechnology:

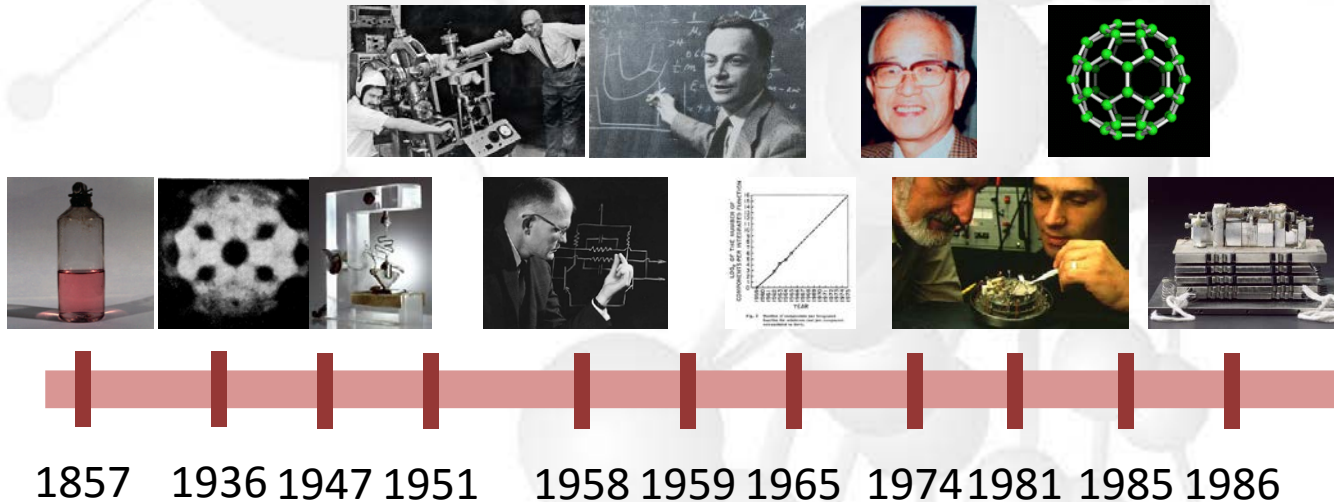


- 1985: Discovery of the Buckminsterfullerene (C_{60} or buckyball).

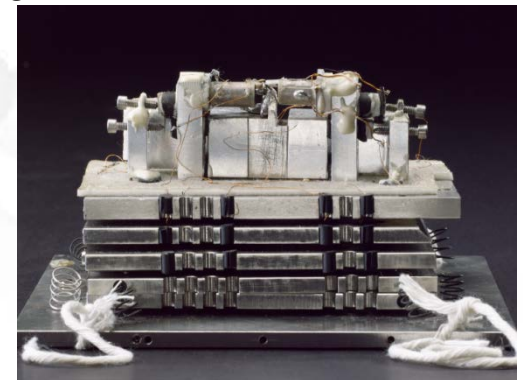


Introduction: Nanotechnology

Some key dates in Nanotechnology:



- 1986: Binnig, Quate and Gerber invented the atomic force microscope.



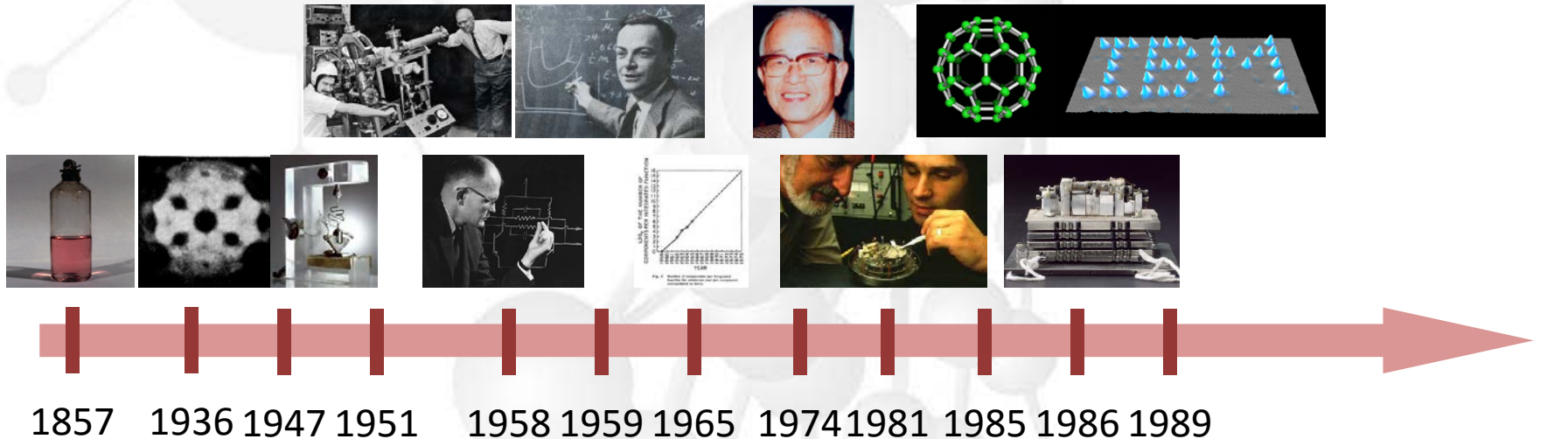
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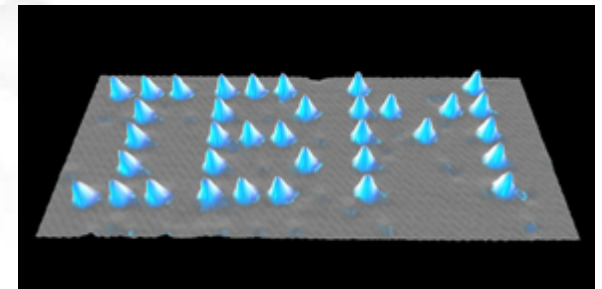


Introduction: Nanotechnology

Some key dates in Nanotechnology:

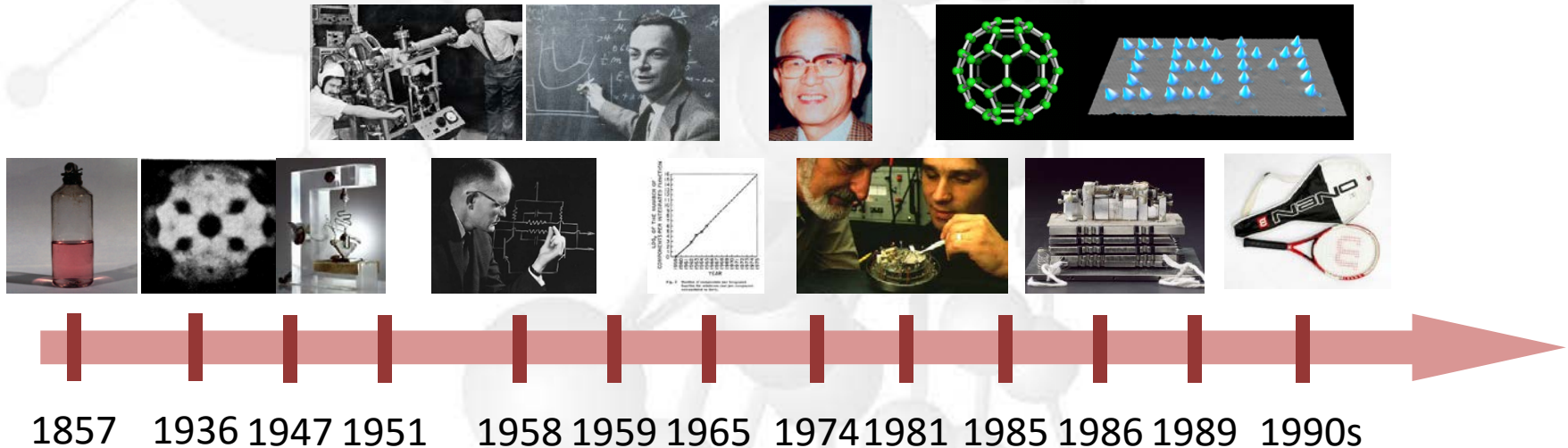


- 1989 Eigler and Schweizer demonstrated the atomic manipulation.



Introduction: Nanotechnology

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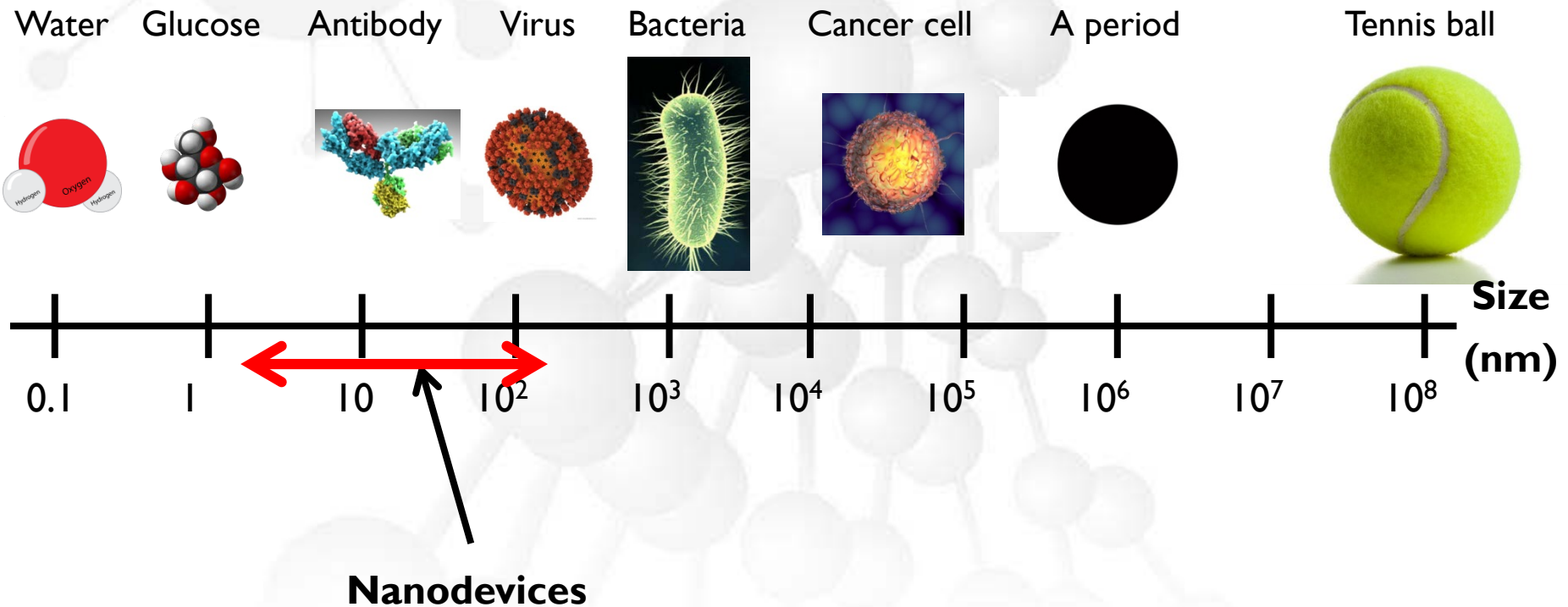


- 1990s: Consumer products making use of nanotechnology!



Introduction: Nanotechnology

How small is Nano?



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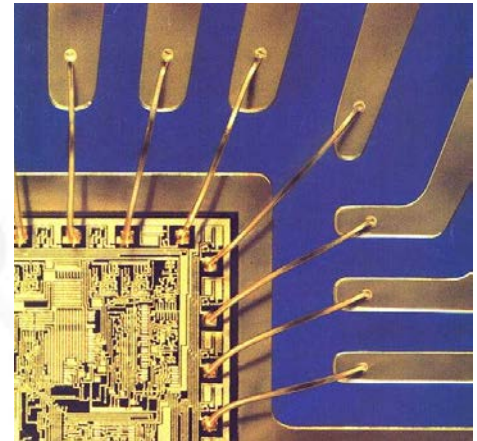
Nanolithography techniques

Nanolithography: Branch of nanotechnology concerned with the study and application of fabricating nanoscale structures, i.e. patterns with at least one dimension between 1 and 100 nm.

Why do we need Nanolithography?

We want to do nanopatterning and fabricated useful devices with nanometric dimensions.

Even though nature provides a few nanometric systems, in general we need to create them artificially.



Nanolithography techniques

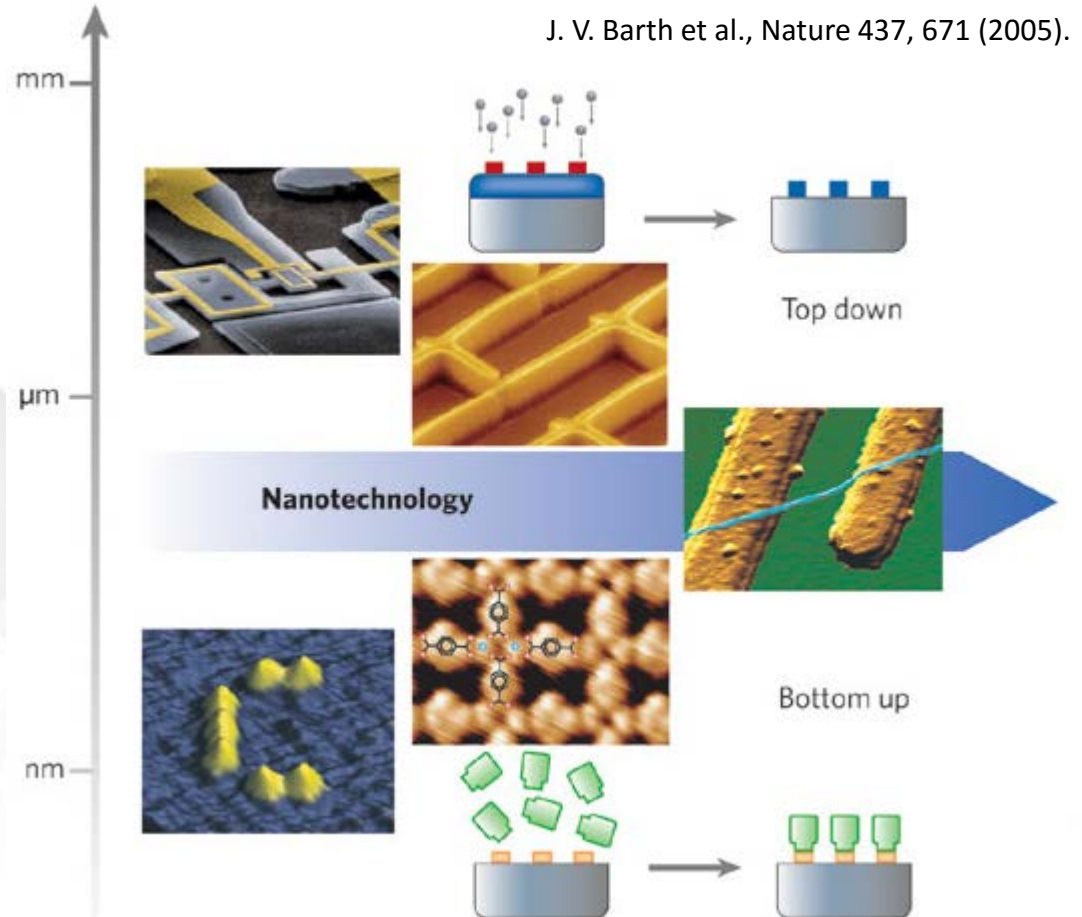
Approaches to control matter at the nanoscale

Top-down approach

Thin film deposition techniques
+
Lithography

Bottom-up approach

Self assembly, self organization



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Nanolithography techniques

Resolution for micro- and nano- fabrication:

10^{-4} m

10^{-5} m

10^{-6} m

10^{-7} m

10^{-8} m

Micrometric range
(10^{-3} - 10^{-6} m)

Nanometric range
(10^{-6} - 10^{-9} m)

Optical lithography

**Electron-beam
lithography (EBL)**

**Ion-beam lithography
(IBL)**

Nanoimprinting (NIL)

**Scanning Probe
Lithography (SPL-AFM)**



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Nanolithography techniques

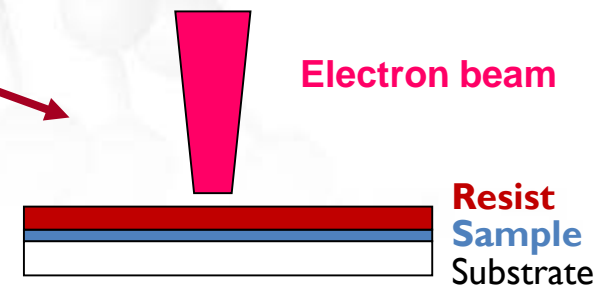
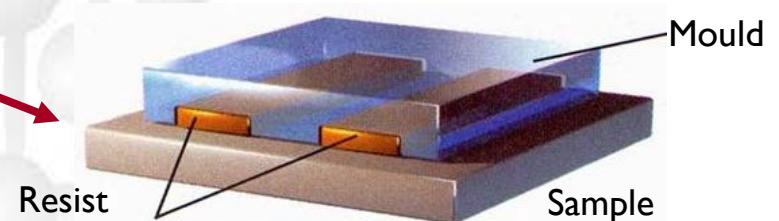
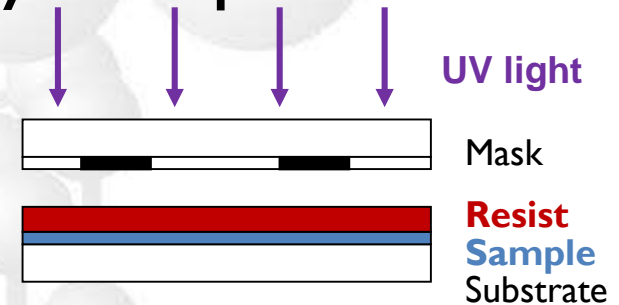
Possible classification of nanolithography techniques:

□ Masked lithography techniques:

- ✓ Photolithography.
- ✓ X-ray lithography.
- ✓ Nanoimprint lithography.

□ Maskless lithography techniques:

- ✓ Electron beam lithography.
- ✓ Ion beam lithography.
- ✓ Scanning probed based lithographies.



Photolithography

Schematically:

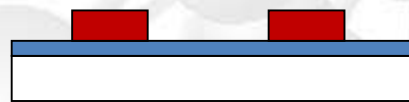
1) Exposure

The resist becomes sensitized



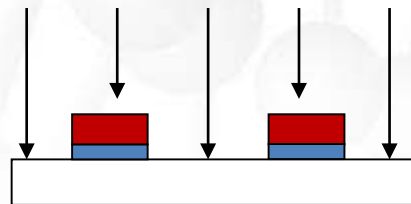
2) Development

Immersion in developer fluid.



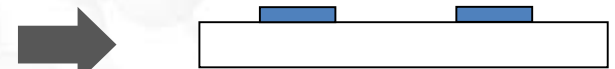
3) Etching

Dry or wet etching.



4) Resist removal

Typically acetone



Result: Sample with the same pattern of the mask

Courtesy of J. M. De Teresa, ICMA-Unizar



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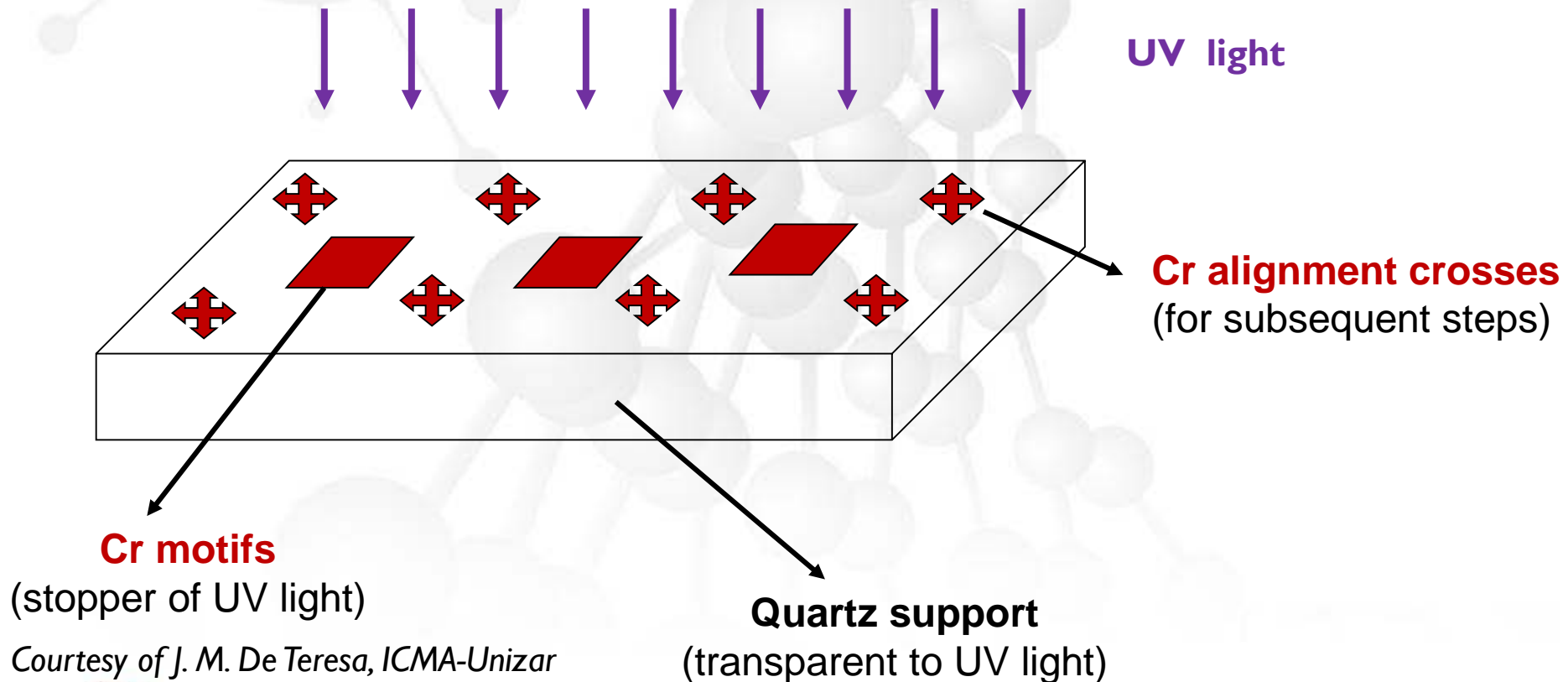
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Photolithography

Going over that a little more slowly:

- **Photolithography masks:**



Courtesy of J. M. De Teresa, ICMA-Unizar



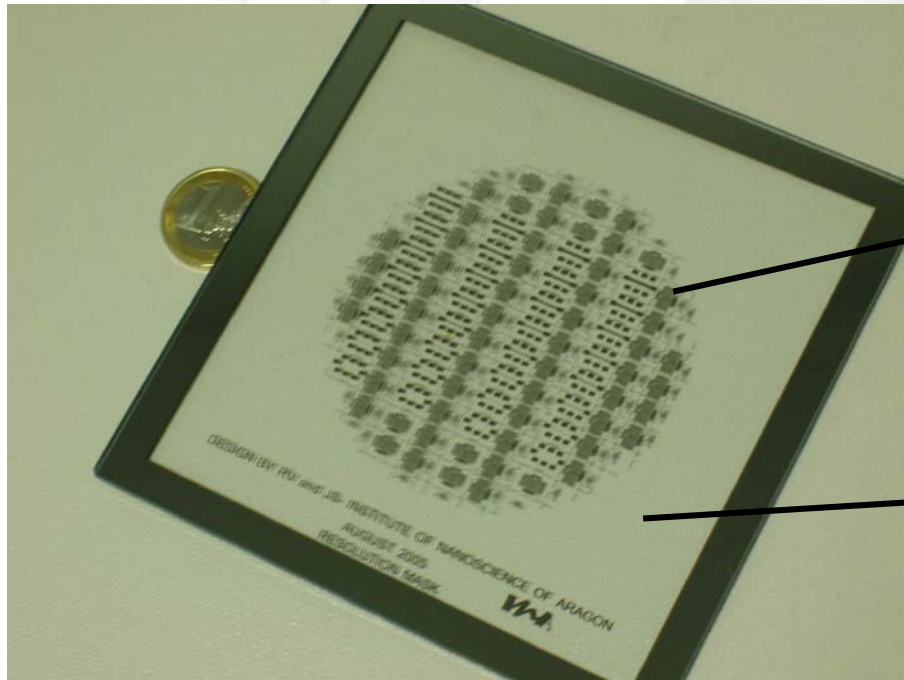
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Photolithography

- **Photolithography masks:**



Cr motifs
(stopper of UV light)

Quartz support
(transparent to UV light)
5" by 5" in area
0.25" in thickness

Courtesy of J. M. De Teresa, ICMA-Unizar



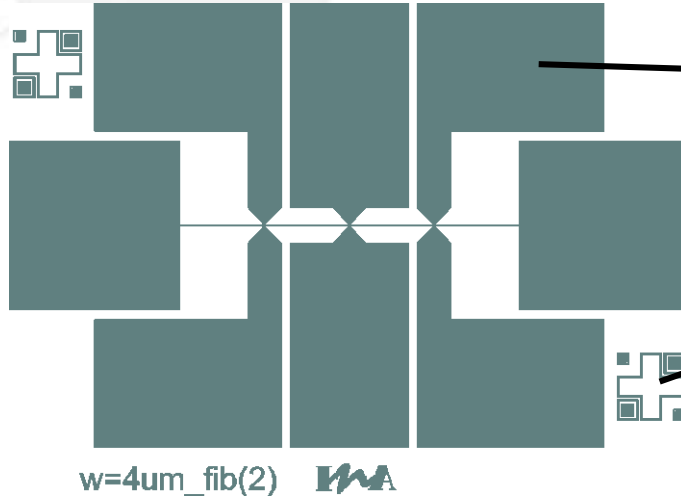
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Photolithography

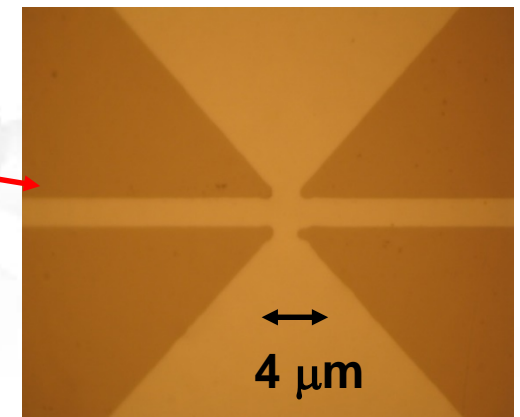
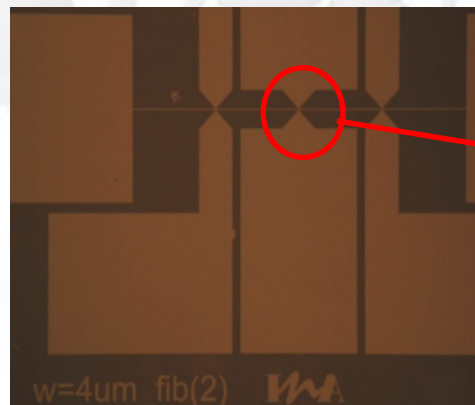
- Photolithography masks:**



Cr motifs
(stopper of UV light)

Cr alignment crosses
(for subsequent steps)

Final sample:
(Optical microscope image)



Courtesy of J. M. De Teresa, ICMA-Unizar



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Photolithography

- **Resists (Photoresists):** Viscous fluid formed by a polymer, a photosensitive component and a solvent.

Polymer: It provides the properties of viscosity, adherence and resilience to chemical etching.

Solvent: It permits to keep the polymer in solution, allowing its application on the sample. Its concentration changes the viscosity/final thickness.

Photosensitive complex: It provides the sensitivity to the UV radiation. This molecule is able to change the solubility of the polymer in the developer.



Photolithography

- Two types of photoresists:

Negative photoresist

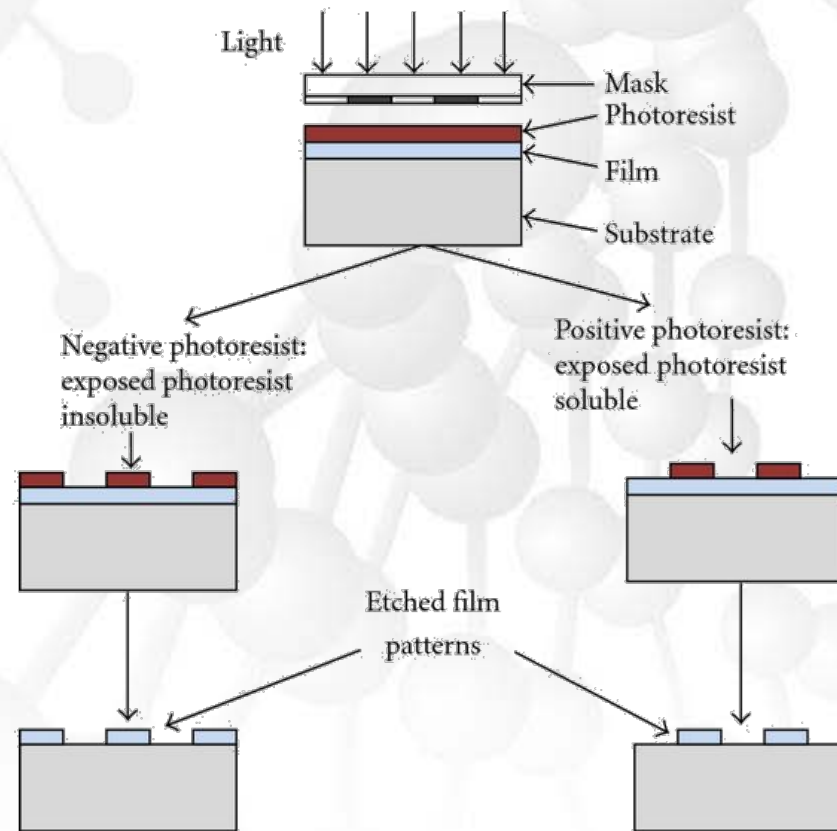
- Exposure to UV light causes it to polymerize and thus be more difficult to dissolve.



- Developer removes unexposed resist.



- It results in a pattern supplementary to that of the mask.



Positive photoresist

- Exposure to UV light makes it more soluble in the developer.



- Exposed resist is washed away by developer so that the unexposed sample remains.

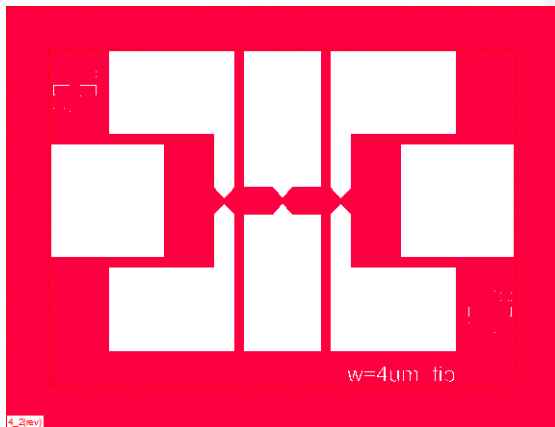


- It results in an exact copy of the original design.

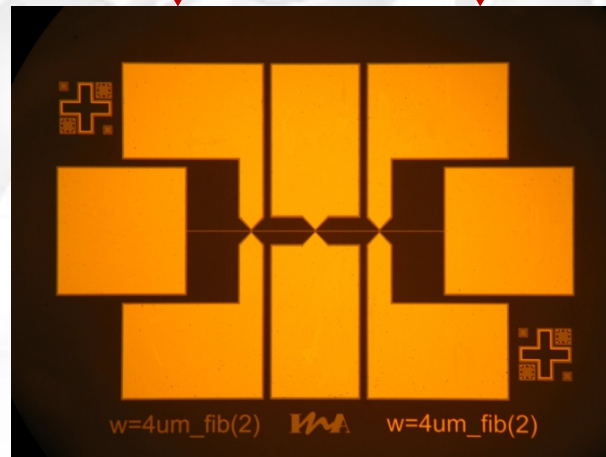
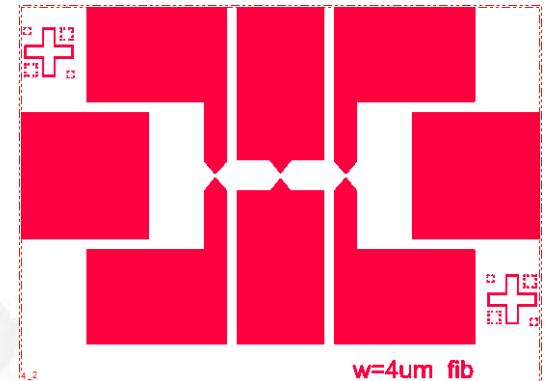
Photolithography

- Two types of photoresists:

Negative photoresist
+
Mask #1



Positive photoresist
+
Mask #2
(supplementary to mask #1)



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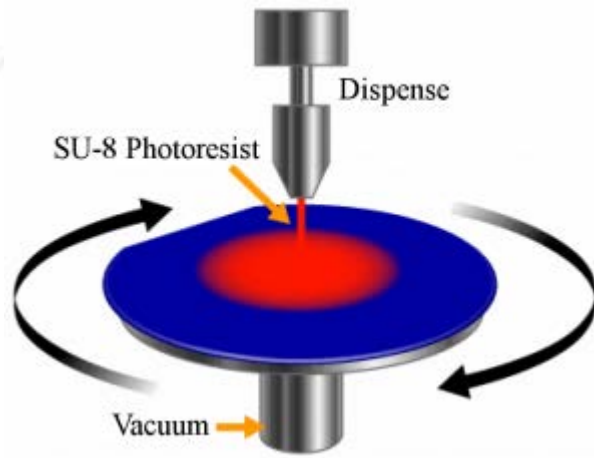
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Photolithography

- Spin coating

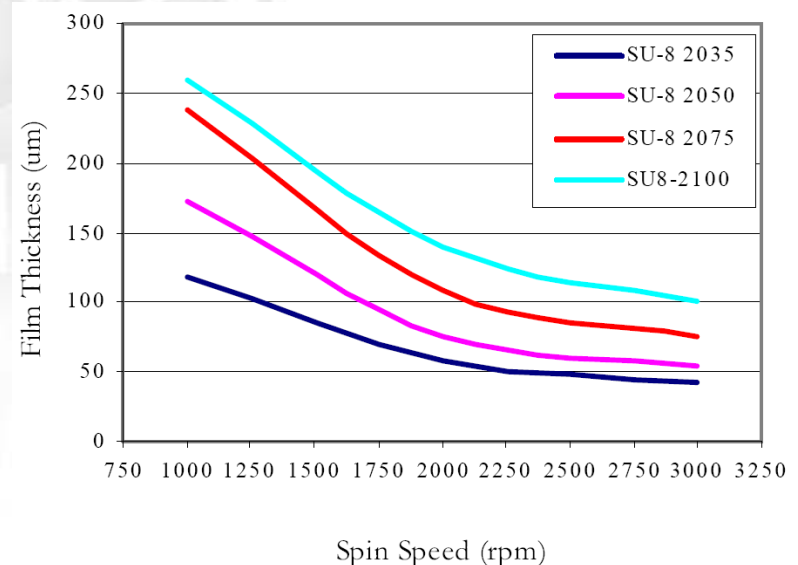


Spin speed:
usually in the range 1000 – 6000 rpm

Final resist thickness:

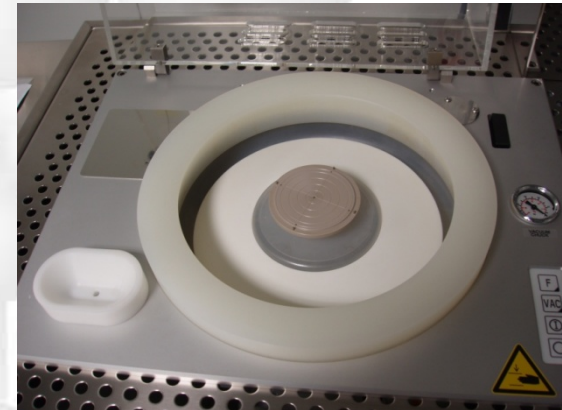
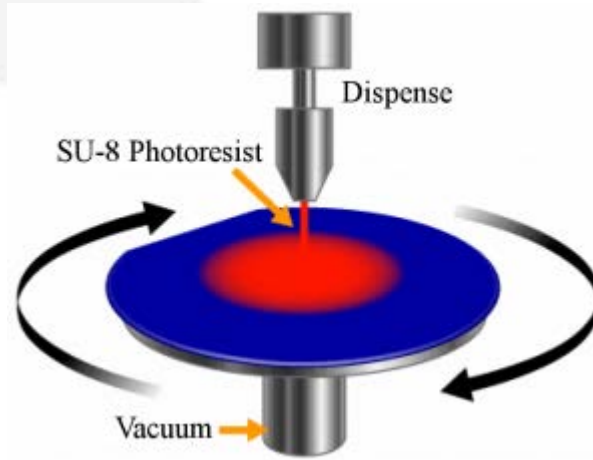
$$t \propto \frac{\eta^2}{\sqrt{s}}$$

η = viscosity.
 s = spin speed.



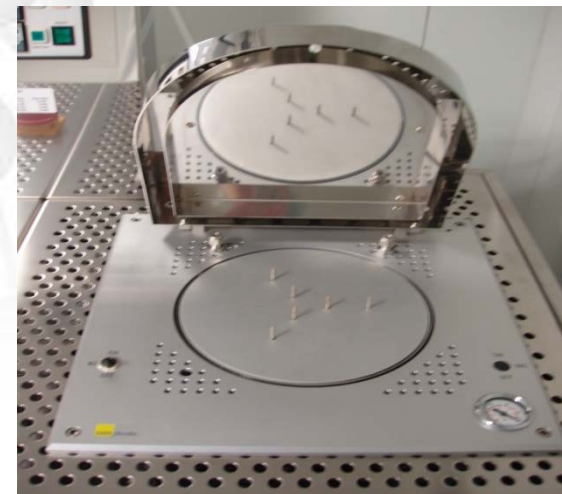
Photolithography

- Real equipment for spin coating:



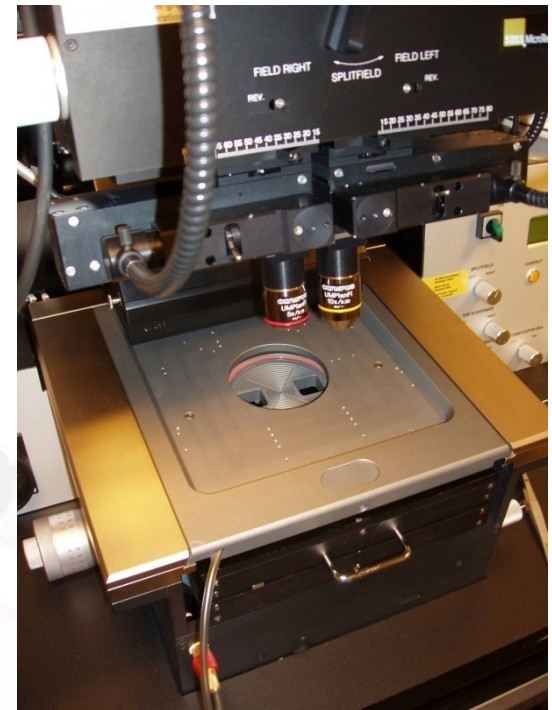
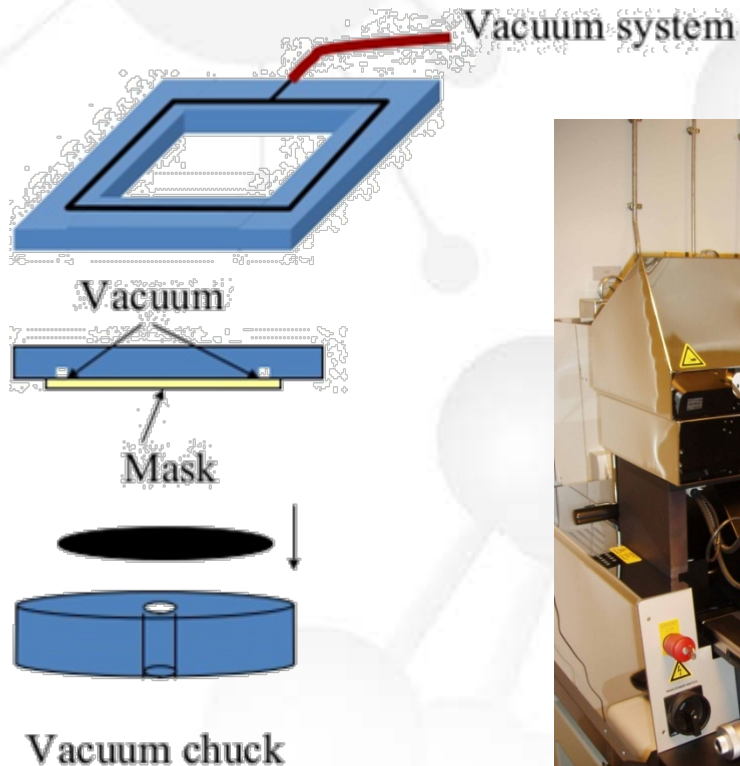
-Soft-bake step:

Heating at T around 100°C to eliminate the solvent.



Photolithography

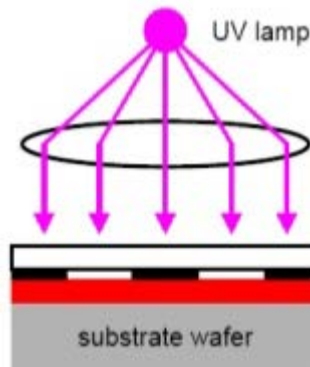
- **Mask aligner: (Exposure system).**



Photolithography

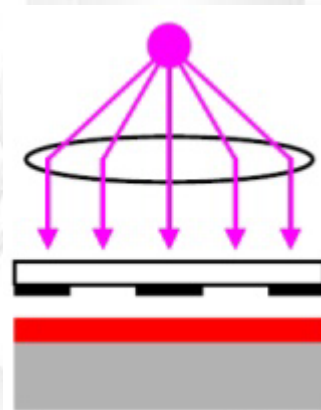
- **Exposure modes:**

Contact:



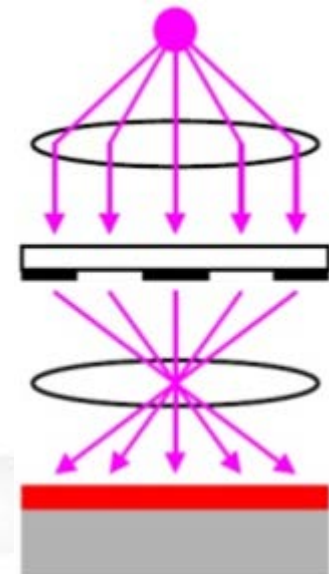
Mask in contact
with the
photoresist film
(gap $\sim 0 \mu\text{m}$)

Proximity:



Gap $\sim 10 \mu\text{m}$
between mask and
photoresist.

Projection:

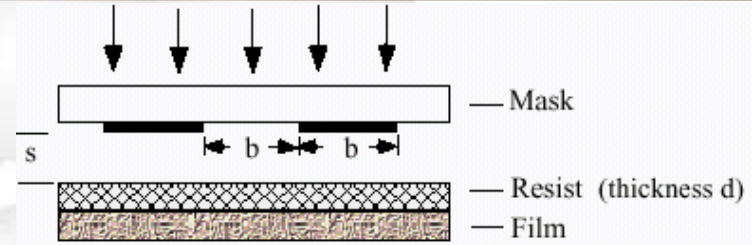


Imaging optics in
between the mask
and the wafer

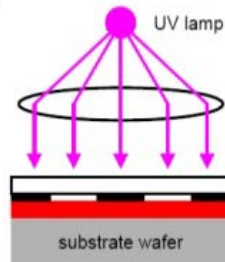


Photolithography

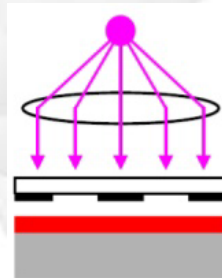
- Exposure modes: Resolution



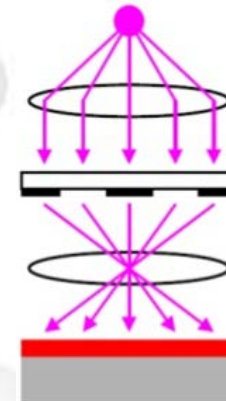
Contact:



Proximity:



Projection:



Depth of focus:
 $\sigma = k\lambda / (NA^2)$

Resolution: $2 b_{min} = 3\sqrt{\lambda d/2}$

$2 b_{min} = 3\sqrt{\lambda s}$

$b_{min} = k\lambda / (NA)$

Example:

$d = 1 \mu m, \lambda = 365 \text{ nm}$

$s = 10 \mu m, \lambda = 365 \text{ nm}$

$k = 0.45, \lambda = 248 \text{ nm}, NA = 0.7$

$b_{min} \approx 640 \text{ nm}$

$b_{min} \approx 2866 \text{ nm}$

$b_{min} \approx 160 \text{ nm}$



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Photolithography

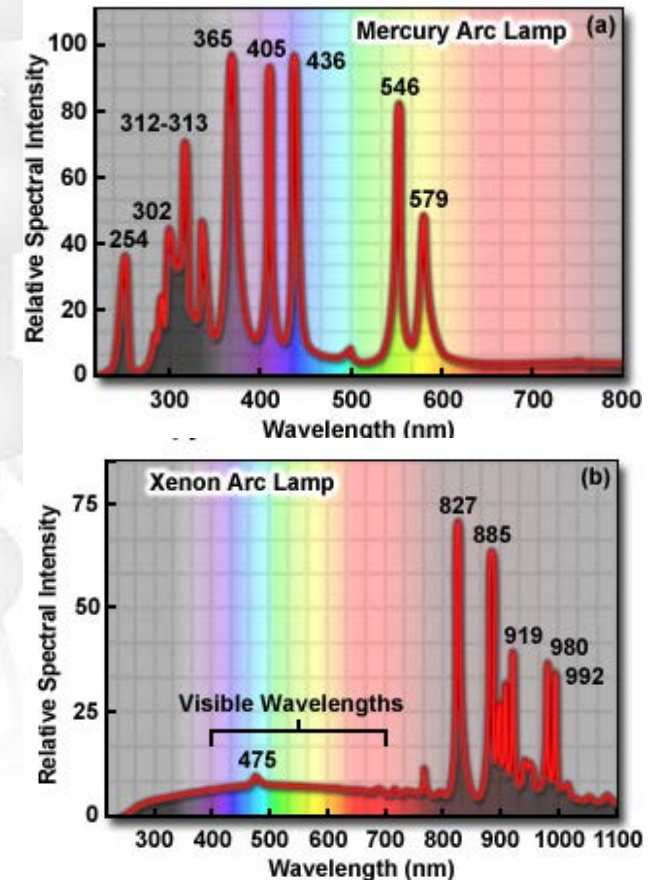
- Mask aligner: Exposure source.

Exposure sources (UV):

-**Xe arc lamps:** Near continuous spectrum in the visible 200-750 nm with Xe lines above 800 nm.

-**Hg arc lamps:** High energy output in the UV with intense lines between 240-600 nm.

-**Hg-Xe arc lamps:** Combination of the spectra from Hg and Xe (Xe gas improves start-up and extends operating life).

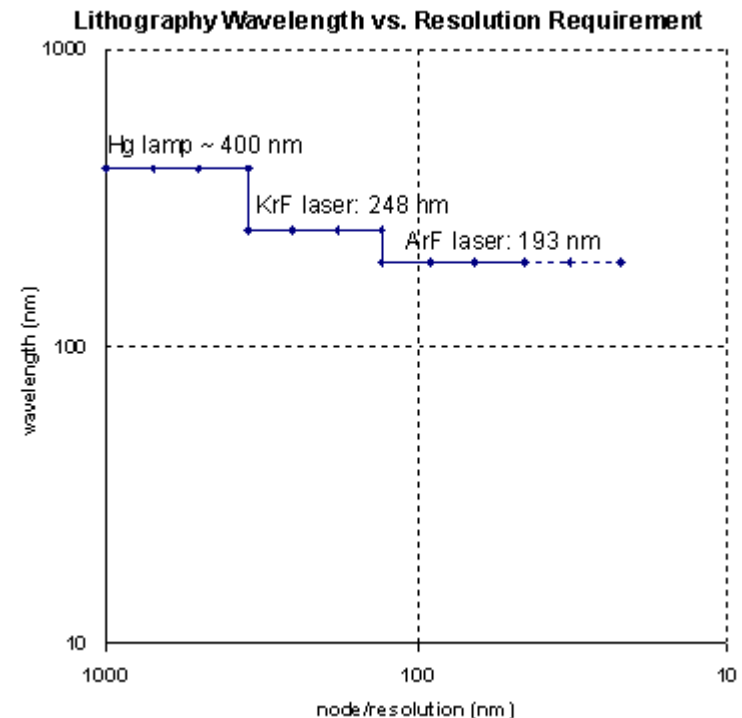


Photolithography

- Mask aligner: Exposure source.

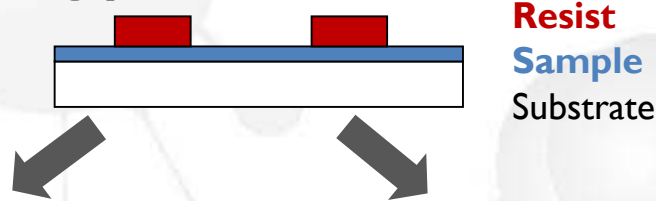
Exposure sources (DUV):

By 1996, transition from an I-line Hg arc lamp to deep-UV excimer laser – KrF (248 nm). The physics of excimer laser allows scaling to higher powers, narrower spectral widths and shorter wavelengths.



Photolithography

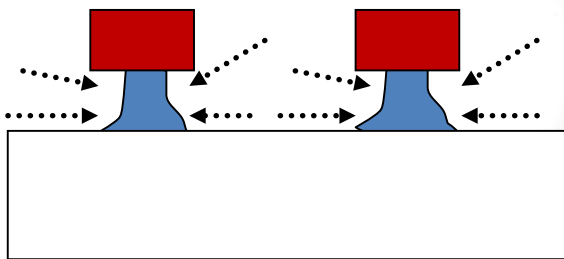
- Etching process:



Resist
Sample
Substrate

Wet etching:

By means of reactive liquids

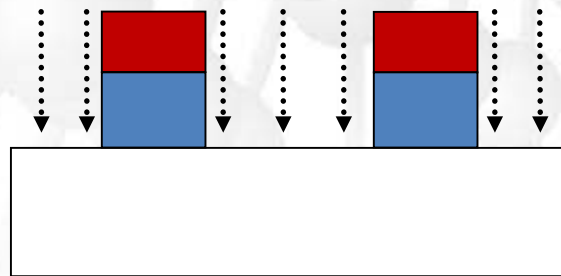


Isotropic etching profile

Courtesy of J. M. De Teresa, ICMA-Unizar

Dry etching:

By means of physical etching (sputtering/ionic bombardement) or chemical etching (plasma / RIE).



Anisotropic etching profile

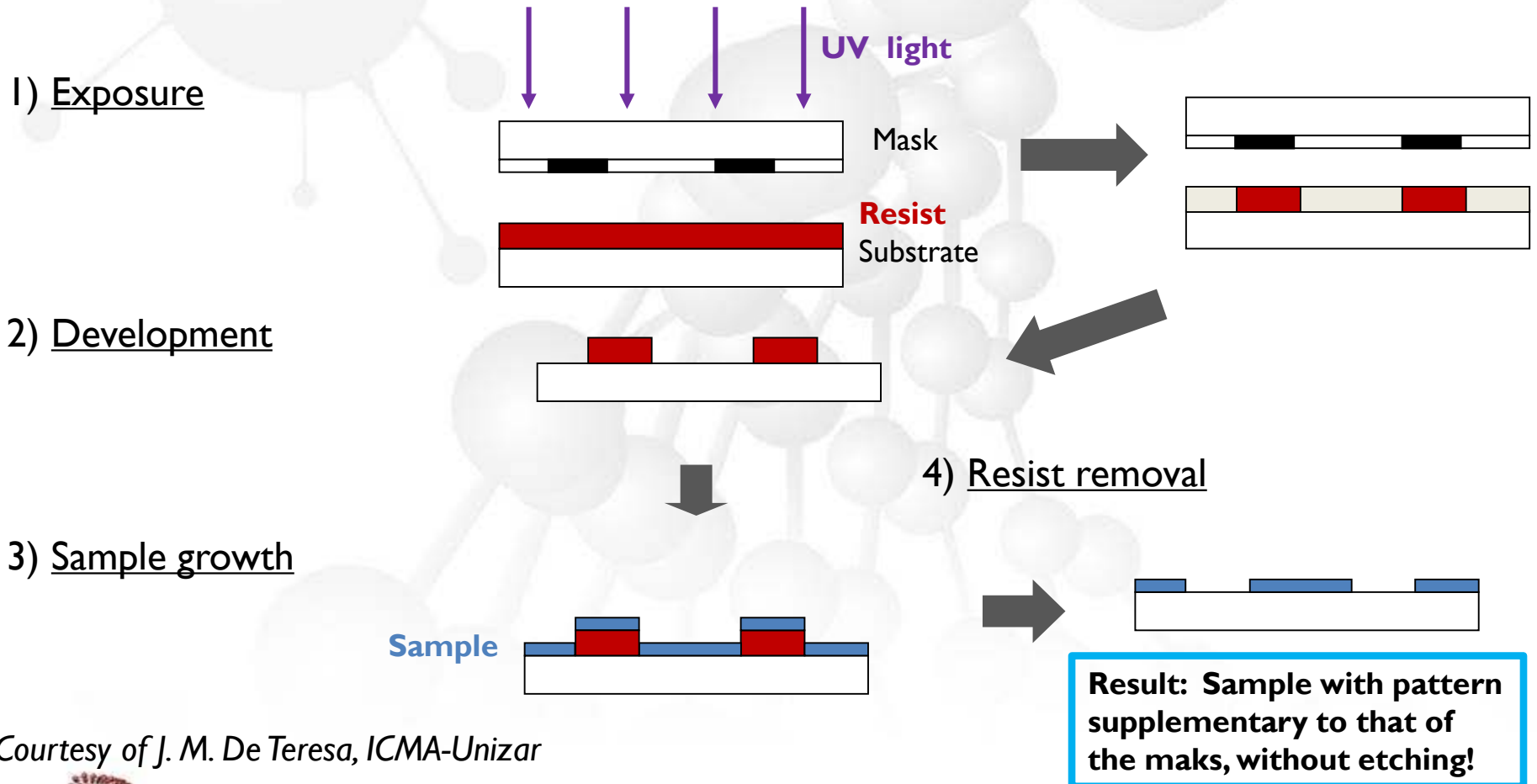
Comparison:

Property	Wet	Dry
Anisotropy	-	+
Resolution	-	+
Homogeneity	-	+
Reproducibility	-	+
Profile	-	+
Risk of burns	-	+
Cost	+	-



Photolithography

- Lift-off process: (positive resist).



Courtesy of J. M. De Teresa, ICMA-Unizar



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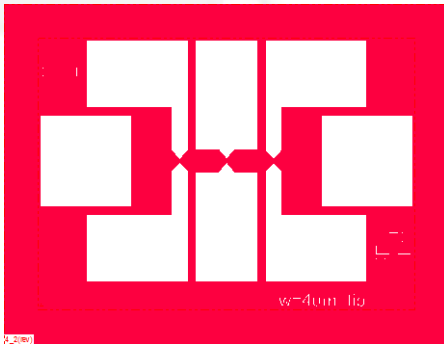
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Photolithography

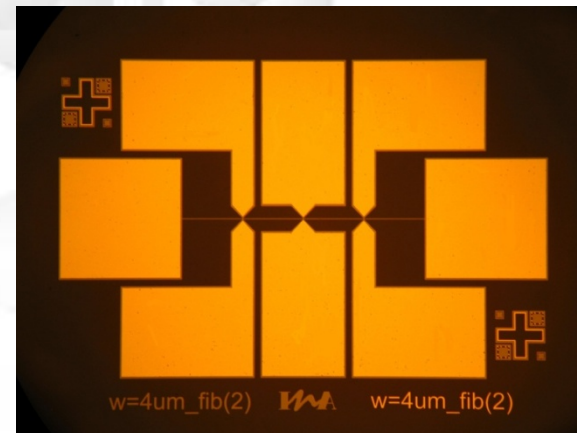
- **Lift-off process:** Real example.

Mask:



+ Positive resist.

After growing the sample and removing the resist:



Courtesy of J. M. De Teresa, ICMA-Unizar



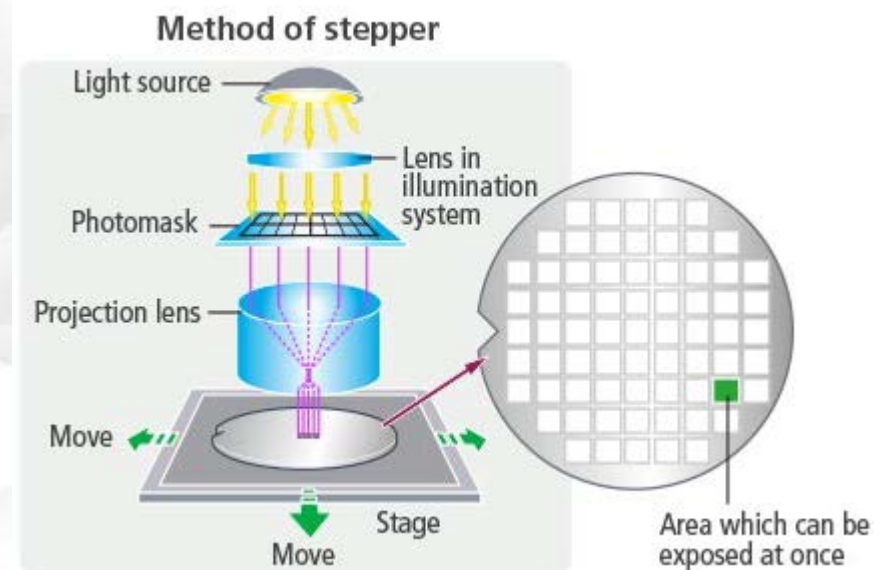
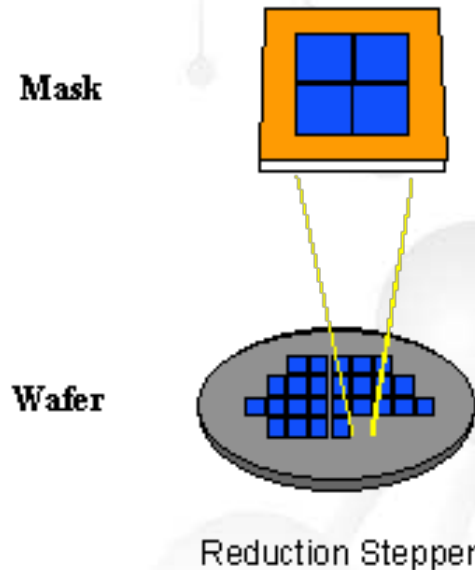
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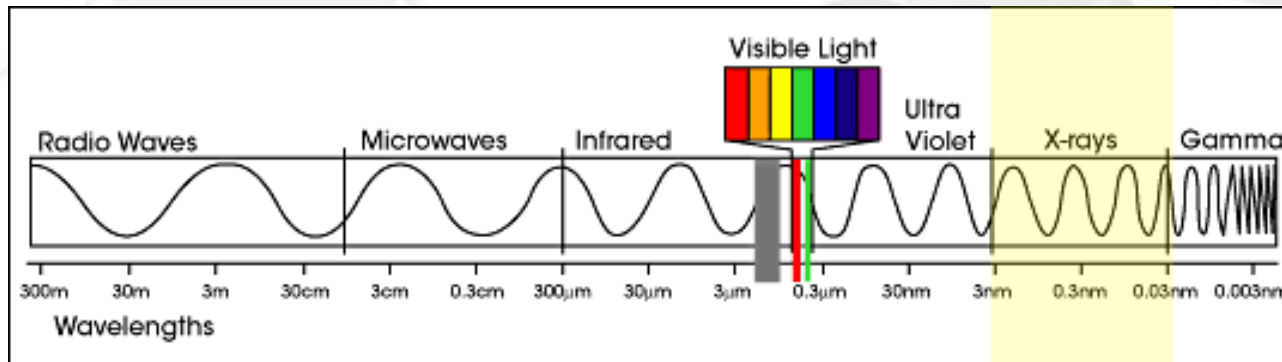
Photolithography

- **Photolithography in IC industry: Stepper.**



X-ray lithography

- **X-rays:**



- Shorter wavelength than UV light → Little diffraction effects.
- Fine features with vertical sidewalls.
- Very large depth of focus → Non-flat wafer is OK.
- No optics needed: “Just” an **x-ray source**, an **x-ray resist** and an **x-ray mask**.



X-ray lithography

- **X-ray source:**

Requirements: Strong, stable, collimated, single frequency...

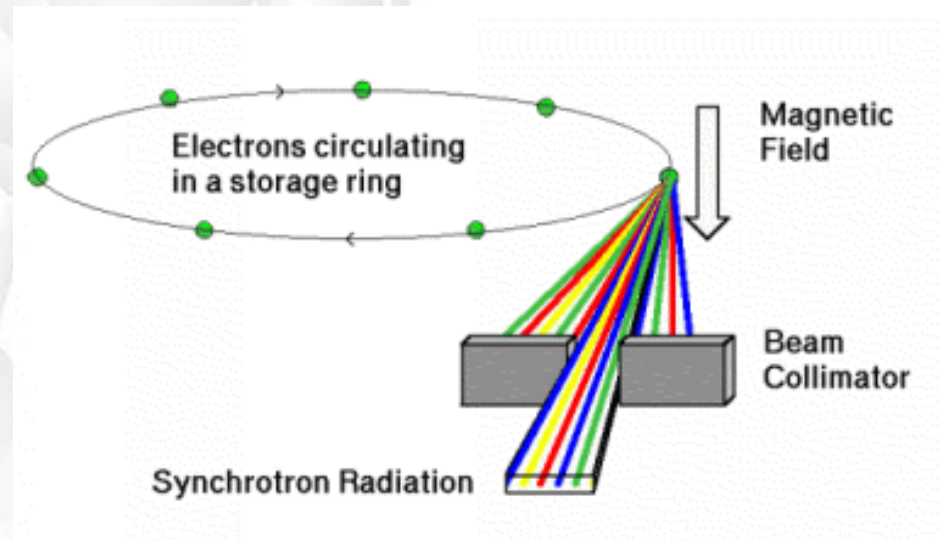
Synchrotron radiation:

Electromagnetic radiation emitted when charge particles are radially accelerated.

High cost!!

But...

- Extremely high intensity.
- Tunable.
- Very low divergence.

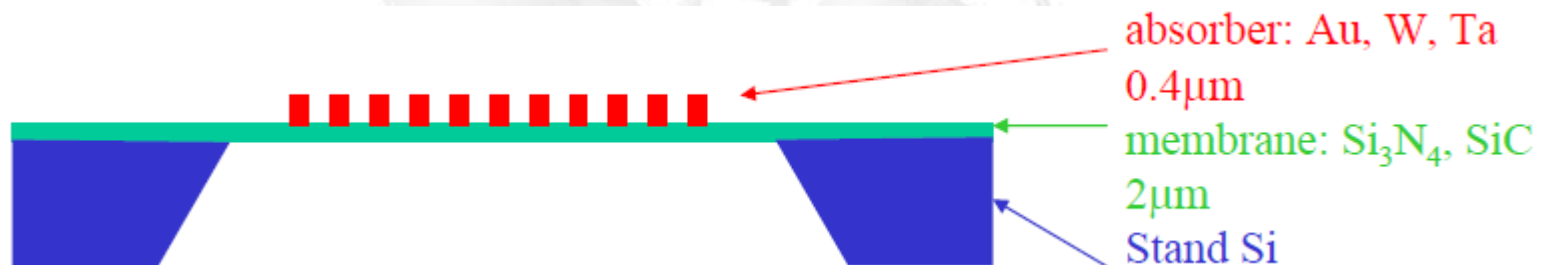


X-ray lithography

X-ray mask:

- **Mask substrate:** Low atomic number thin membrane.
- **Absorber:** High attenuation, stability under radiation, low microstructural defect density: Au, W, Ta, alloys.

Silicon	0 (50% transmission at $5.5 \mu\text{m}$ thickness).
SiC	0 (50% transmission at $2.3 \mu\text{m}$ thickness).
Diamond	0 (50% transmission at $4.6 \mu\text{m}$ thickness).



X-ray lithography

- **X-ray resist:**

- Absorption of x-ray does not produce resist modification.
 - Photoelectrons and Auger electrons are responsible for resist modification.
- ↓
- Any resist for electron beam lithography (PMMA) can be used.

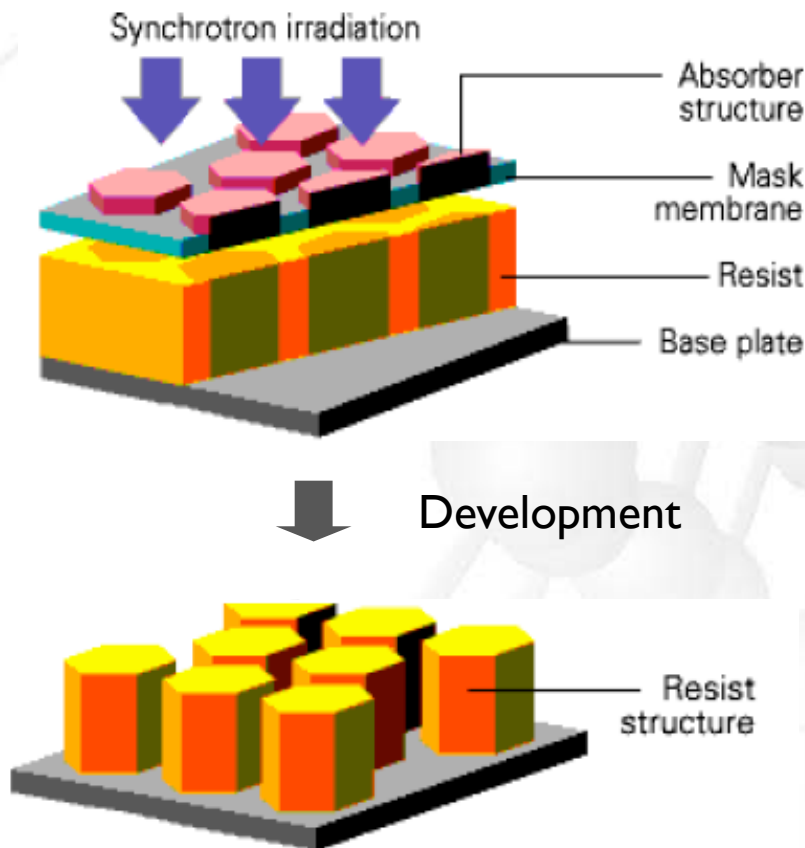
Exposure to x-ray (that generates Auger electrons...) cut the PMMA chains, leading to smaller molecular weight that dissolves faster in developers.

Novolak-based resist	EBL sensitivity ($\mu\text{C}/\text{cm}^2$)	EBL contrast	XRL sensitivity (mJ/cm^2)	XRL contrast
PMMA	100	2.0	6500	2.0



X-ray lithography

- **Basic process:**

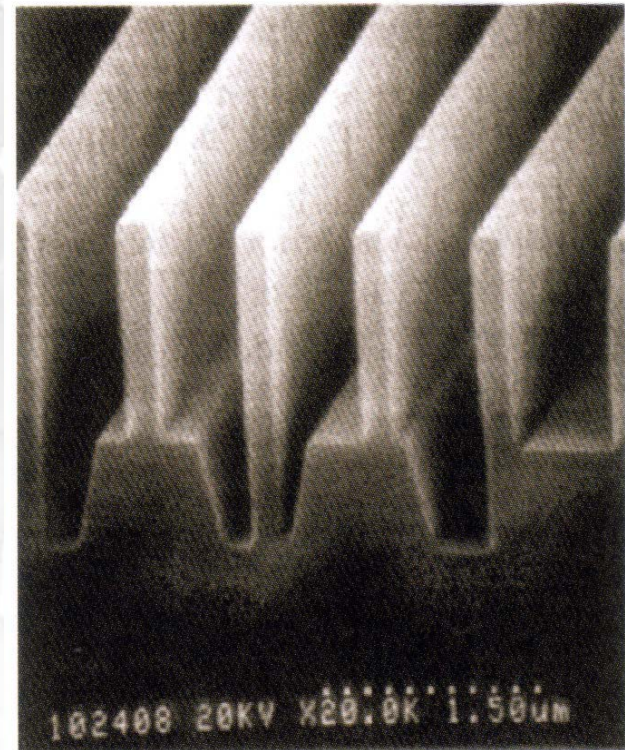
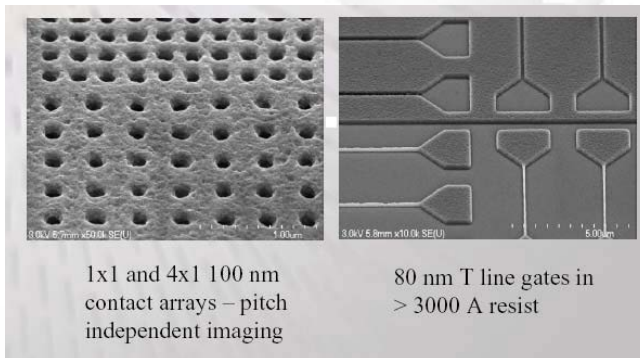
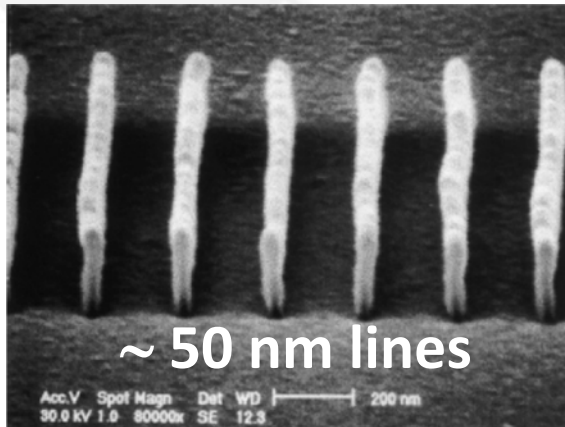


Ideal to pattern high resolution and high aspect ratio nanostructures!



X-ray lithography

- Examples:



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



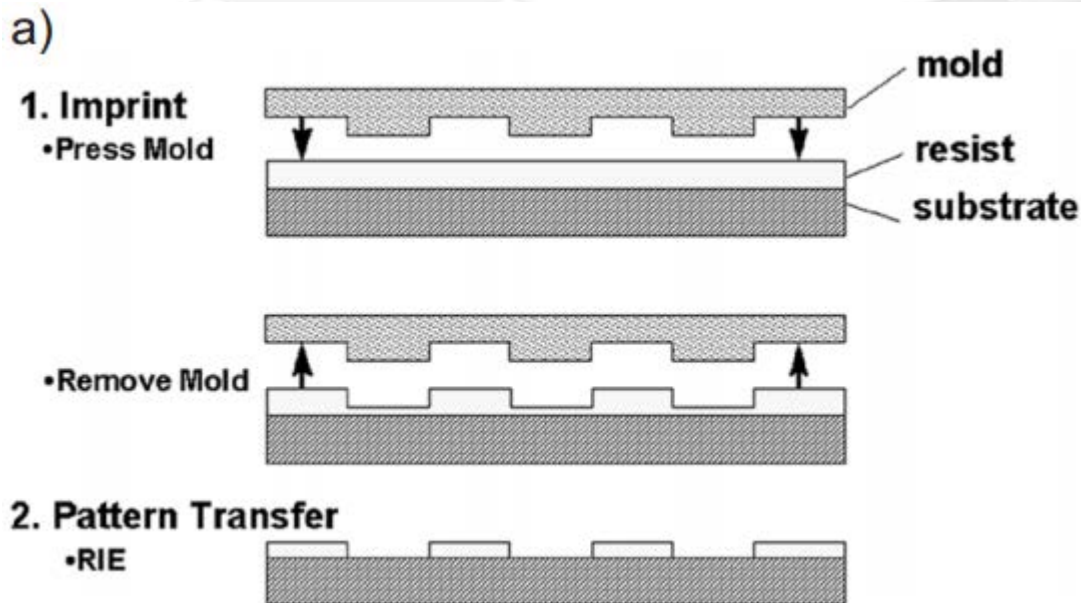
Overview of the main nano-lithography techniques

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Nanoimprint lithography

- Basic process:



- Much simpler in comparison to alternatives!
- High throughput.
- Low cost for a next-generation technology.

High resolution
+ high throughput
+ low cost!!

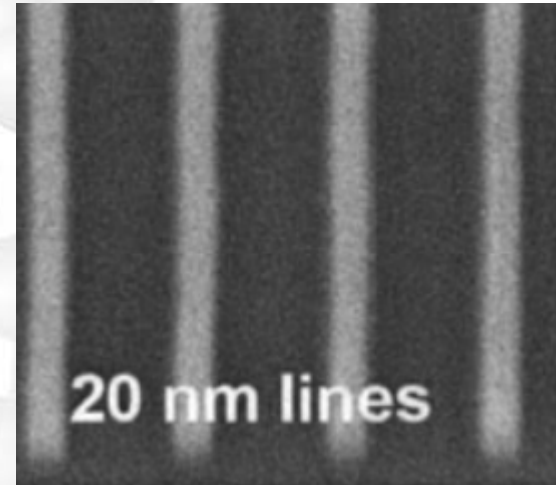
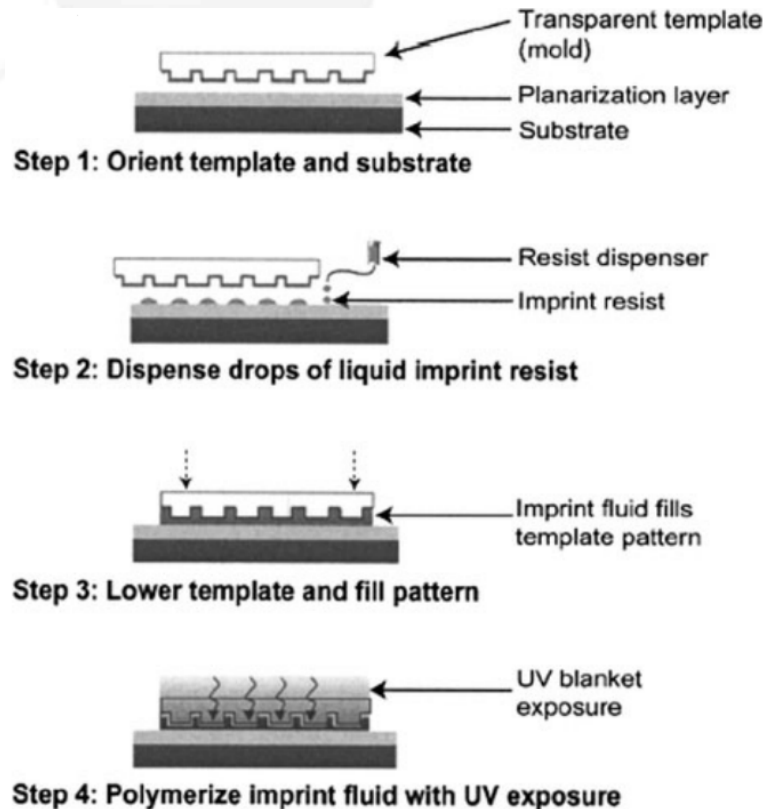
- Mechanical deformation of the imprint resist.

L. Jay Guo, *Adv. Mater.* 19, 495 (2007).



Nanoimprint lithography

- Improved process: Step-and-flash imprint lithography (SFIL).



**Candidate technology
for future IC production.**

L. Jay Guo, *Adv. Mater.* 19, 495 (2007).



Overview of the main nano-lithography techniques

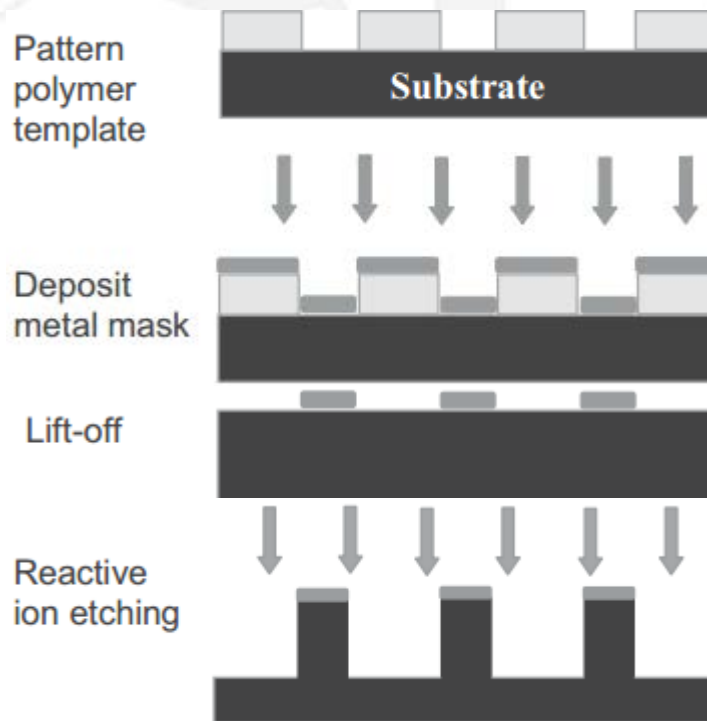
Soraya Sangiao, Jaca, July 18th, 2016



Nanoimprint lithography

- **NIL molds:**

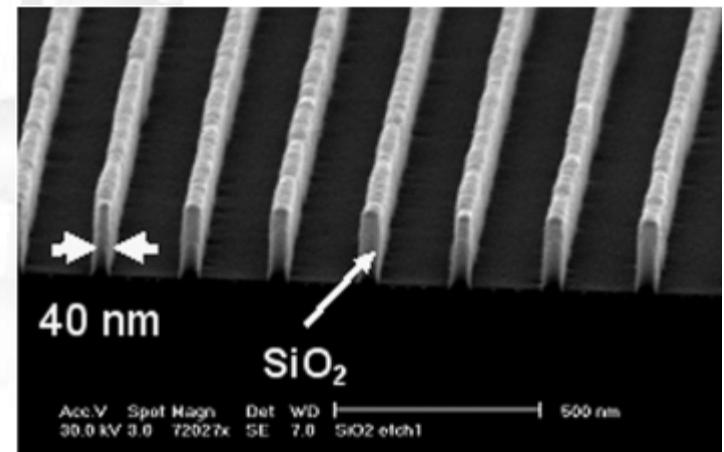
Fabrication:



Material requirements:

- Sufficient Young's modulus.
- High strength and durability.

SEM micrograph:



L. Jay Guo, Adv. Mater. 19, 495 (2007).



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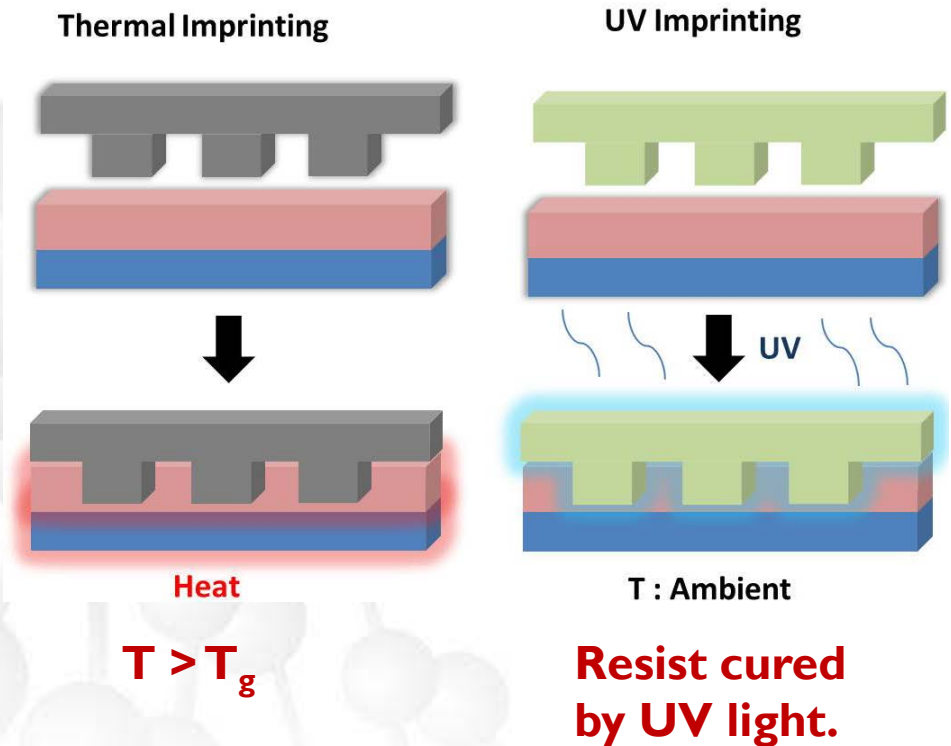


Nanoimprint lithography

- **NIL resists:**

Material requirements:

- Young's modulus lower than that of the mold.
- Sufficiently low viscosity.



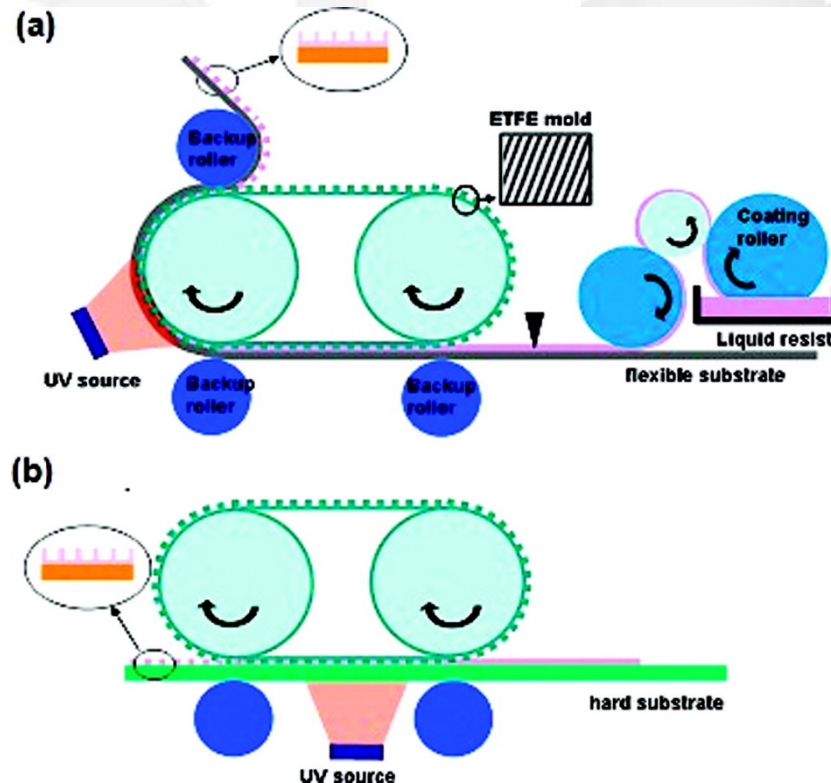
- Good mold-releasing properties.
- Good plasma-etching resistance.

L. Jay Guo, Adv. Mater. 19, 495 (2007).



Nanoimprint lithography

- Large area Roll-to-Roll and Roll-to-Plate NIL:
High-Throughput application of continuous NIL



S. Hyun Ahn and L. Jay Guo, *ACS Nano* 3, 2304 (2009).



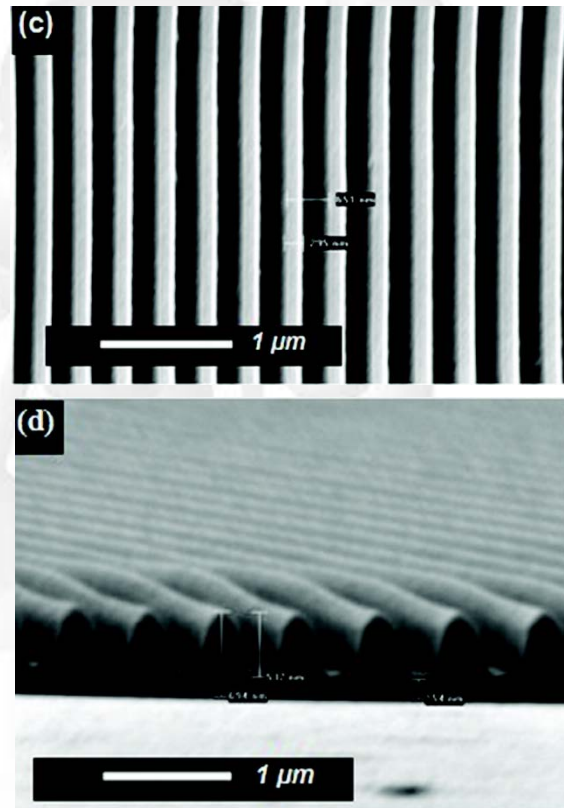
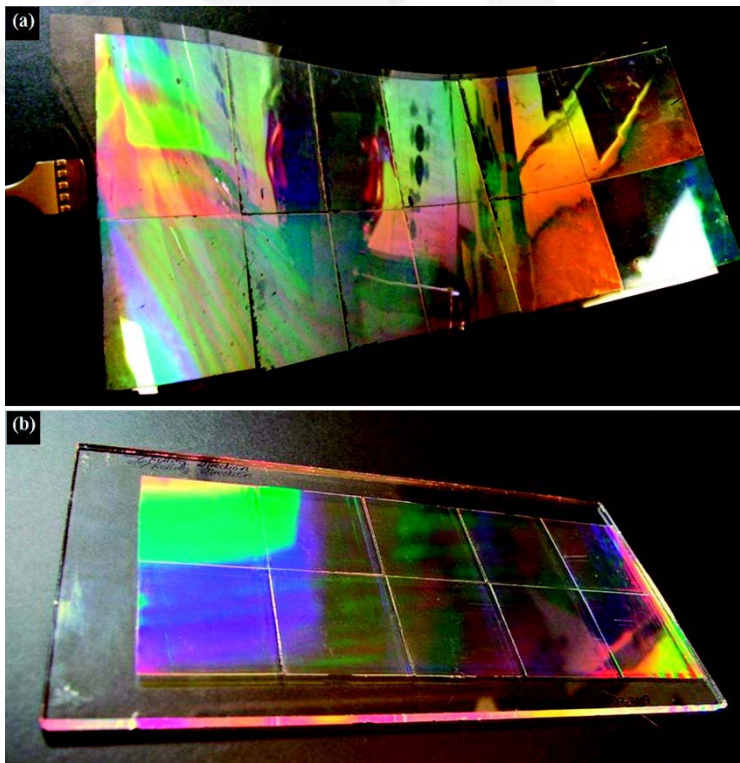
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Nanoimprint lithography

- Large area Roll-to-Roll and Roll-to-Plate NIL:
High-Throughput application of continuous NIL



**300 nm linewidth,
600 nm height
with greatly
enhanced
throughput.**

S. Hyun Ahn and L. Jay Guo, *ACS Nano* 3, 2304 (2009).



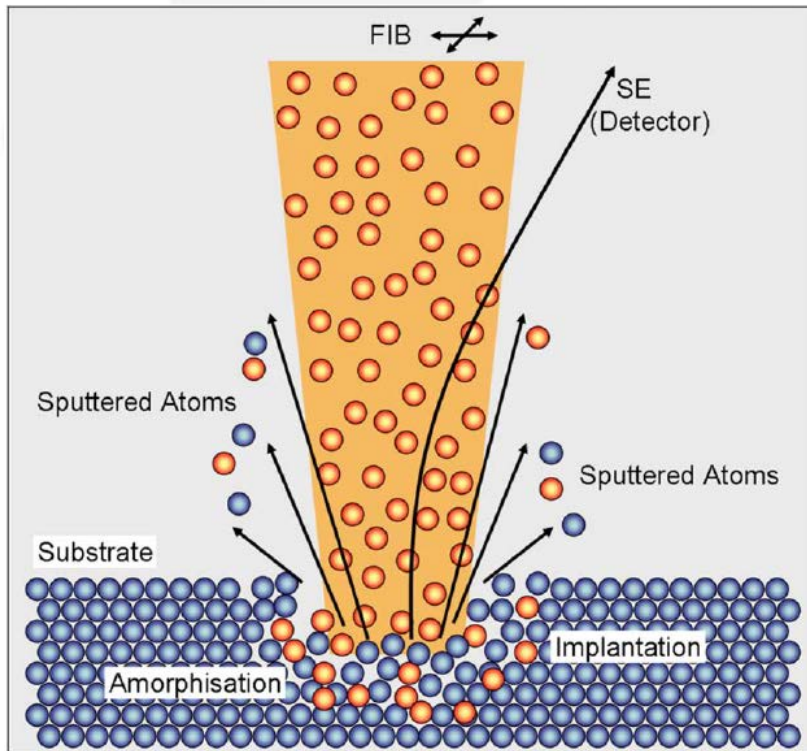
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Ion beam lithography

- **Ion beams: Interaction with matter**



Focused ion beam (around 30 keV):

- **Slow heavy atoms:** Sputtering of atomic and molecular species from the surface.

Focused ion beam lithography:

- Direct writing lithography! (No mask)
- Sub-100 nm resolution.

I. Utke et al., *Int. J. Vac. Sci. Technol. B* 26, 1197 (2008).



Overview of the main nano-lithography techniques

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Ion beam lithography

- Focused Ion Beams sources:

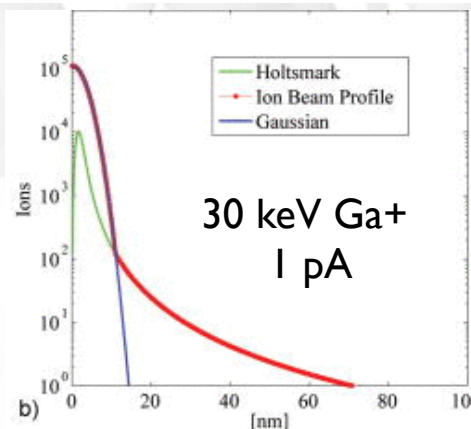
Type of ion source	Ion species	Unnormalized brightness ($\text{A}/\text{cm}^2 \text{ sr}$)	Current density on sample (A/cm^2)	Minimum beam diameter (nm) (at 30 kV)
Liquid metal	Ga^+	3×10^6	10	10
Liquid metal alloy ^a	Au/Si/Be	$\sim 10^5$ depends on the % of the desired species in beam	0.1–1.0	50
Gas field ion (supertip)	He^+	5×10^9	1000	5
Gas field ion source	He^+	4×10^9	...	0.6
Multicusp plasma	Kr^+	0.55×10^3	1.2×10^{-2}	100

→ High brightness

→ Cryogenic temperature.

→ Less brighter but robust.

FIB profile:
(spatial distribution)



I. Utke et al., *Int. J. Vac. Sci. Technol. B* 26, 1197 (2008).



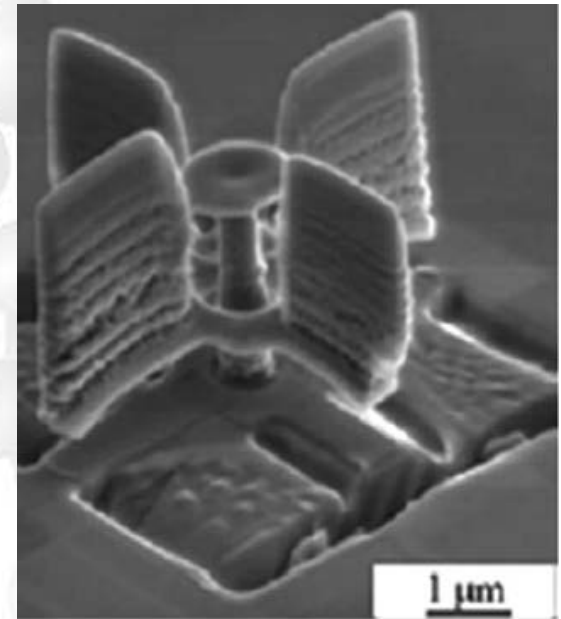
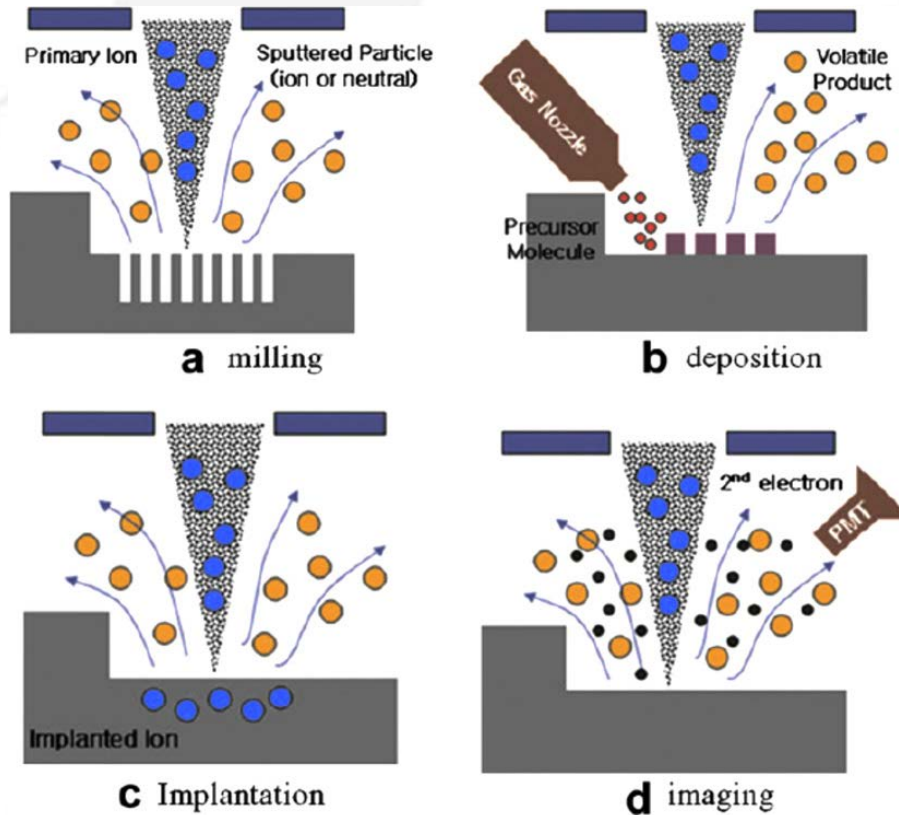
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Ion beam lithography

FIB processes:



Nanorotor produced by FIB.

A. Santos et al., *Nanotechnol.* 26, 042001 (2015).

X.Wang et al., *Chem. Mater.* 25, 2819 (2013).



Overview of the main nano-lithography techniques

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Summary

Lithography Technique	Minimum Feature Size	Throughput	Applications
Photolithography (contact & proximity printings)	2-3 μm ^[22]	very high	typical patterning in laboratory level and production of various MEMS devices
Photolithography (projection printing)	a few tens of nanometers (37 nm) ^[2]	high - very high (60-80 wafers/hr) ^[1]	commercial products and advanced electronics including advanced ICs ^[1] , CPU chips
Electron beam lithography	< 5 nm ^[23]	very low ^[1, 3] (8 hrs to write a chip pattern) ^[1]	masks ^[3] and ICs production, patterning in R&D including photonic crystals, channels for nanofluidics ^[23]
Focused ion beam lithography	~20 nm with a minimal lateral dimension of 5 nm ^[2]	very low ^[3]	patterning in R&D including hole arrays ^[125, 134] , bull's-eye structure ^[132] , plasmonic lens ^[137]
Soft lithography	a few tens of nanometers to micrometers ^[2, 13] (30 nm) ^[2]	high	LOCs for various applications ^[13, 96]
Nanoimprint lithography	6-40 nm ^[14, 15, 18]	high (> 5 wafers/hr) ^[1]	bio-sensors ^[17] , bio-electronics ^[18] , LOCs: nano channels, nano wires ^[97, 102, 104]
Dip-pen lithography	a few tens of nanometers ^[39, 40, 43]	very low – low, possibly medium ^[39]	bio-electronics ^[43] , bio-sensors ^[40] , gas sensors ^[42]

A. Pimpin et al., *Enginner. J.* 16, 37 (2011).



Overview of the main nano-lithography techniques

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A faint, light gray molecular structure is visible in the background, consisting of various sized spheres connected by lines, resembling a complex network or a biological molecule. A horizontal brown line is positioned above the main text.

Thank you for your attention!



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