# Nanofabrication

PH 673
Nanoscience and nanotechnology
December 3, 2025

**“I think there is a world market for maybe five computers.”**

Thomas Watson,
Chairman of IBM, 1943

**“There is no reason for any individual to have a computer in their home.”**

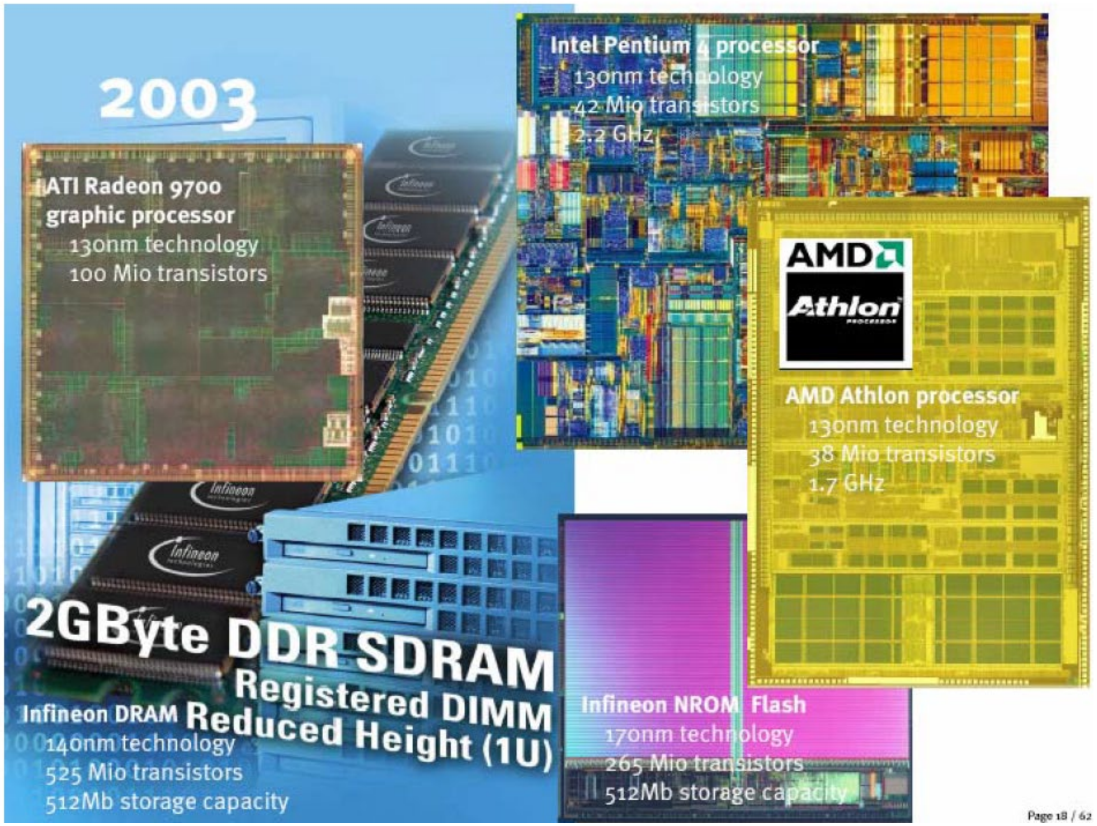
Ken Olson,
President, Chairman and Founder of Digital Equipment Corp., 1977

**“640K ought to be enough for anybody.”**

Bill Gates, Microsoft founder, 1981

1958 1 transistor = 10 US$;
first integrated circuit with 4 transistors: 150 US$
market $218 \cdot 10^6$ US$

2000 for 10 US$, you receive $50 \cdot 10^6$ transistors (with passive components, interconnects, ...)




| Semiconductor manufacturing processes |
|---|
| •10 µm – 1971<br>•6 µm – 1974<br>•3 µm – 1977<br>•1.5 µm – 1982<br>•1 µm – 1985<br>•800 nm – 1989<br>•600 nm – 1994<br>•350 nm – 1995<br>•250 nm – 1997<br>•180 nm – 1999<br>•**130 nm** – 2001<br>•90 nm – 2004<br>•65 nm – 2006<br>•45 nm – 2008<br>•32 nm – 2010<br>•22 nm – 2012<br>•14 nm – 2014<br>•10 nm – *2016*<br>•7 nm – *2018*<br>•5 nm – *2020* |

Wikipedia

"x nm process" = half-distance between identical features

Semiconductor manufacturing processes

- 10 µm – 1971
- 6 µm – 1974
- 3 µm – 1977
- 1.5 µm – 1982
- 1 µm – 1985
- 800 nm – 1989
- 600 nm – 1994
- 350 nm – 1995
- 250 nm – 1997
- 180 nm – 1999
- **130 nm** – 2001
- 90 nm – 2004
- 65 nm – 2006
- 45 nm – 2008
- 32 nm – 2010
- 22 nm – 2012
- 14 nm – 2014
- 10 nm – *2016*
- 7 nm – *2018*
- 5 nm – *2020*

Intel Pentium 75-100 MHz

Intel Pentium II

Intel Pentium 4

Intel Core I7

35 nm gate length

1 nm equivalent oxide thickness, with 0.7 nm transition layer

Intel Core I7 980x extreme edition

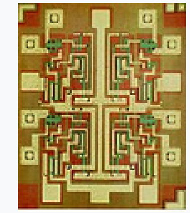
Intel Core I7 Ivy Bridge (25 nm gate length)

Intel Core M (e.g. in Ultrabook laptops) (15 nm gate length)

Samsung 64 GB multi-media card; flash memory

NVIDIA H100/200 GPU, Apple MacBook Pro, iPhone 15 Pro

**Semiconductor device fabrication**



MOSFET scaling (process nodes)

- 20 µm – 1968
- 10 µm – 1971
- 6 µm – 1974
- 3 µm – 1977
- 1.5 µm – 1981
- 1 µm – 1984
- 800 nm – 1987
- 600 nm – 1990
- 350 nm – 1993
- 250 nm – 1996
- 180 nm – 1999
- 130 nm – 2001
- 90 nm – 2003
- 65 nm – 2005
- 45 nm – 2007
- 32 nm – 2009
- 28 nm – 2010
- 22 nm – 2012
- 14 nm – 2014
- 10 nm – 2016
- 7 nm – 2018
- 5 nm – 2020
- **3 nm** – 2022

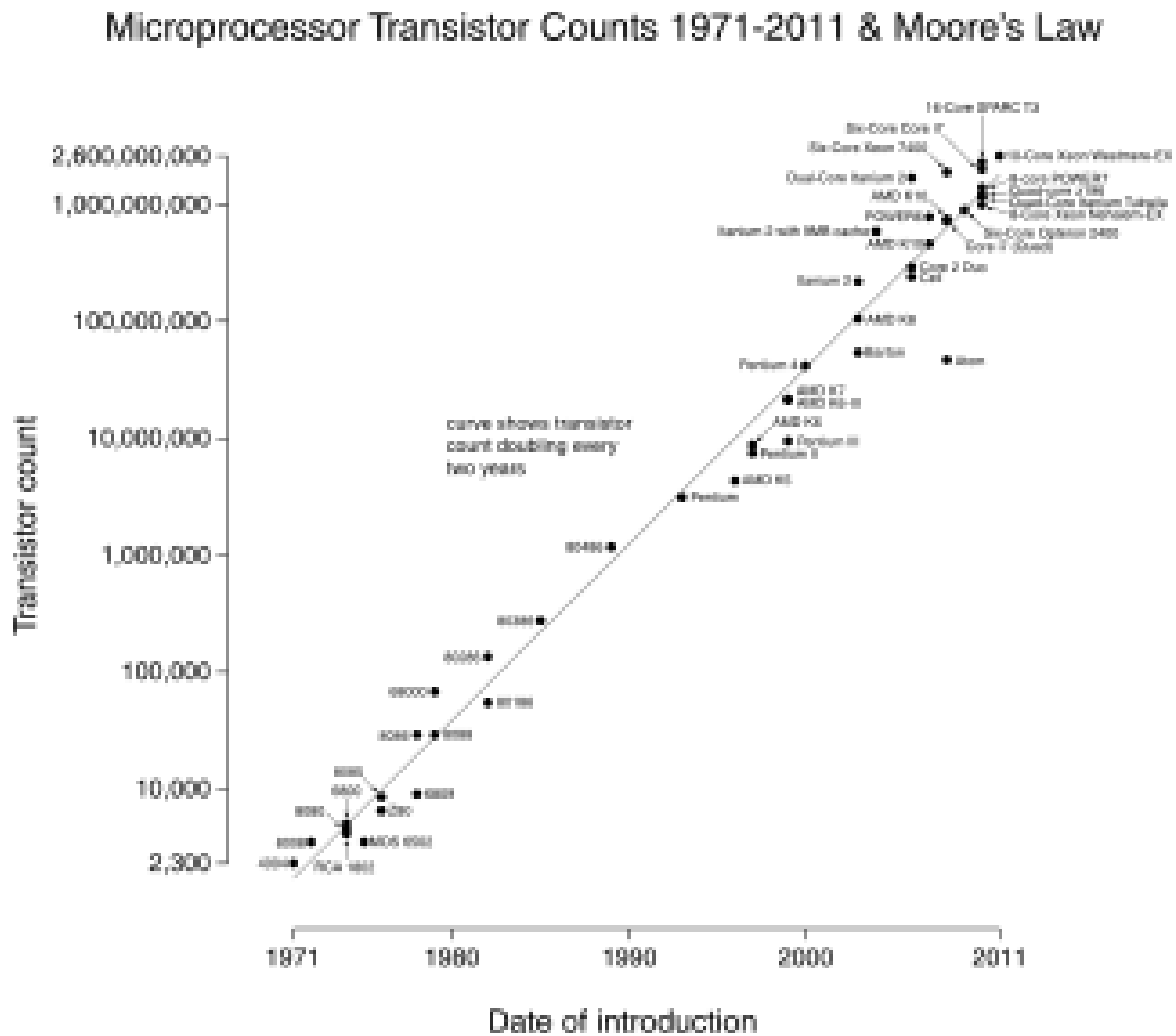
Future

- 2 nm ~ 2025
- 1 nm ~ 2027

HPC (IBM, Samsung)

Moore’s law (1965):

the number of [transistors](#) in a dense [integrated circuit](#) doubles approximately every 2 years.




2010 update:
Slow down in 2013 to doubling every 3 years

Moore, Gordon E. (1965). ["Cramming more components onto integrated circuits“ Electronics Magazine](#). p. 4.

going really nano, i.e. <100nm ?

top-down approach:

extend current techniques to smaller sizes

(EUV-L, x-ray lithography., nano-imprint, flip-up principle, i.e.: horizontal/vertical exchange, etc…)

problem: precision, costs

bottom-up approach:

start from individual atoms/molecules

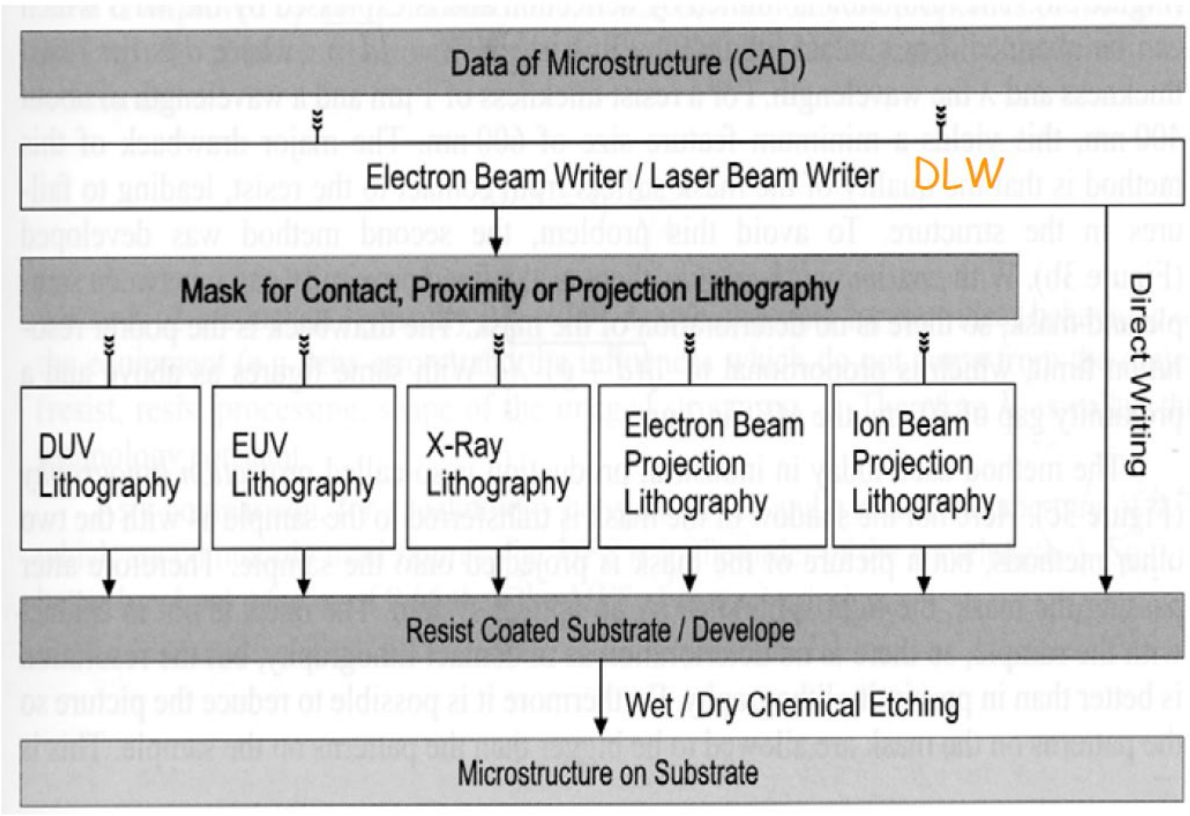
use principles of self-organization (self-assembly; inspiration from biology, biochemistry, chemistry)

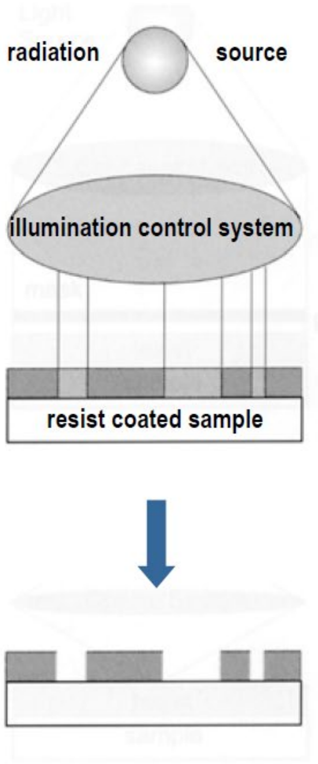
problem: long-range order difficult to achieve

➔ in practice: combination of both routes

- Conventional Lithography: use photons, electrons, ions; minimize wavelength and scattering (e.g. EUV lithography for 3 nm technology uses 13.5 nm EUV light)
- Improved lithography: use tricks like interference patterns to improve resolution
- Various soft lithography methods – use printing, SPM, etc.

# Lithography/direct writing overview



# Overview of photolithography (ctnd.)

- *Lithography* consists of patterning substrate by employing the interaction of beams of photons or particles with materials.
- *Photolithography* is widely used in the integrated circuits (ICs) manufacturing.
- The process of IC manufacturing consists of a series of 10-20 steps or more, called *mask layers* where layers of materials coated with resists are patterned then transferred onto the material layer.

# Overview of photolithography (ctnd.)

- A photolithography system consists of a light source, a mask, and a optical projection system.

- *Photoresists* are radiation sensitive materials that usually consist of a photo-sensitive compound, a polymeric backbone, and a solvent.

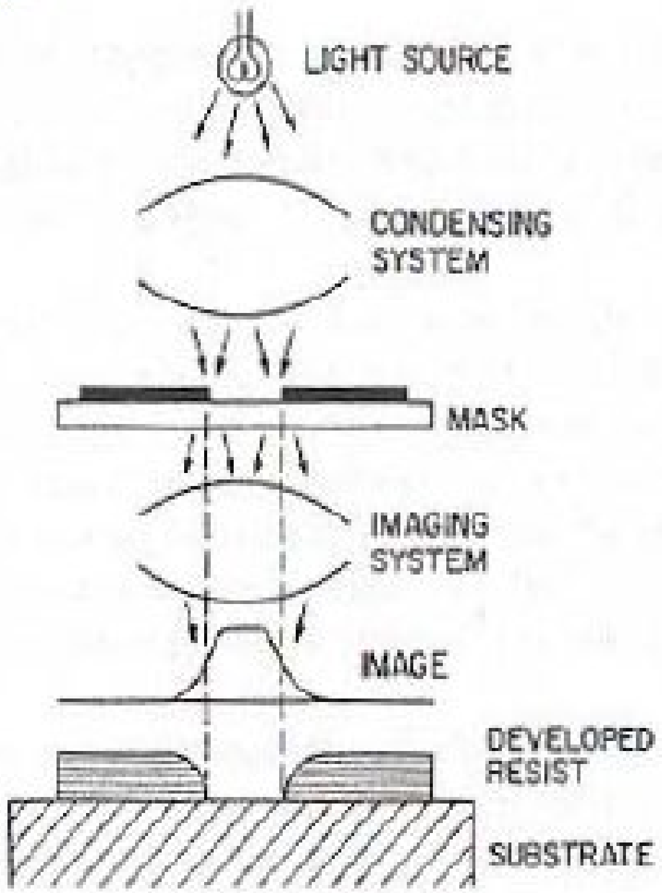
- Resists can  be classified upon their solubility after exposure into: *positive resists* (solubility of exposed area increases) and *negative resists* (solubility of exposed area decreases).

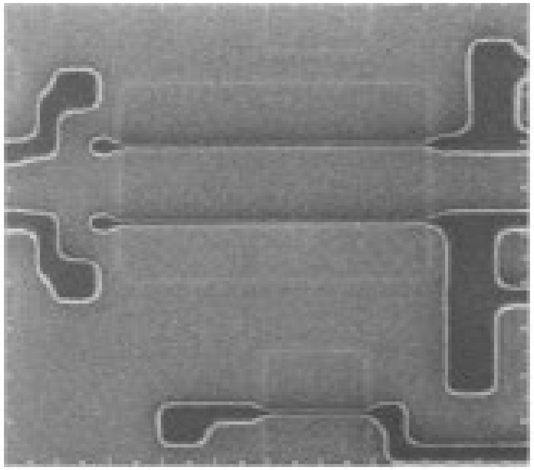
# Optical lithography

source wavelengths:
optical: > 450nm
UV: 365nm-435nm
DUV: 157nm-250nm
EUV: 11nm-14nm
x-ray: < 10nm

| Wavelength [nm] | Source | Range |
|---|---|---|
| 436 | Hg arc lamp | G-line |
| 405 | Hg arc lamp | H-line |
| 365 | Hg arc lamp | I-line |
| 248 | Hg/Xe arc lamp; KrF excimer laser | Deep UV (DUV) |
| 193 | ArF excimer laser | DUV |
| 157 | $F_2$ laser | Vacuum UV (VUV) |
| ~10 | Laser-produced plasma sources | Extreme UV (EUV) |
| ~1 | X-ray tube; synchrotron | X-ray |

# Overview of photolithography



Projection photolithography

# Optical lithography

photoresists

positive

made soluble upon exposure

(chain scission)

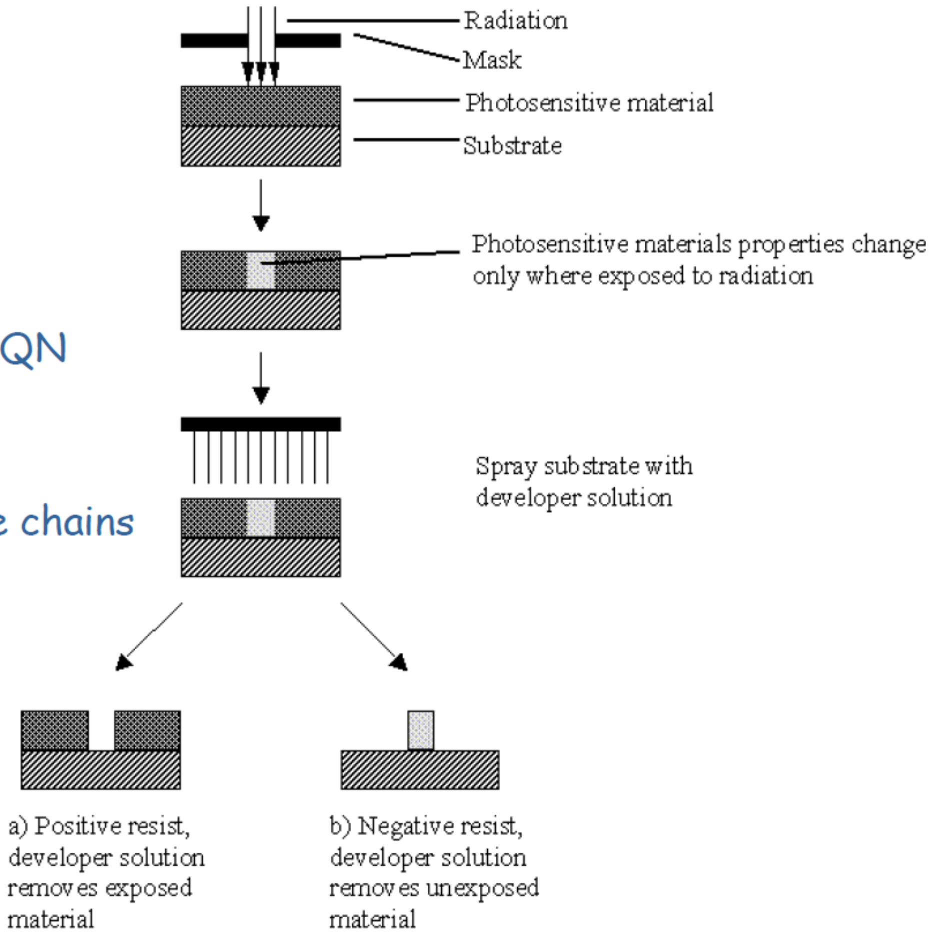
e.g. PMMA (DUV, e-beam), DQN

negative

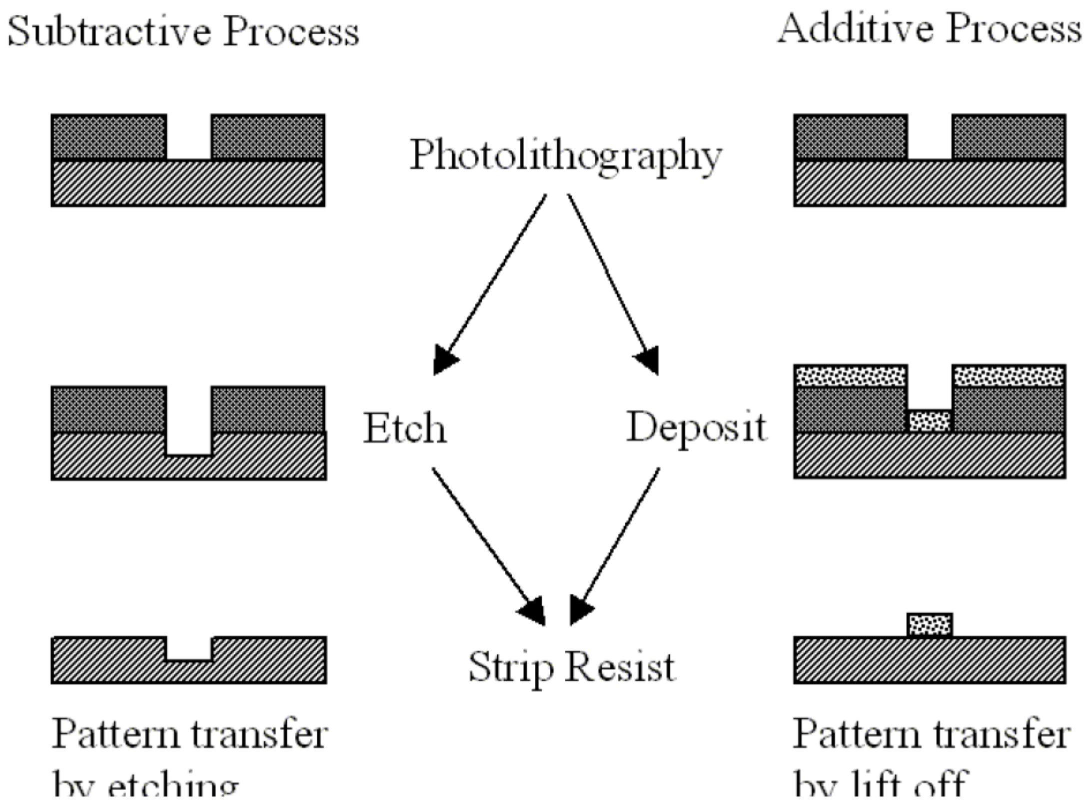
initiates cross-linking of side chains

or polymerization of mono-/oligomeric species

e.g. maN400



# Optical lithography



# Resolution of photolithography

Contact lithography limited by Fresnel diffraction:

$$W_{min} = \sqrt{\lambda g}$$

where $\lambda$ is wavelength employed and g is mask-resist gap.

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Projection lithography limited by Rayleigh's criterion:

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

where $\lambda$ is wavelength employed, NA is numerical aperture of lense ($NA = \sin \alpha$), and $k_1$ is a constant (typically $k_1 = 0.6 - 0.8$)

# Resolution of photolithography: example

**Question:**

An x-ray contact lithography system uses photons of energy of 1 keV. If the separation between the mask and the wafer is 20 µm, estimate the diffraction-limited resolution that is achievable by this system

**Answer:**

The energy $E_p$ of photons is related to their wavelength λ through:

$$E_p = \frac{hc}{\lambda}$$

where h = 6.626× $10^{-34}$ $m^2$ kg/s is Planck's constant, and c = 3 x $10^8$ m/s is the speed of light.

Thus, the wavelength of the photons employed is:

$$\lambda = \frac{6.626x10^{-34} \cdot 3x10^{8}}{1000 \cdot 1.6x10^{-19}}$$

$$\lambda = 1.24 \text{ nm}$$

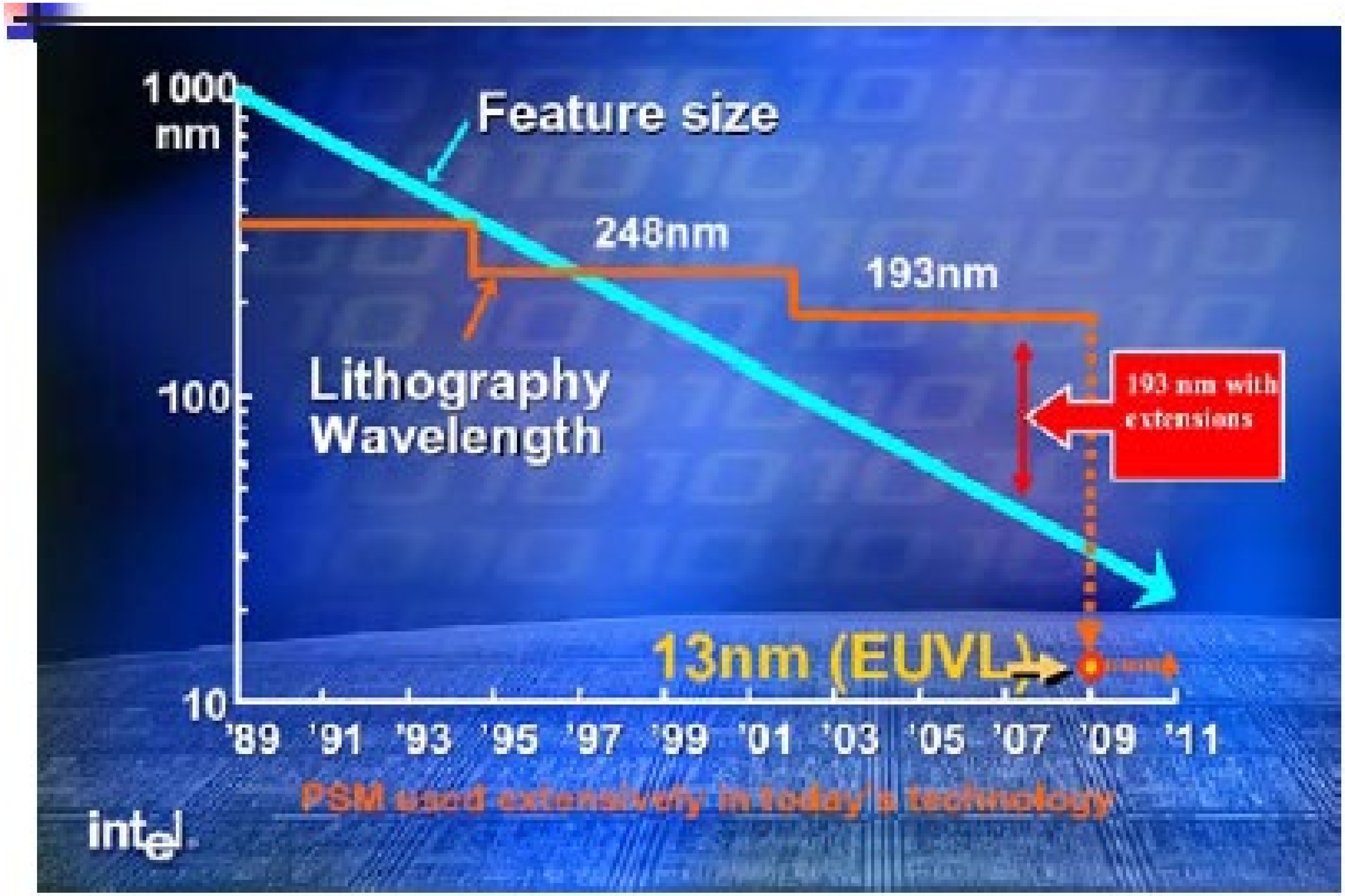
The minimum feature size that can be resolved is:

$$W_{min} = \sqrt{\lambda g}$$

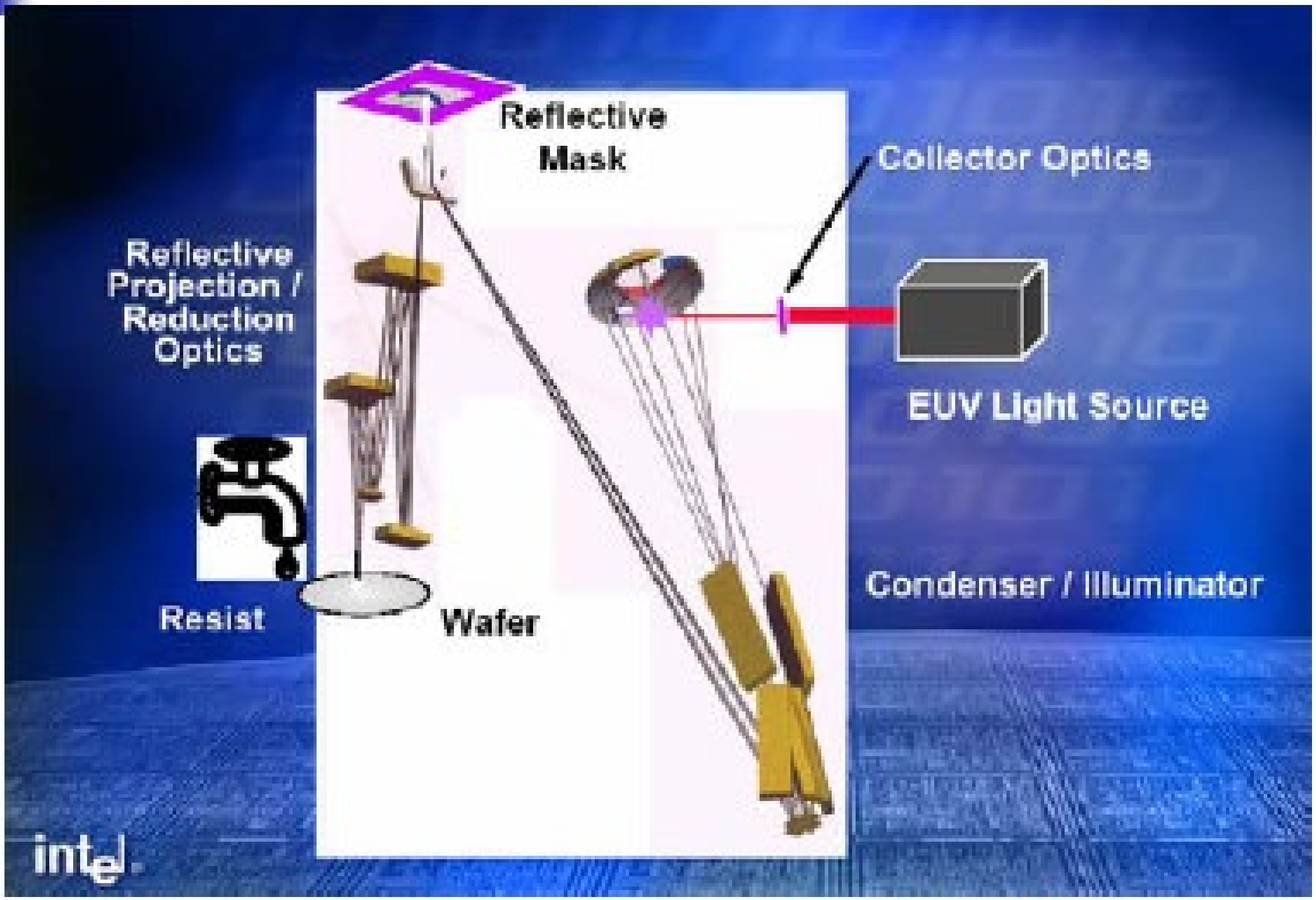
$$W_{min} = \sqrt{1.24x10^{-9} \cdot 20x10^{-6}}$$

$$W_{min} = 157 \text{ nm}$$

# Intel lithography road map



# EUV lithography system



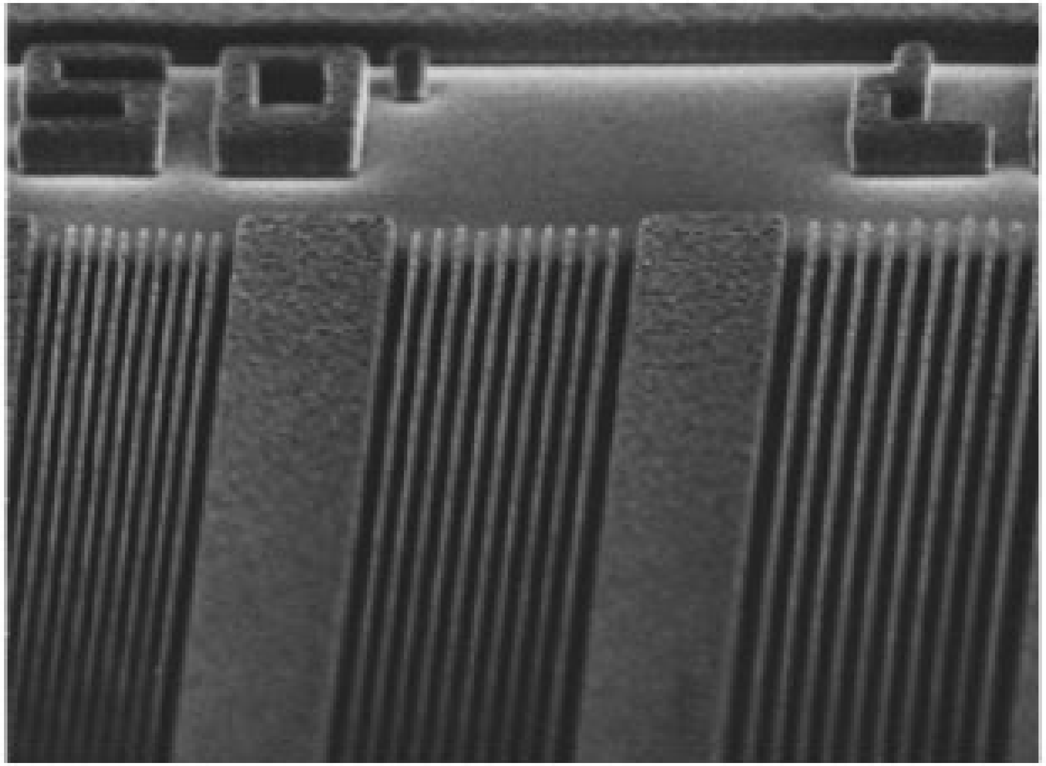

EUV Systems to employ reflective instead of refractive optics

13.5 nm:
4d – 4f transitions
$Sn^{4+}$ -$Sn^{13+}$

- Sn droplets injected in a vacuum chamber at high speed
- Laser pulses (CO2) vaporize the droplet creating plasma (ionized Sn)
- Sn ions emit 13.5 nm

Problem: can't use neutral atoms – need to produce multi-charged ions in discharge- or laser-induced plasma (Xe, Sn, Li plasma sources); need high efficiency; lack of coherence

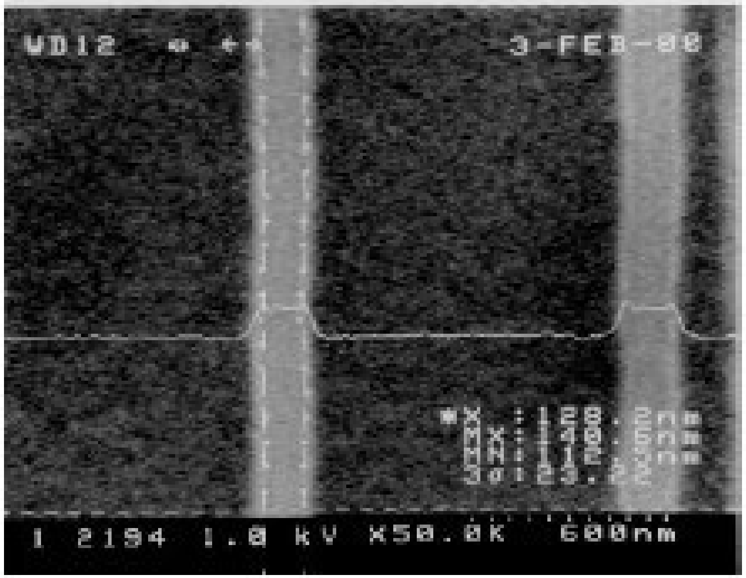
# EUV lithography system (ctnd.)



50 nm lines fabricated with EUV lithography (~1999)
30 nm features now routinely achieved

ASML is the leader in EUV lithography systems (https://www.asml.com/en) (Netherlands)
Inpria is the leader in EUV resists (https://www.inpria.com/,  Corvallis)

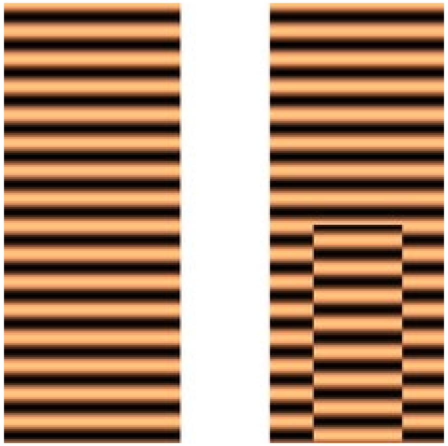
# Structures produced with X-ray litho. (ctnd.)



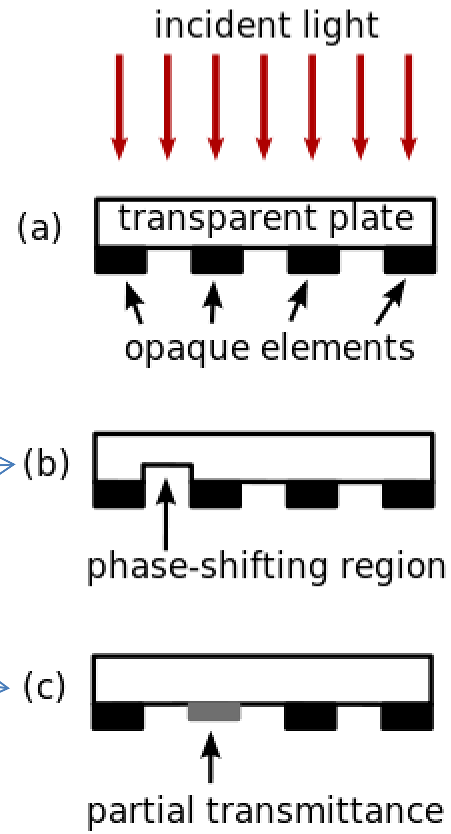

125 nm feature exposed with SAL

Source: SAL, Inc.

# Phase-shift masks: use interference patterns to improve resolution



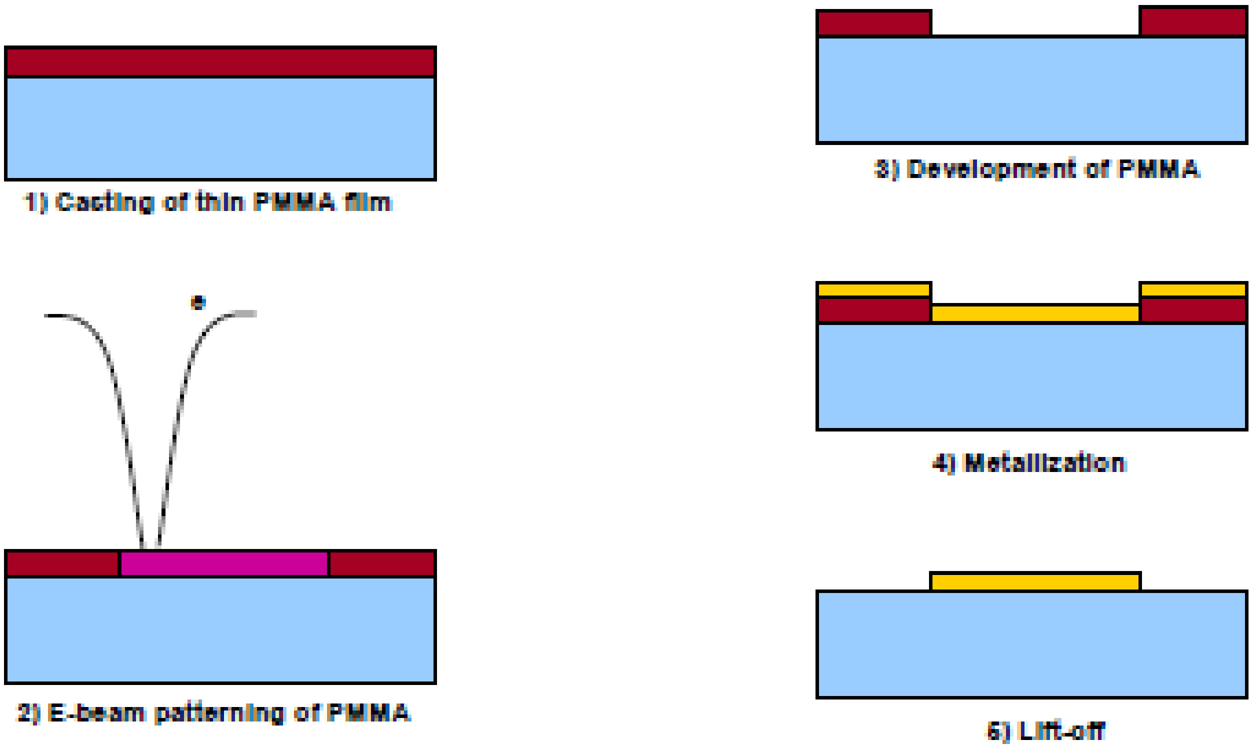
Right: the effect of introducing in the path of the wave a transparent mask with a 180° phase-shifting region.




Used in <=65 nm technologies

Further trick: use immersion (water) lithography (increase NA) – used in <=45 nm technologies

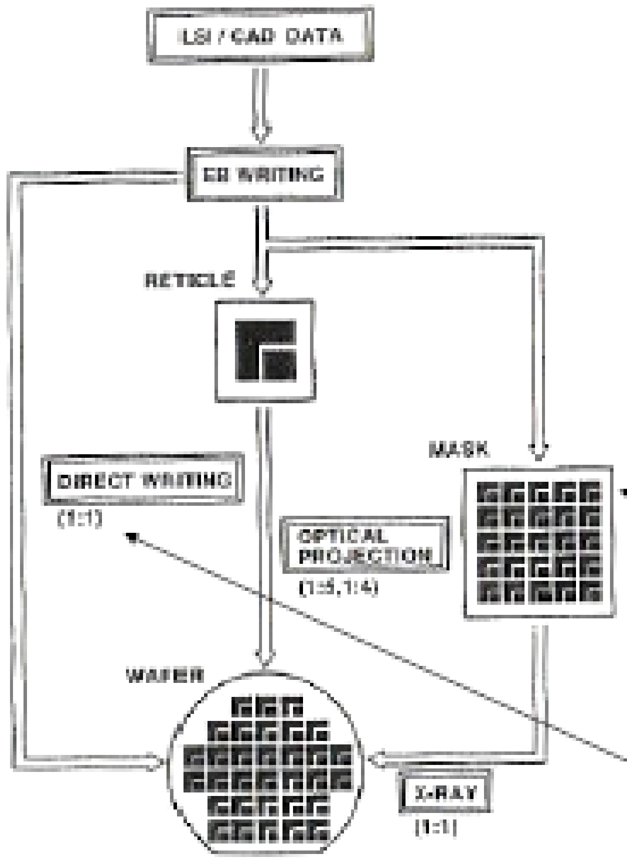
# Electron beam lithography

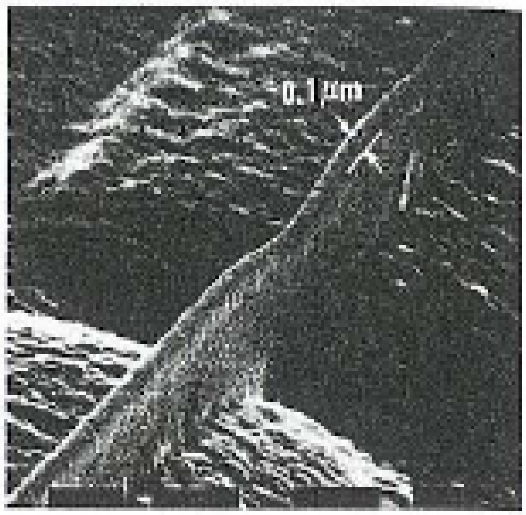



Employs a beam of electron instead of photons

Advantage: Fast turn-around time
Disadvantage: Slow throughput

# Applications of electron beam lithography

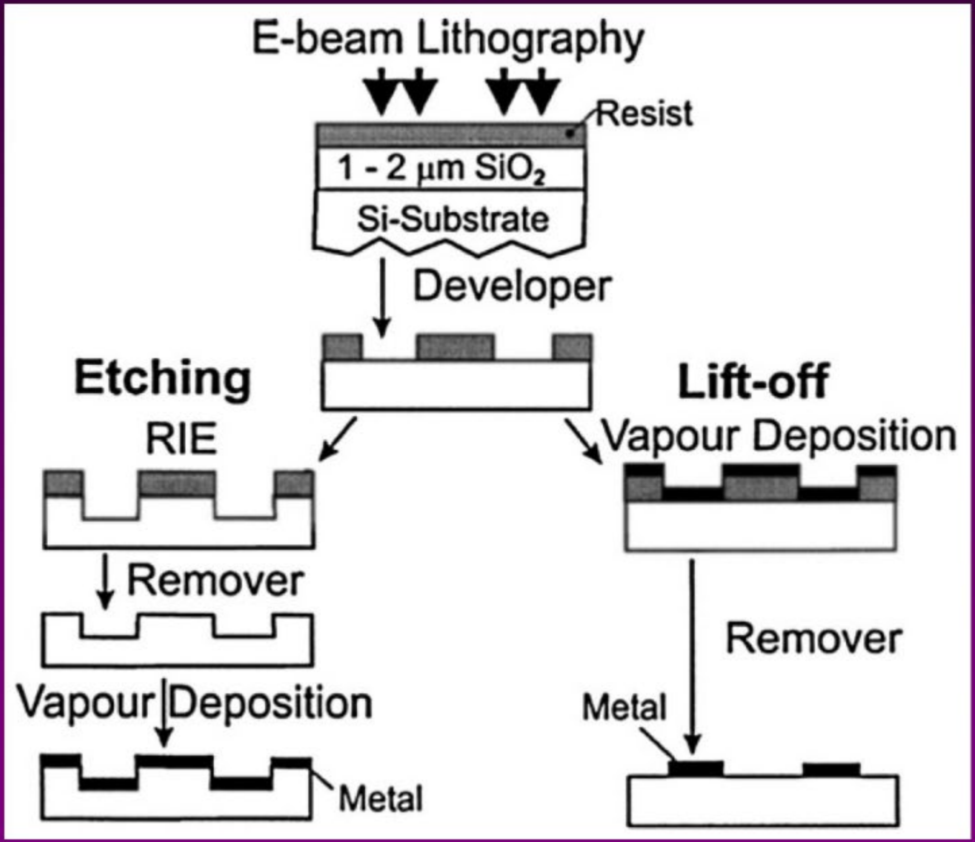



Mainly employed for the fabrication of photomasks

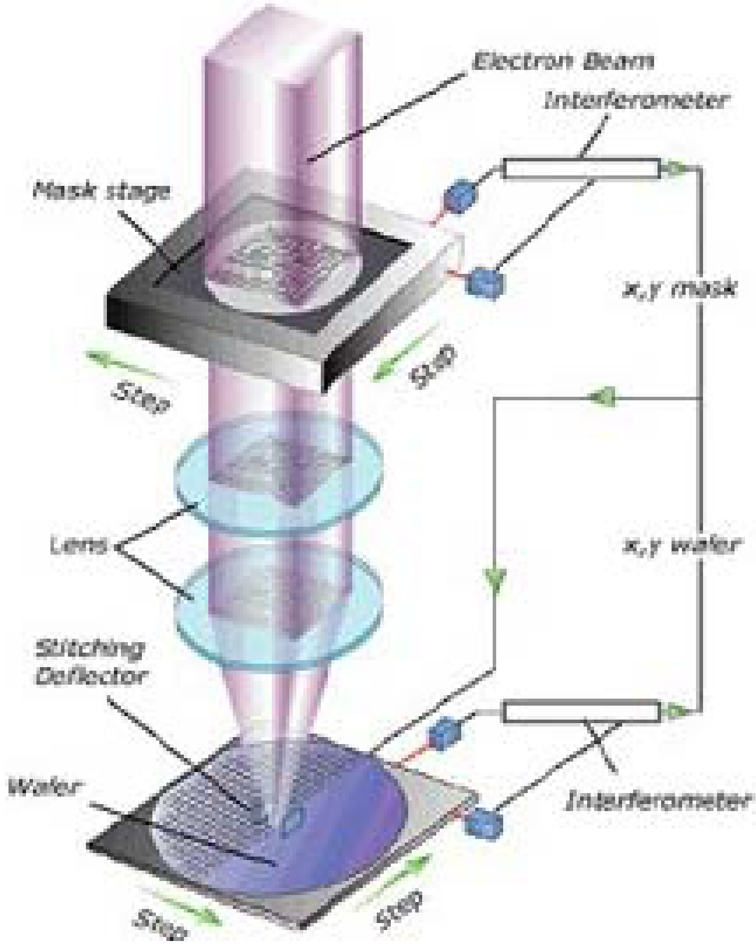
Also used to write patterns directly on wafer

# EBL



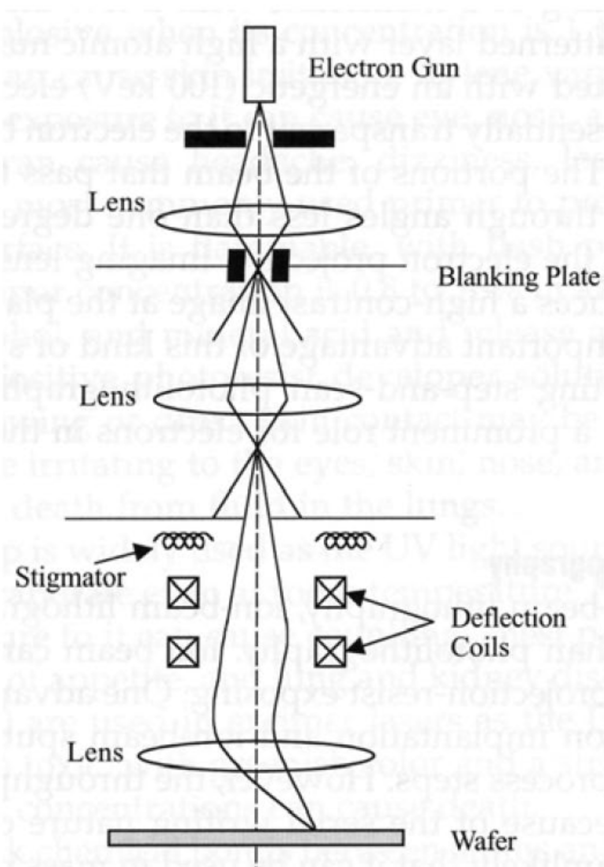

M. Kahl et al., Sensors and Actuators B-Chemical, 51 (1998), p. 285

# Electron beam projection lithography (EPL)



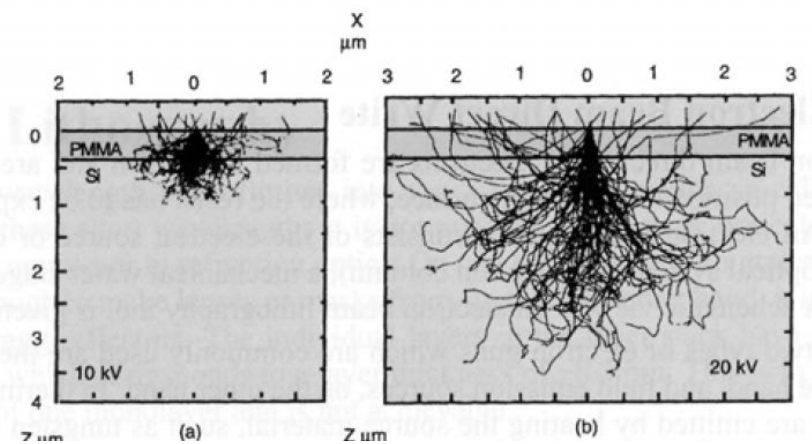

SCALPEL System (Lucent Technologies)

# electron beam lithography (EBL)

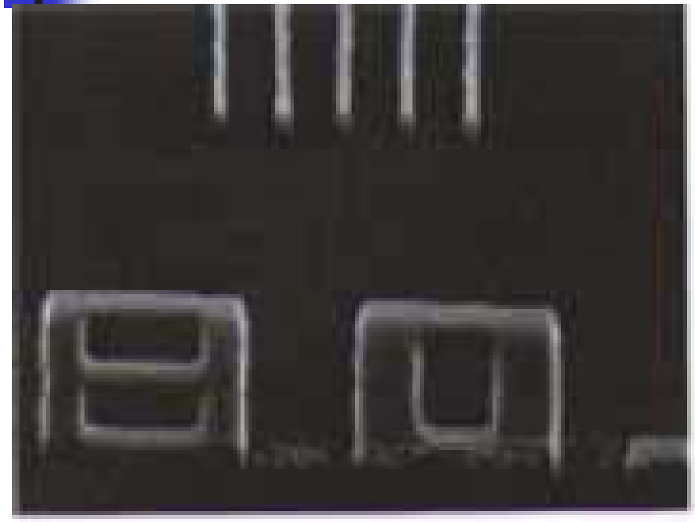


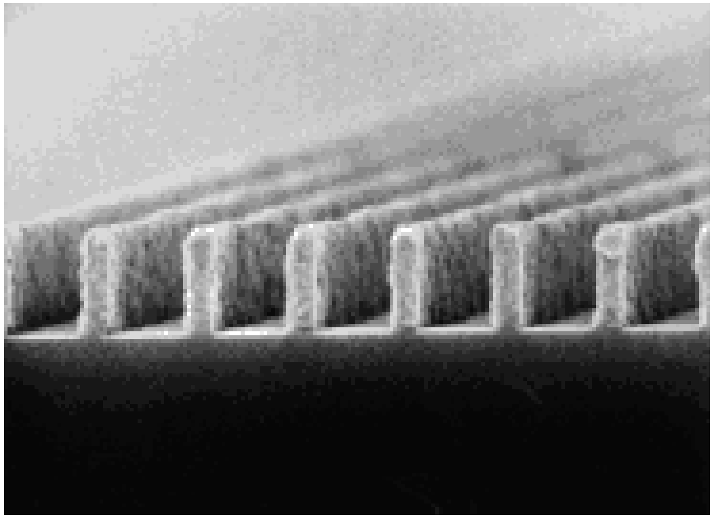

precise (energy, dose)
relatively slow
(industrial application: parallel beams)
resolution limit ~ 10nm (50nm)
no mask
large DOF

large scattering of electrons



# Structures produced by EPL





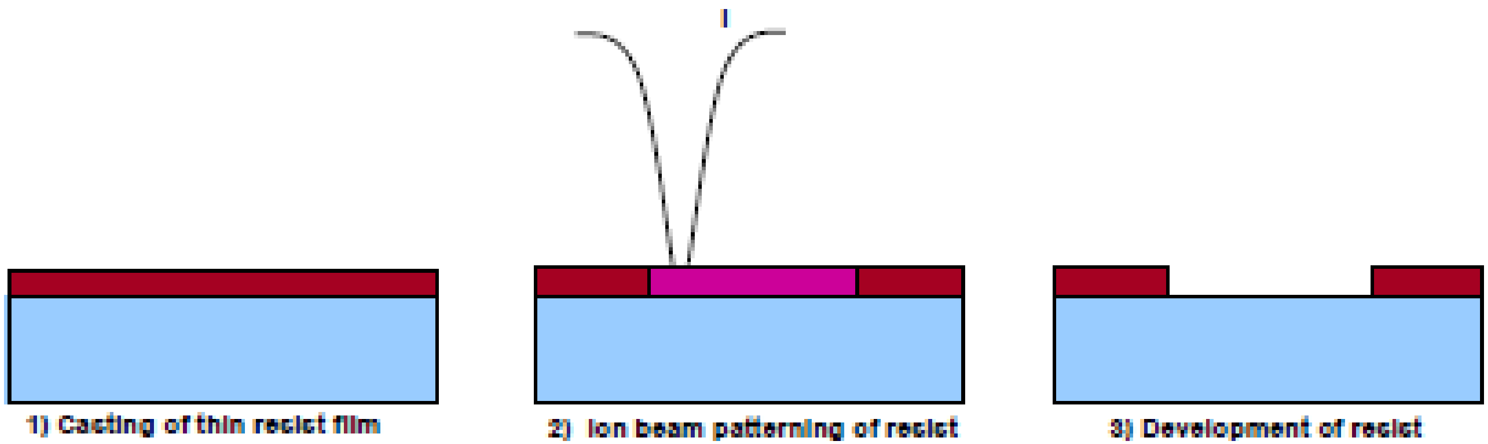
Technology was a serious contender for future sub-70 nm nodes

Relatively low throughput and high cost of mask precluded its viability

Eventually abandoned (~2001) in favor of EUV ($\lambda$ = 13.5 nm) optical systems

EPL = electron projection lithography

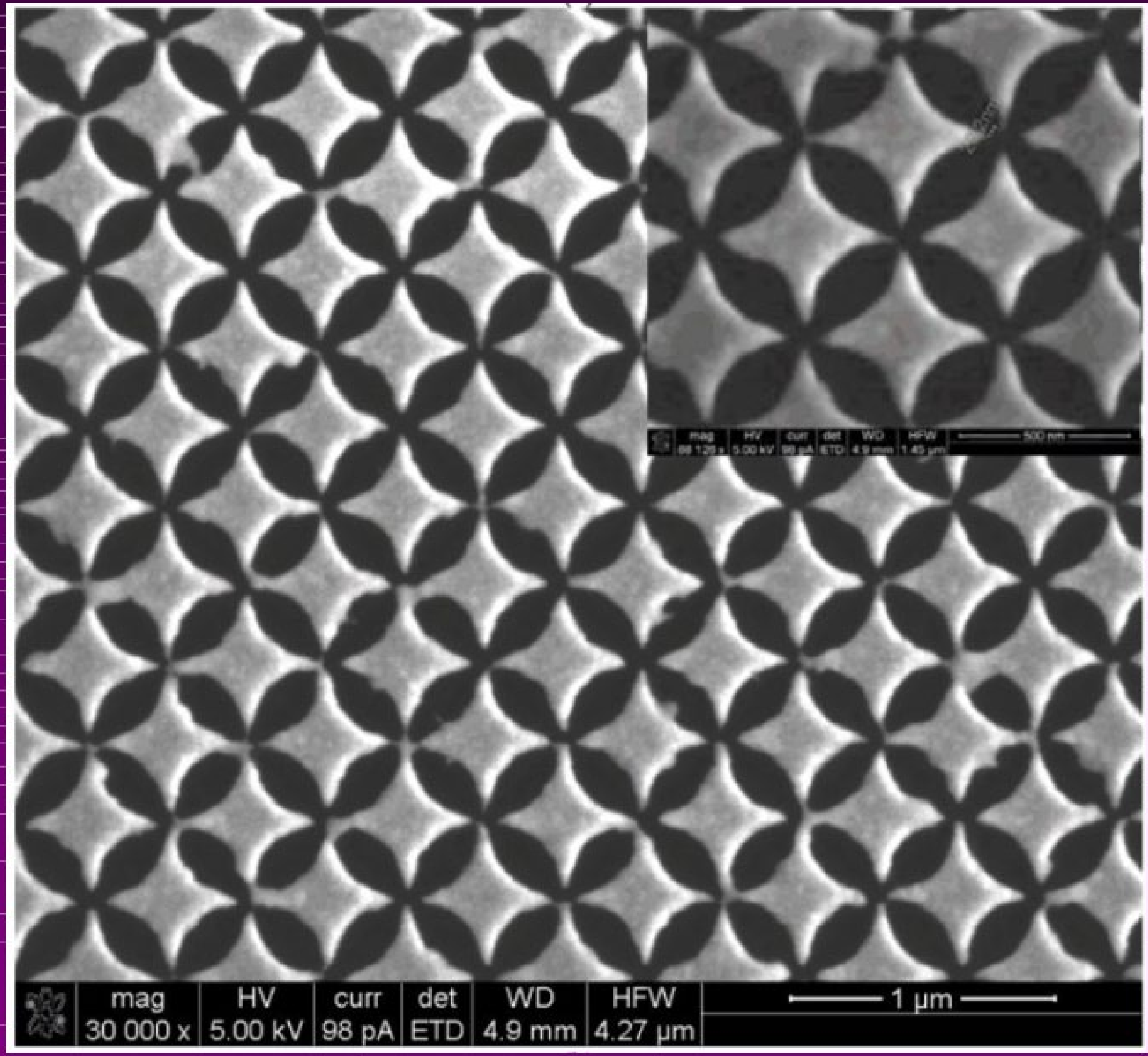
# Ion beam lithography




- Advantages of ion beams:
  - Enhanced resists sensitivity
  - Can be focused to narrower linewidth
  - Reduced scattering
  - Allows hybrid processes such as ion-induced etching and implantation

- FIB lithography is superior to EBL:
  - Higher resolution
  - Higher resist sensitivity
- Additionally to EBL:
  - Local ion beam etching (subtractive lithography)
    - 3D patterning
  - Local deposition of materials (additive lithography)
  - Direct patterning of hard mask layers
- Multi-beam systems

# FIB, Au, thickness 60 nm

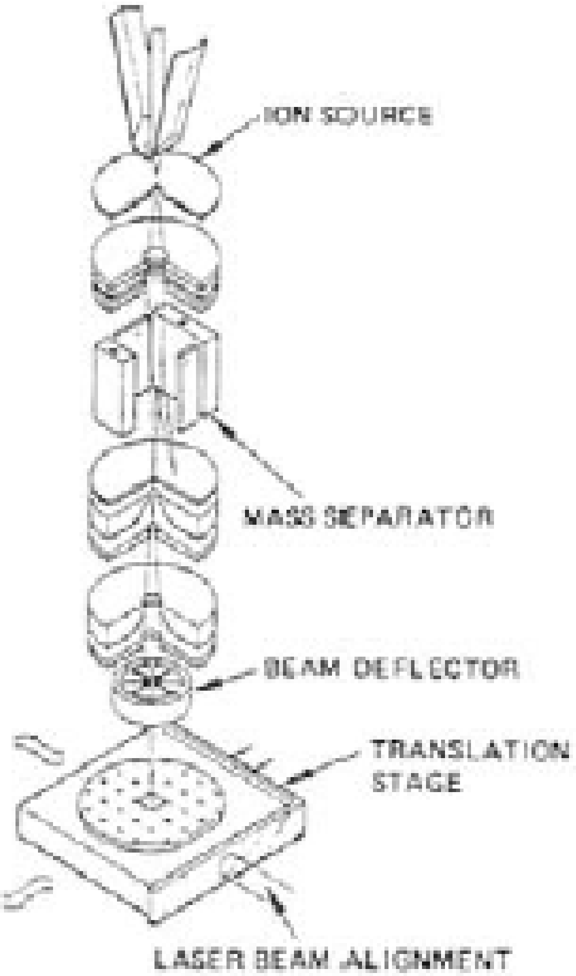



Nanofabrication, InTech, 2011, p. 247

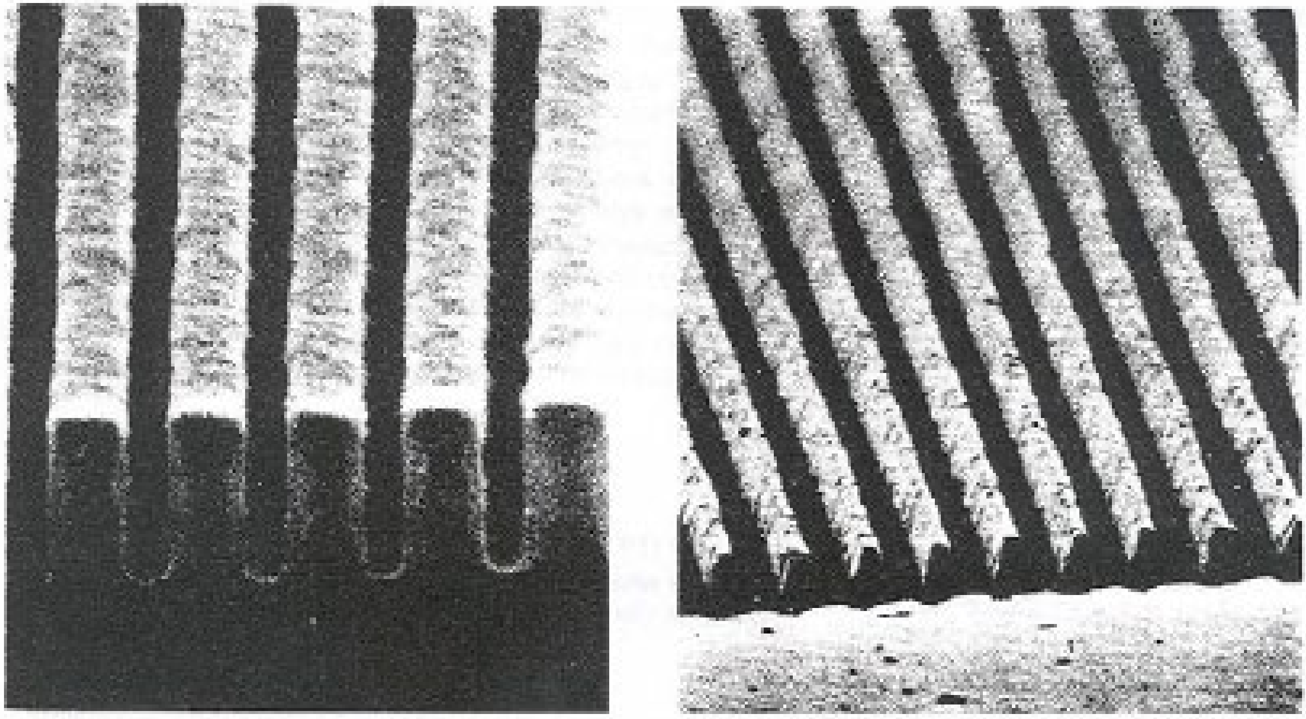
# Focused ion beam lithography

- FIBL components:
  - Ion source
  - Ion optics column
  - Sample displacement table

- Specifications:
  - Accelerating voltage 3-200 kV.
  - Current density up to 10 A/cm$^2$ .
  - Beam diameter 0.5-1.0 µm.
  - Ions: $Ga^+$ , $Au^+$ ,$Si^+$ ,$Be^+$ etc.



# FIB fabricated nanostructures



(a) 0.1 μm

(b) 1 μm

# Issues in FIBL

- Effects of the ion beam on the substrate:
  - Displacement of atoms.
  - Emission of electrons.
  - Chemical effect like change of solubility of the resist.
  - Sputtering of substrate atoms by low energy ions.
- May result in resist heating as high as 1500° C

# Fabrication of planar SERS substrates

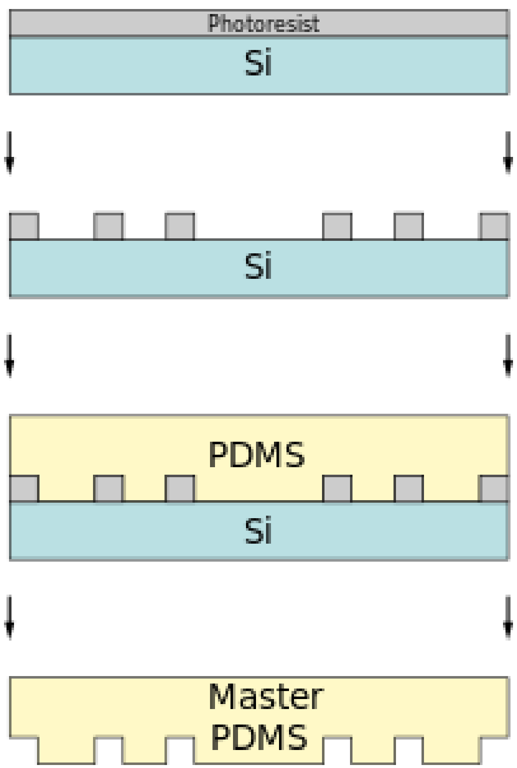
- Deposited films (self-organized metal islands)
- Beam lithography (ring, crescent, dimer...)
  - EBL
  - FIB
- Interference lithography
- Nanoimprint
- Template assisted lithography
  - Porous polymers (polycarbonate membranes)
  - Porous anodic alumina $Al_2O_3$
  - Nanosphere lithography (NSL)

# Alternate Nanolithography Techniques

- Micro-contact Printing
- Nanoimprint Lithography
- Scanned Probe Lithography
- Dip-pen Lithography

# Microcontact printing:

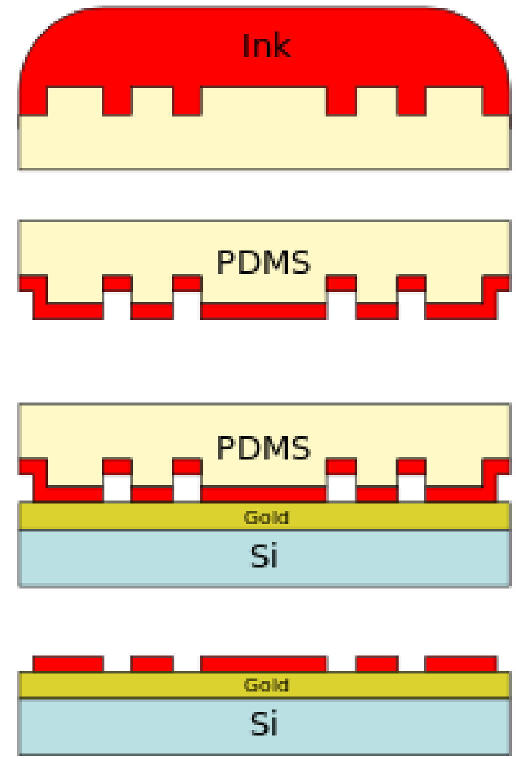
soft lithography that uses the relief patterns on a master polydimethylsiloxane (PDMS) stamp to form patterns of self-assembled monolayers (SAMs) of ink on the surface of a substrate




PDMS master is created by patterning silicon, pouring and curing the PDMS, and peeling away from the substrate

Why PDMS?

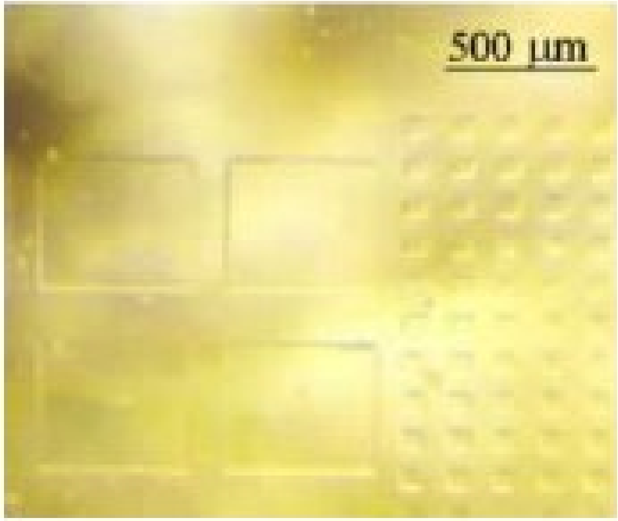
- Low Young modulus
- Low shrinkage
- Inert and non-reactive
- Gas permeable
- Transparent 240-1100 nm
- Non-adhesive (low surface energy)




Thiol is poured over the stamp and let dry. Conformal contact is made with the substrate and pattern is left behind.

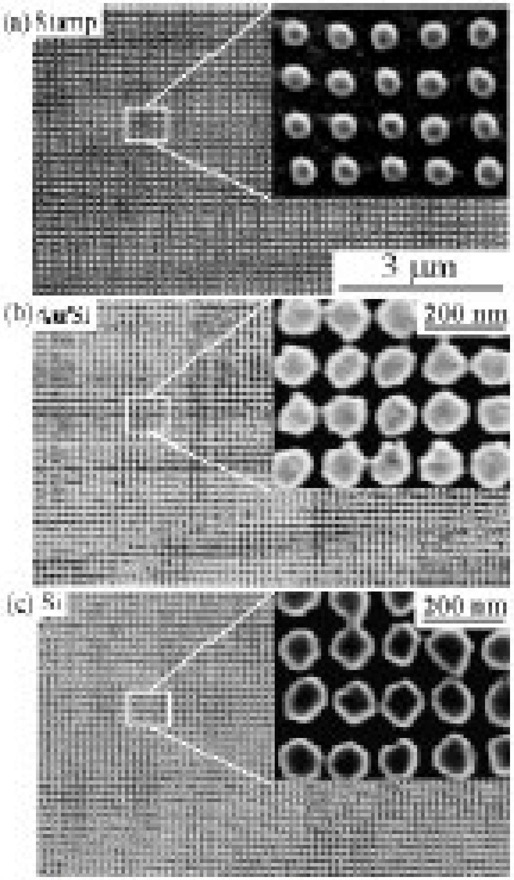
Used in microelectronics, micromachining, organic semiconductor devices, biology

# Micro-contact printing




Printing of PDMS

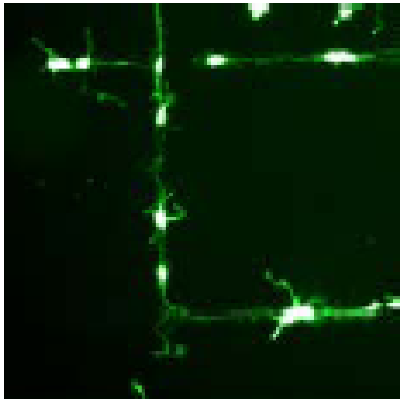
Source: Winograd Group, Penn State




High resolution µCP of 60 nm dots

Source: IBM Zurich

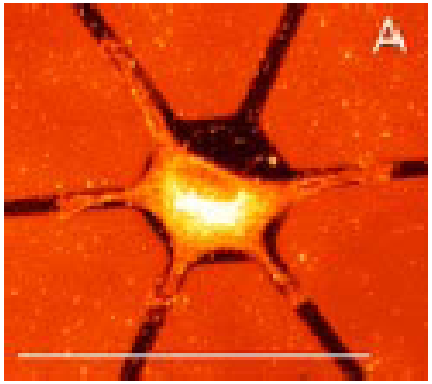
# Selective growth of neurons on printed surfaces



Biological interactions that underlie neuron cell attachment and growth are being employed to produce defined networks of neurons.

Microcontact printing has been used to place chemical, biochemical, and/or topographical cues at designated locations.

Important potential for the interfacing of solid state electronics with nerve cell biology, and for the fundamental electrical studies of single nerve cells.

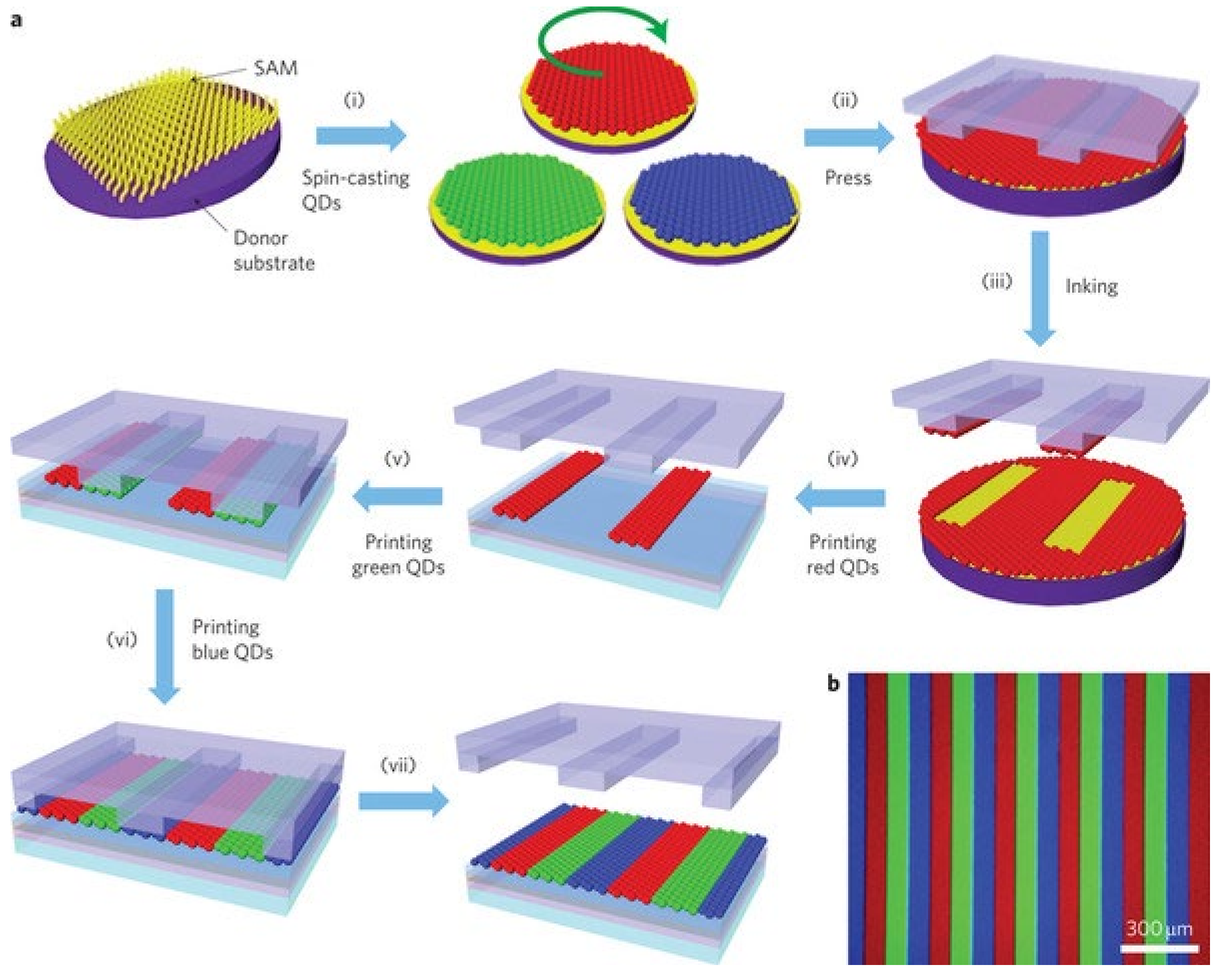



Source: Craighead Group, Cornell

Selective growth of neurons on chemically patterned Si (C. D. James *et al.*)

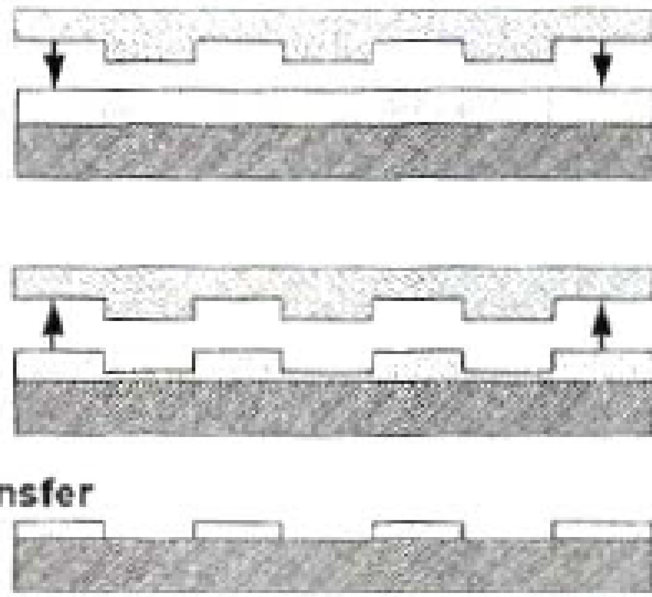
# Full-color quantum dot displays fabricated by transfer printing

T. Kim et al.




Nature Photonics 5, 176–182 (2011); doi:10.1038/nphoton.2011.12

# Nanoimprint Lithography

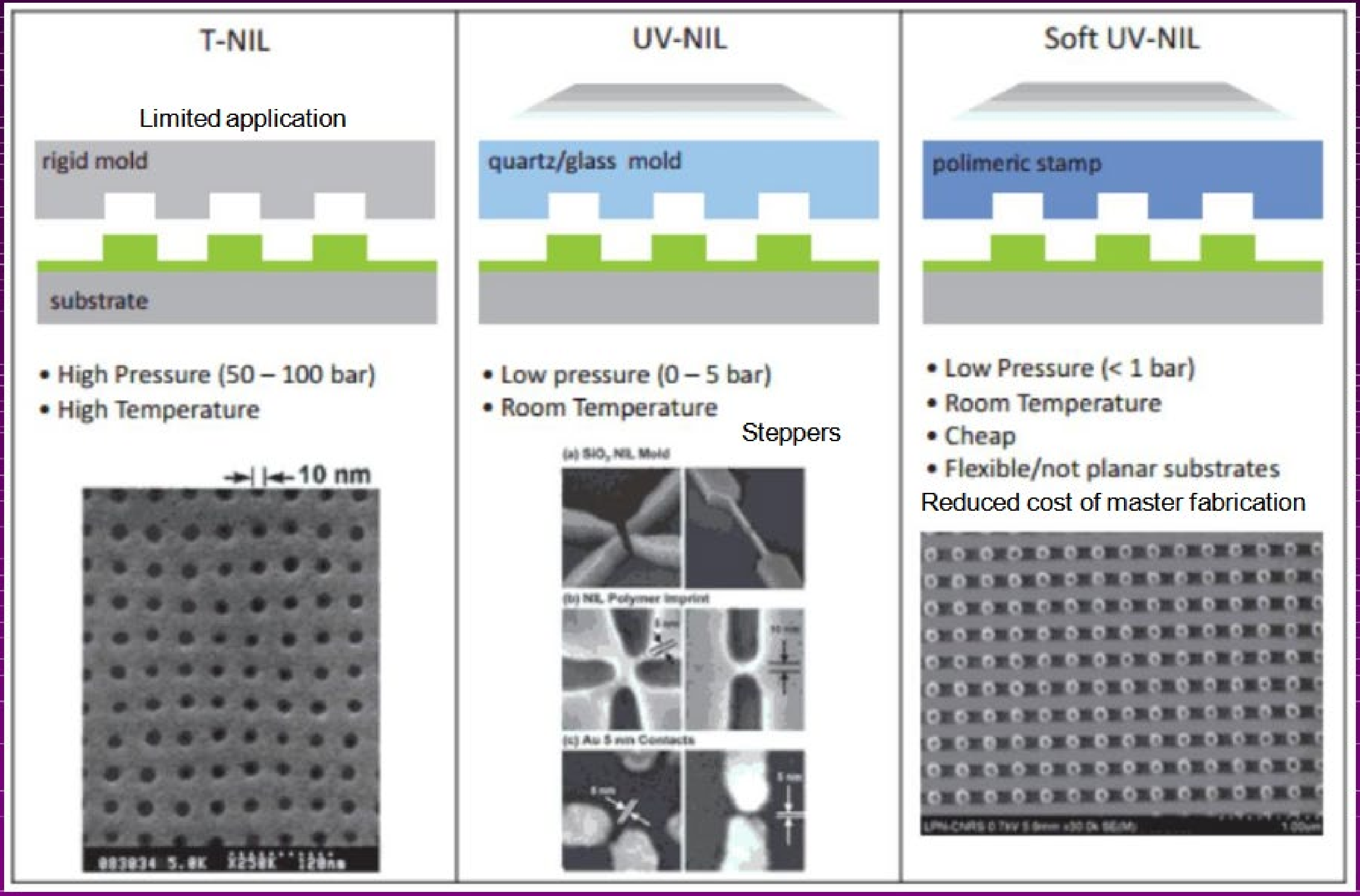



**Consists of pressing a mold onto the resist above its glass transition temperature $T_g$**

More ? Check out S. Y. Chou, Princeton

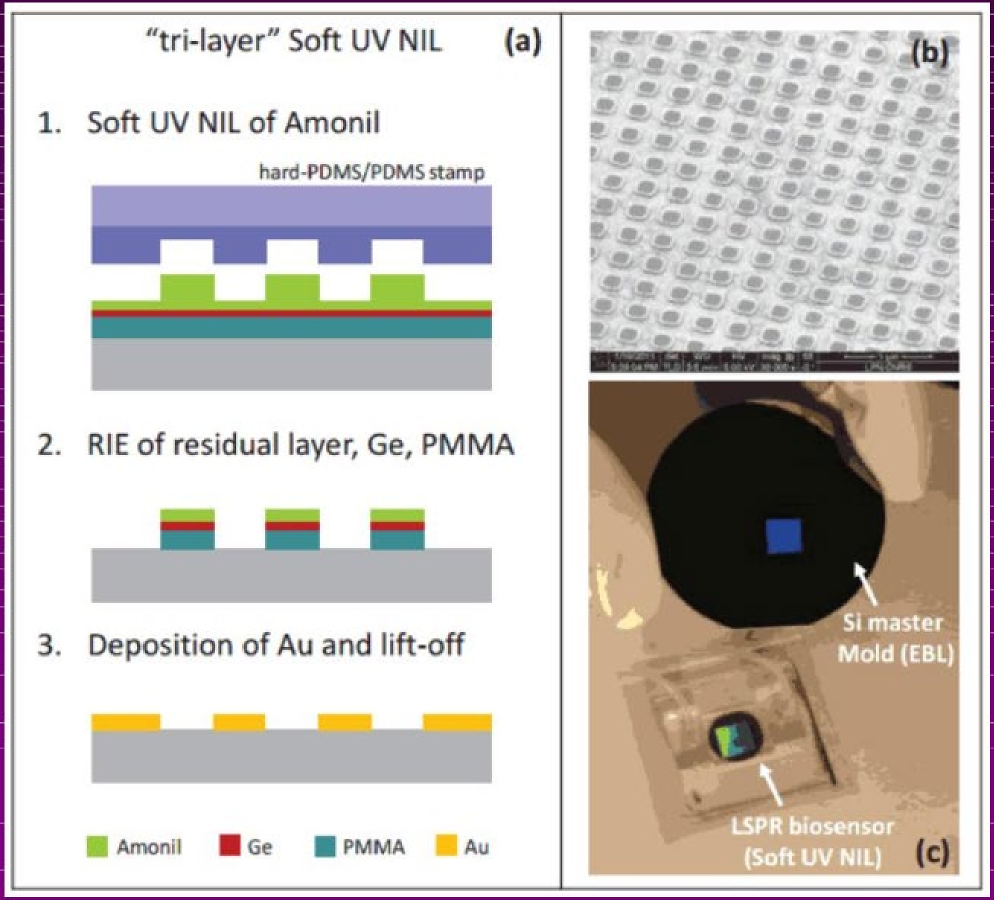
• Creates patterns by mechanical deformation of imprint resist and subsequent processes. The imprint resist is typically a monomer or polymer formulation that is cured by heat or UV light during the imprinting. Adhesion between the resist and the template is controlled to allow proper release.

# Nanoimprint




Recent Advances in Nanofabrication Techniques and Applications, InTech, 2011, p. 140

# Plasmonic nanocavities 200 nm, pitch 400 nm

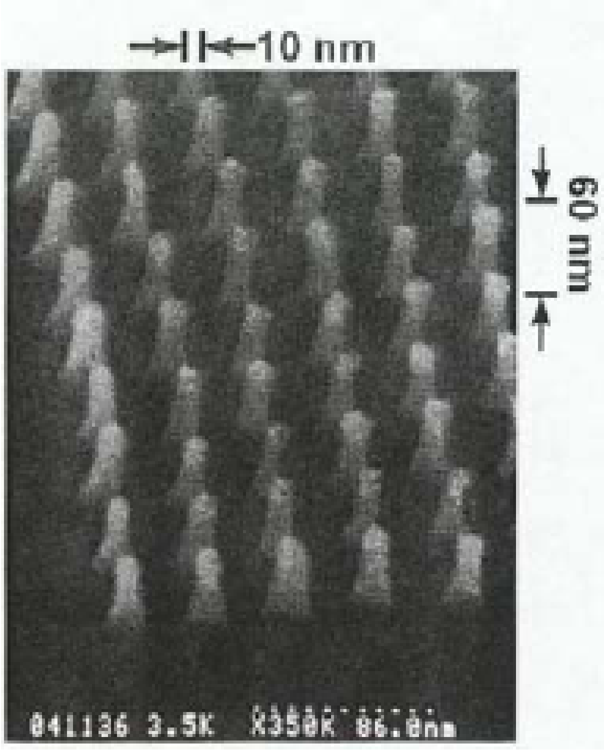



Glass substrate, large surface < 1cm$^2$,
Au/dielectric/Au islands
Ge -10 nm thick to improve the selectivity Amonil/PMMA
Amonil (NIL resist) is not soluble in solvents

A. Cattoni et al., Nanoletters, 2011, pp. 3557-3563

# NIL master

- $SiO_2$ pillars with 10 nm diameter, 40 nm spacing, and 60 nm height fabricated by e-beam lithography.
- Master can be used tens of times without degradation

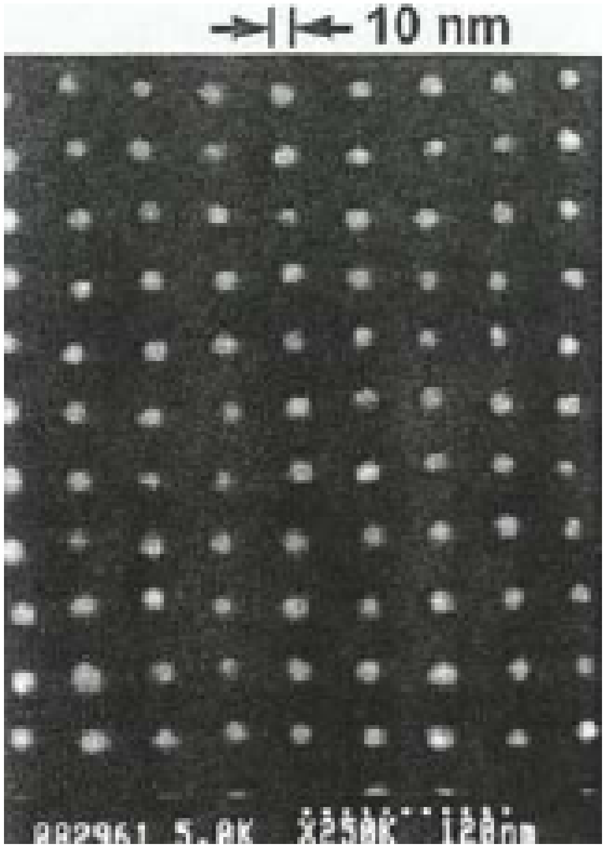


# NIL pattern in PMMA

- Mask is pressed into 80 nm thick layer of PMMA on Si substrate at 175° C ($T_g$=105 ° C), P= 4.4 MPa.
- PMMA conforms to master patterng, resulting in ~10 nm range holes

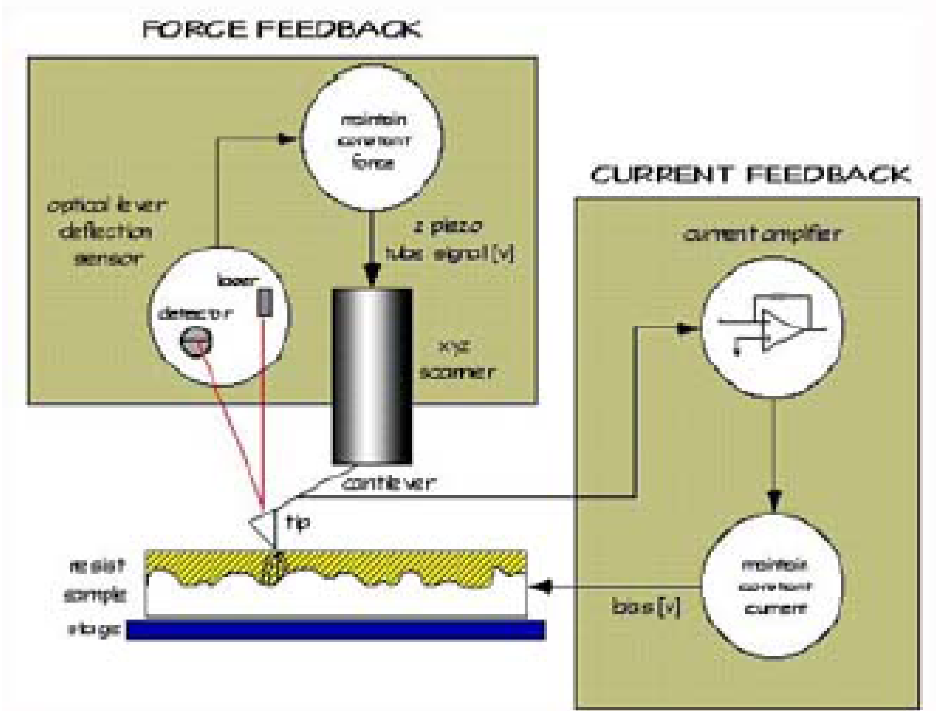
# Metal dots by NIL

- Reactive ion etching is used to cut down resist thickness until shallow regions are completely removed
- Ti/Au is deposited onto resist.
- Resist and metal-coating is removed by solvent leaving behind metal dots where resist had been removed.




Photonic and plasmonic devices, nanofluidics, single electron memory, organic TFTs

# Scanned Probe Lithography




Use STM or AFM:

Material modification, removal, or addition at nanoscales

**REVIEW ARTICLE**

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## Nanofabrication by scanning probe microscope lithography: A review

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**J. Vac. Sci. Technol. B 23(3), May/Jun 2005**

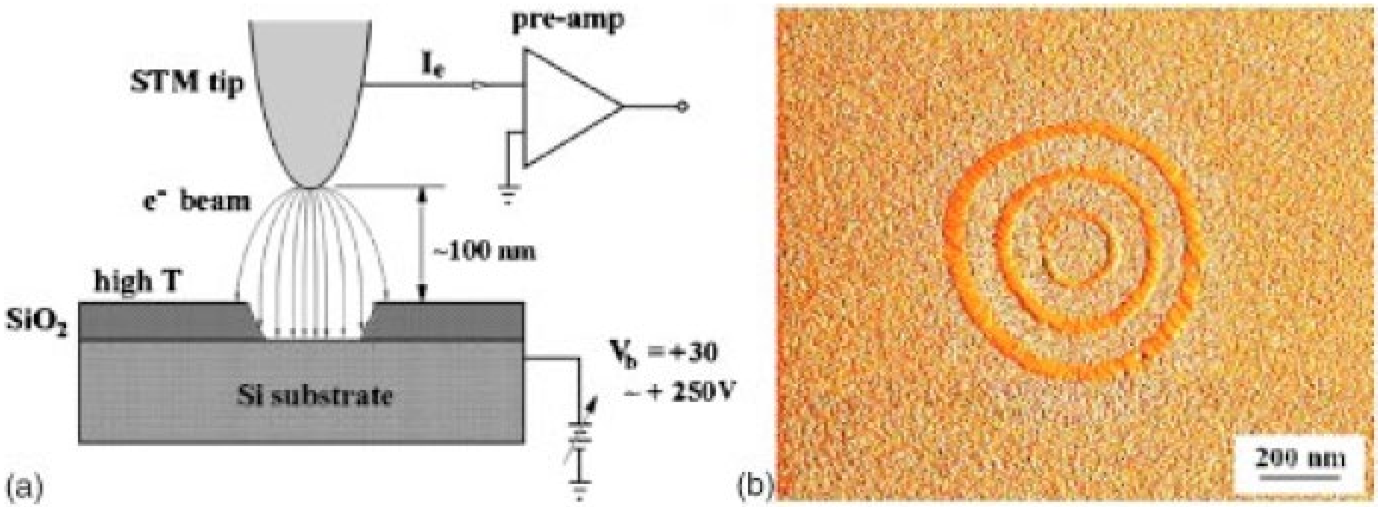



FIG. 6. Material removing by STM induced thermal decomposition: (a) schematic of decomposition of $SiO_2$ layer by an STM tip with negative bias and (b) concentric ring pattern with a minimum linewidth of 25 nm fabricated by STM tip scanning using computer controller (courtesy of Hiroshi Iwasaki of Osaka University, Japan).

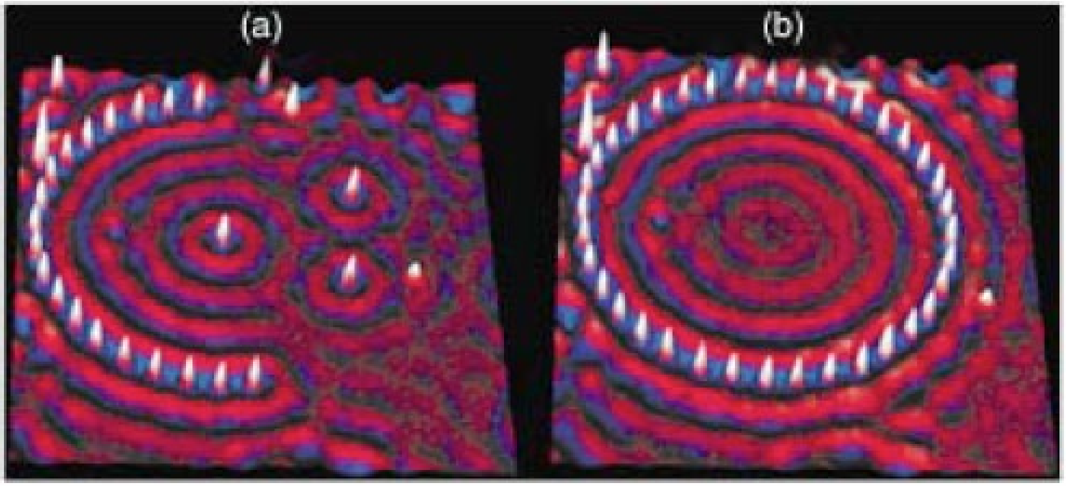



FIG. 7. STM images of quantum corral nanostructure (diameter 31.2 nm) composed of 36 Ag atoms (white protrusions) on Ag(111): (a) during construction and (b) after completion of the corral (after Ref. 39).

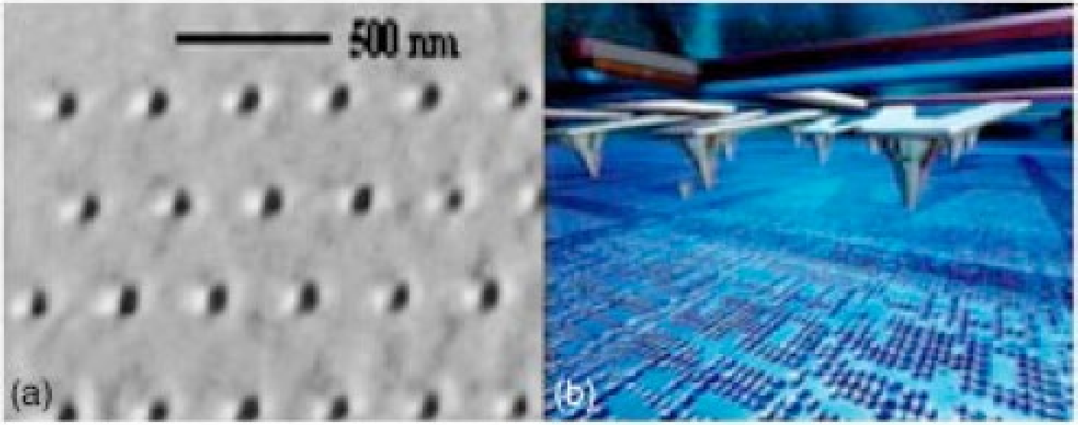
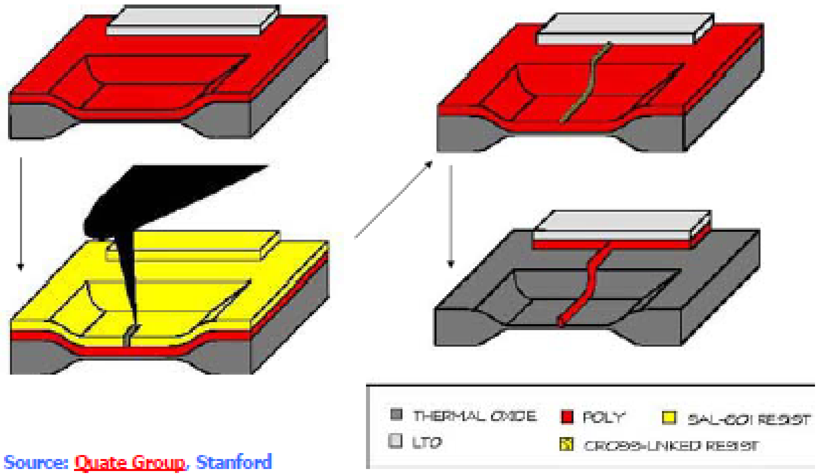


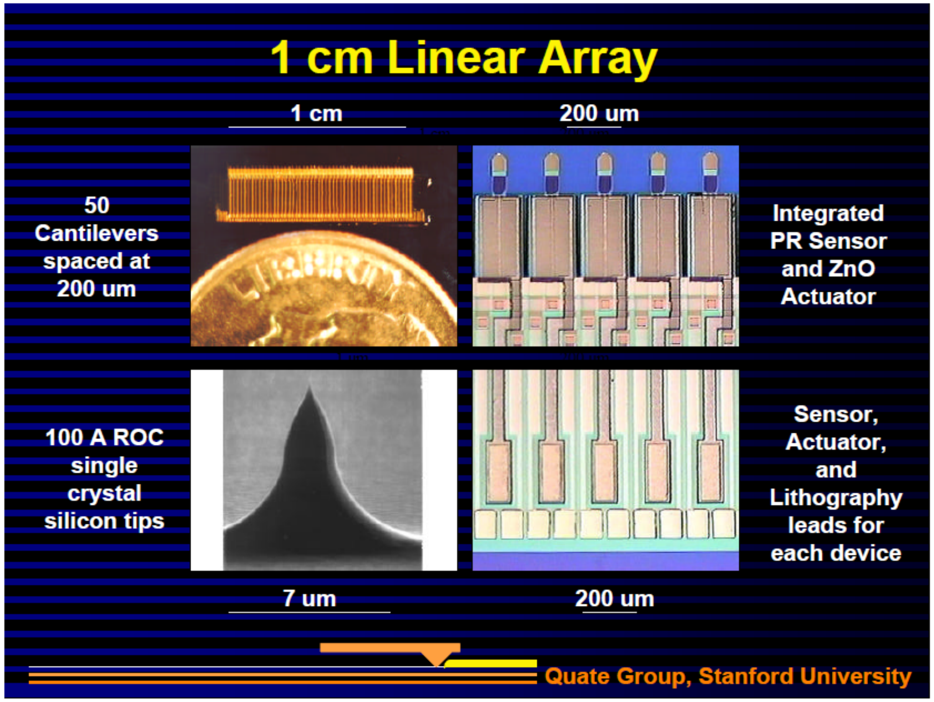

FIG. 9. Thermomechanical writing by AFM: (a) AFM image of sub-100 nm dot array written on polycarbonate using electrically heated sharp-cantilever tip with 35 mW, 4 ms pulses (after Ref. 55) and (b) schematic of IBM Millipede (courtesy of IBM).

## Fabrication of CMOS gate using SPM lithography



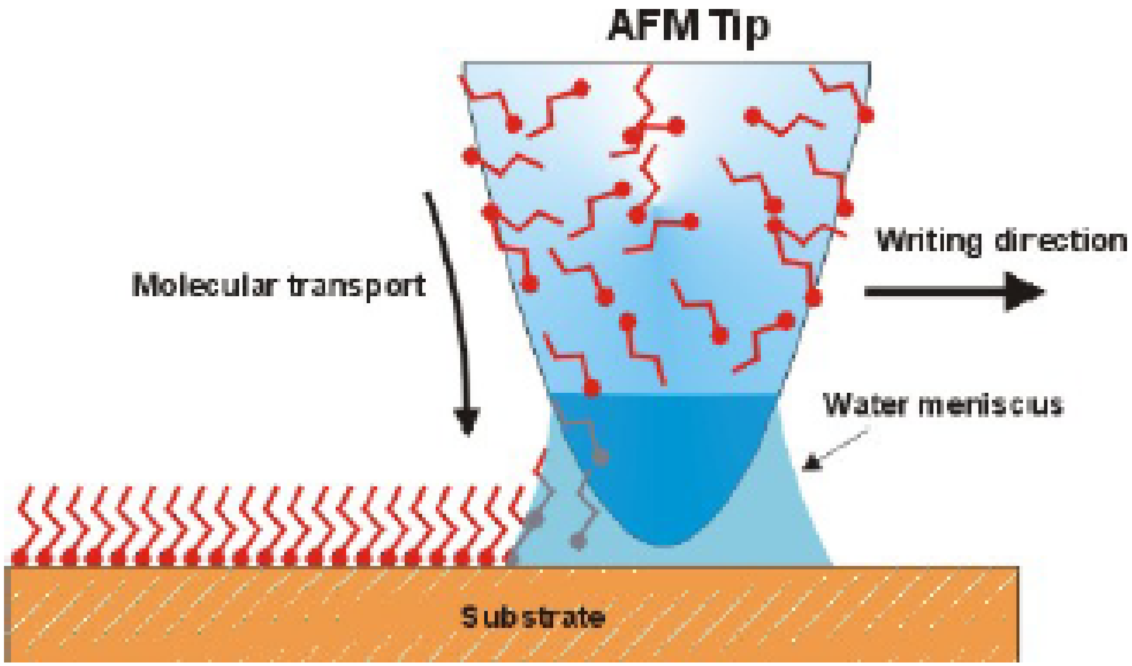

Source: Quate Group, Stanford

Attempts to scale-up:



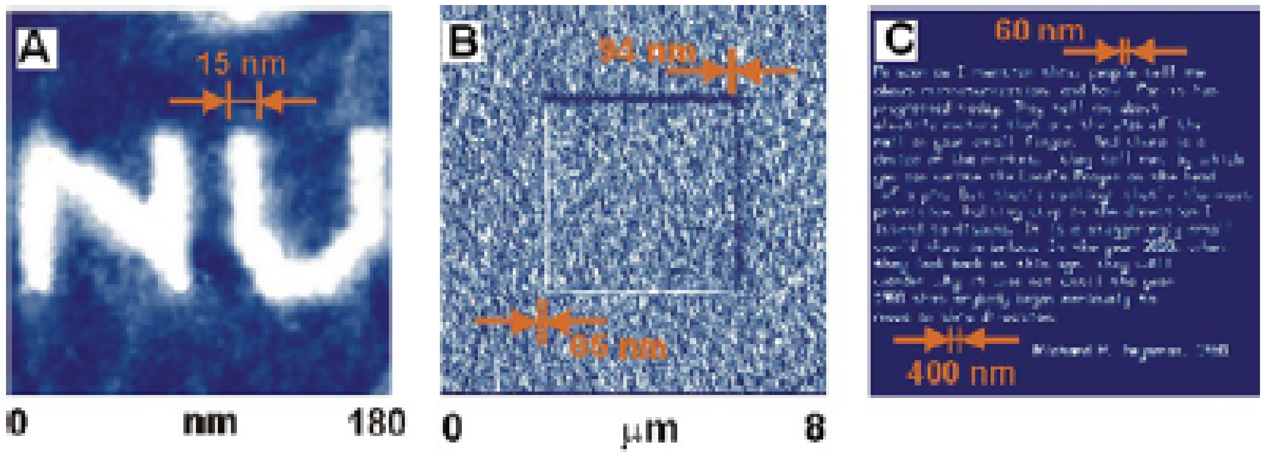

Quate group at Stanford

# Dip-pen lithography




Source: Mirkin Group, NWU

# Dip-pen lithography




A) Ultra-high resolution pattern of mercaptohexadecanoic acid on atomically-flat gold surface. B) DPN generated multi-component nanostructure with two aligned alkanethiol patterns. C) Richard Feynmann's historic speech written using the DPN nanoplotter

Source: Mirkin Group, NWU

TABLE I. Comparison of SPM-based techniques.

| Type | Technique | Strengths | Weaknesses |
|---|---|---|---|
| ALL SPM | All Techniques | • Nanoscale resolution<br>• Accurate alignment and repositioning<br>• Real-time imaging of patterned areas<br>• Multitip parallel operation demonstrated<br>• Low-cost facilities and uncomplicated procedures | • Low throughput, especially in serial operations<br>• Lack of appropriate control strategy for multitip parallel automation and feedback signals |
| STM | All techniques | • Higher resolution | • Vacuum or controlled environment required |
| | Material modification | • Minimum proximity effect<br>• Suitable for high-resolution resists | • Limited resist thickness<br>• Conducting substrate required |
| | Material deposition | • Deposition of a wide range of materials<br>• Precise control over deposition rate and geometry for CVD processes | • Limited pattern uniformity<br>• Low reproducibility in direct material transfer processes |
| | Material removal | • Precise control over material removal rate and geometry | • Limited processing speed |
| | Atom manipulation | • Atomic level resolution | • Low temperature, extremely high precision and high vacuum required<br>• Very low processing speeds |
| AFM | All techniques | • Operation in normal ambient environment | • Low probe–tip lifetime |
| | Thermally induced modification | • Good reproducibility | • Limited processing speed or long phase changing (thermal relaxation) time |
| | Local oxidation | • Good reproducibility<br>• Appropriate for a wide range of materials | • Limited oxide thickness<br>• Limited processing speed |
| | Material deposition | • Deposition of a wide range of materials<br>• Precise control over deposition rate and geometry in CVD processes | • Limited pattern uniformity<br>• Low reproducibility in direct material transfer processes |
| | Material removal | • A wide variety of materials can be handled by direct scratching<br>• Uncomplicated concept and operation in using direct scratching<br>• Precise control over etching rate and geometry using chemical etching | • Debris formation in direct scratching<br>• Very low tip lifetime in direct scratching<br>• Limited processing speed in chemical etching |
| | Dip-pen lithography | • Compatible with self assembly processes<br>• Precise control over assembly rate and geometry | • Resolution limited by tip shape<br>• High instrument complexity, especially synchronization of every dip-pen with each pattern assembly. |

Tseng et al.,

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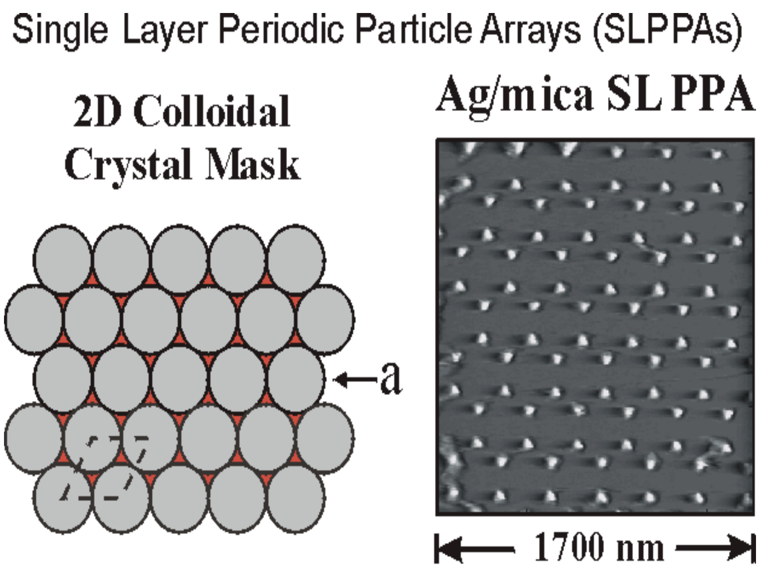
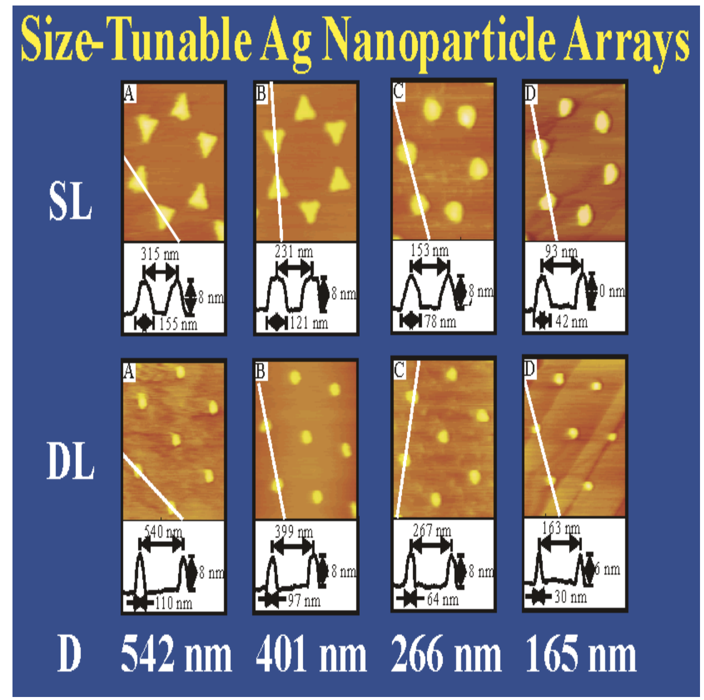
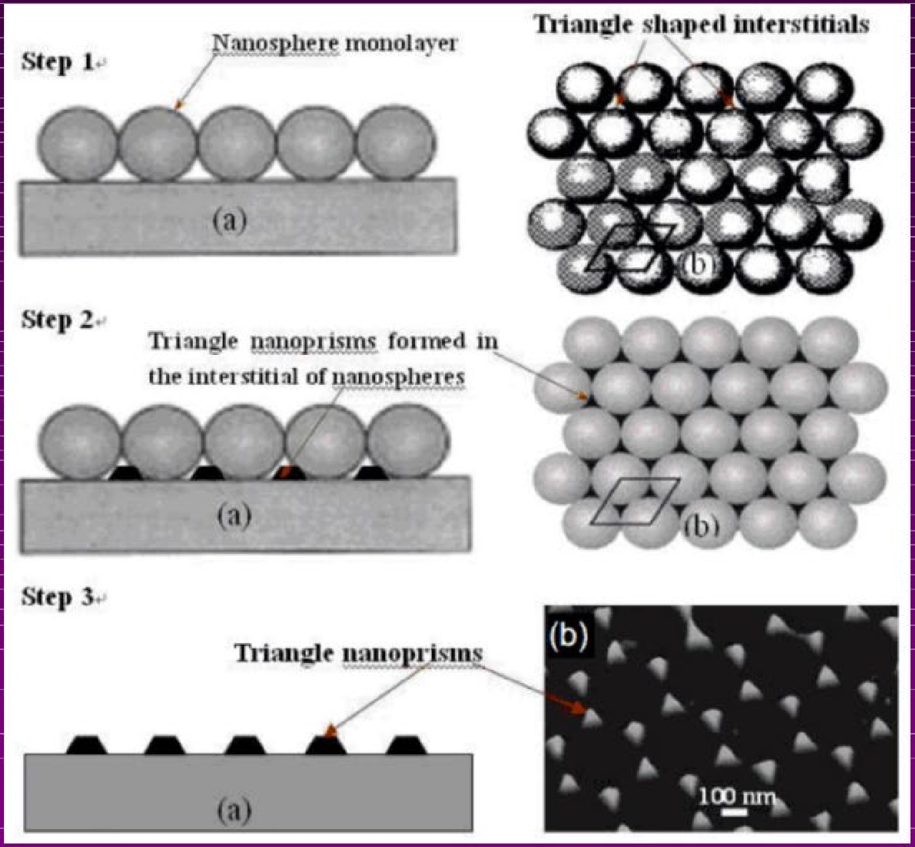
# Other methods: e.g. Nanosphere Lithography
(van Duyne group, Northwestern)



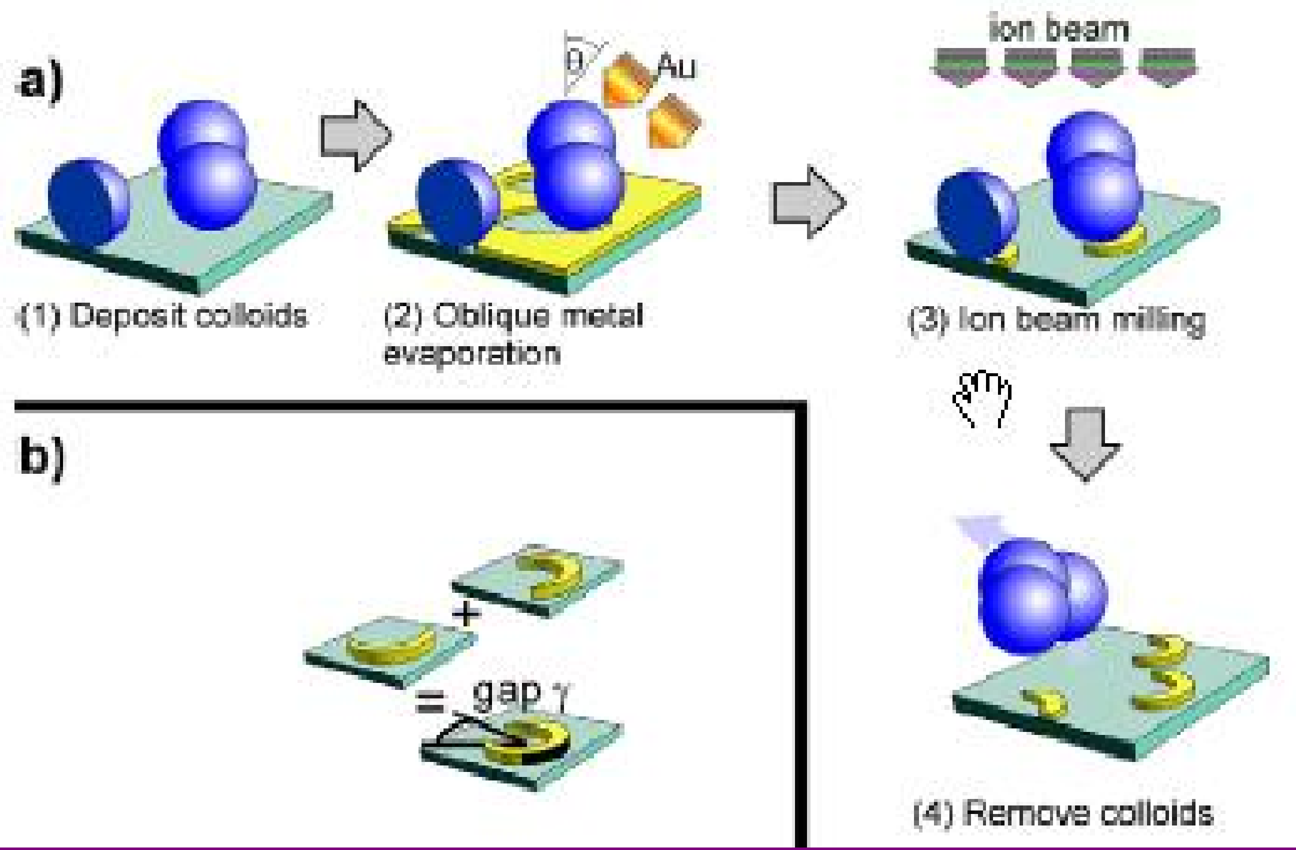
# NSL

Dip-coating, drop-coatin, spin on.
Problems for < 100 nm spheres: surface roughness




Recent Advances in Nanofabrication Techniques and Applications, InTech, 2011, p. 508

# Nanocrescents fabricated by nanosphere lithography

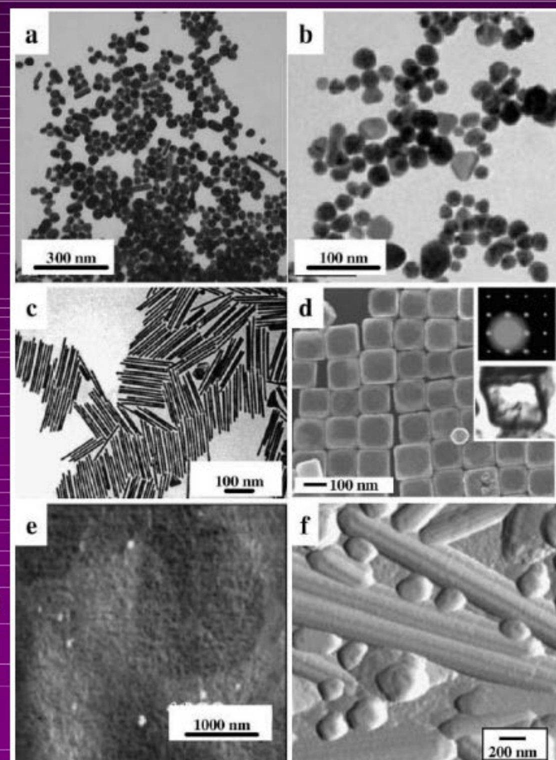



H. Rochholz *et al.*, New Journal of Physics, **9** (2007) 53

# Metal colloids for plasmonics

- Mainly Au, Ag or Cu nanoparticles (diameter 10 – 80 nm) in water
- Produced by:
  - Chemical reduction (co-precipitation and reducing). Process depends on:
    - Kind of metal
    - Reducing reagent
      - $AgNO_3$ in sodium citrate (Lee and Meisel, 1982). Average 60 nm
      - $HAuCl_4$ (Frens, 1973 and Natan 1995). Range 16 – 150 nm
    - Temperature (boiling 1 h)
    - Stabilizing agents
    - Metal ion concentration
  - Laser ablation
  - Photoreduction

# Images of metal colloids




TEM of Ag citrate colloid
$\lambda_{max}$= 406 nm

TEM of Au borohydride colloid,
Au particles 20-70 nm,
$\lambda_{max}$= 535 nm

TEM of Au nanorods,
$\lambda_{max}$= 525 nm and 885 nm

TEM of Au nanosquares

AFM of Au nanospheres embedded
in film of biopoymer chitosan
(inert organic matrix)

AFM of Ag nanowires
in dendrimer matrix

R.F. Aroca et al. / Advances in Colloid and Interface Science 116 (2005) 45–61