MESA+
Institute for Nanotechnology

University of Twente
The Netherlands

Nanofabrication principles

Summer School in Nanofluidics
ICTP, Trieste, Italy

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University of Twente
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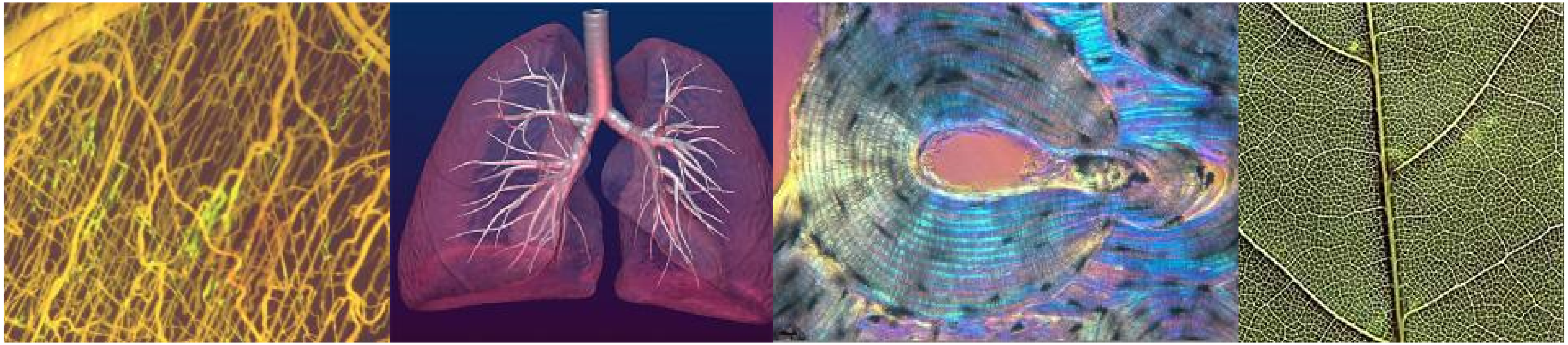
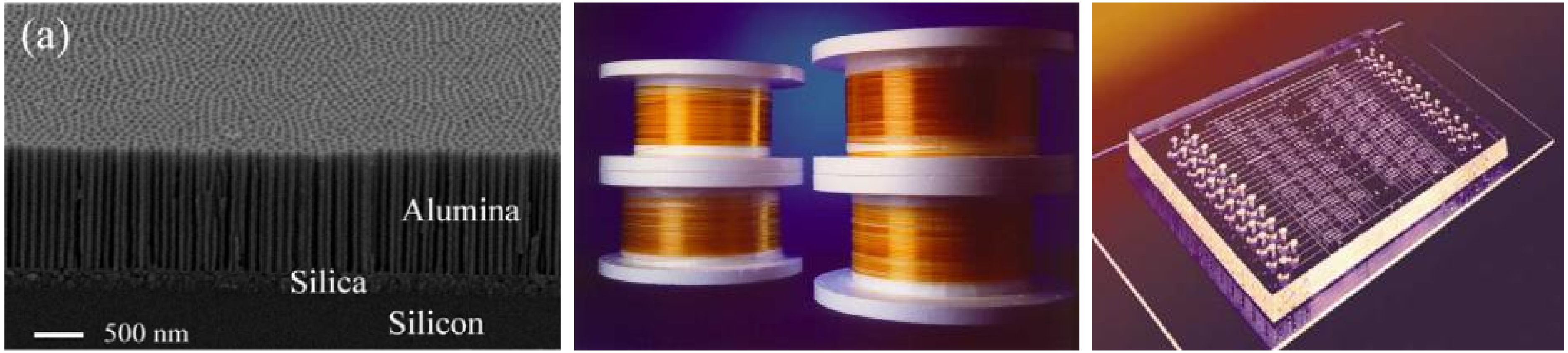
The micro/nanofluidic world

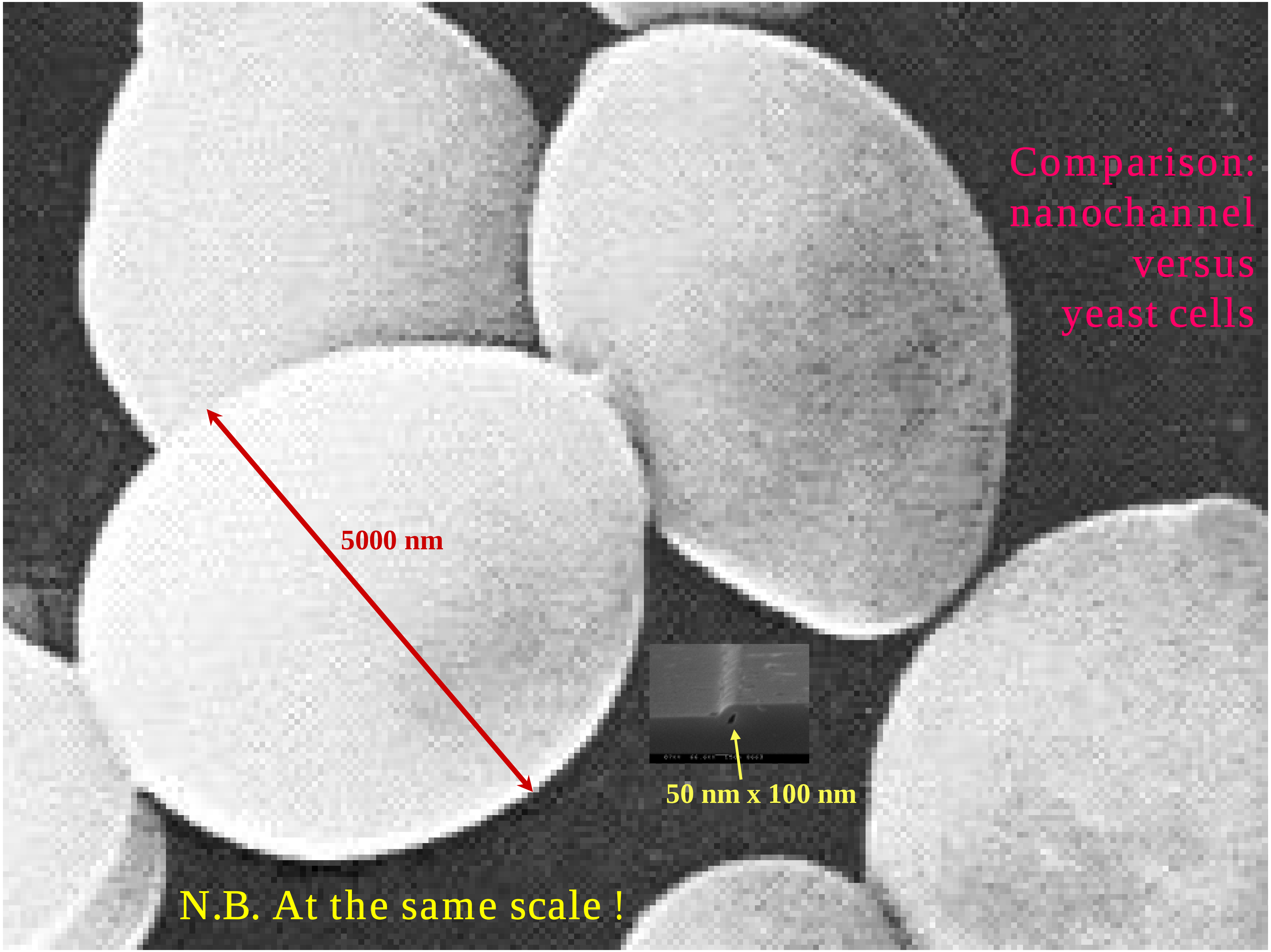


Biological flow systems: animal blood / lung / bone capillaries, plant veins

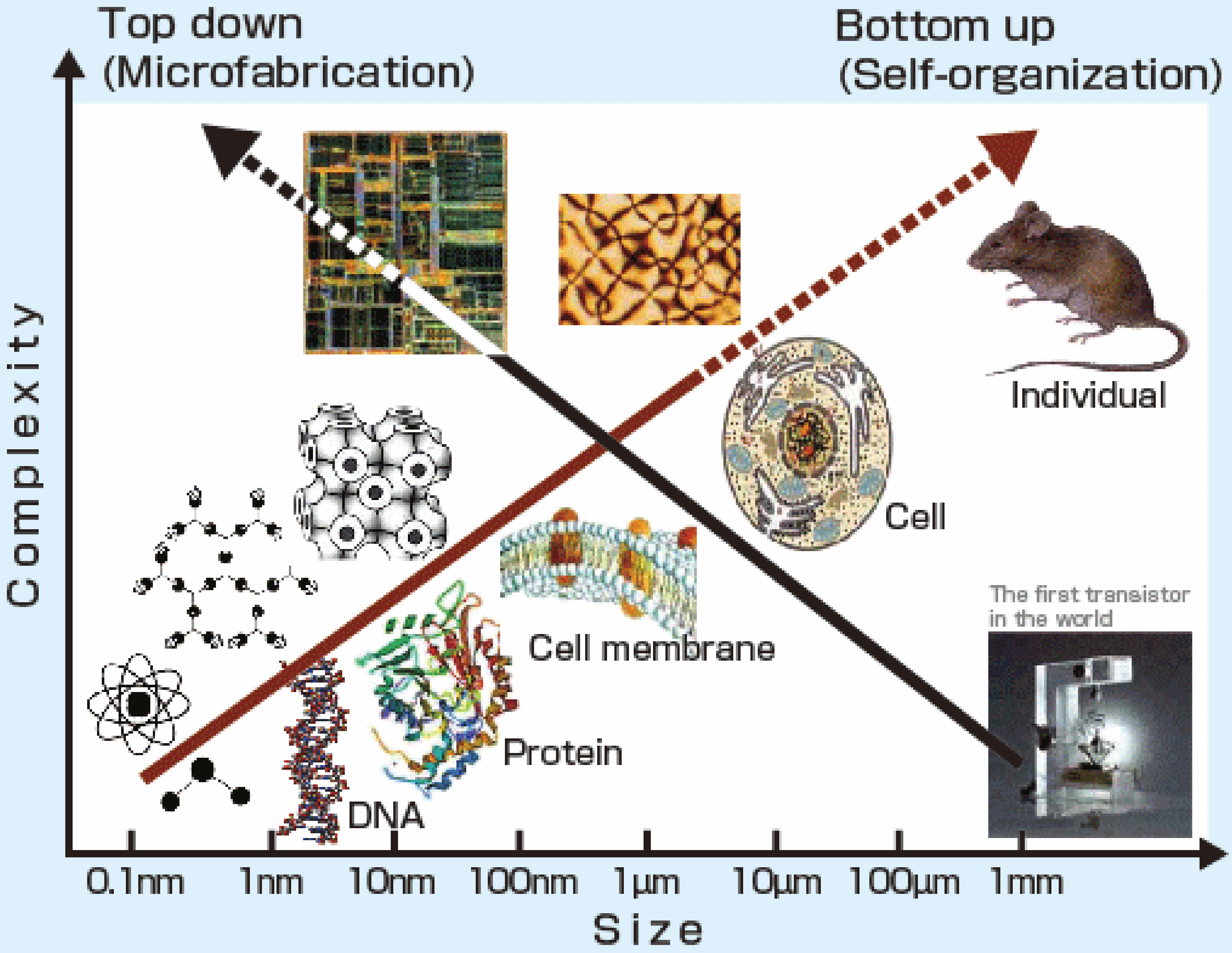


Man-made flow systems: porous solids, glass capillaries, fluidic chips

Comparison: nanochannel versus yeast cells



N.B. At the same scale !

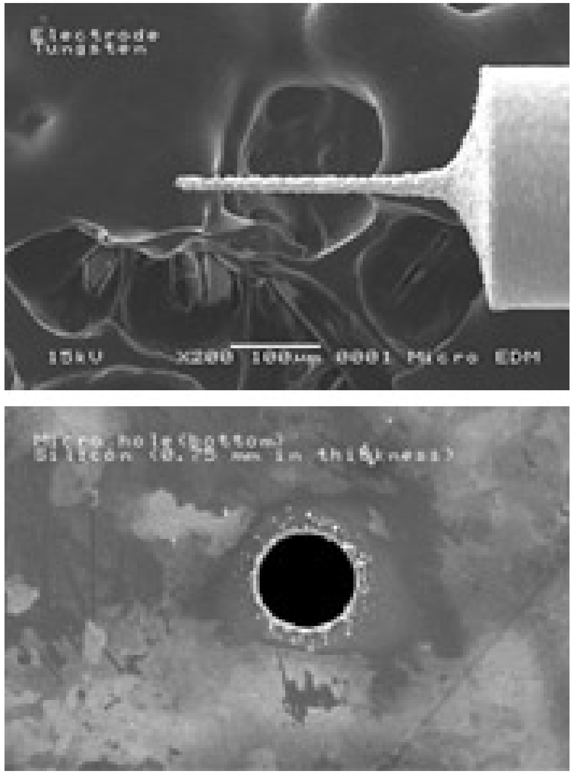


http://www.aist.go.jp/aist_e/aist_today/2007_23/nanotec/nanotec_02.html

Top-down approach:
same principle, smaller tools

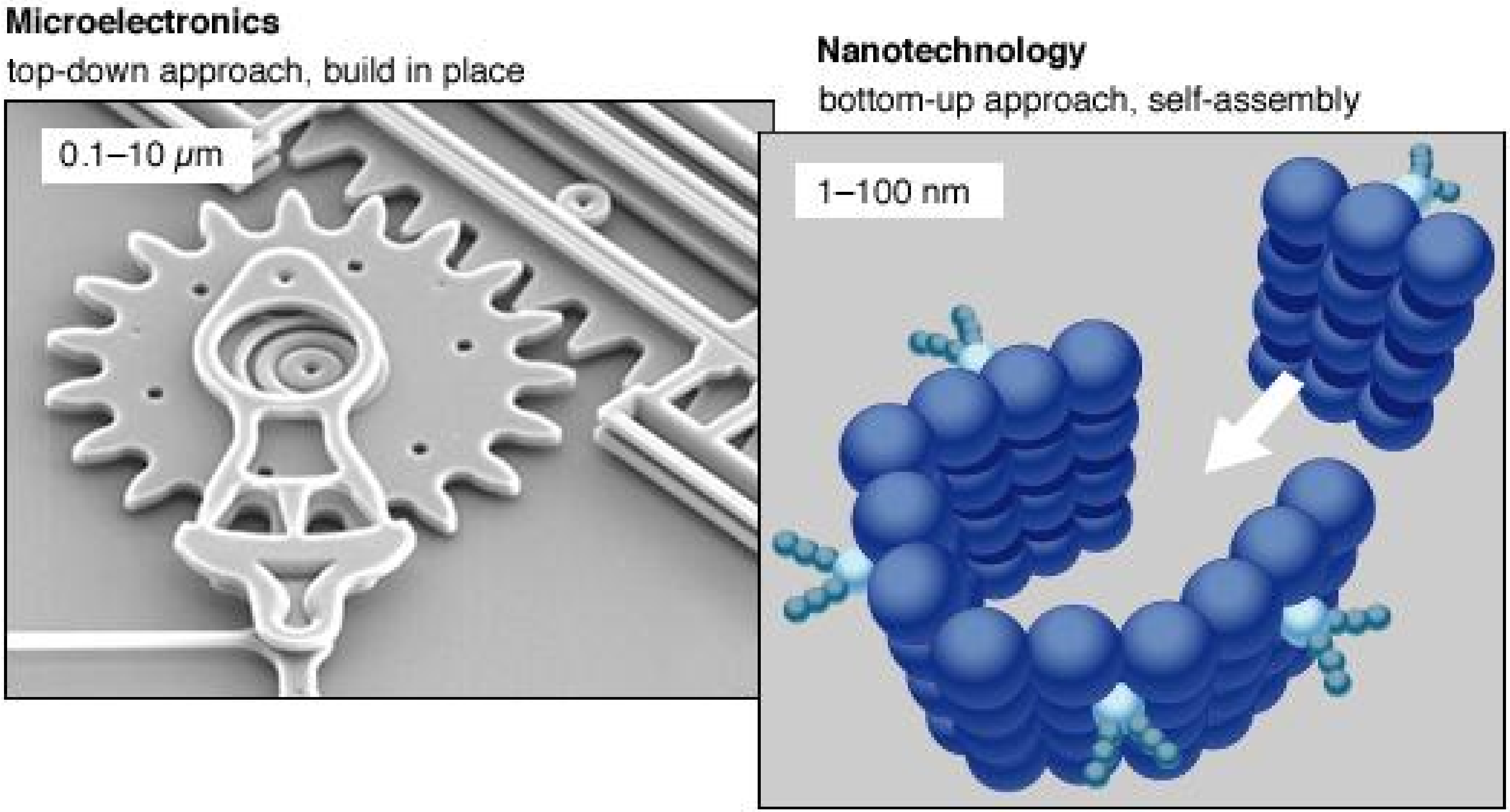
from meters

to millimeters



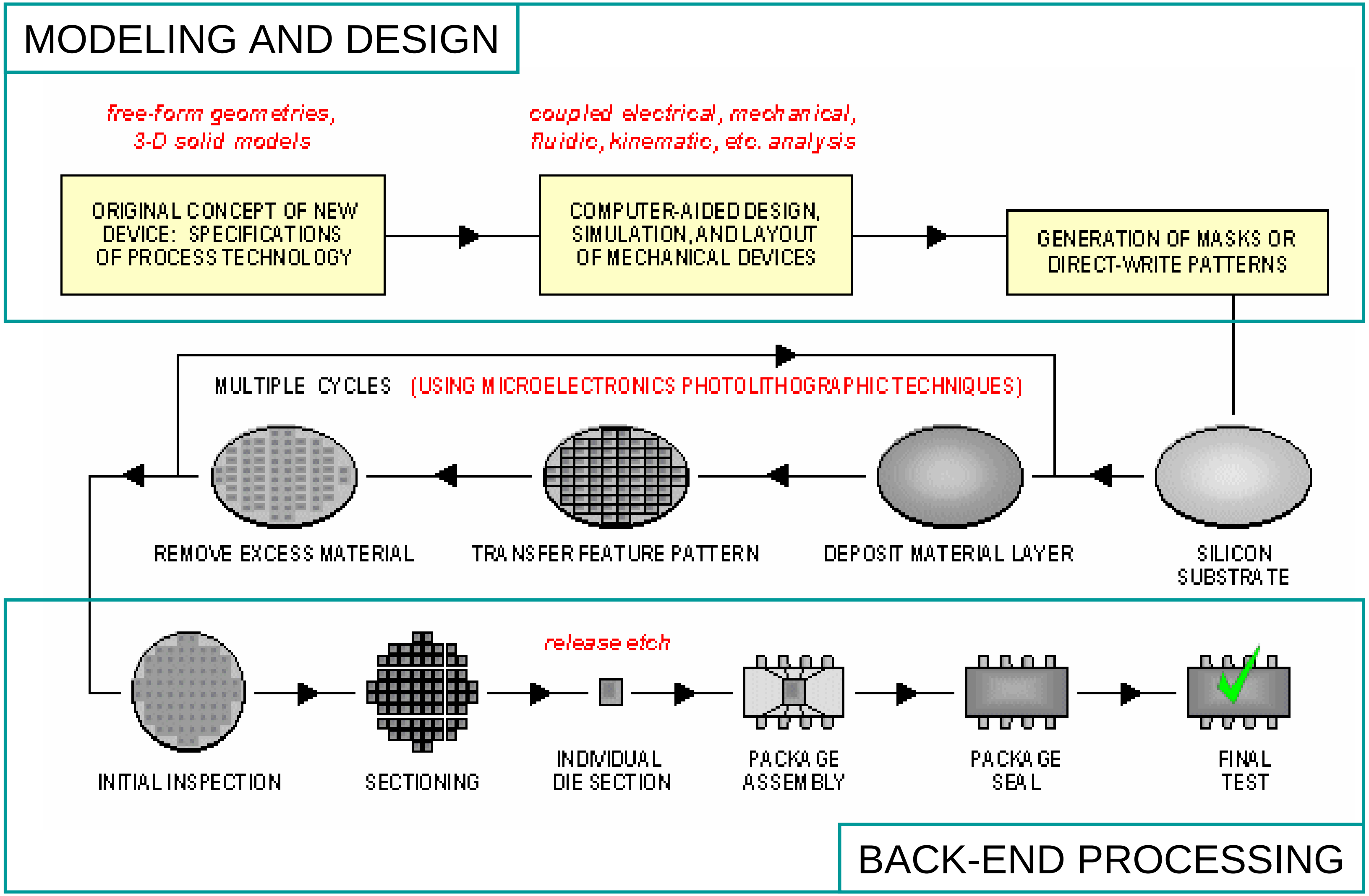
to micrometers

Top-down and bottom-up nanofabrication



http://www.britannica.com/eb/art-73017/

Batch microfabrication process (IC's)



MODELING AND DESIGN

free-form geometries, 3-D solid models

coupled electrical, mechanical, fluidic, kinematic, etc. analysis

ORIGINAL CONCEPT OF NEW DEVICE: SPECIFICATIONS OF PROCESS TECHNOLOGY

COMPUTER-AIDED DESIGN, SIMULATION, AND LAYOUT OF MECHANICAL DEVICES

GENERATION OF MASKS OR DIRECT-WRITE PATTERNS

MULTIPLE CYCLES (USING MICROELECTRONICS PHOTOLITHOGRAPHIC TECHNIQUES)

SILICON SUBSTRATE

DEPOSIT MATERIAL LAYER

TRANSFER FEATURE PATTERN

REMOVE EXCESS MATERIAL

INITIAL INSPECTION

SECTIONING

release etch

INDIVIDUAL DIE SECTION

PACKAGE ASSEMBLY

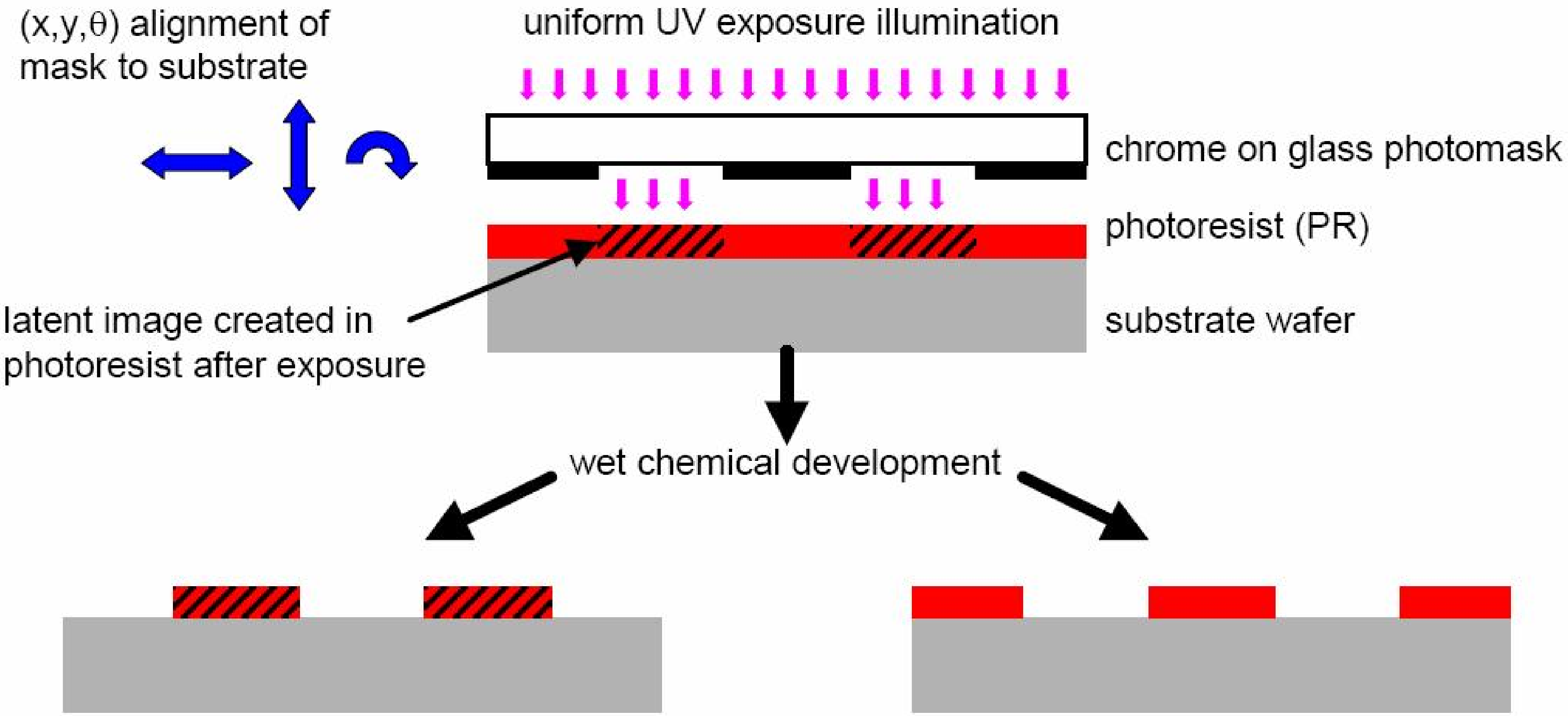
PACKAGE SEAL

FINAL TEST

BACK-END PROCESSING

copied from: MEMS Tutorial by M.A. Michalice

The core technology: photolithography



(x,y,θ) alignment of mask to substrate

uniform UV exposure illumination

chrome on glass photomask

photoresist (PR)

substrate wafer

latent image created in photoresist after exposure

wet chemical development

NEGATIVE PHOTORESIST

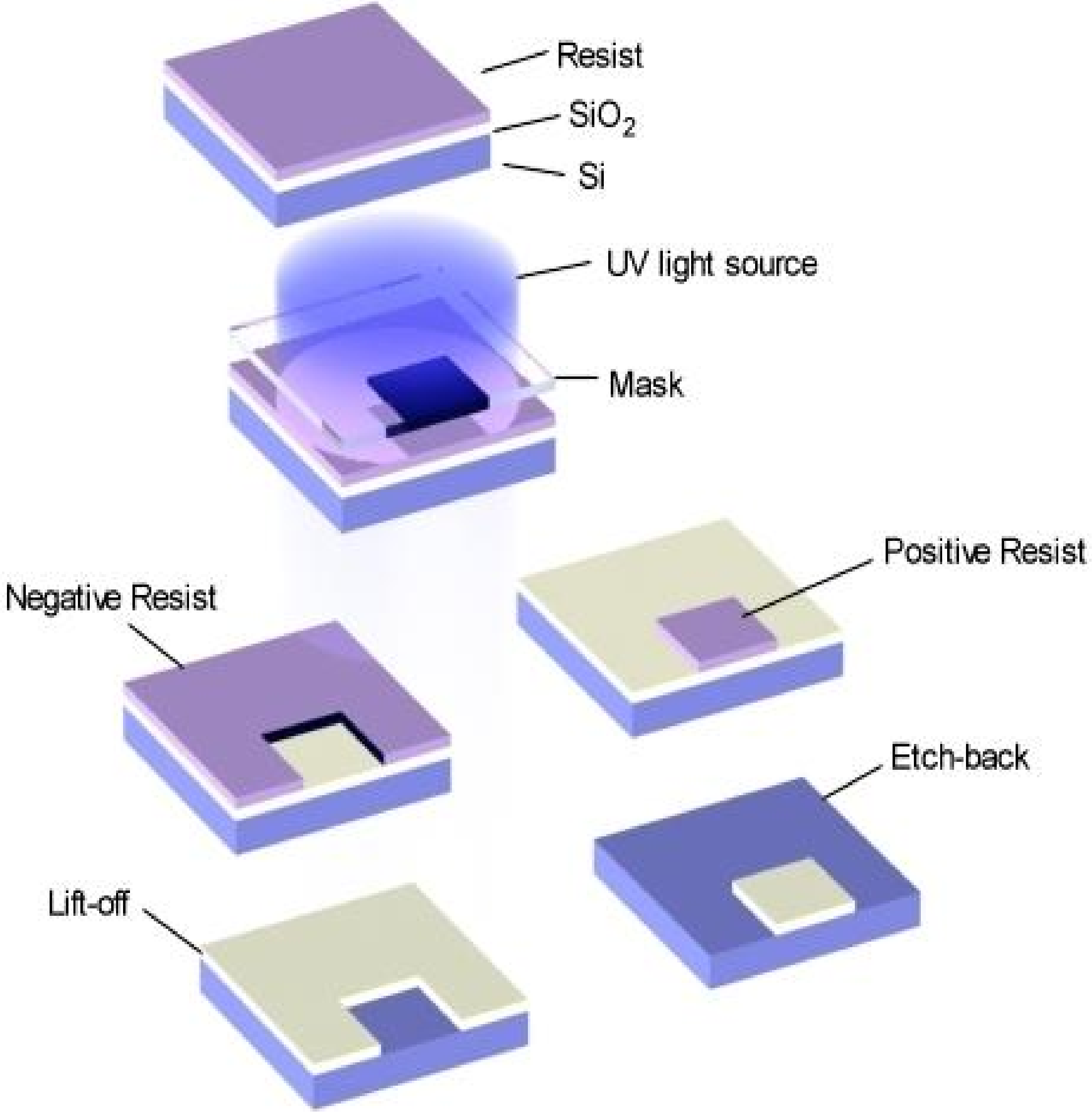
Photoresist is photopolymerized where exposed and rendered insoluble to the developer solution.

POSITIVE PHOTORESIST

Exposure decomposes a development inhibitor and developer solution only dissolves photoresist in the exposed areas.

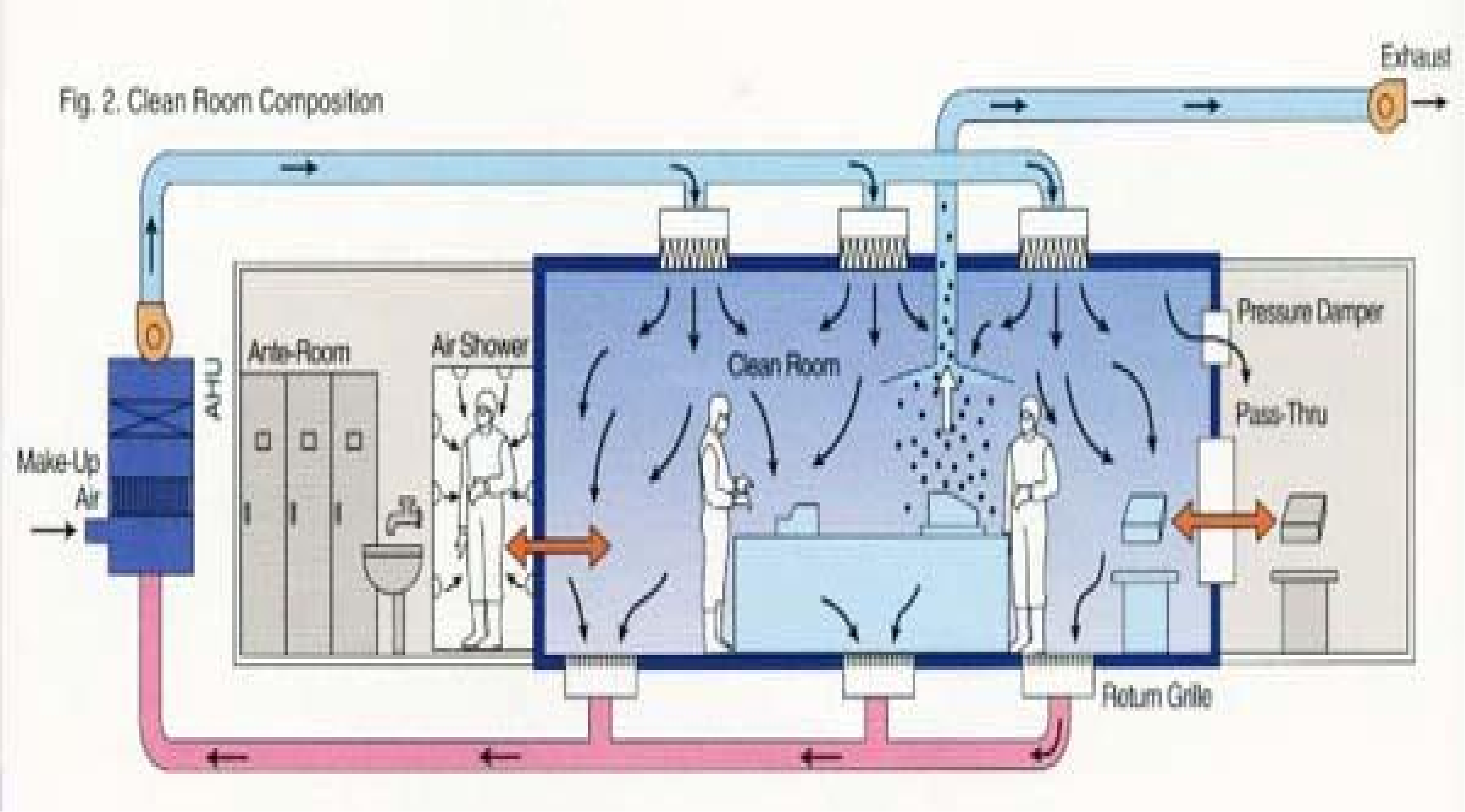
R. B. Darling / EE-527

Photolithography and pattern transfer

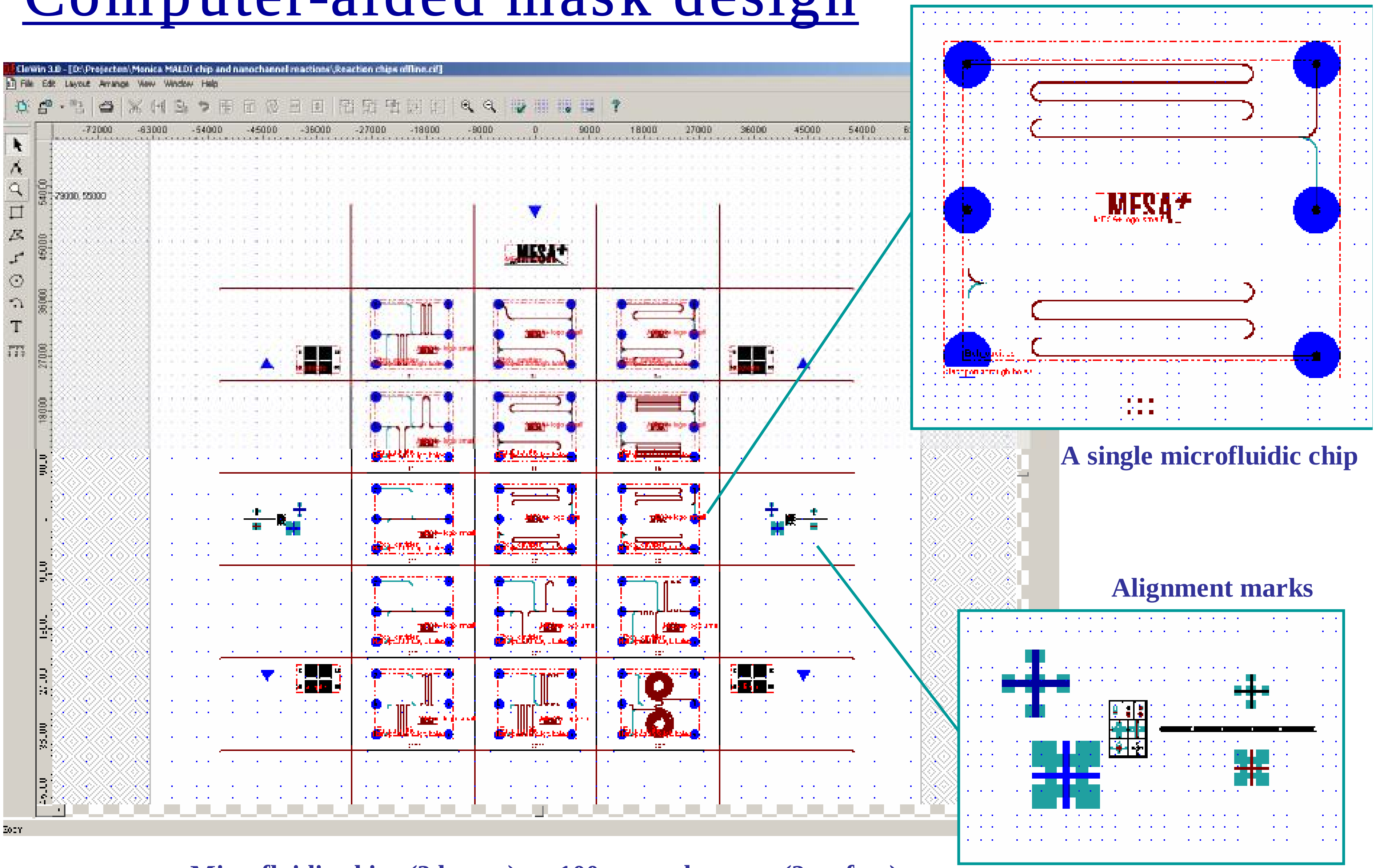


Typical equipment: mask aligners

Working environment: clean room



Computer-aided mask design



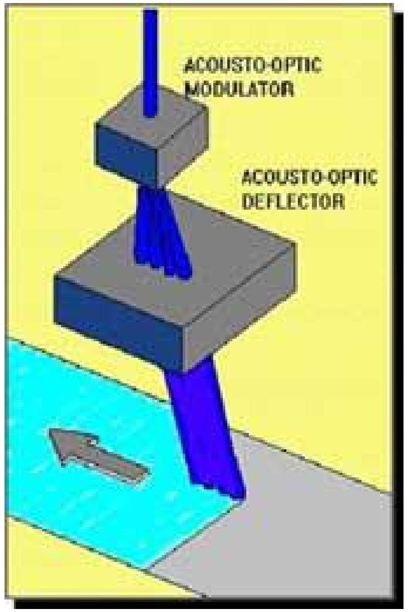
A single microfluidic chip

Alignment marks

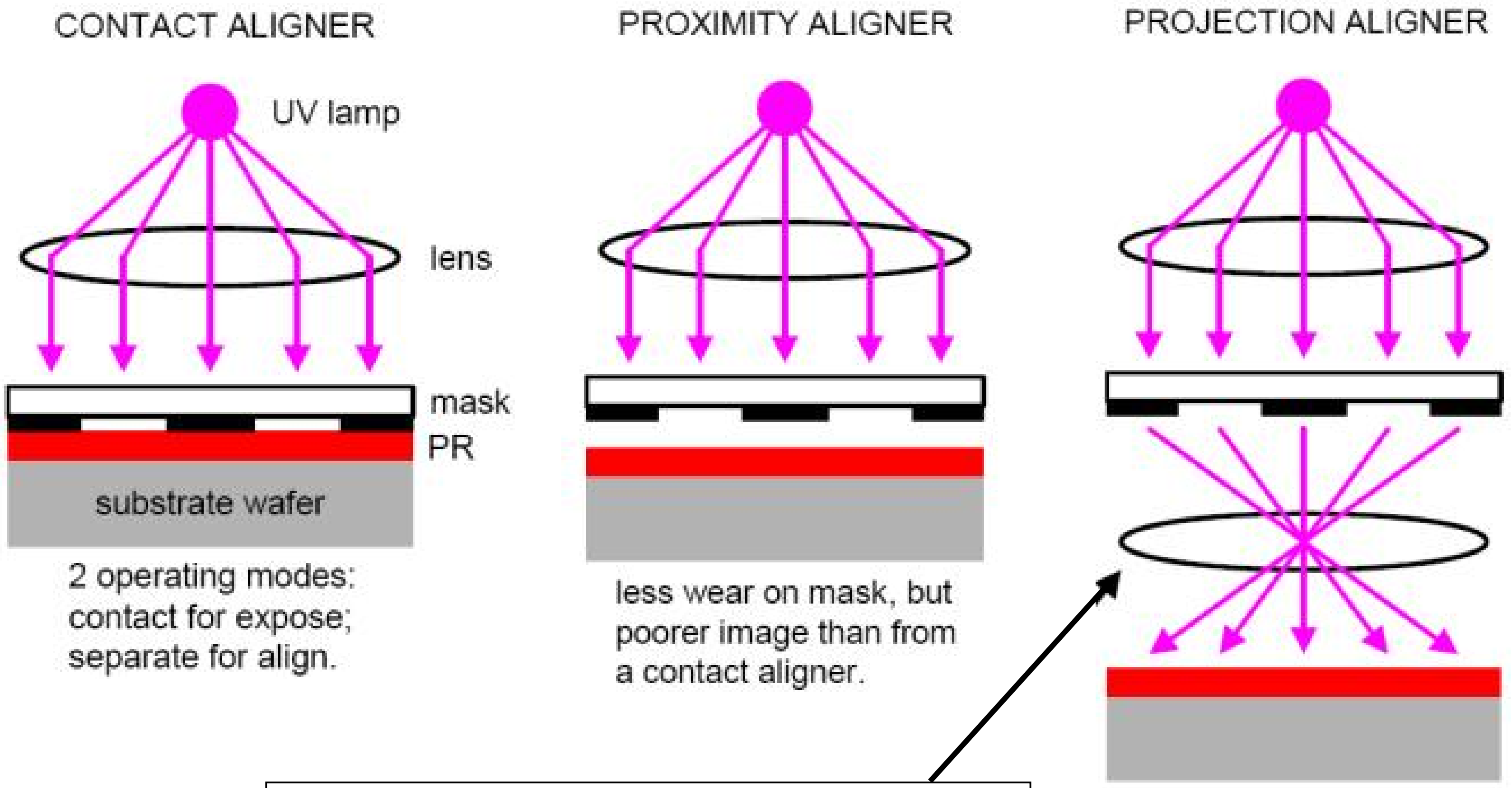
Microfluidic chips (3 layers) on 100 mm substrates (2 wafers)
Different colours represent different material layers / processes

Mask fabrication e.g. by laser beam writing

High Accuracy Photomask and Direct Write Lithography Systems



Alignment and exposure systems



2 operating modes:
contact for expose;
separate for align.

less wear on mask, but
poorer image than from
a contact aligner.

Projection systems use imaging optics in between the mask and the wafer that reduce the image by a factor 4-5

Limitations of optical lithography

Projection lithography works at Rayleigh diffraction limit.

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

NA=numerical aperture (0.5-0.6)

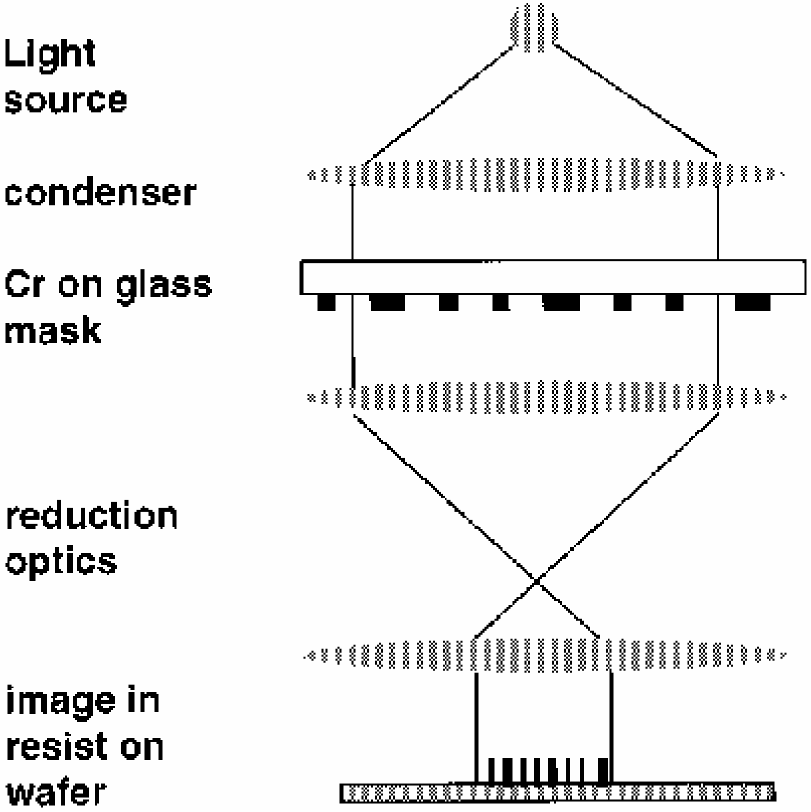
λ=wavelength

k_1 depends on process (0.4-0.8)

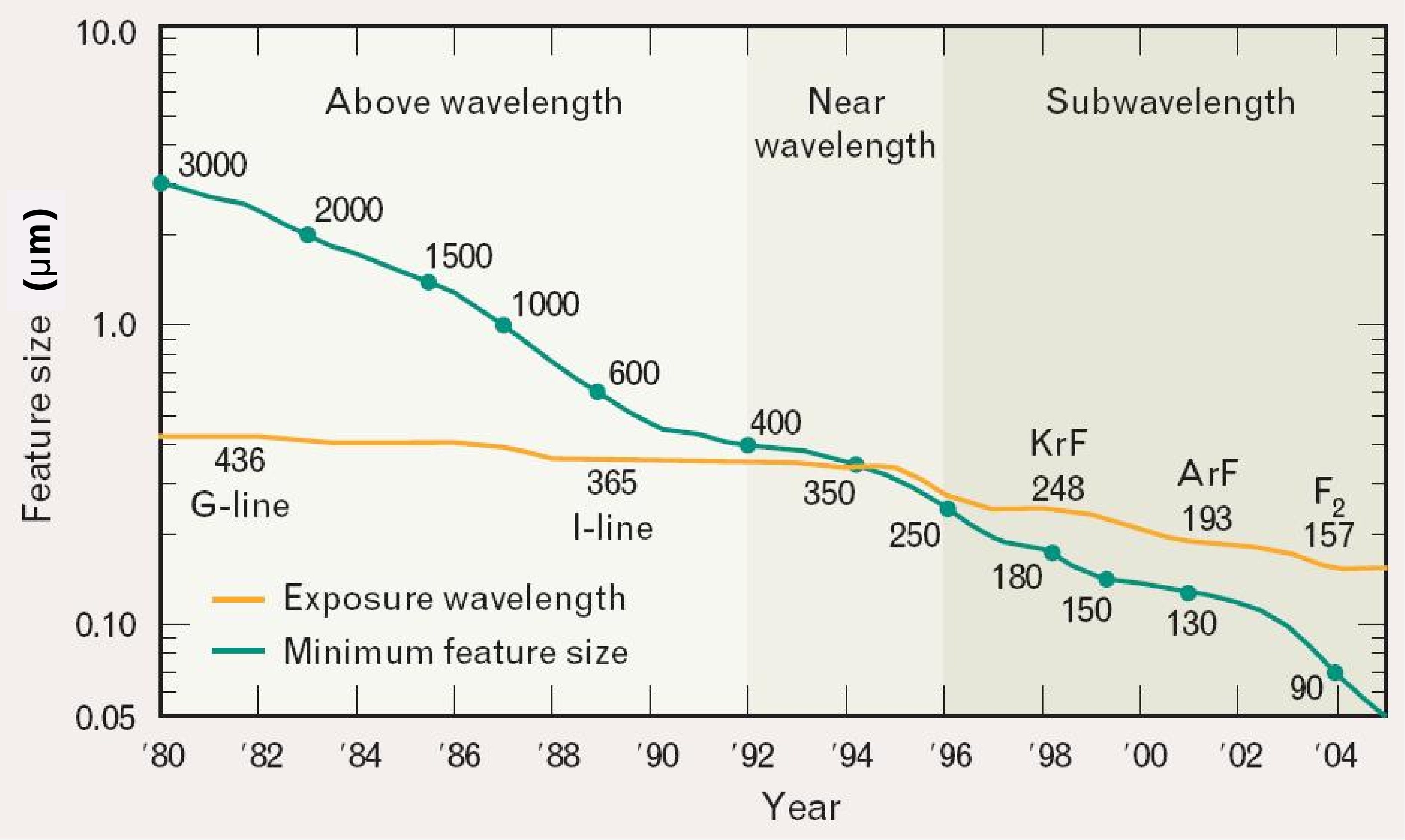
Note: for these values, $R \approx \lambda$

Depth of focus: $$DOF = k_2 \frac{\lambda}{(NA)^2}$$

Advanced litho: k_2=0.7



Timeline optical lithography



Today:

M. Rothschild et al, Lincoln Lab. J. vol.14, nr.2, 2003, p.221

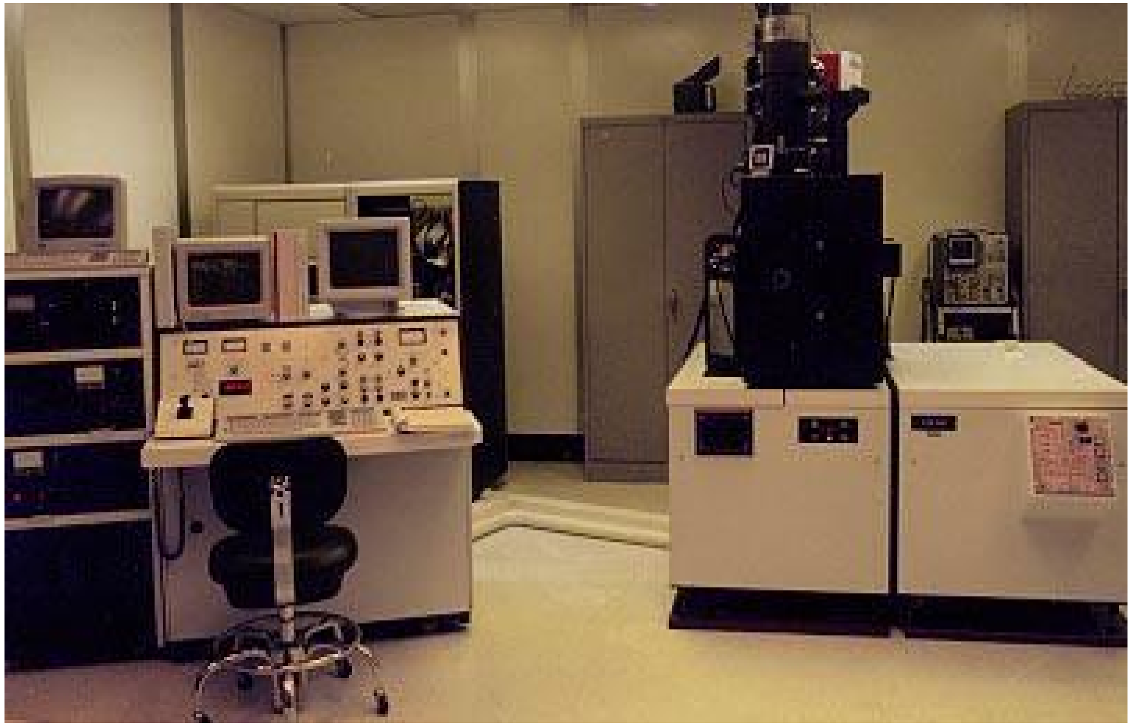
Towards optical nano lithography

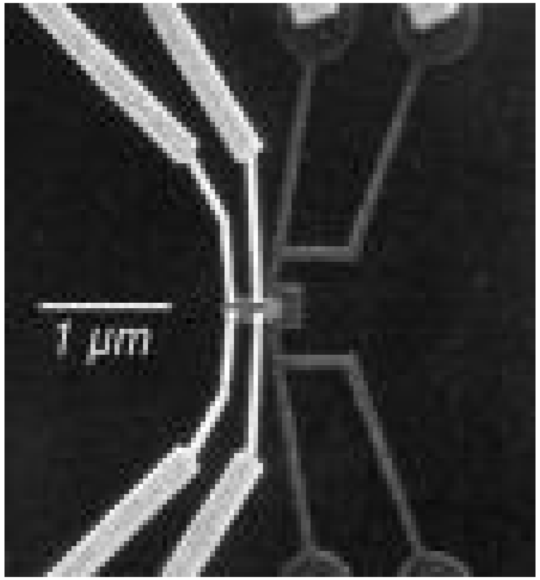
- Lower wavelengths: deep-UV excimer lasers KrF 248 nm, ArF 193 nm, F_2 157 nm* (lens/mask transmission issues)
- X-ray: $\lambda \approx 0.8$ nm (synchrotron source needed)
- Higher contrast photoresists (theoretical limit lines & spaces: k_1=0.25*)
- Improved optics & immersion lithography, i.e. liquid between lens and substrate (***NA***=1.3* with water; absorption issues)

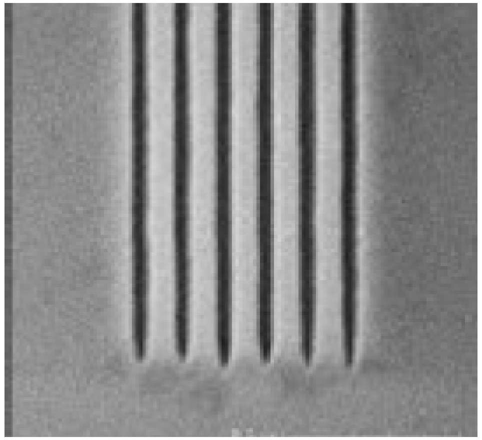
*R = 30 nm, DOF = 65 nm

- scanning beam lithography: next slide

Direct-write electron beam lithography







33nm Trenches

At 100-keV e-beam energy, $\lambda = 3.7$ pm
With typical NA ≈ 0.001, R ≈ 4 nm

Limitations: charging, speed

Mask-less photolithography

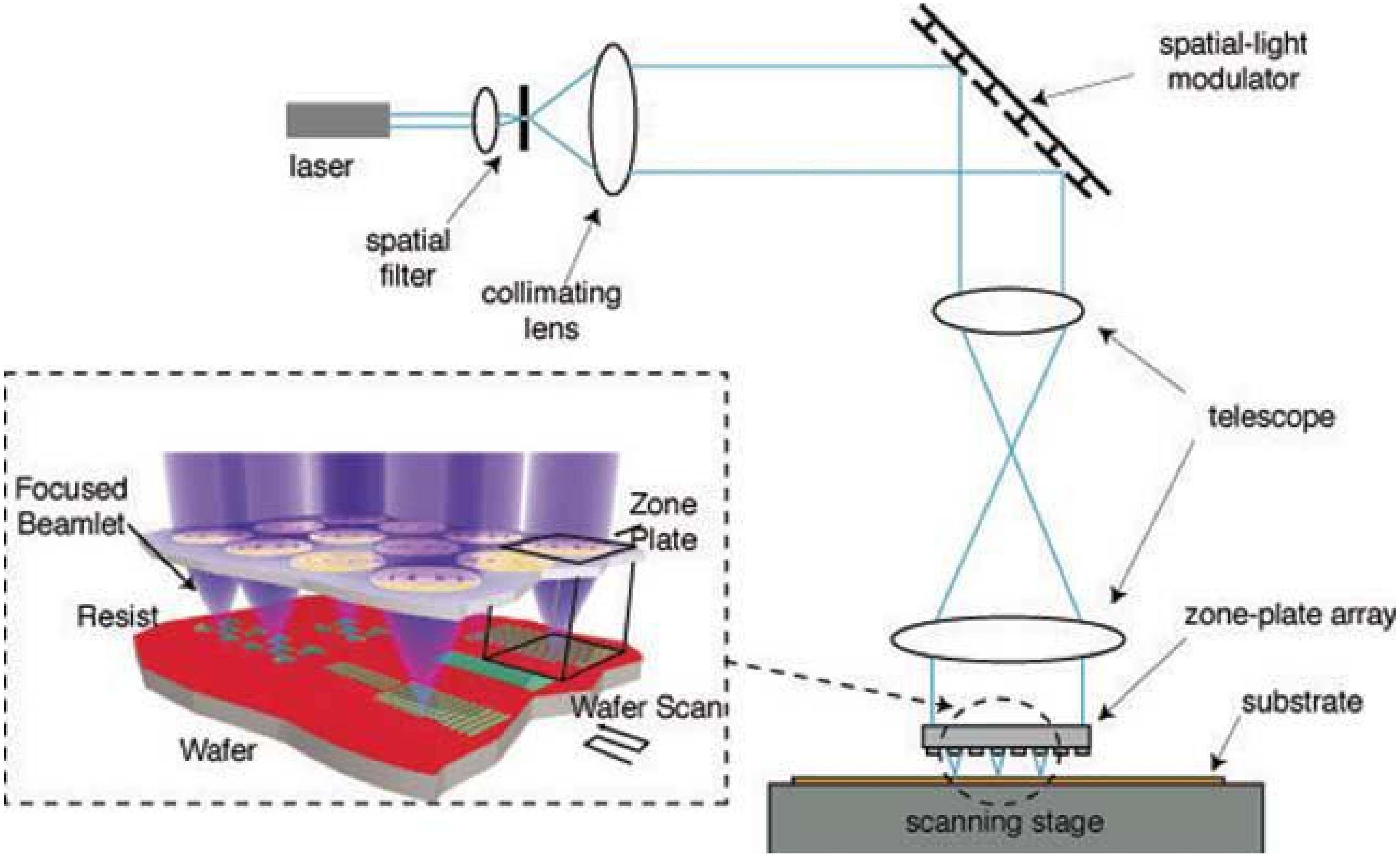
Scanning electron-beam writing - see before
(also possible with focused ion beams -see after)

Zone-plate array lithography

Holographic (interferometric) lithography

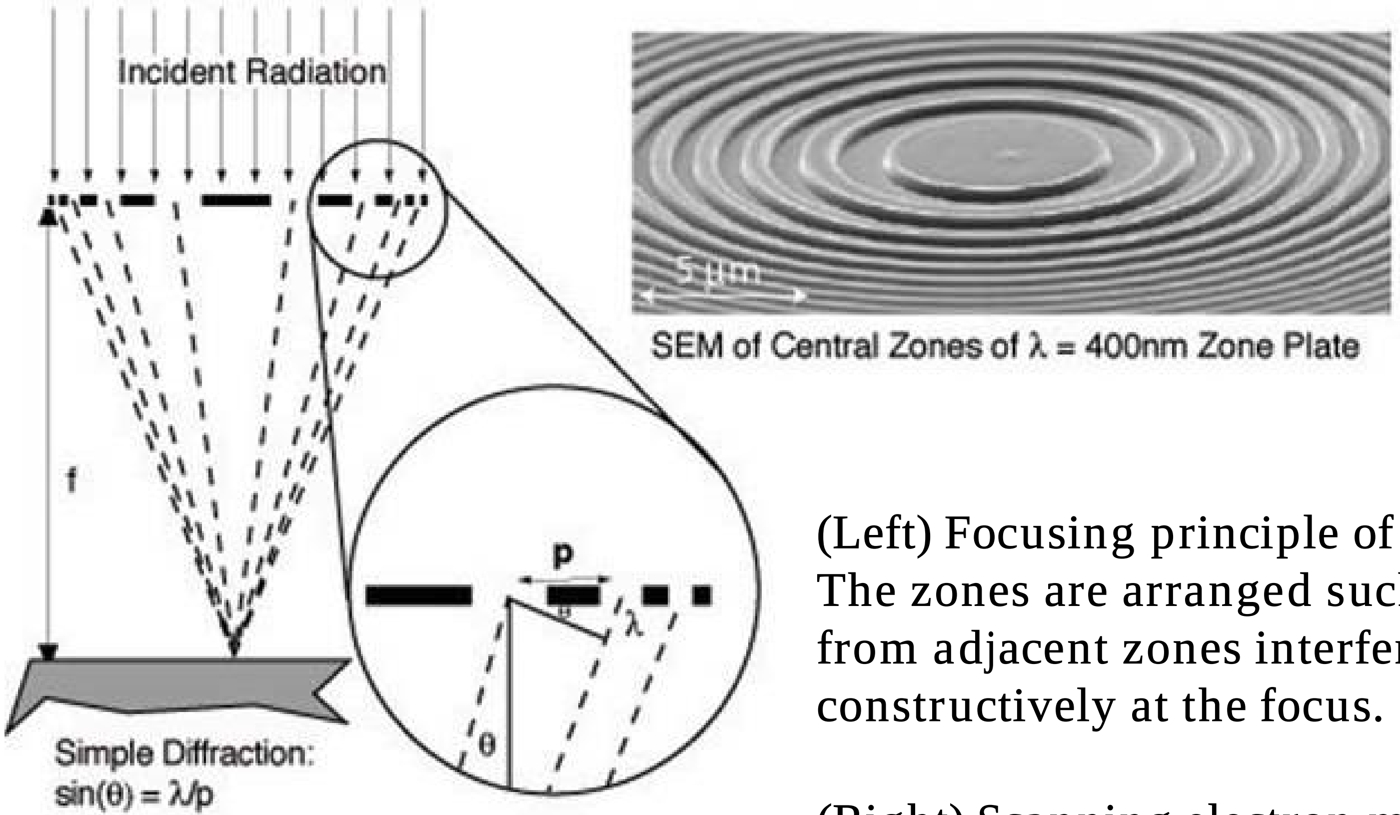
"Soft" lithography (imprint lithography)

Zone-plate array lithography



R. Menon et al., Materials today, Feb. 2005, p. 26

Zone-plate array lithography



SEM of Central Zones of λ = 400nm Zone Plate

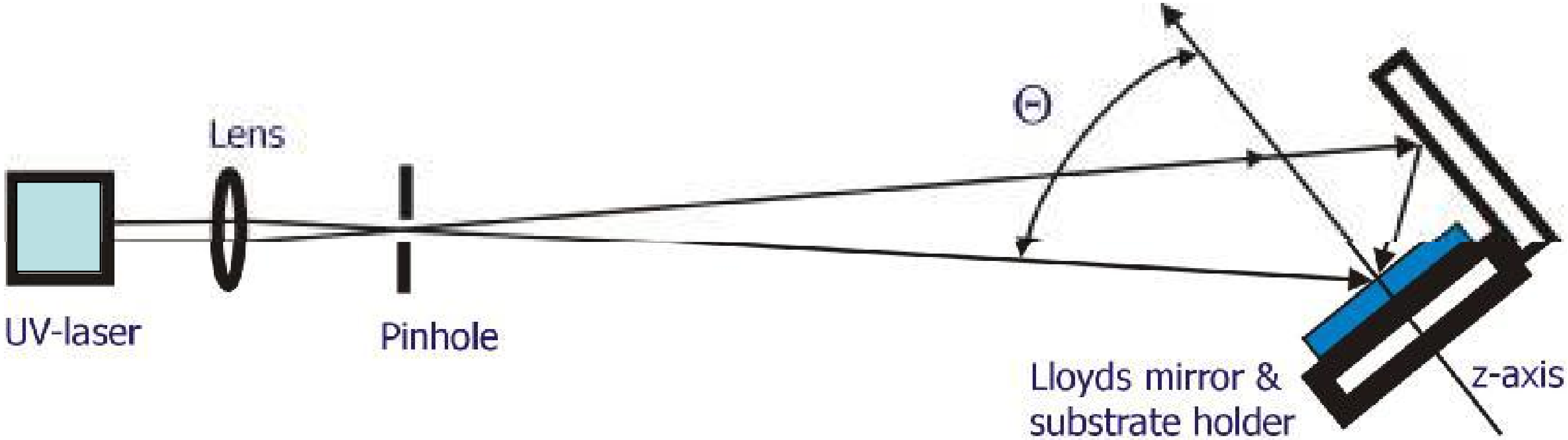
(Left) Focusing principle of a zone plate. The zones are arranged such that light from adjacent zones interferes constructively at the focus.

(Right) Scanning electron micrograph of the central zones of a zone plate.

$\boldsymbol{k_1}$=0.32, $\boldsymbol{NA}$=0.85, λ=193nm: $\boldsymbol{R}\approx$70 nm

R. Menon et al., Materials today, Feb. 2005, p. 26

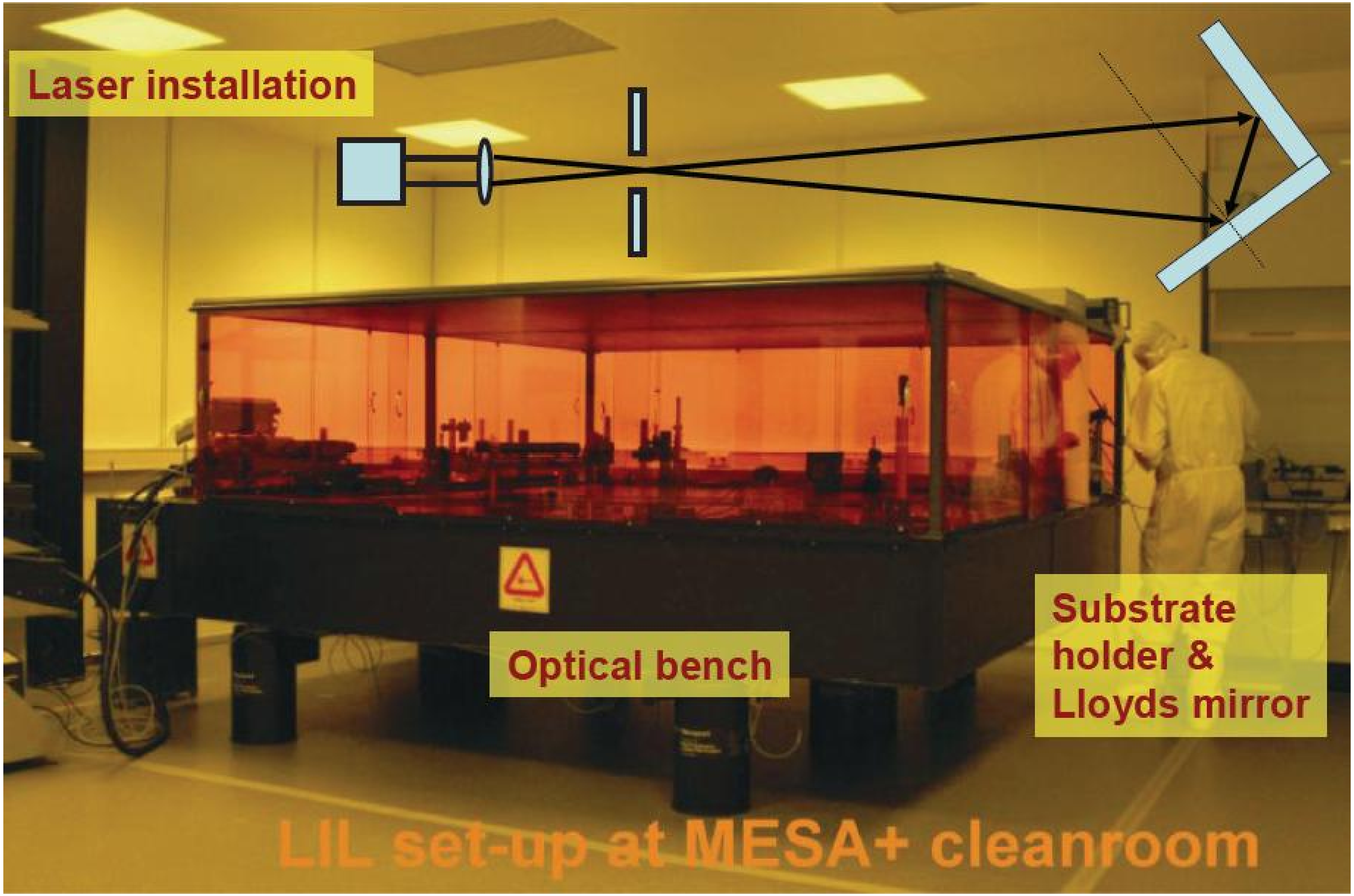
Laser interference lithography



Principle: interference of two beams creates sinusoidal intensity gradient across substrate with photoresist. Period of interference pattern is:

$$p = \frac{l}{2\sin\Theta}$$

Thus, the exposed pattern can have a pitch smaller than λ

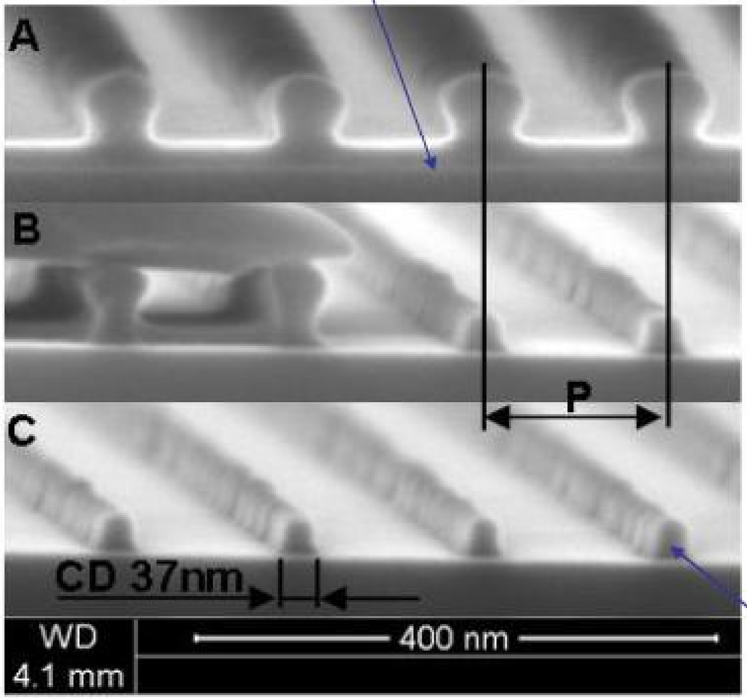


LIL set-up at MESA+ cleanroom

Some results: parallel lines in silicon

PEK/BARC on Silicon

Cleaved edge, silicon wafer



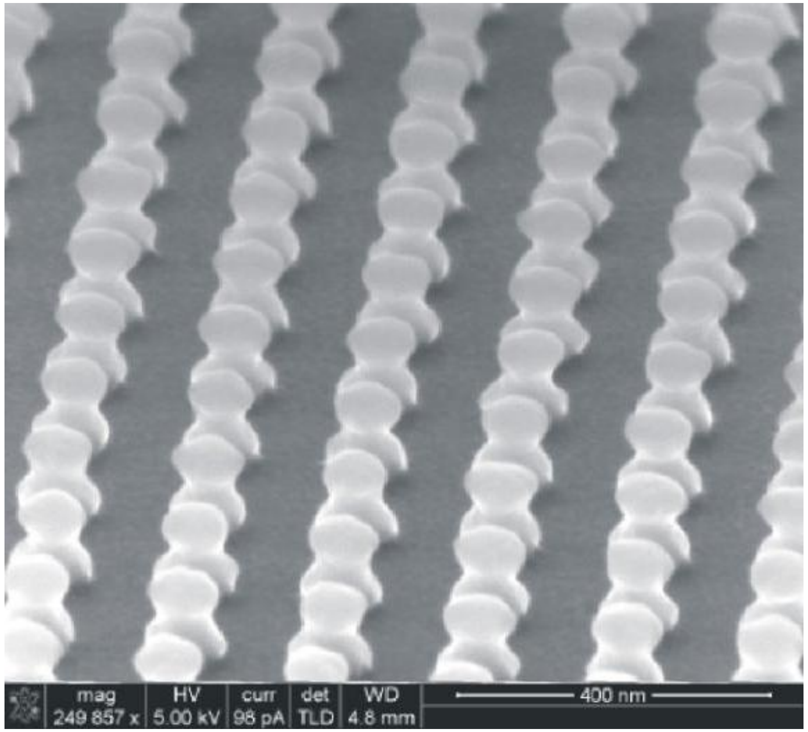
P = 140nm (Θ=72°)

- Resist thickness ca. 70nm
- BARC breakthrough etch using O_2 flash (100mTorr, 20sccm, 100W, 15s).
- RIE in O_2:CHF_3 fluorine plasma (30mTorr, 5sccm:25sccm, 350W, 1min).
- Gratings at P=140nm.

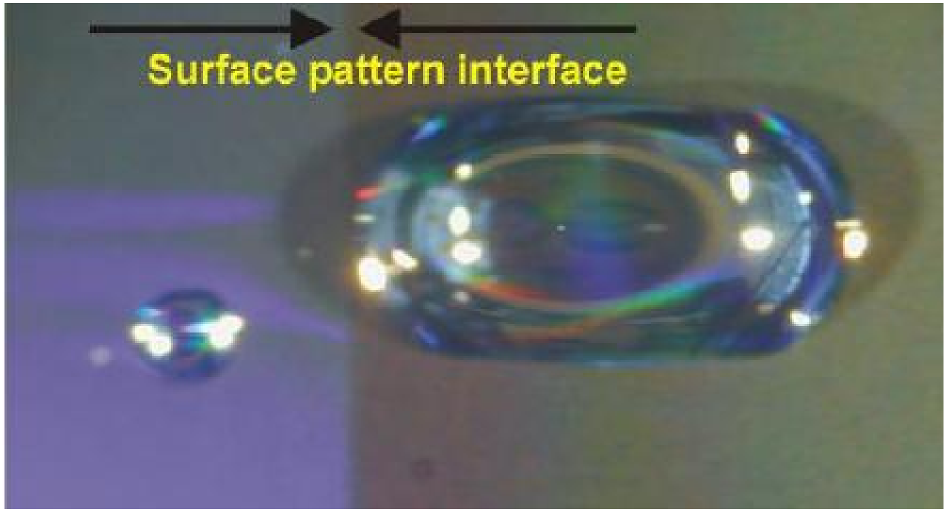
Residual BARC layer on a silicon ribbon of 10-15nm thickness.

R. Luttge et al., Laser interferometric nanolithography using a new positive chemical amplified resist, J. Vac. Sci. Technol. B, in press

Multiple exposure interference litho

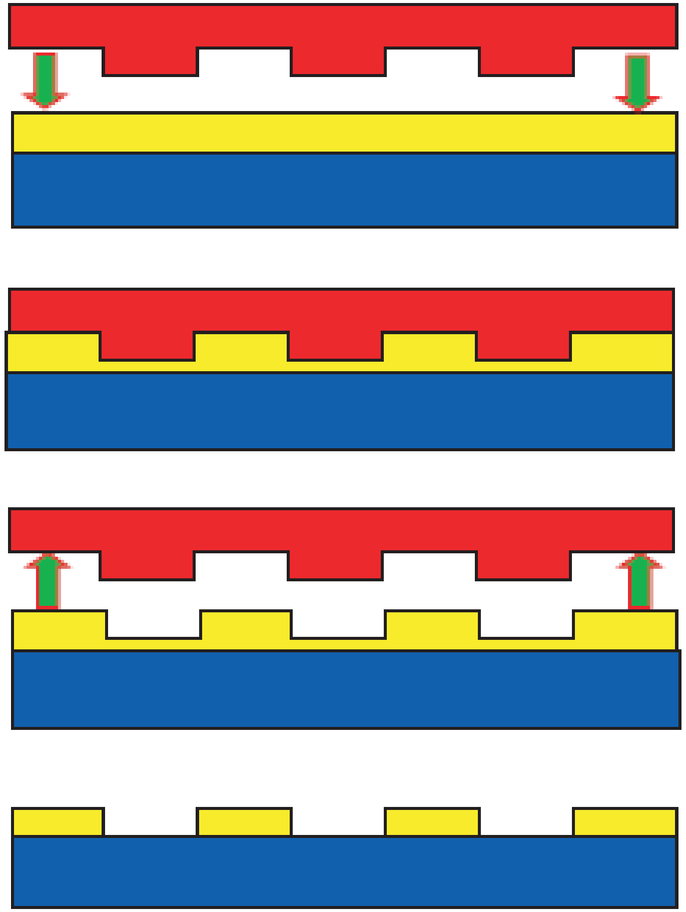


18 Gbit/inch^2 array of photoresist dots on sputtered platinum thin film
(R. Luttge et al. J. Vac. Sci. Technol. B, in press)

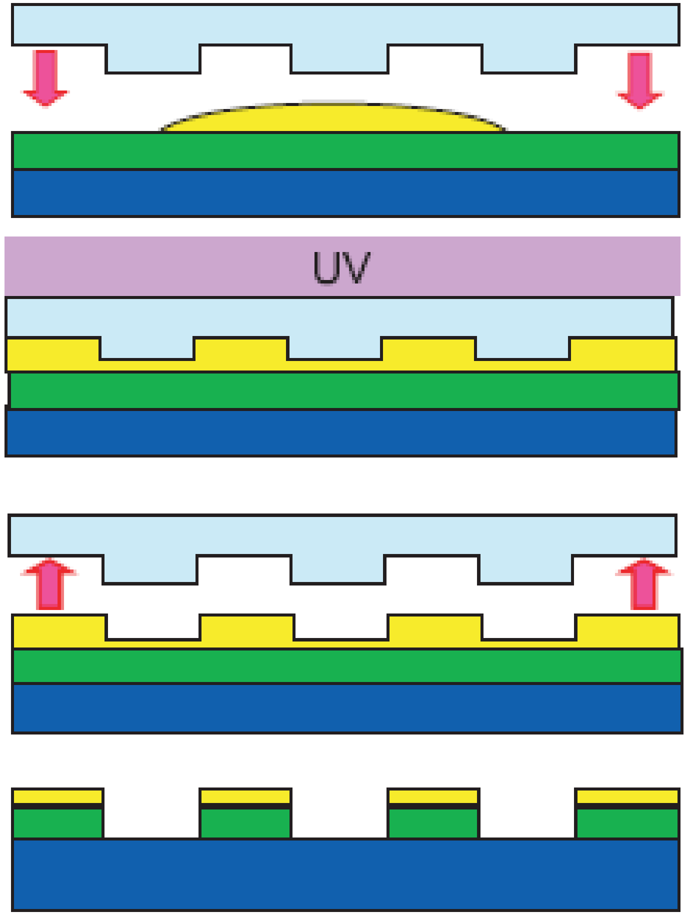


Change in nano-dot pattern leads to change in anisotropic wetting properties (R. Luttge, unpublished)

Soft lithography concepts



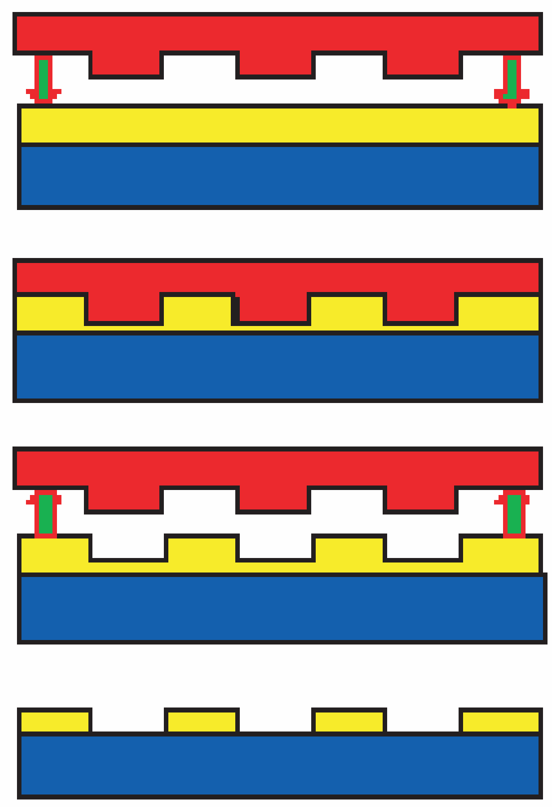
NIL, nano imprint lithography, uses hot embossing



SFIL, step-and-flash imprint lithography, uses a liquid resist which is cross-linked by UV

L.J. Guo, J. Phys. D: Appl. Phys. 37 (2004) R123–R141

Nano imprint lithography (NIL)



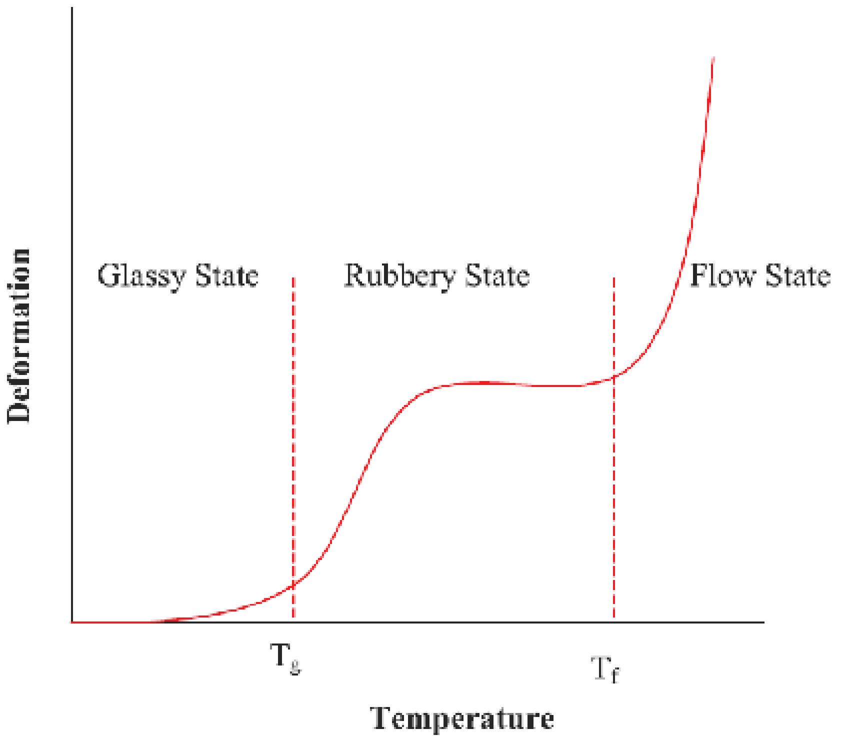
hard stamp (Si)

polymer (PMMA)

imprint: $T>T_g$, high p

release at $T<T_g$

residual layer removal (RIE)

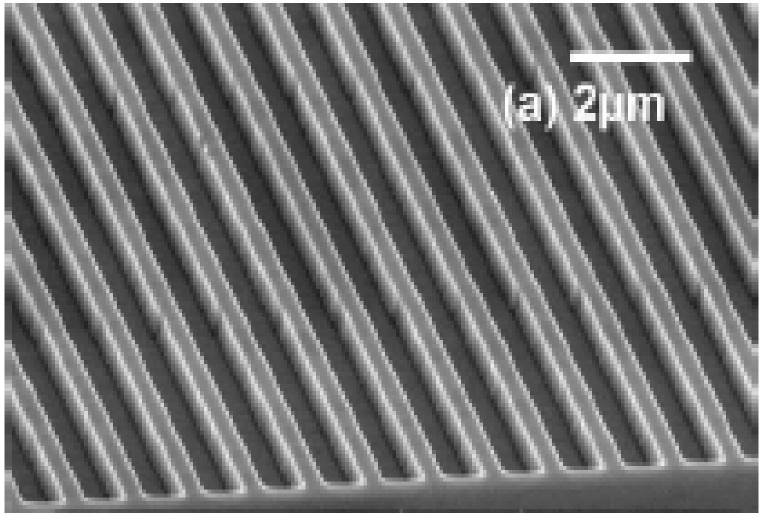


Glassy state: no flow; rubbery state: reversible deformation;
flow state: irreversible, viscous flow

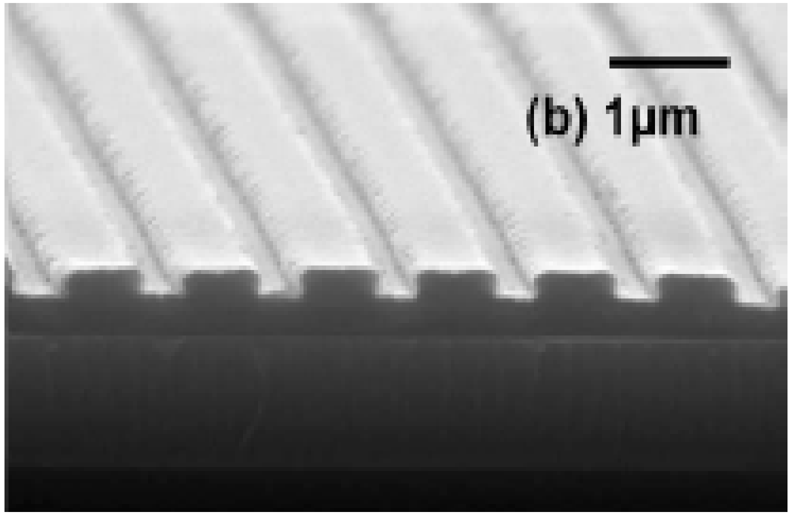
For NIL: flow state needed: thermoplastic, non-crosslinked polymer (e.g. PMMA or PS)
Empirical rule: Imprint at 70 to 100 °C above T_g

Example nanoimprint lithography

Silicon stamp (made by e-beam)



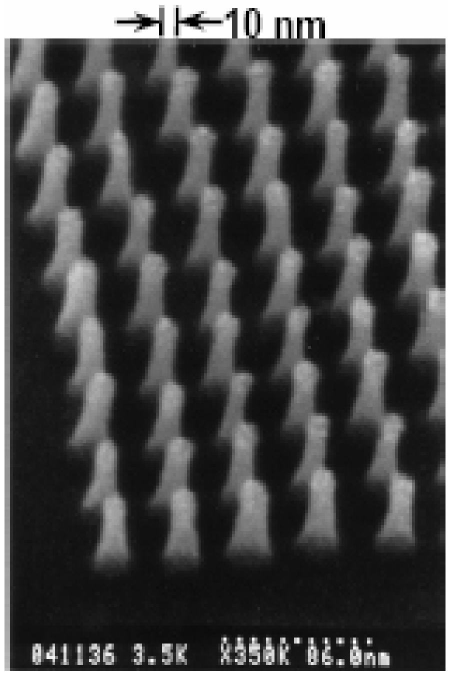
Imprint into PMMA



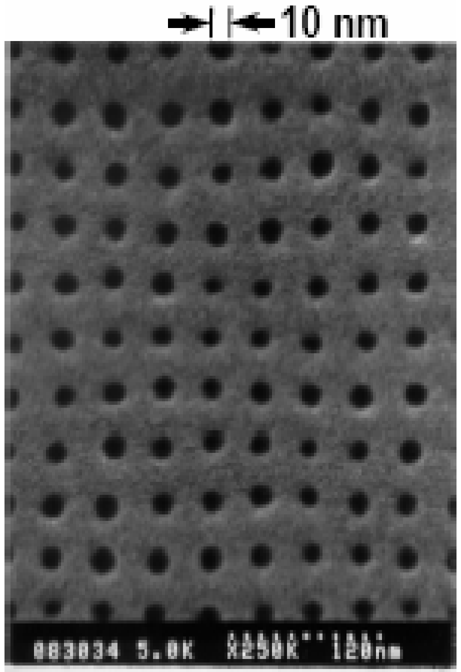
Review: C.M. Sotomayor Torres et al. Mater. Sci. Eng. C 23, 2003, p. 23

Example nanoimprint lithography

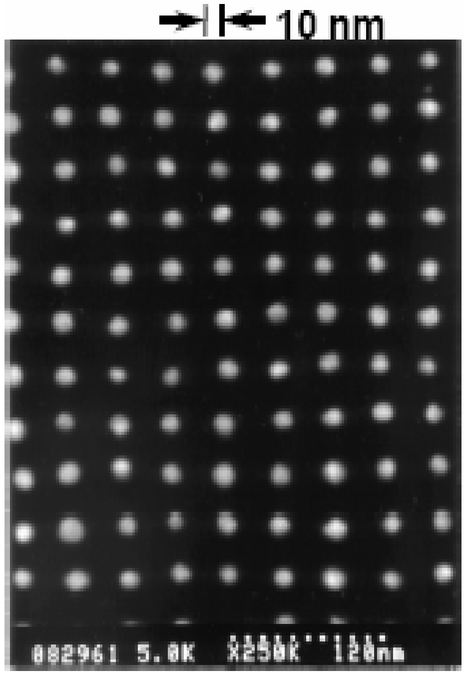
High resolution NIL:



master in SiO_2



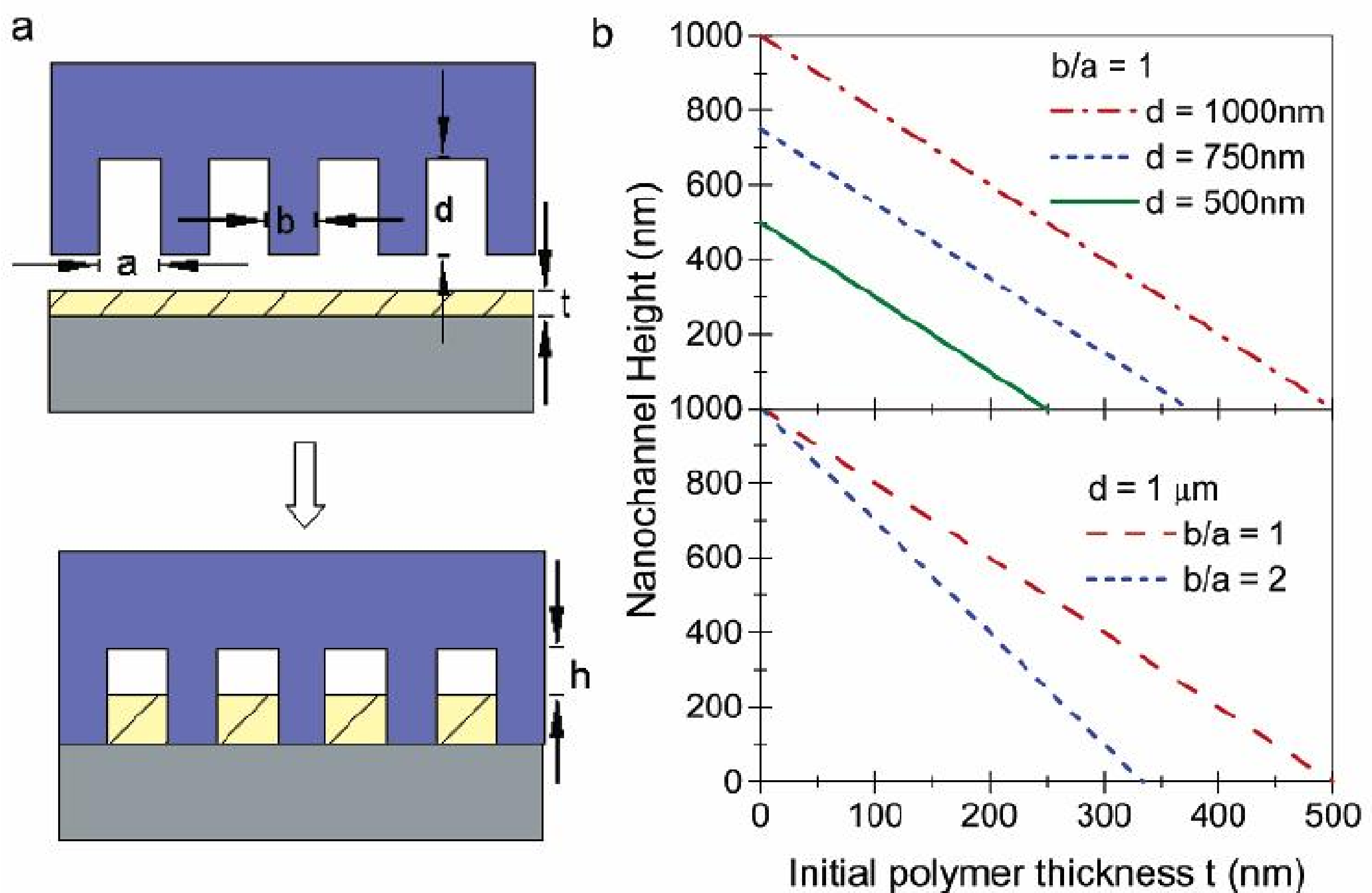
imprint in PMMA

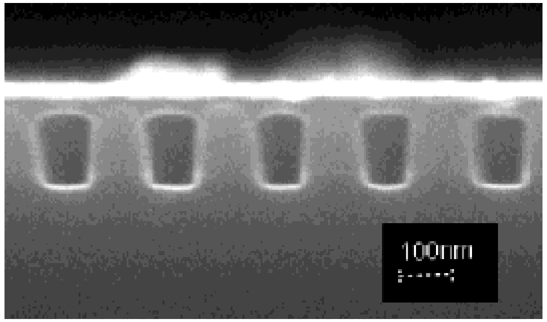


metal structures
after lift-off

S. Y. Chou, Nanoimprint Lithography, Ch. 2 in: Alternative Lithography,
C.M. Sotomayor Torres, Ed. 2003, Kluwer Academic, NY

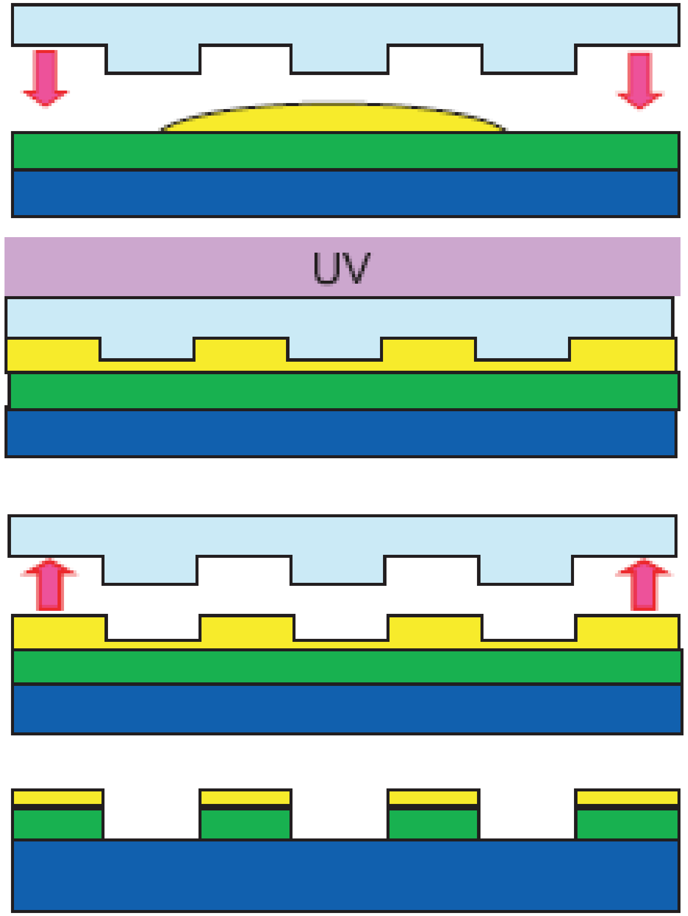
Nanochannels by NIL





L.J. Guo e.a. Nano Lett. 4, 2004, p. 69

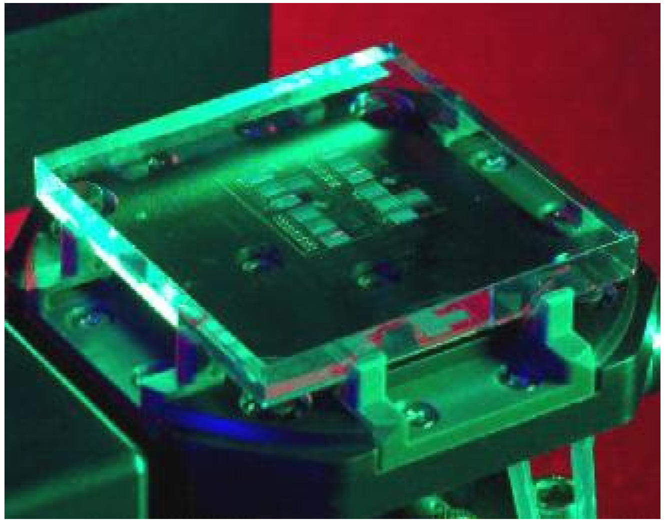
Step-and-flash imprint lithography (SFIL)



imprint into low viscosity, photocurable organosilicon liquid

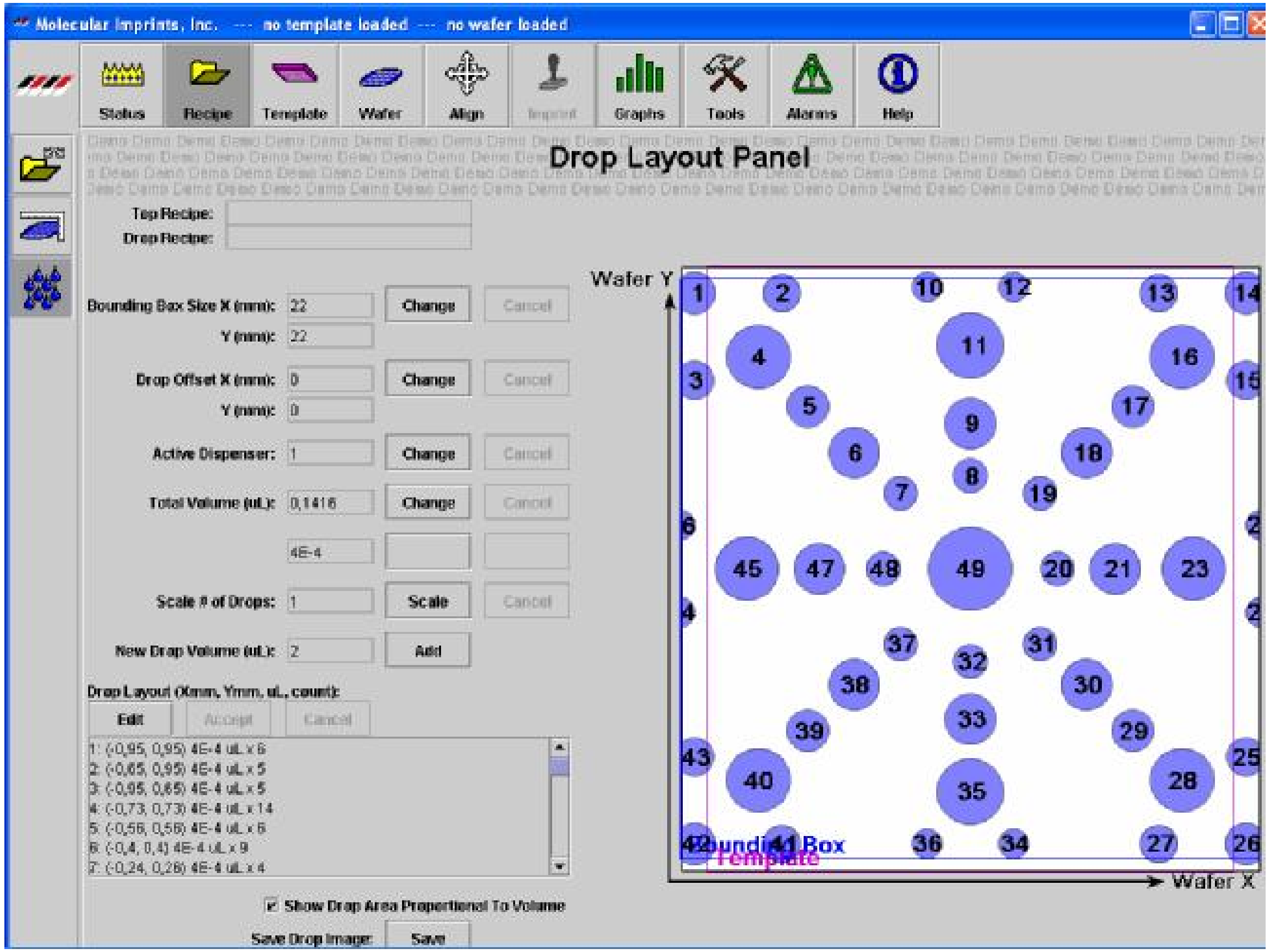
UV flood exposure for curing

stamp is:
  a) hard & transparent (silica, quartz) for UV-NIL
  b) soft & transparent (PDMS) for "soft UV-NIL"



Picture property of Molecular Imprints Inc.

Resist dispensing pattern



Top Recipe:
Drop Recipe:

Bounding Box Size X (mm): 22 Change Cancel
Y (mm): 22

Drop Offset X (mm): 0 Change Cancel
Y (mm): 0

Active Dispenser: 1 Change Cancel

Total Volume (uL): 0,1416 Change Cancel

4E-4

Scale # of Drops: 1 Scale Cancel

New Drop Volume (uL): 2 Add

Drop Layout (Xmm, Ymm, uL, count):

Edit Accept Cancel

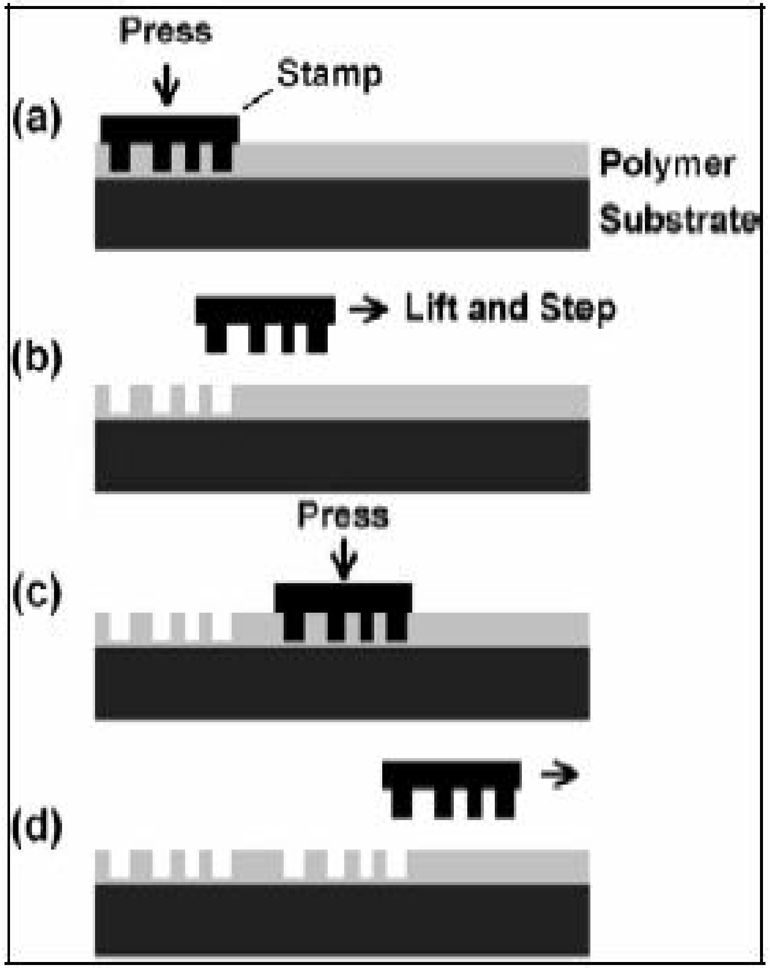
```
1: (-0,95, 0,95) 4E-4 uL x 6
2: (-0,65, 0,95) 4E-4 uL x 5
3: (-0,95, 0,65) 4E-4 uL x 5
4: (-0,73, 0,73) 4E-4 uL x 14
5: (-0,56, 0,56) 4E-4 uL x 6
6: (-0,4, 0,4) 4E-4 uL x 9
7: (-0,24, 0,26) 4E-4 uL x 4
```

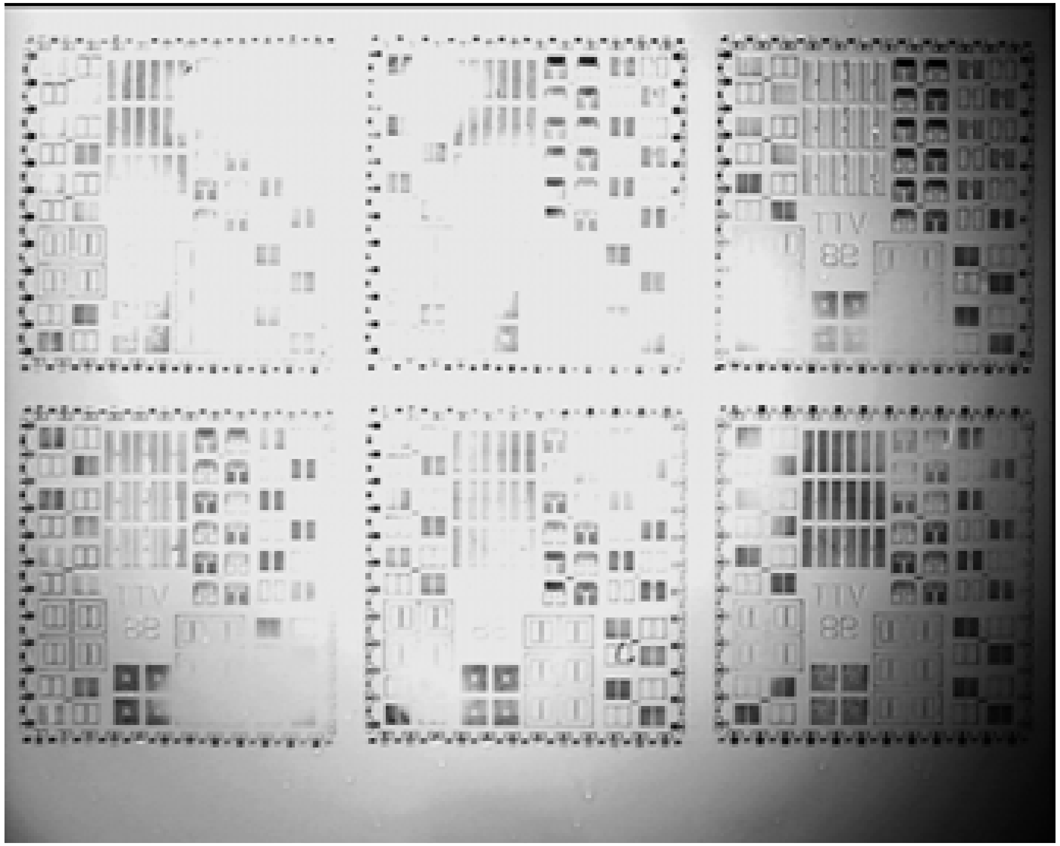
☑ Show Drop Area Proportional To Volume

Save Drop Image: Save

Picture property of Molecular Imprints Inc.

Step-and-stamp lithography



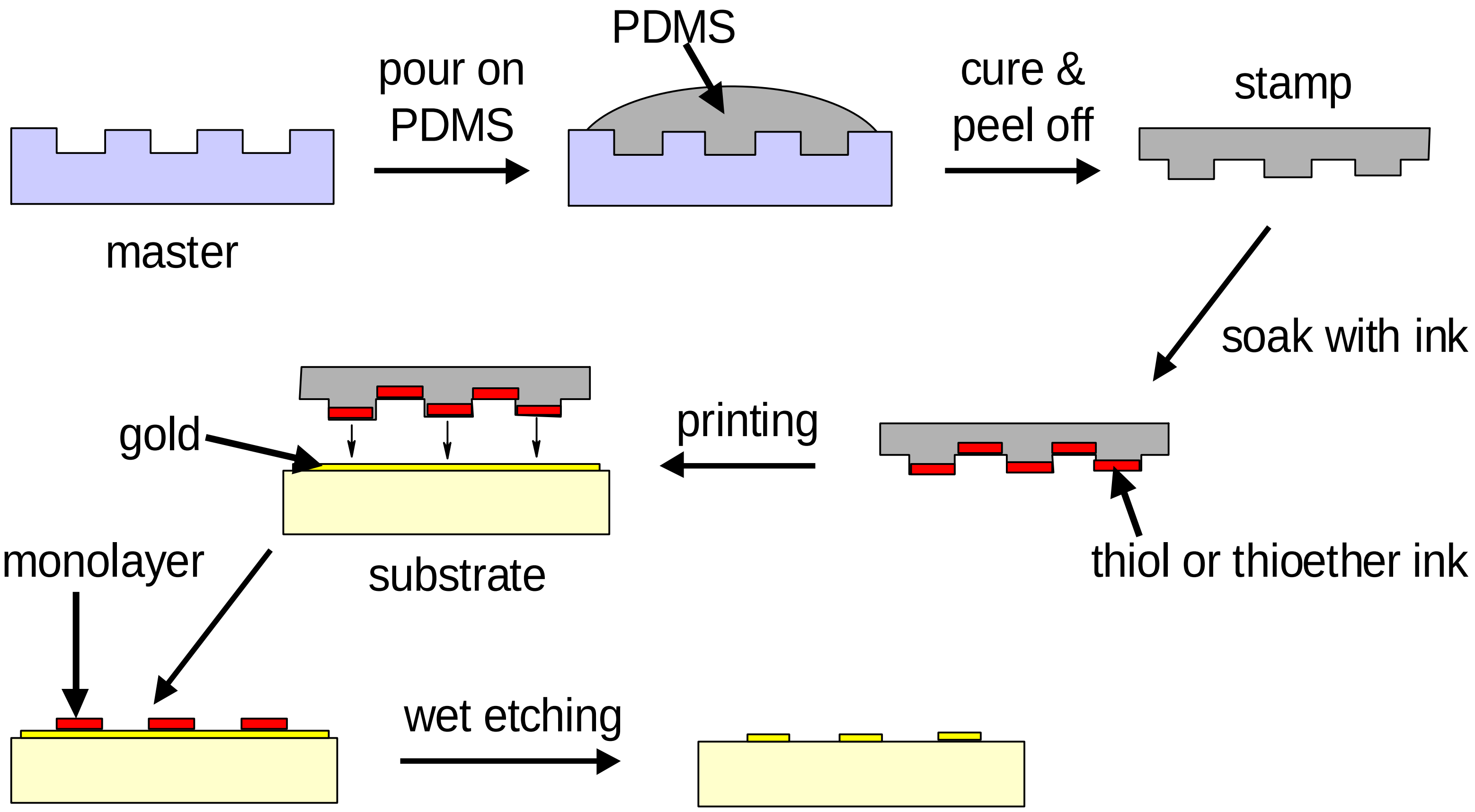


Repeated imprints into PPM

J. Ahopelto, T. Haatainen, Step and Stamp Imprint Lithography, Ch. 6 in: Alternative Lithography, C. M. Sotomayor Torres, Ed. 2003, Kluwer Academic, NY

Microcontact printing (μCP)

Example: Application of monolayers on gold

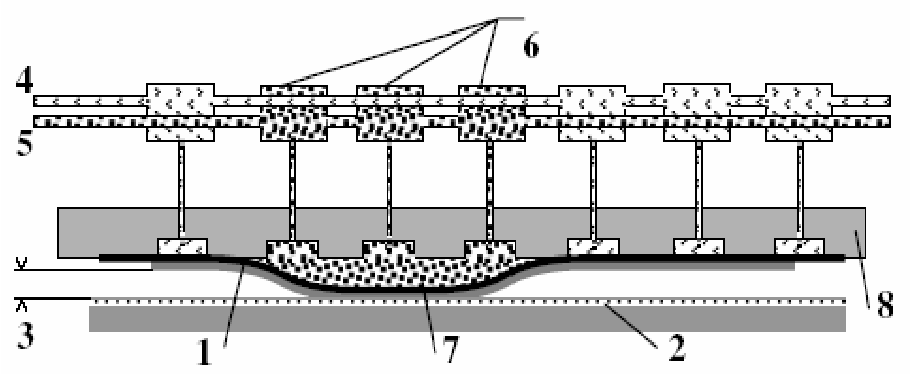


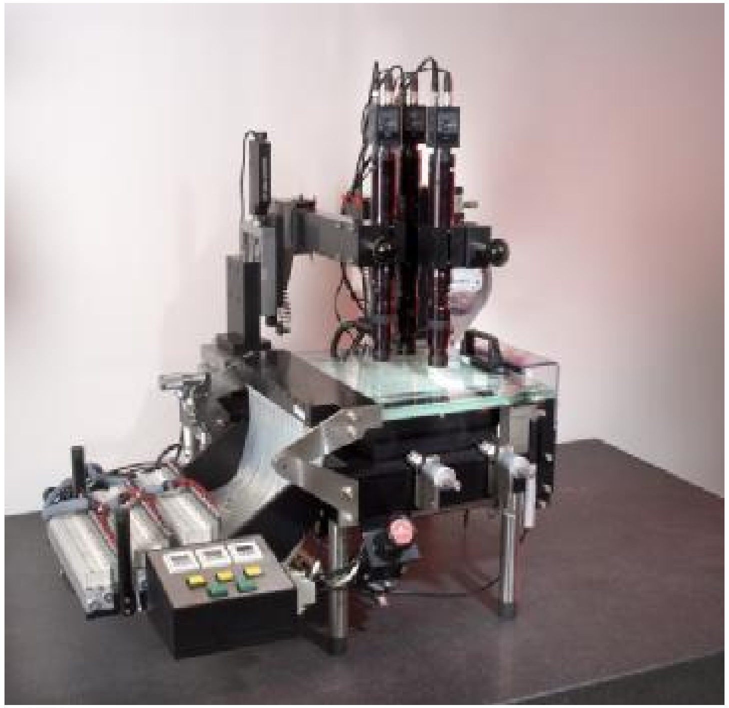
Slide courtesy of Jurriaan Huskens, MNF, MESA+
Y. Xia and G.M. Whitesides, Angew. Chem. Int. Ed. 37, 1998, 550

MESA+ Institute for Nanotechnology

University of Twente
The Netherlands

Industrial μCP: Philips' wave printer





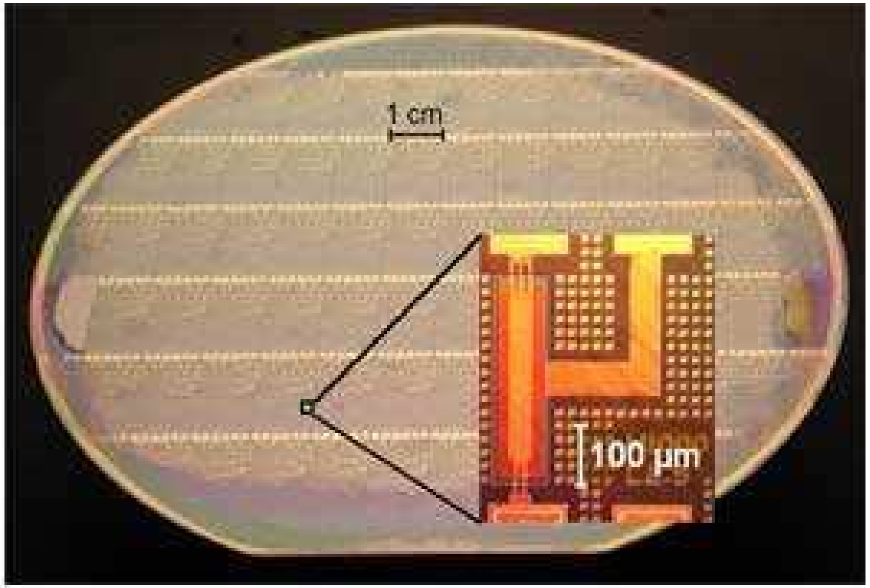


Fig.4 Six inch silicon wafer comprising repeating 2x1cm^2 units of bottom gate plastic electronic test circuits with microcontact wave printed gate and source-drain gold electrodes.

M.M.J. Decré et al., MRS Symp. Proc. 2004, Vol. EXS-2, 59

Master & stamp fabrication

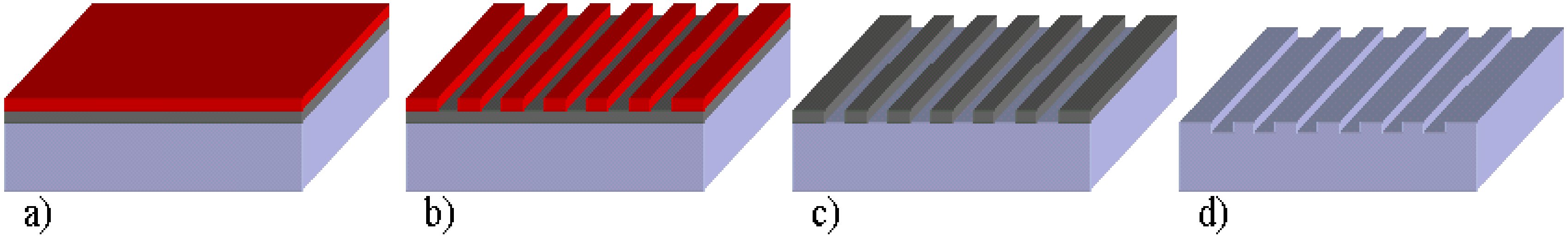
Hard, non-transparent stamps (NIL, SSIL):

Si processing (optical lithography, e-beam)

Soft stamps (mCP, CFL, soft UV-NIL):

hard masters via Si processing followed by replica molding

Hard, transparent stamps (UV-NIL, SFIL): silica/quartz processing:



fused silica with Cr and e-beam resist

patterning by e-beam

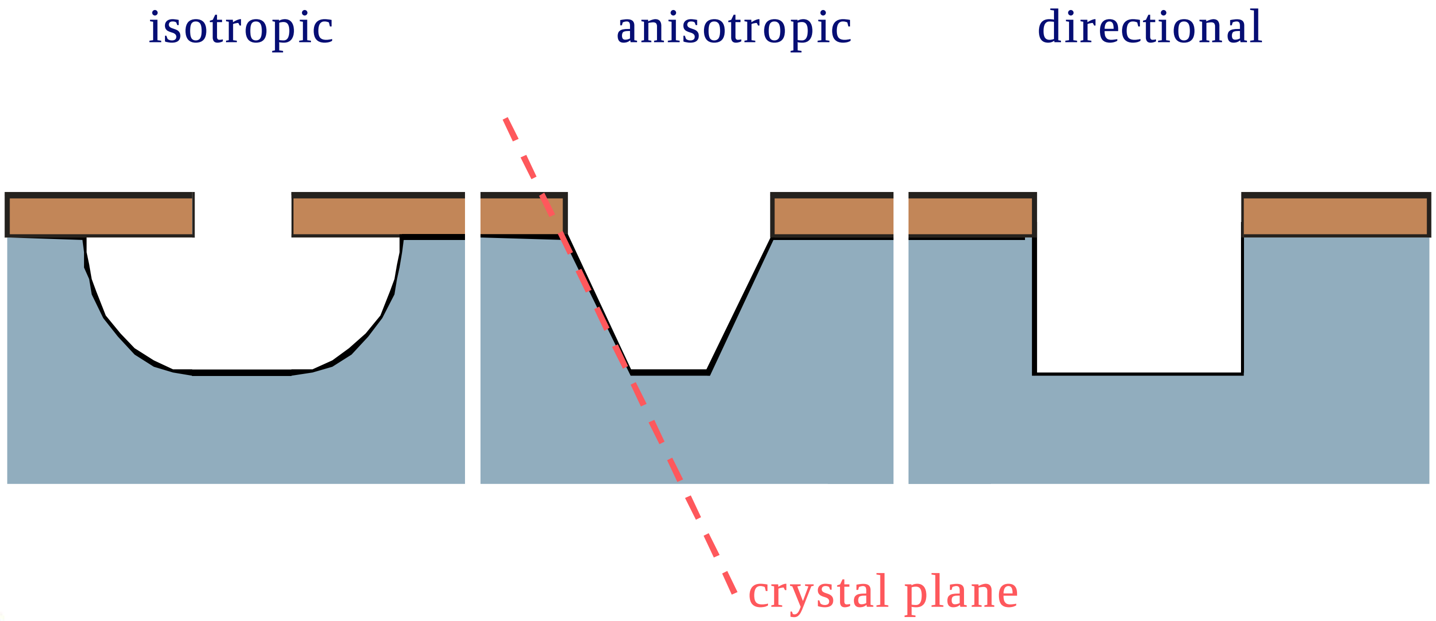
etching into Cr

etching into silica by RIE

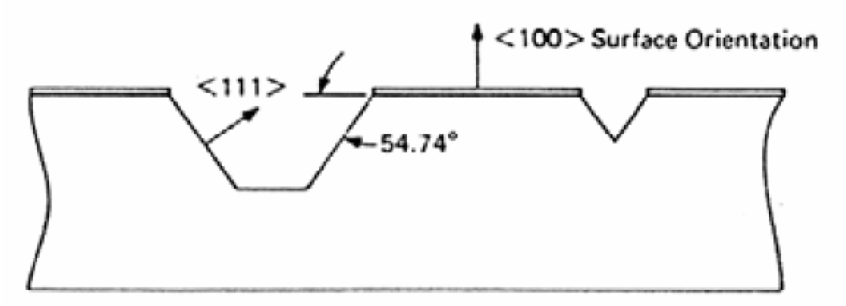
Pattern transfer: Bulk machining

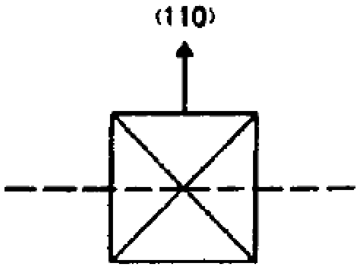
General procedure:

- Application of a masking (protective) material
- Patterning of material by photolithography and selective layer etching
- Selective bulk etching

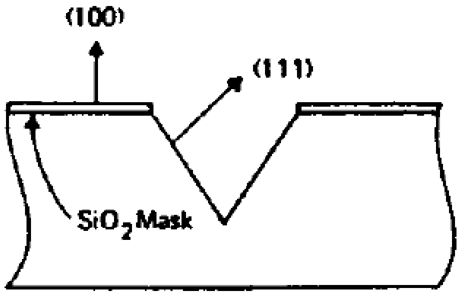


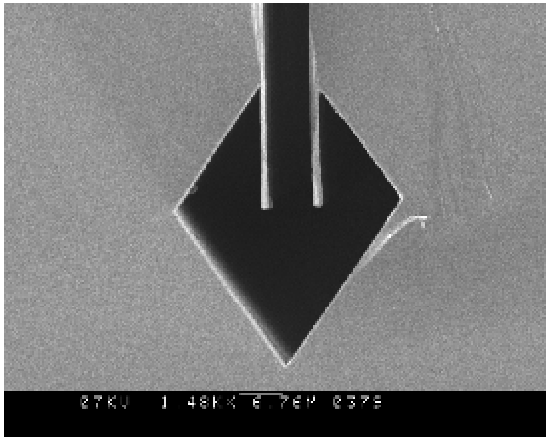
Example: anisotropic etching of silicon

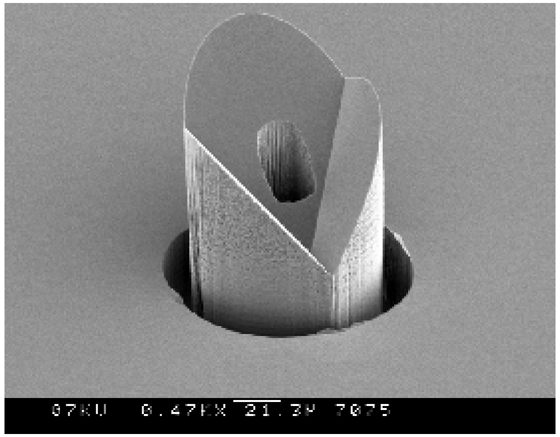


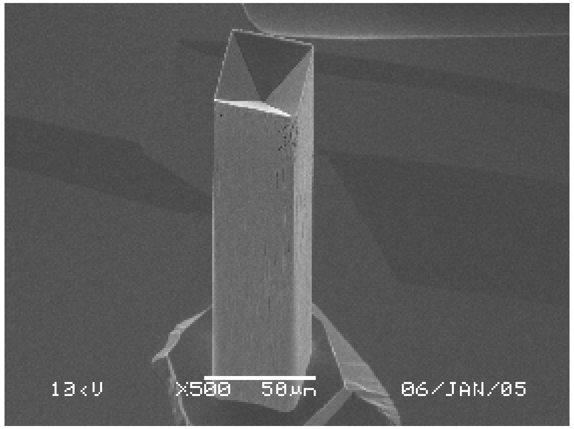


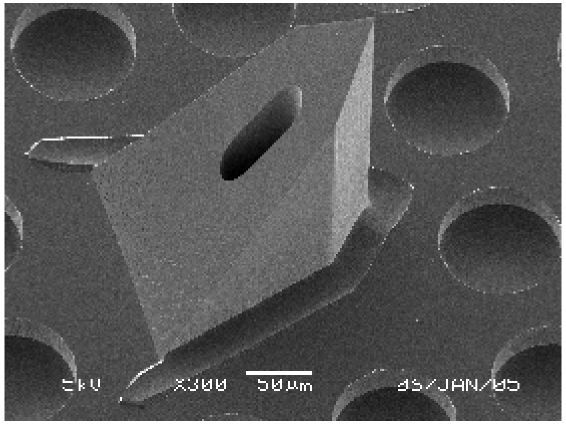
pyramidal shape

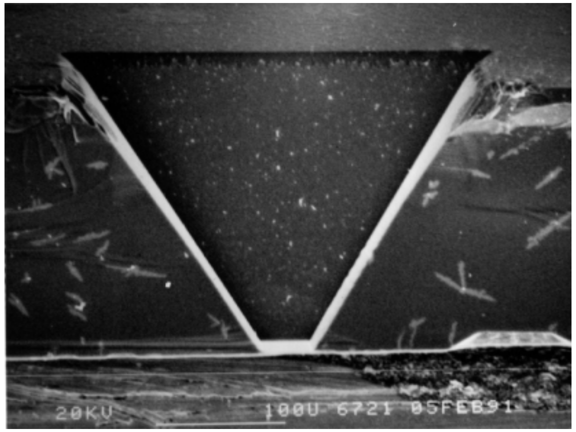




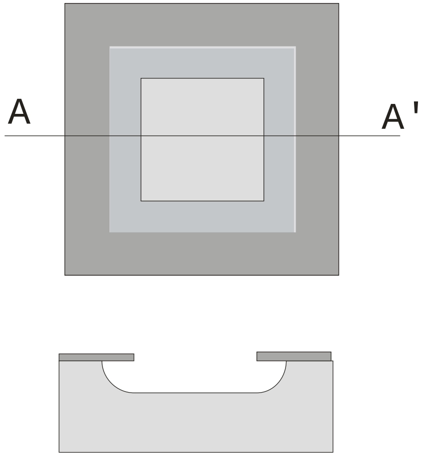


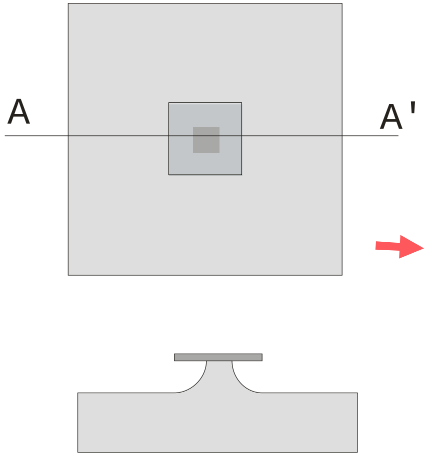


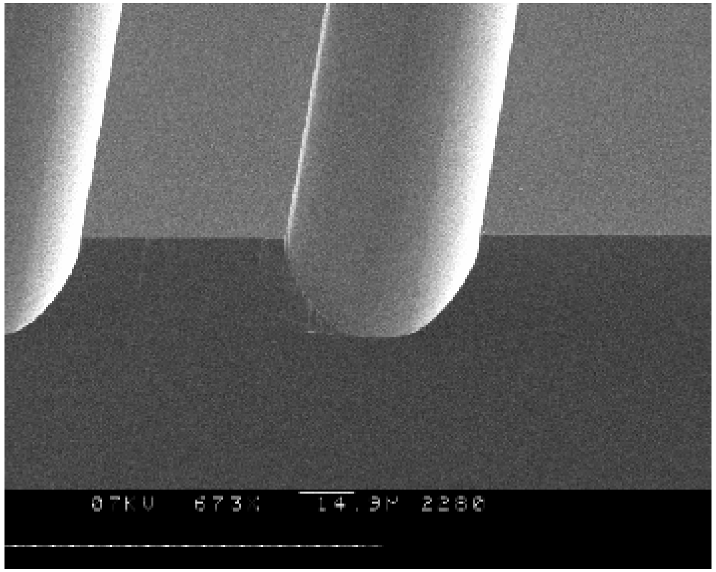


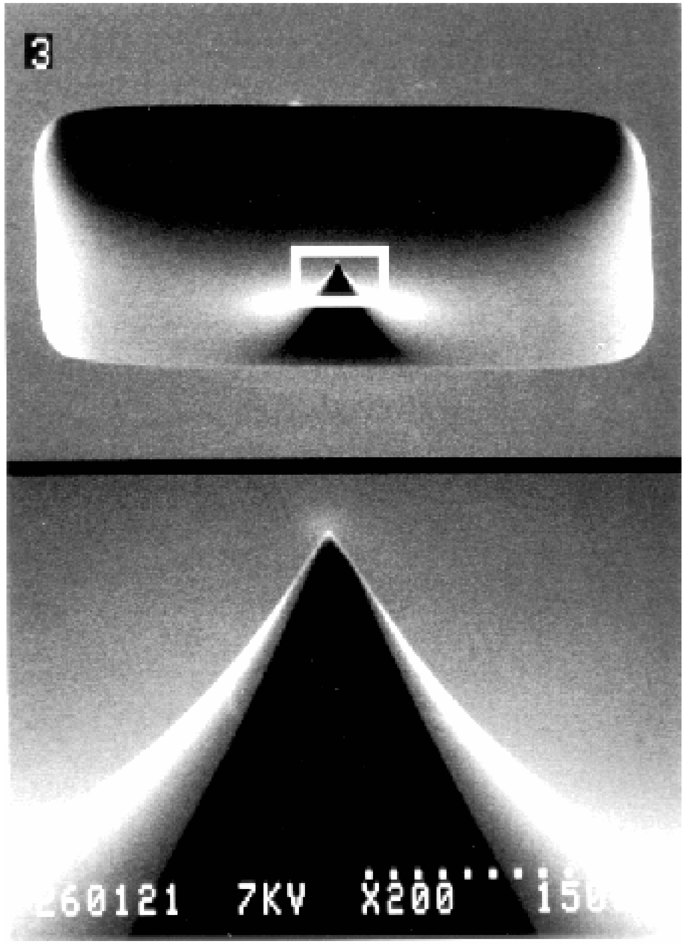


Example: Isotropic etching of silicon





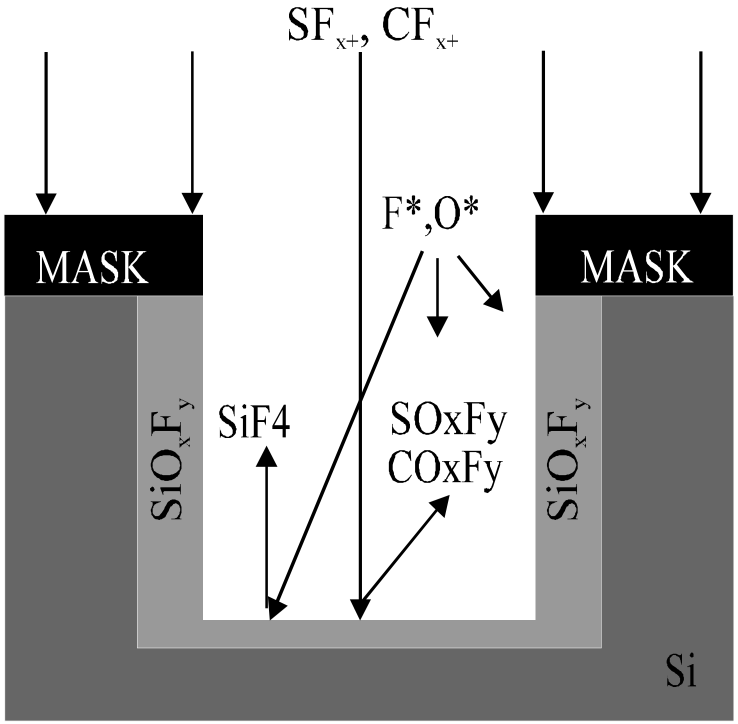


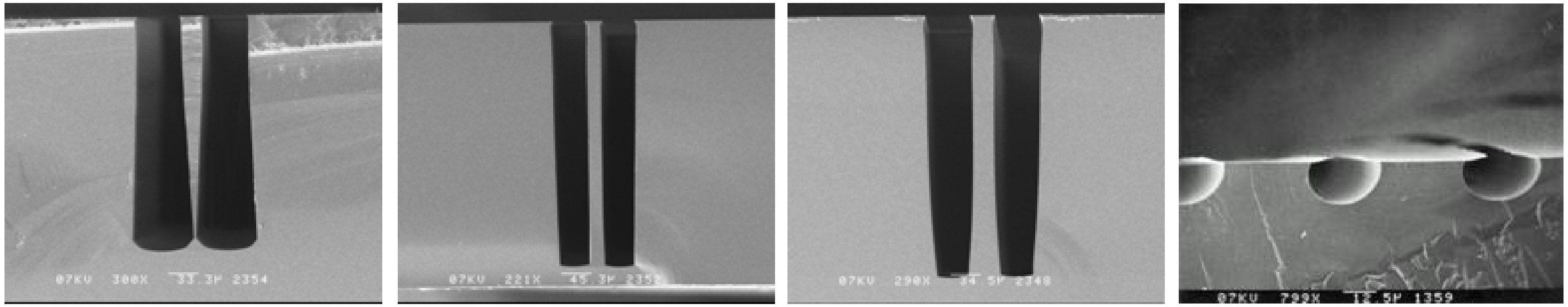


Deep Reactive Ion Etching (DRIE)

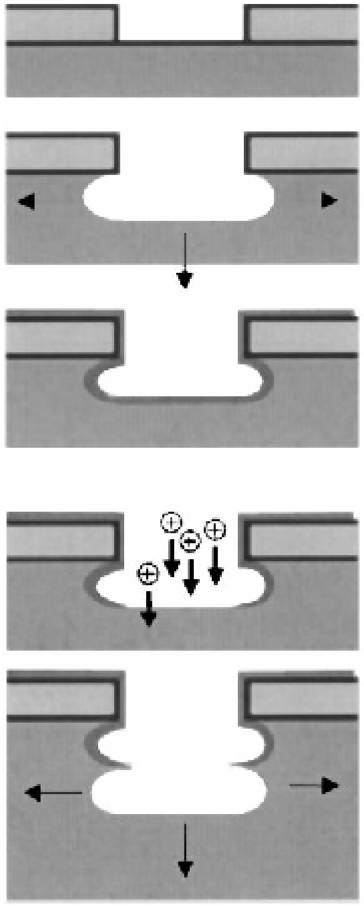
Principle: SF_6 gas etches the silicon
O_2 gas passivates the sidewalls

Isotropic or directional, depending on the settings





Deep RIE via "Bosch process"

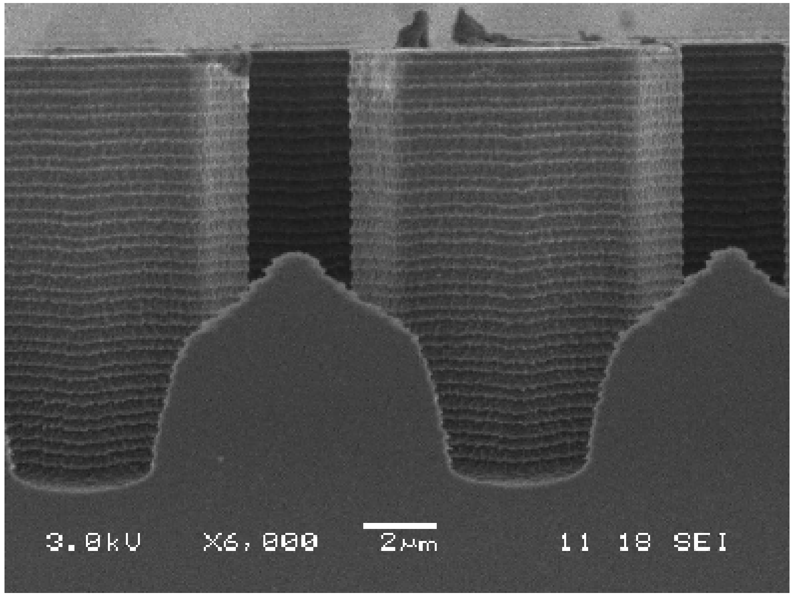


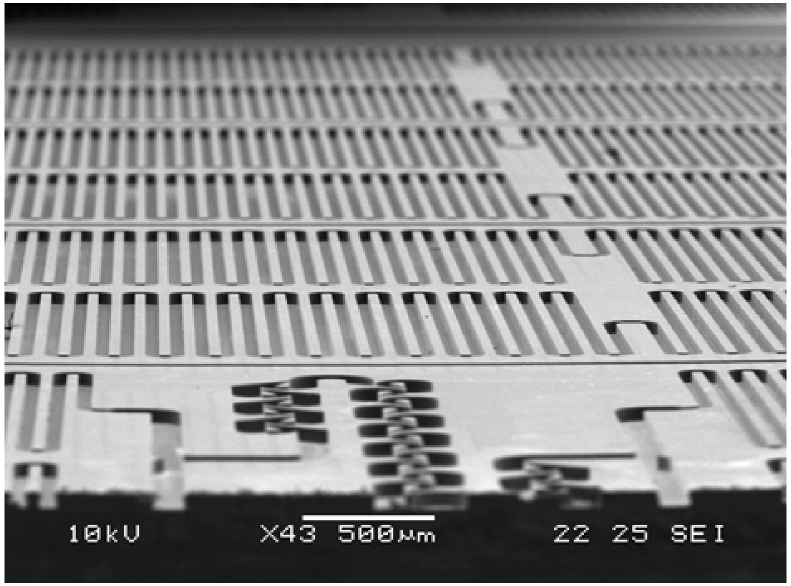
First Etch

Passivate

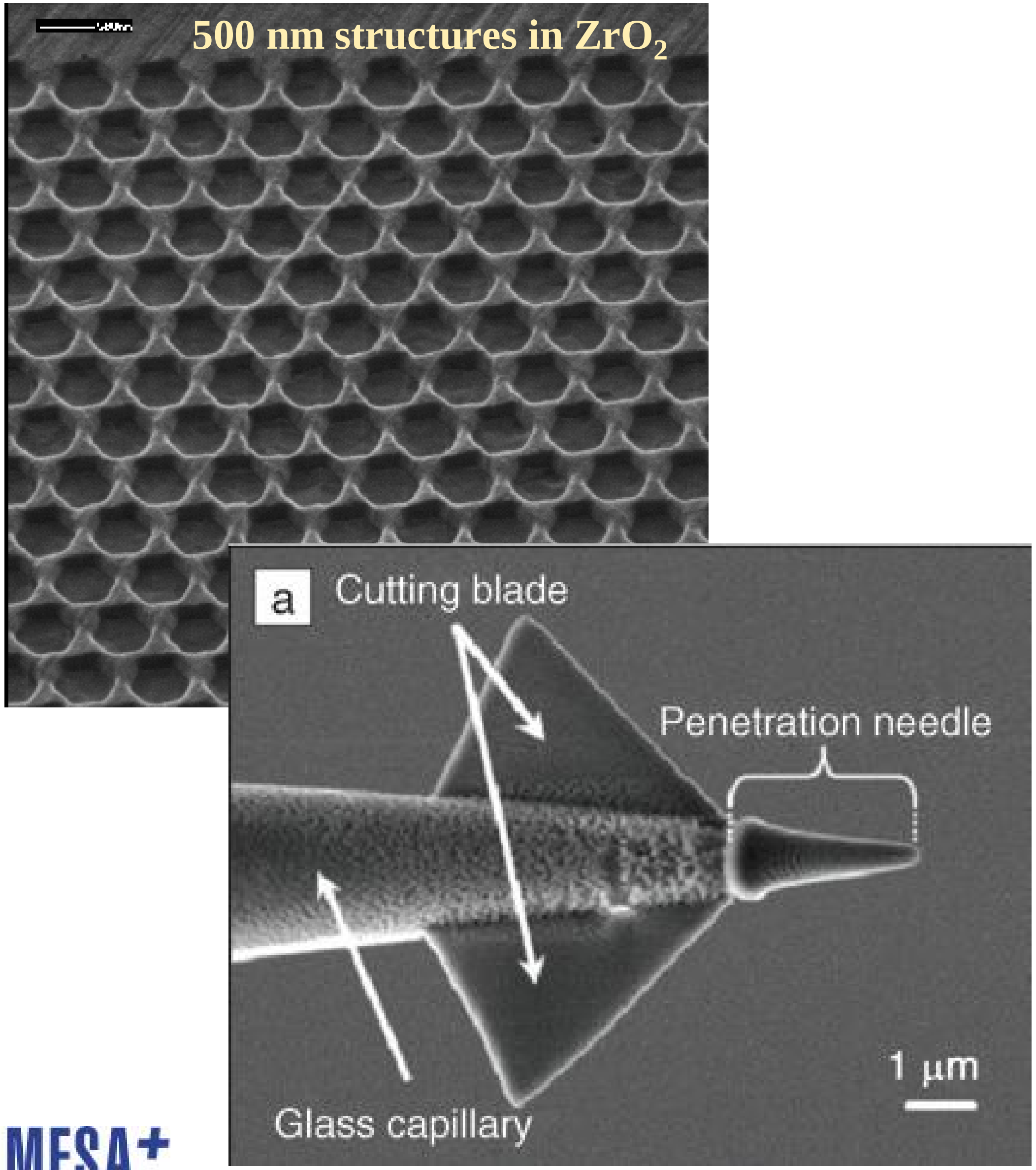
Start of Second Etch

Second Etch Continues

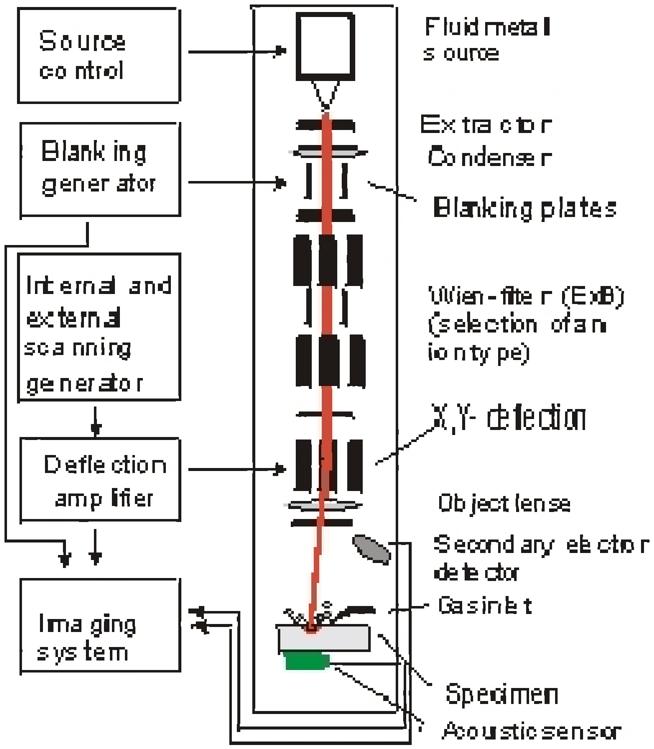

"scallops"
p ≈ 700 nm

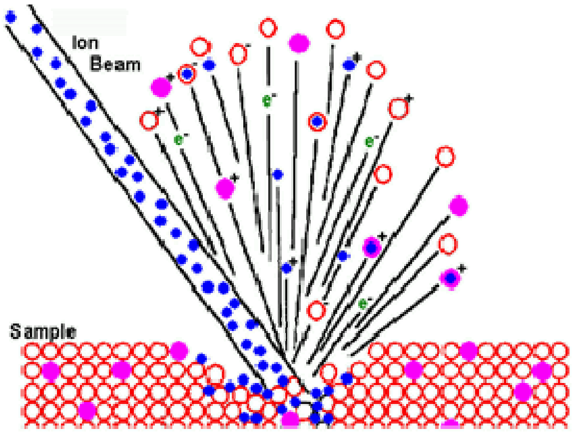


Focused ion beam etching

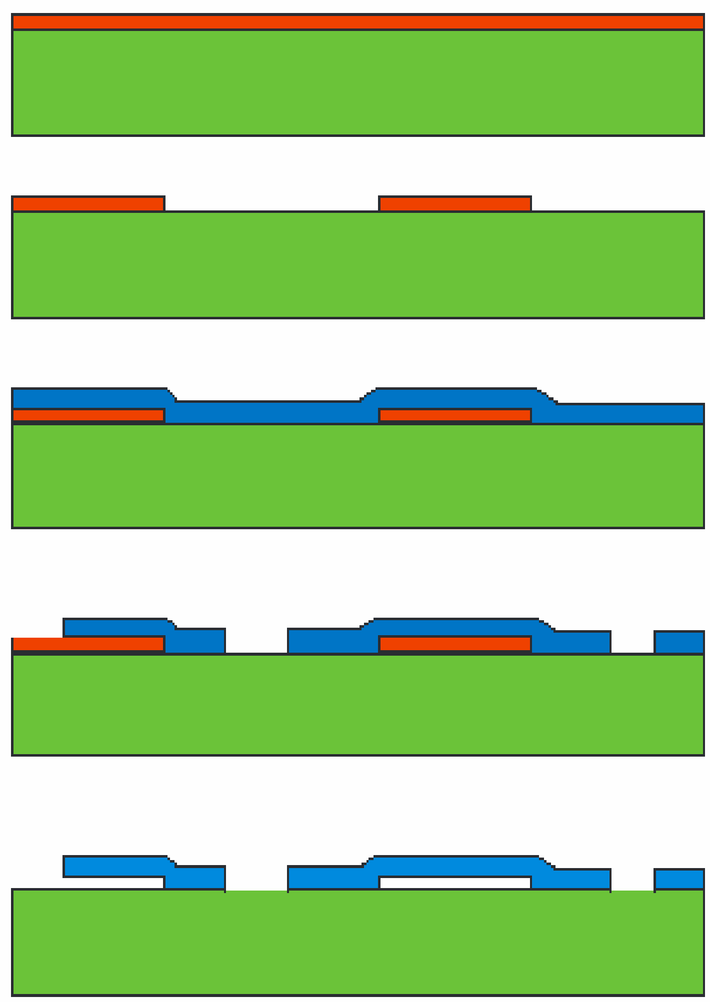


W.J. MoberlyChan e.a. MRS Bull. May 2007, p.424





Surface micromachining: basic scheme



deposition of sacrificial layer

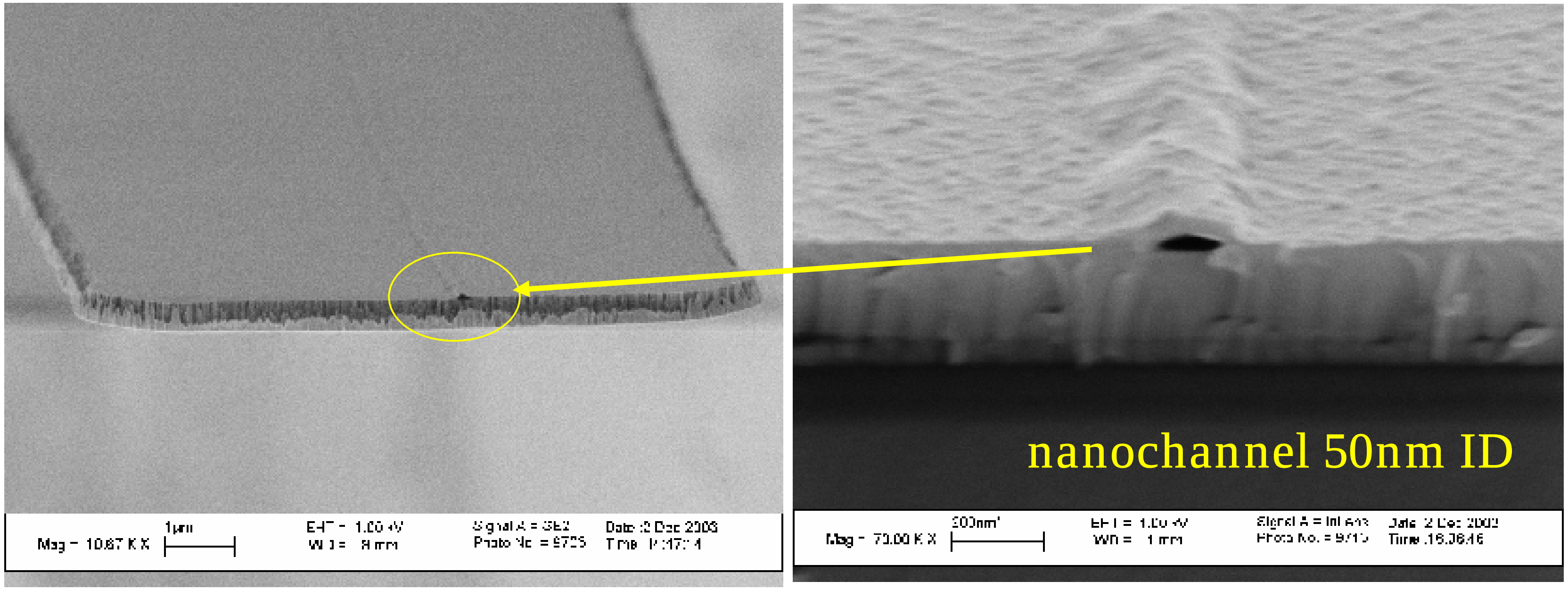
patterning of sacrificial layer

deposition of structural layer

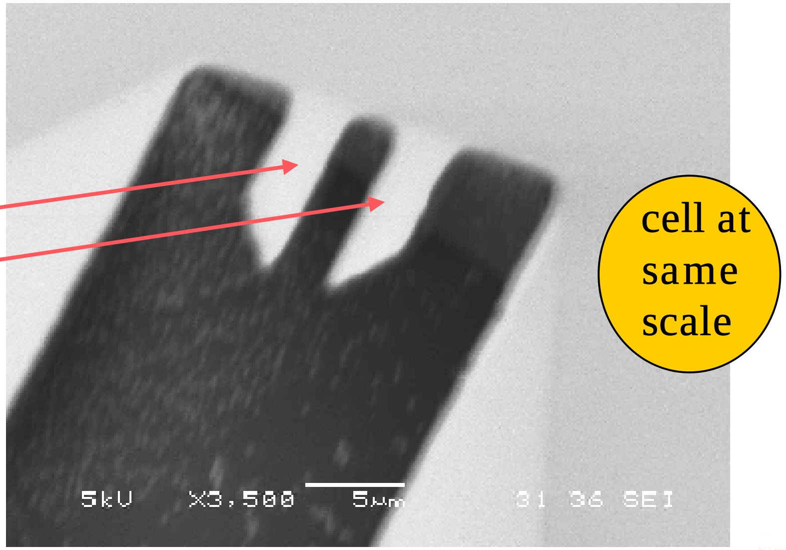
patterning of structural layer

release etch

Nano needles by surface micromachining



nanochannel 50nm ID

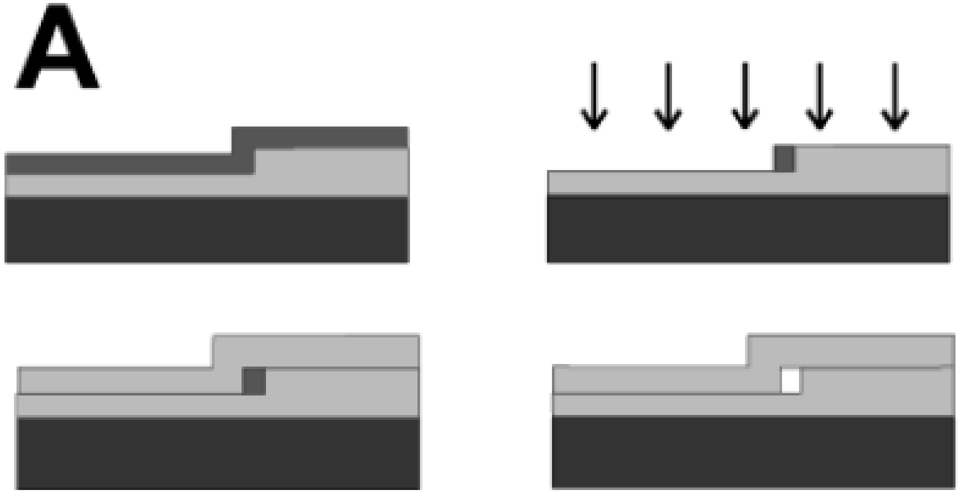


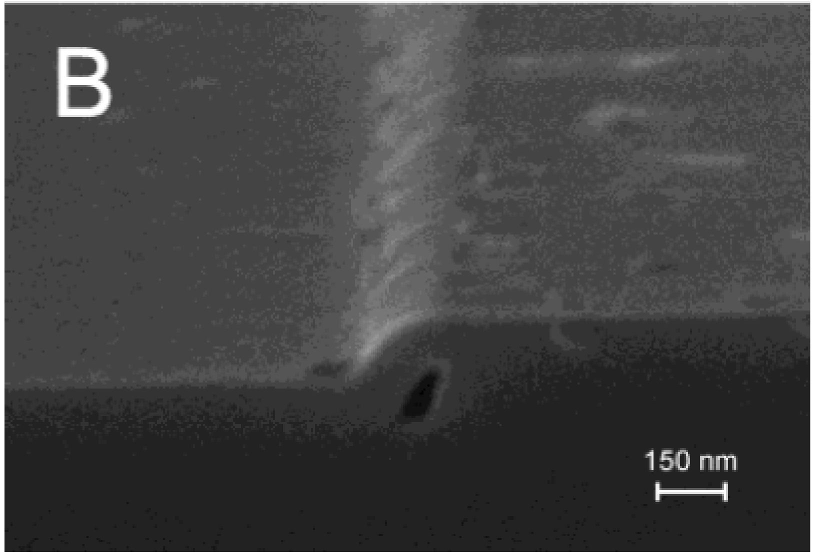
cell at
same
scale

Microneedles
15 x 5 x 0.4 µm^3

J.Emmelkamp, An integrated micro bi-directional dosing system for single cell analysis on-chip, PhD thesis, Univ. of Twente, 2007

Nanochannels by directional etching and sacrificial layer etching



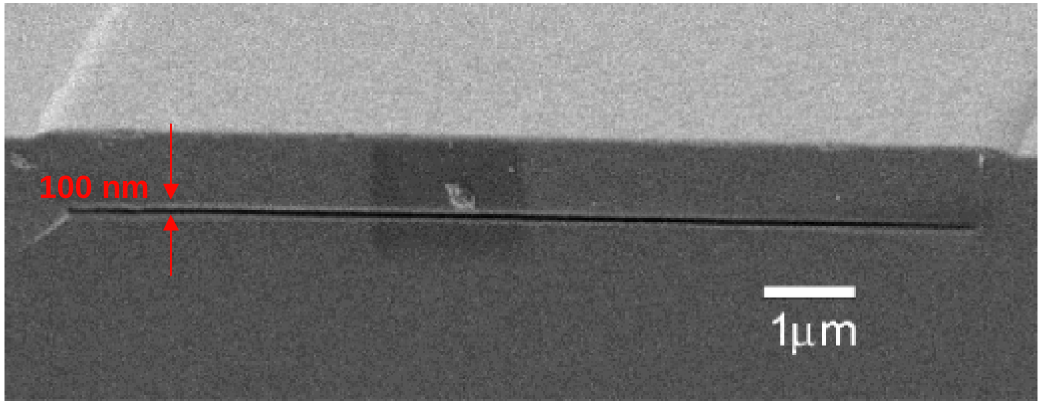


Step A from: Kim e.a. Appl. Phys. Lett. 79, 2001, p.3812
Complete proces: Tas e.a. Nanolett. 2, 2002, p.1031

Etching time (L = 0.64 mm) is 15 hrs !

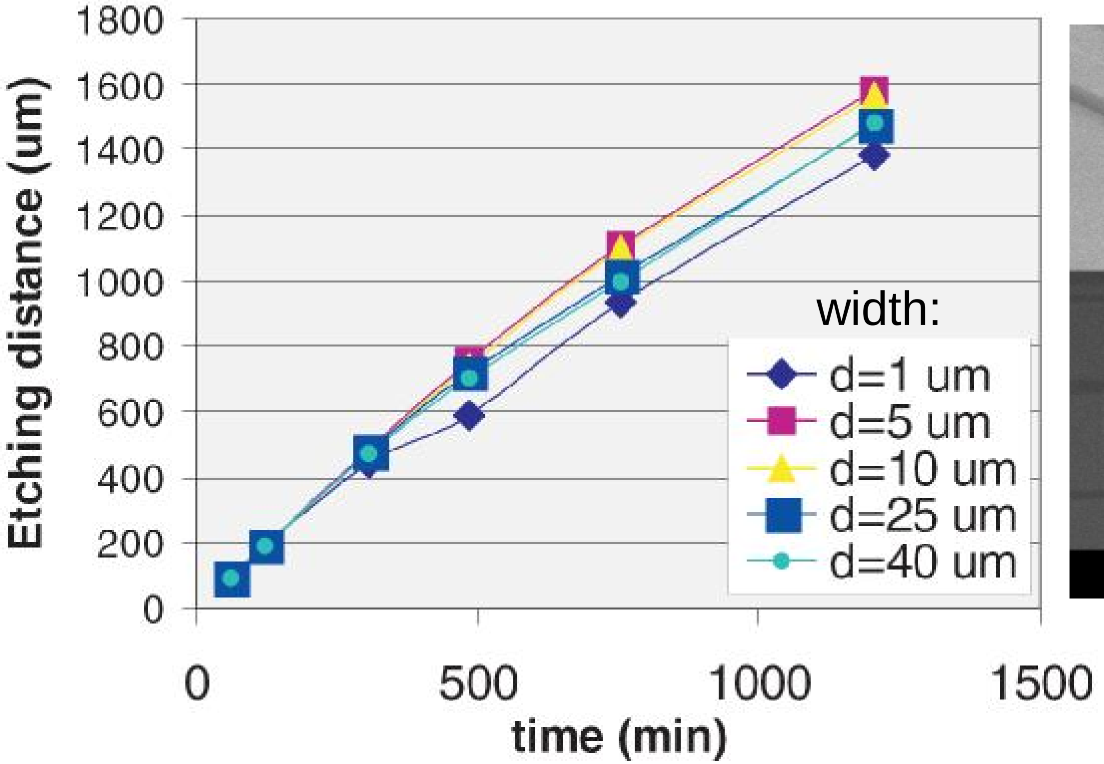
Sacrificial layer removal requires patience

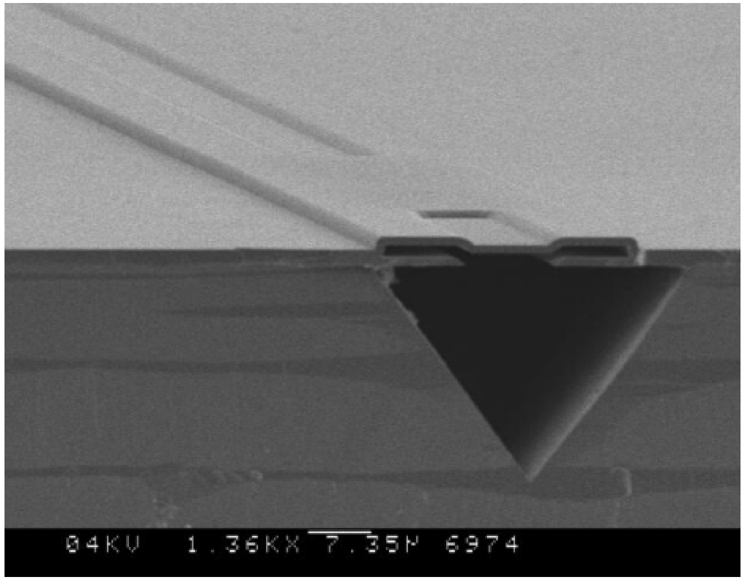
It took tens of ppms of the age of the universe (i.e. million years) for nature to remove the softer layer and create the arch



It takes tens of ppms of the age of a microfabrication expert (i.e. 100,000 seconds) to remove the sacrificial layer and create the nanochannel

Removal of layer in microchannel

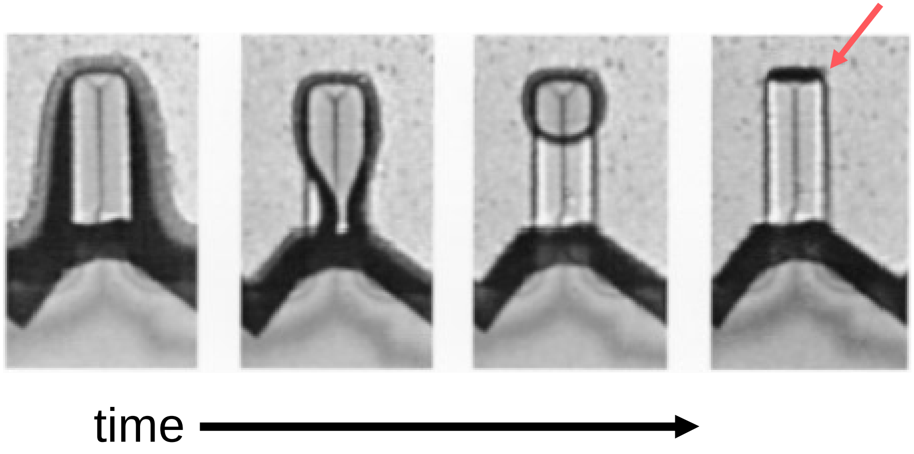


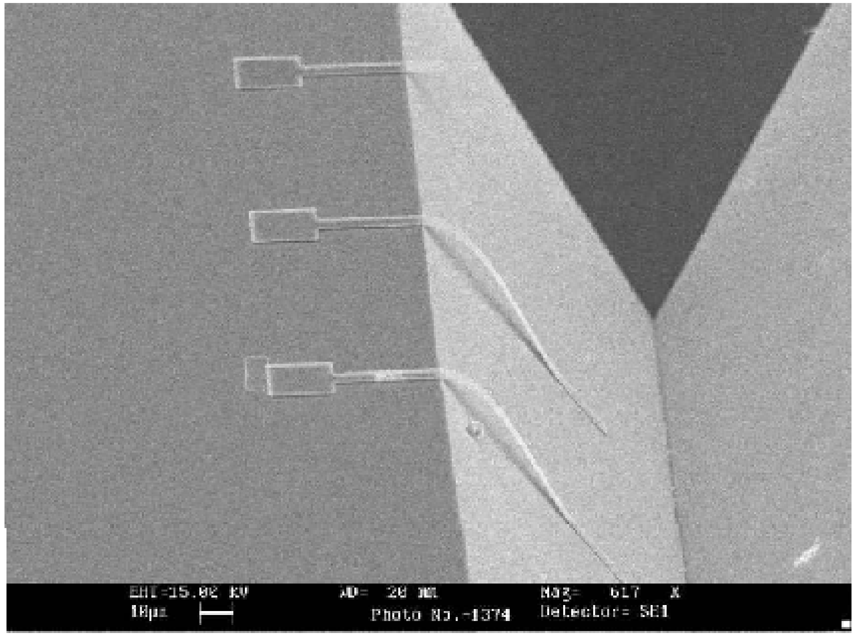


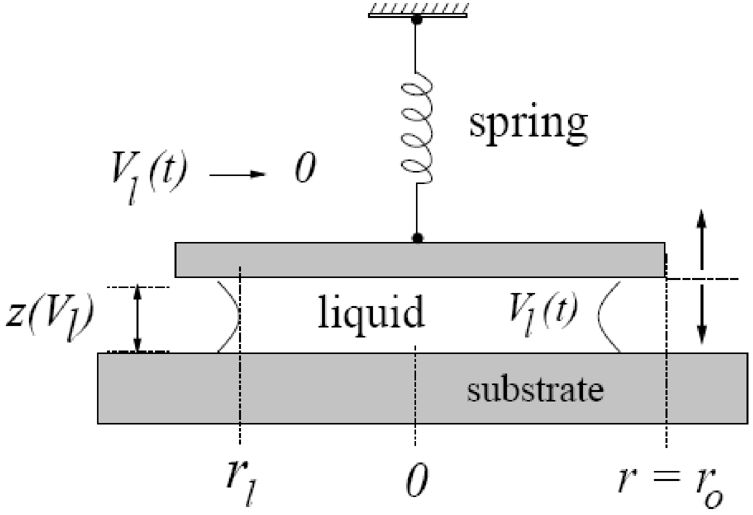
2 μm poly-Si layer in 25 wt% KOH solution at 74 ◦C

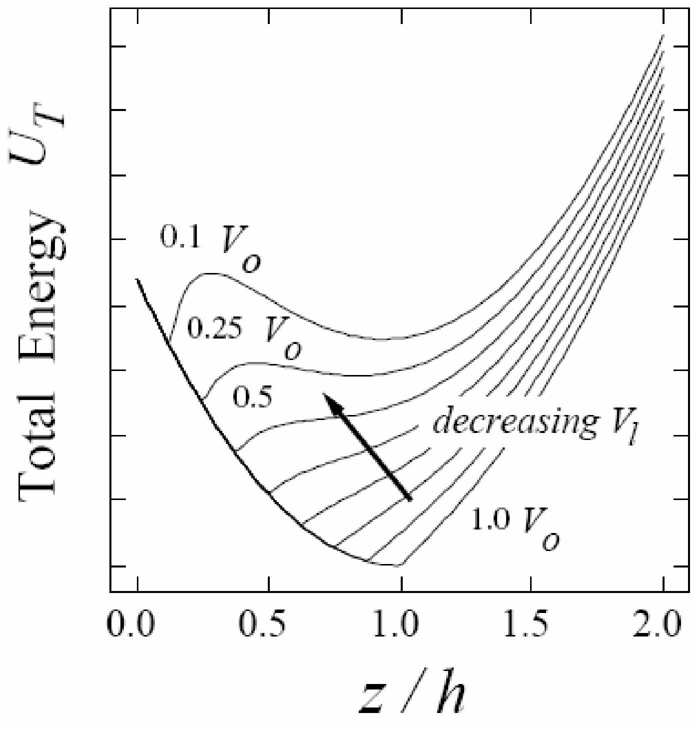
J.W. Berenschot e.a. J. Micromech. Microeng. 12, 2002, p.621

Stiction caused by surface tension during drying





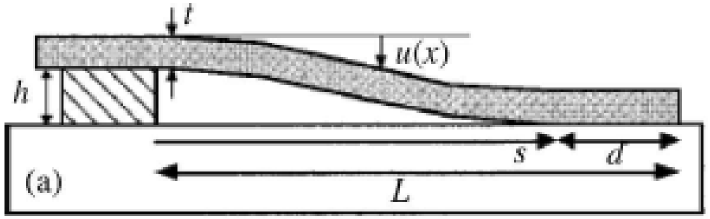




MESA+
Institute for Nanotechnology

Review: Zhao e.a. J.Adhesion Sci.Technol.17, 519-546 (2003)
Theoretical model: Mastrangelo e.a J.MEMS 2, 44 (1993)

Maximum dimensions without stiction



$$L_{\max} = \left(\frac{3Et^3h^2}{8W_a}\right)^{1/4}$$

For other structures:

$$L_{\max}, w_{\max}, R_P\big|_{\max} = \left(\frac{b+\sqrt{b^2+4c}}{2}\right)^{1/2}$$

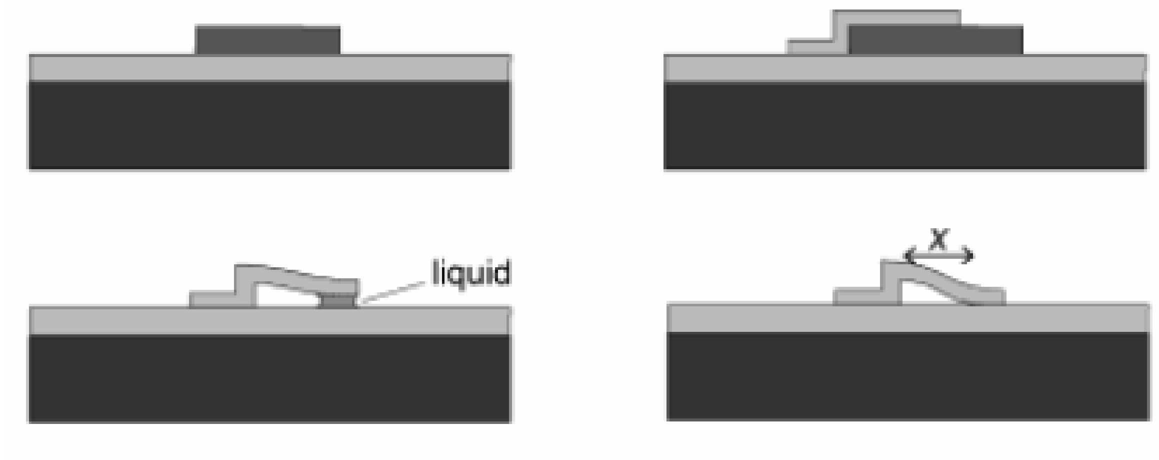
Microstructure	b	c
Doubly clamped beam	$\frac{512}{105}\frac{\sigma_R h^2 t}{W_a}$	$\frac{128}{5}\left[1+\frac{256}{2205}\left(\frac{h}{t}\right)^2\right]\frac{Et^3h^2}{W_a}$
Square plate	$\frac{5022}{301}\frac{\sigma_R h^2 t}{W_a}$	$\left[1+\frac{12}{31}\left(\frac{h}{t}\right)^2\right]\frac{186Et^3h^2}{(1-\nu^2)W_a}$
Circular plate	$\frac{17}{4}\frac{\sigma_R h^2 t}{W_a}$	$\frac{40Et^3h^2}{3(1-\nu^2)W_a}$

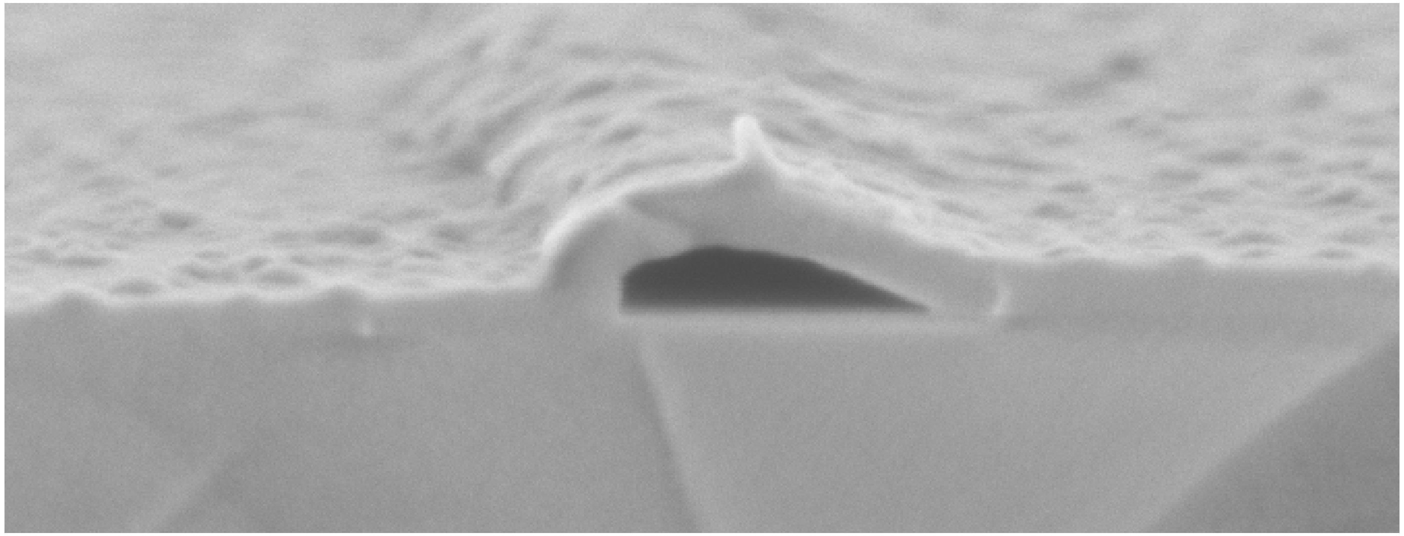
ν: Poisson's ratio
σ_R: residual stress
E: Young's modulus

L, w, R_p are the length of the doubly clamped beam, width of the square plate and radius of the circular plate, respectively

Zhao e.a. J.Adhesion Sci.Technol.17, 519-546 (2003)

How to use stiction

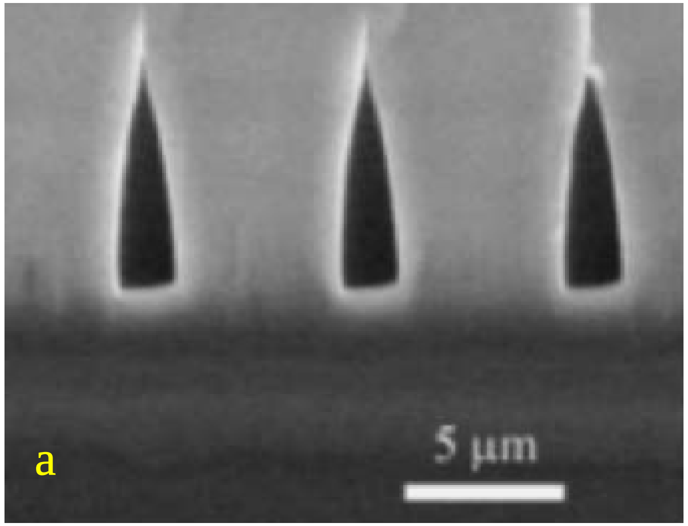


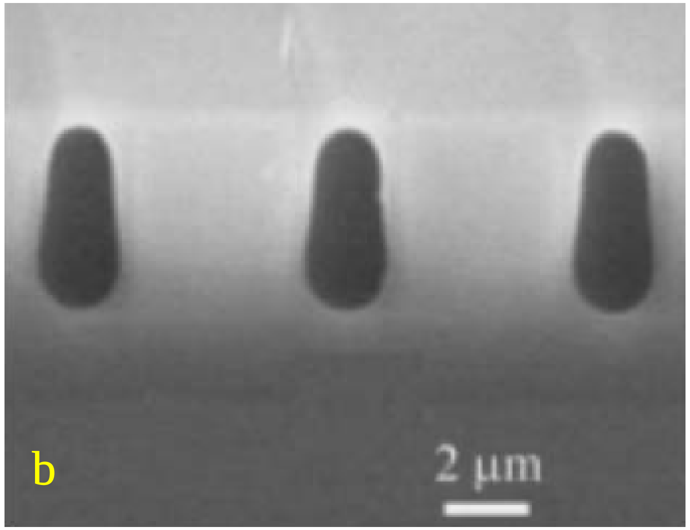


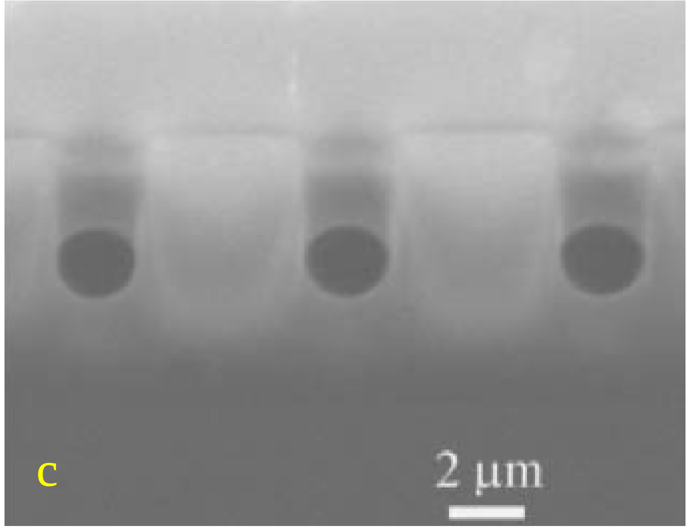
Tas e.a. Nanolett. 2, 2002, p.1031

Etching time is 4 min.

Nanochannels by etching and sealing



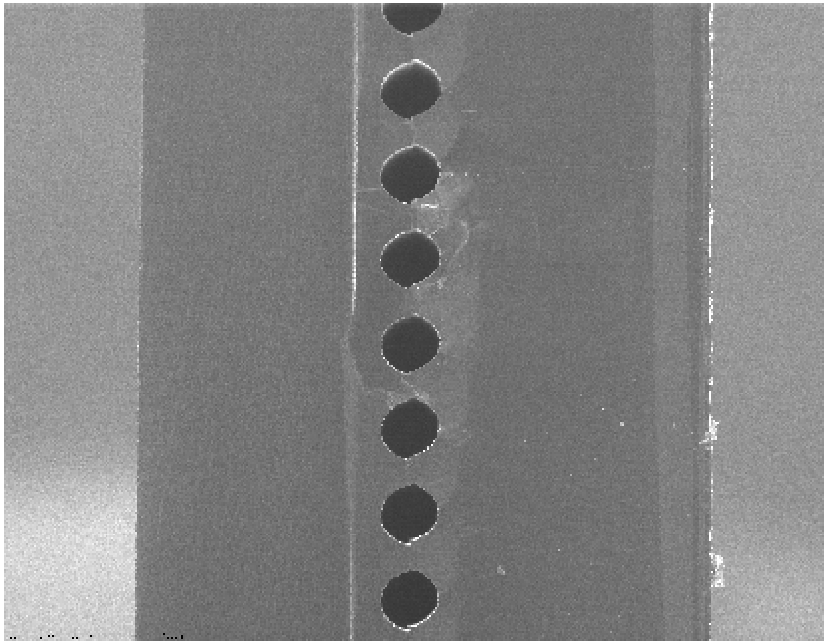




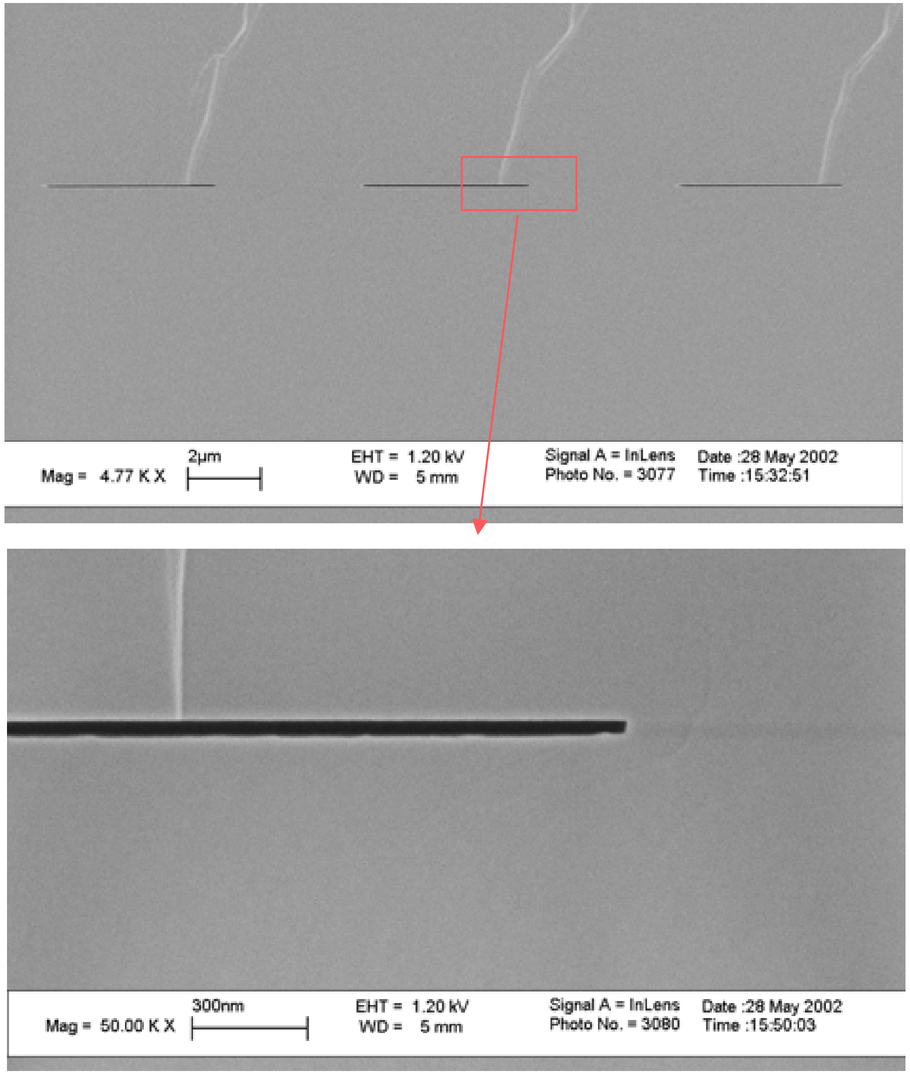
Void formation in a 6-µm-thick BPSG glass layer deposited over template ridges with ***h***=6.4µm, ***w***=4µm and ***d***=3µm: a. as deposited, b. and c. annealed at 1050 °C for 4 and 12 hrs, resp. Annealing causes reflow of the glass layer

Callender e.a. J. Mater. Res. 20, 2005, p. 759

Nanochannels by etching and sealing



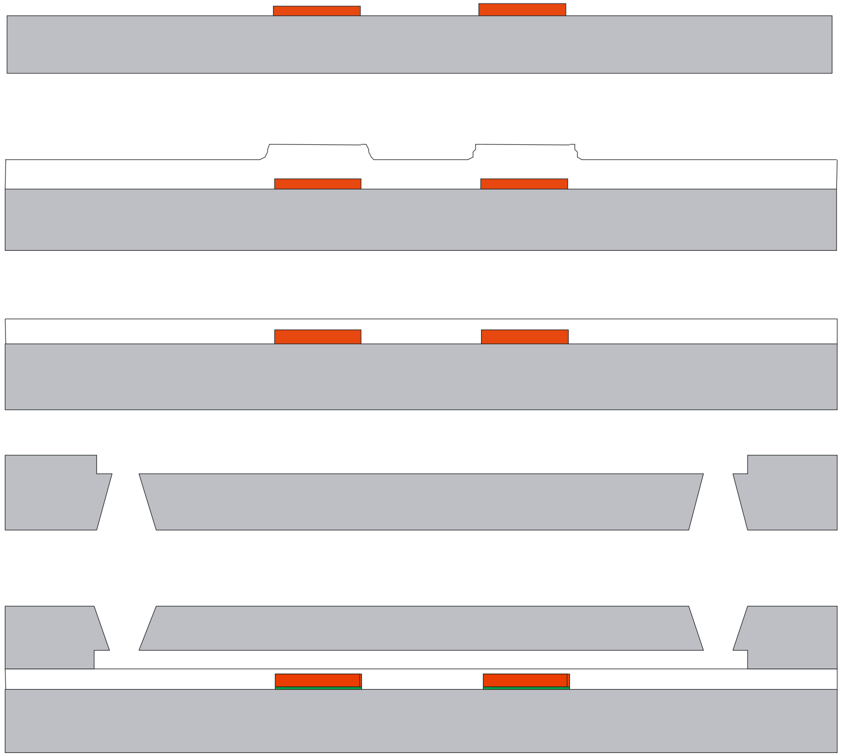
bonded surface



height 50 nm

J. Haneveld e.a. J. Micromech. Microeng. 13, 2003, p. S62

Channels with integrated electrodes



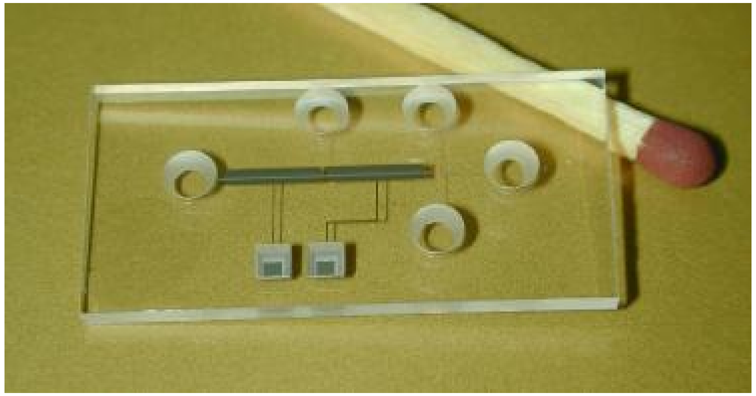
Electrode deposition

Deposition silica insulation

CMP

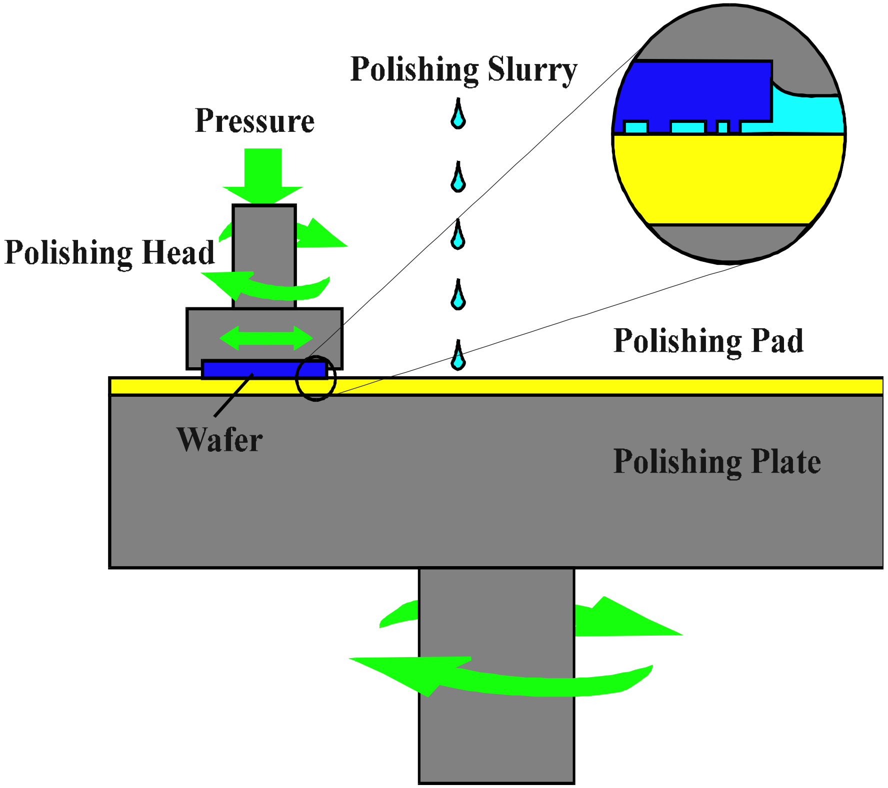
Channel etching

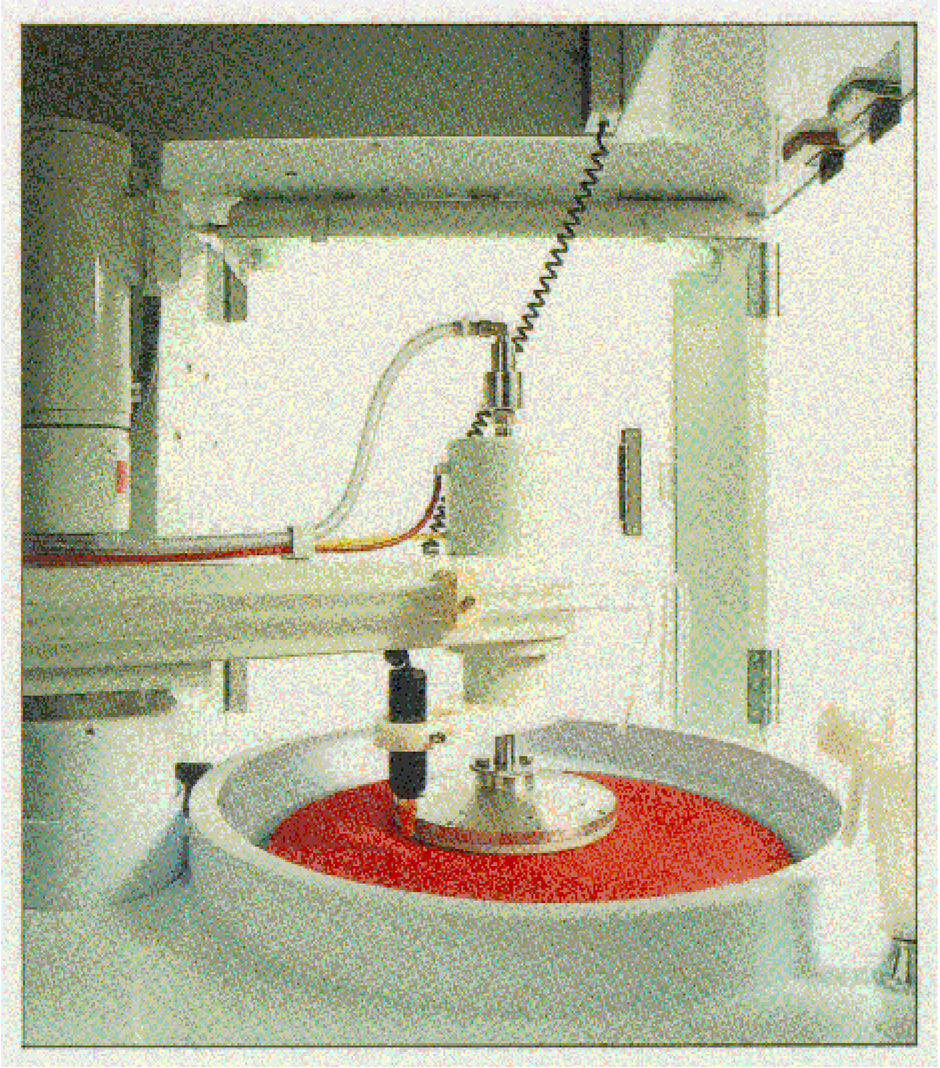
Direct bonding



E.J. van der Wouden e.a.
Coll. Surf. A 267, 2005, p. 110

Chemical mechanical polishing, CMP

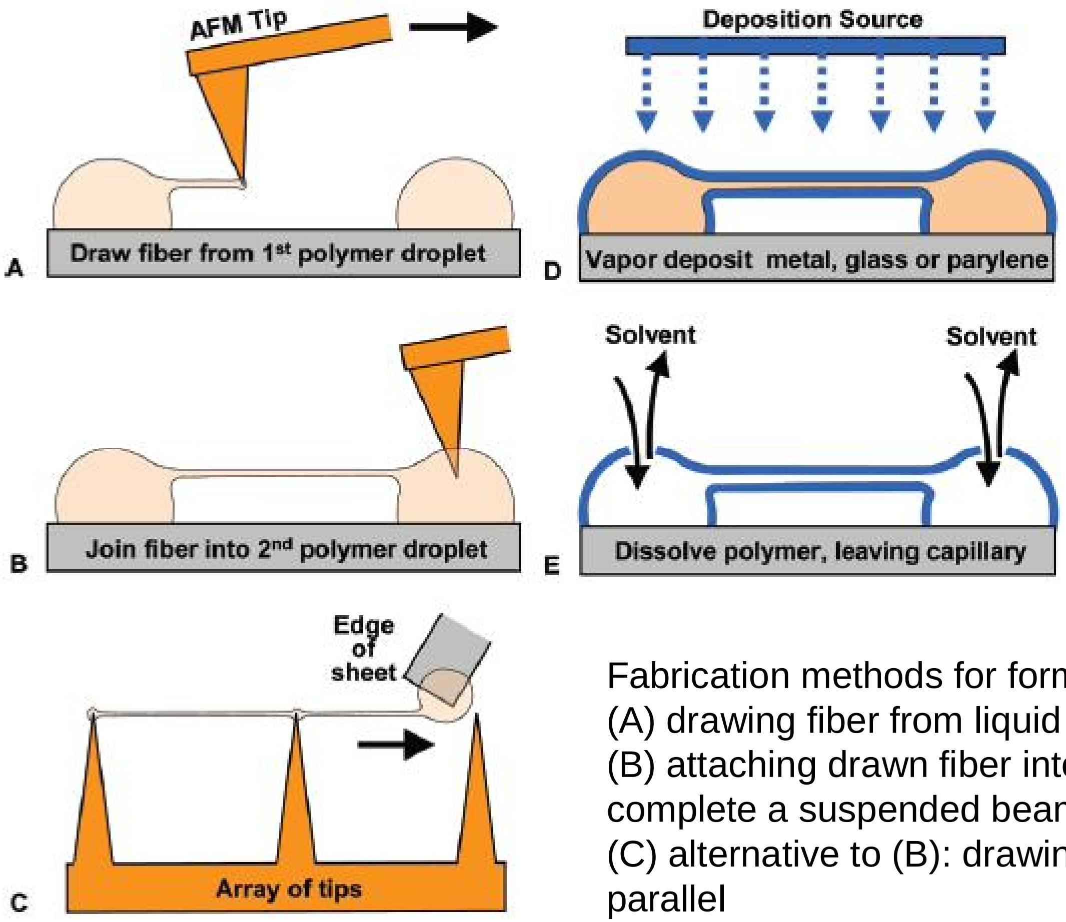




Effects of CMP:

- Reduction of roughness
- Surface (chemical) conditioning
- Planarization

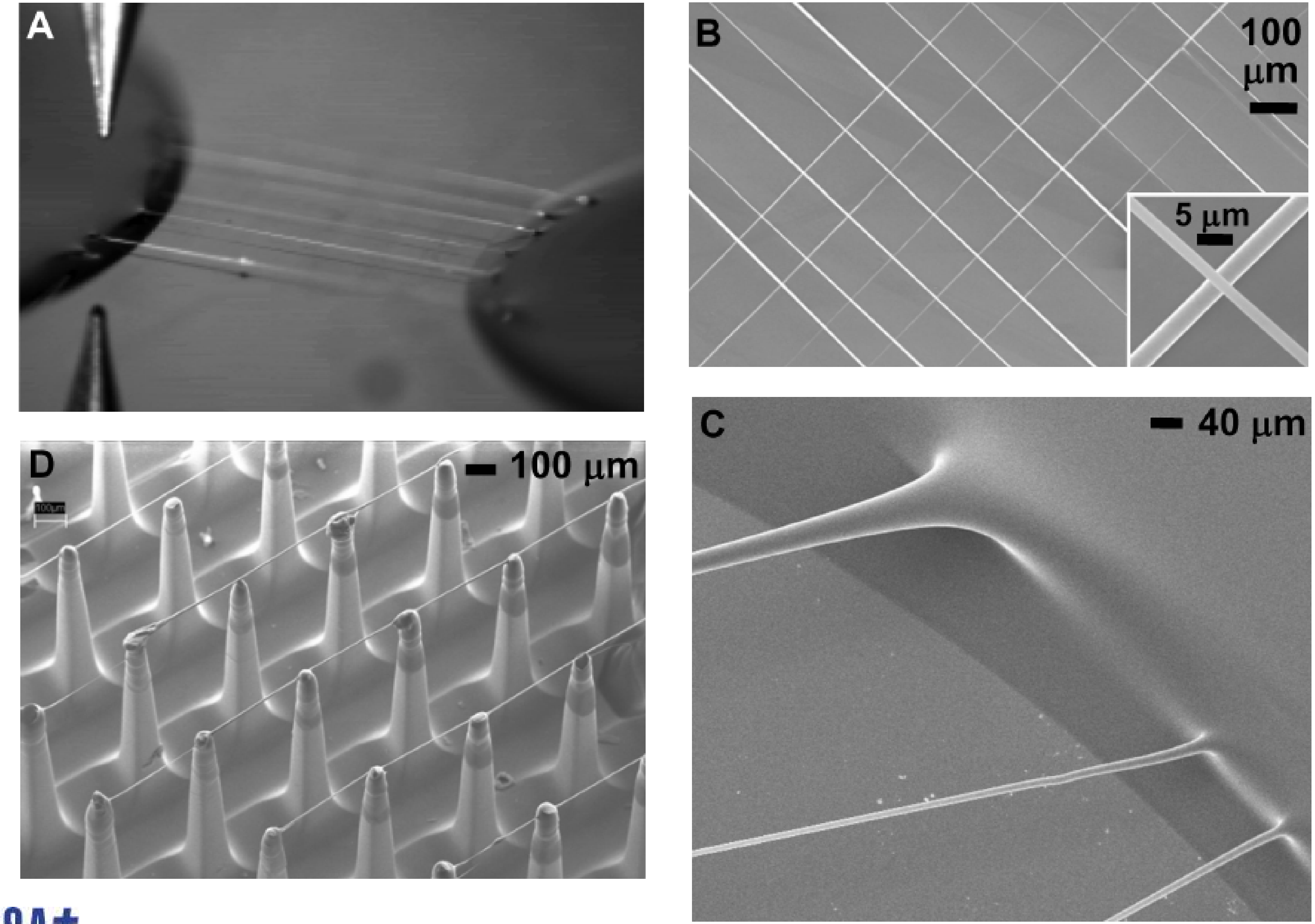
Nanochannels by assembly



Fabrication methods for forming and using polymer fibers.
(A) drawing fiber from liquid polymer droplet
(B) attaching drawn fiber into second droplet to complete a suspended beam
(C) alternative to (B): drawing multiple suspended fibers in parallel
(D) overcoating polymer network
(E) dissolution of the polymer to produce a suspended capillary network

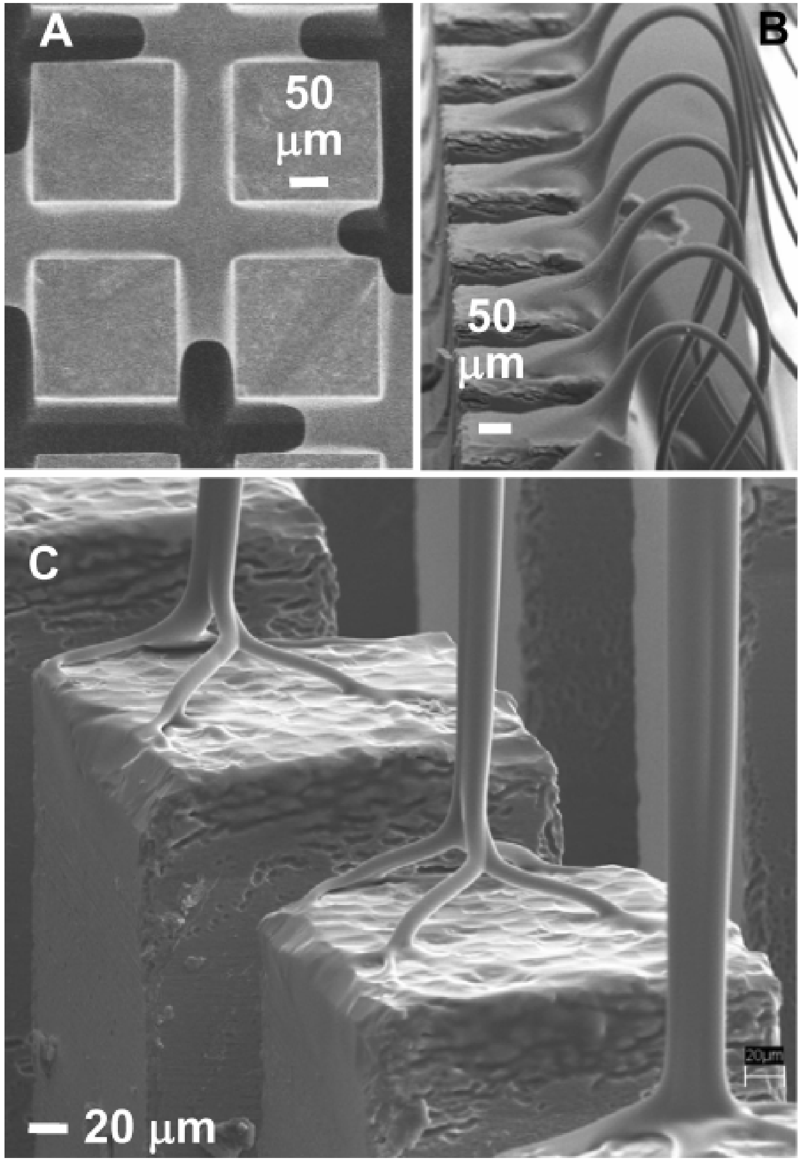
Harfenist e.a. Nanolett. 4, 2004, p.1931

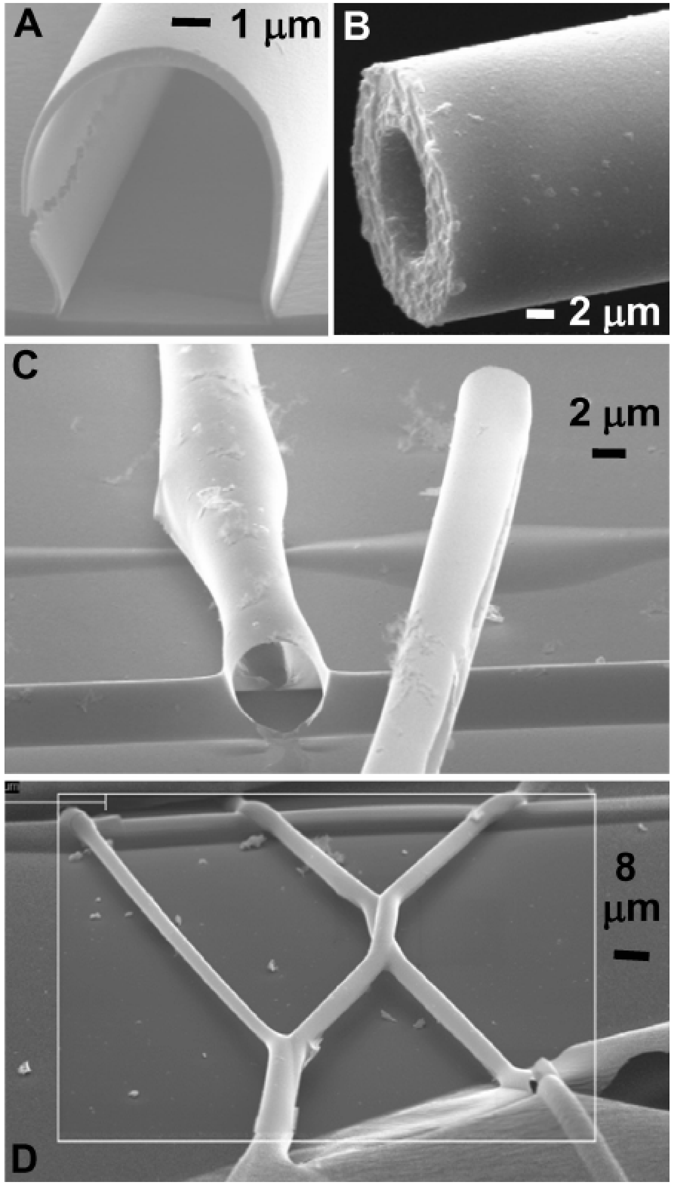
Nanofluidic interconnections



Harfenist e.a. Nanolett. 4, 2004, p.1931

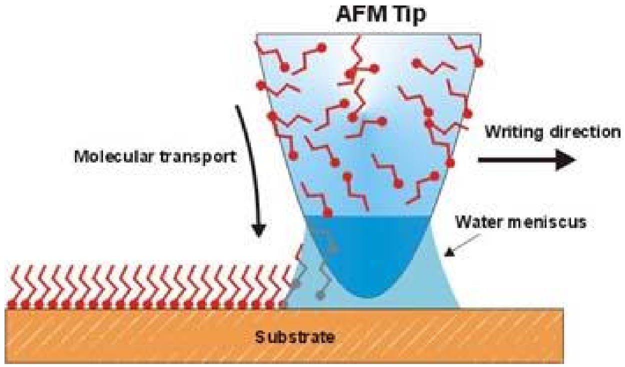
Nanofluidic interconnections

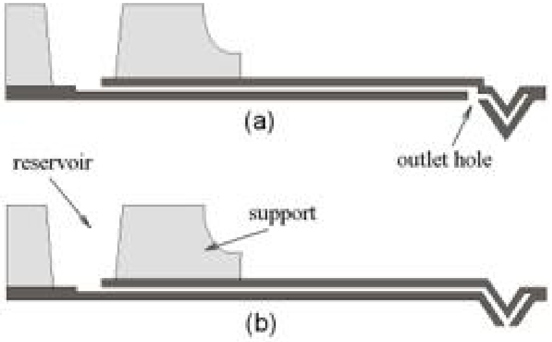




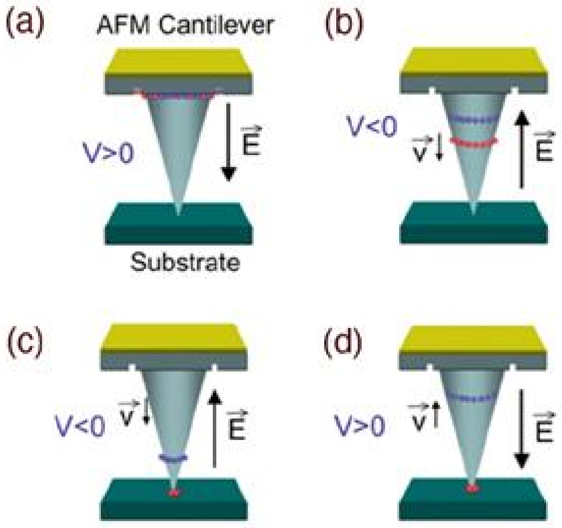
Harfenist e.a. Nanolett. 4, 2004, p.1931

Bottom-up nanotechnology: atomic/molecular assembly using AFM

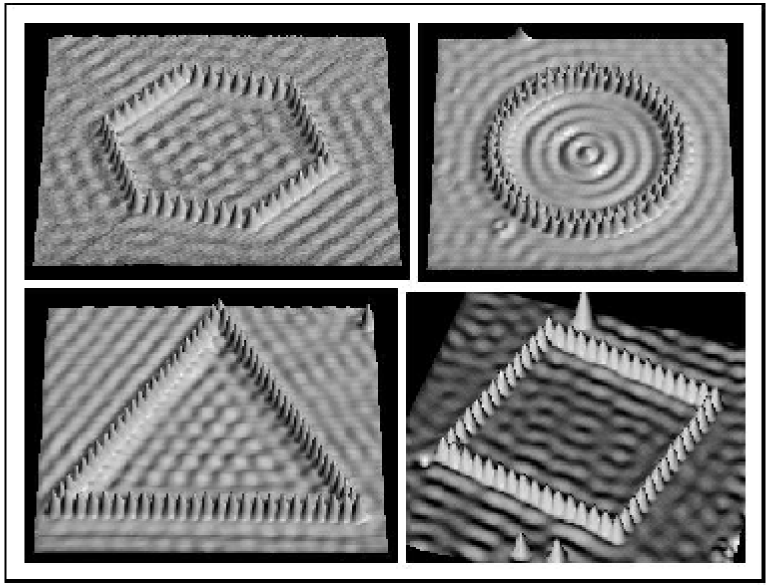




Left: Dip-pen
Right: Fountain pen



AFM with electrophoretic control of molecules

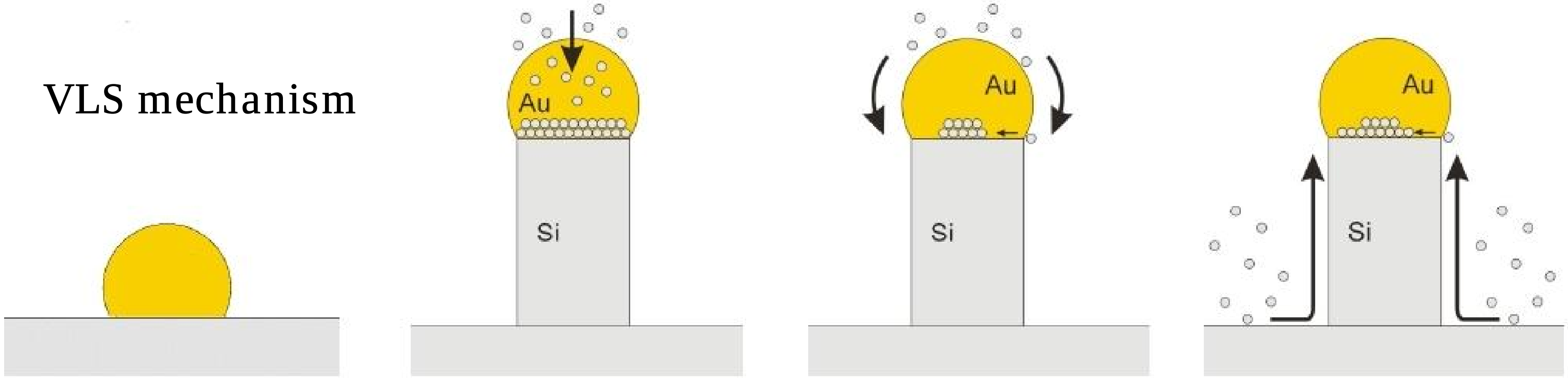


Confinement of electrons to "quantum corrals" on a metal surface, using STM

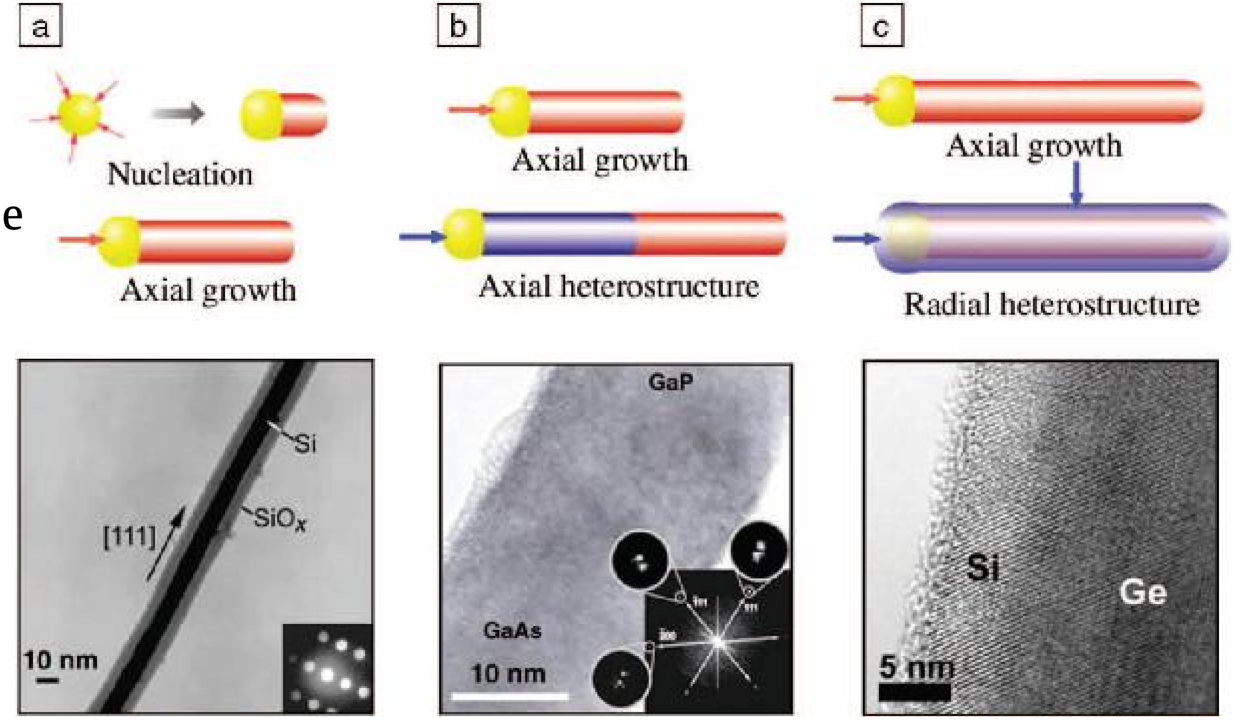
R.D. Piner e.a. Science 283, 1999, p. 661
S. Deladi e.a. Appl. Phys. Lett. 85, 2004, p. 5361
K. Unal e.a. Appl. Phys. Lett. 88, 2006, p. 183105
M.F. Crommie a.a., Science 262, 1993, p.218

Nanowires and nanotubes

VLS mechanism



Growth and representative structures of (a) uniform single-crystal semiconductor nanowires, (b) axial nanowire heterostructures, and (c) radial nanowire heterostructures.



C.M. Lieber, MRS Bulletin July 2003, p. 486

Carbon nanotubes

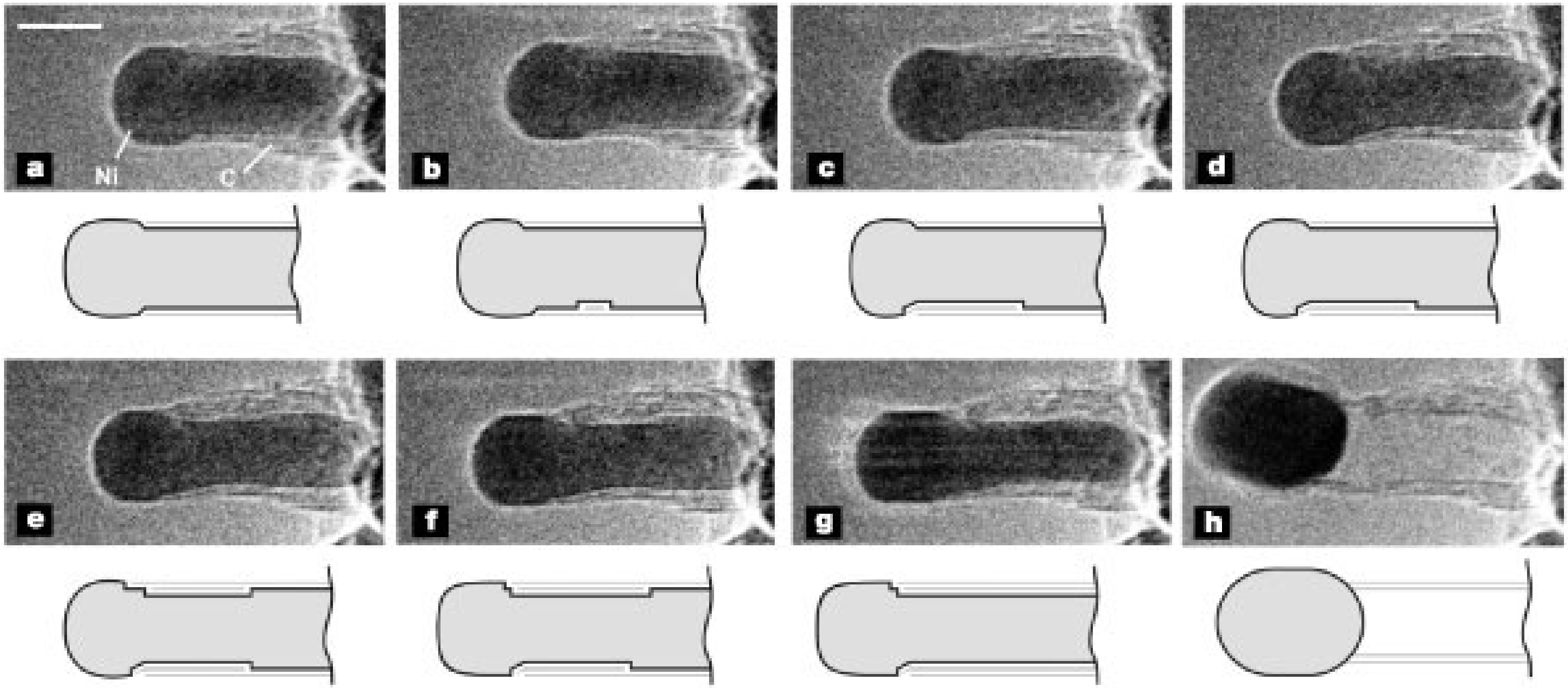
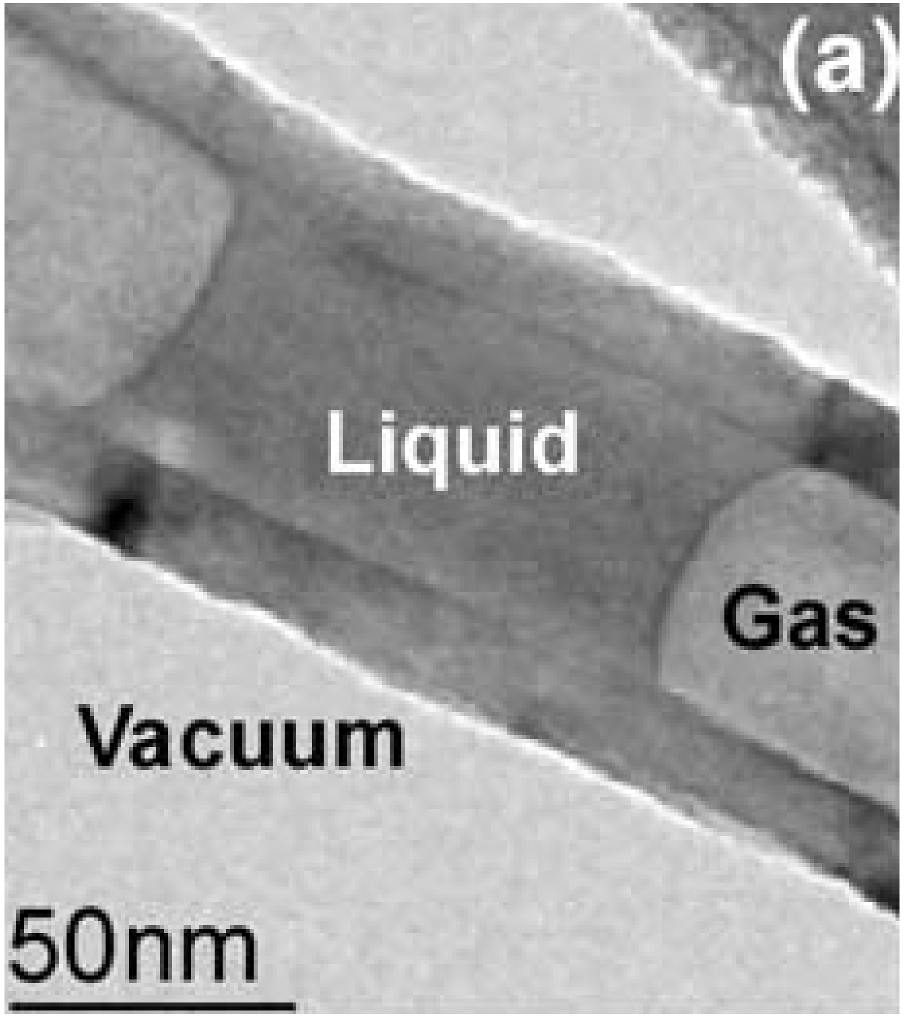


Image sequence of a growing carbon nanofibre. The images are acquired with TEM *in situ* with CH_4:H_2 = 1:1, total pressure 2.1 mbar, sample heated to 536 °C. Scale bar, 5 nm.

Atomic-scale imaging of carbon nanofibre growth
S. Helveg et al., *Nature* **427,** 426–429 (2004)

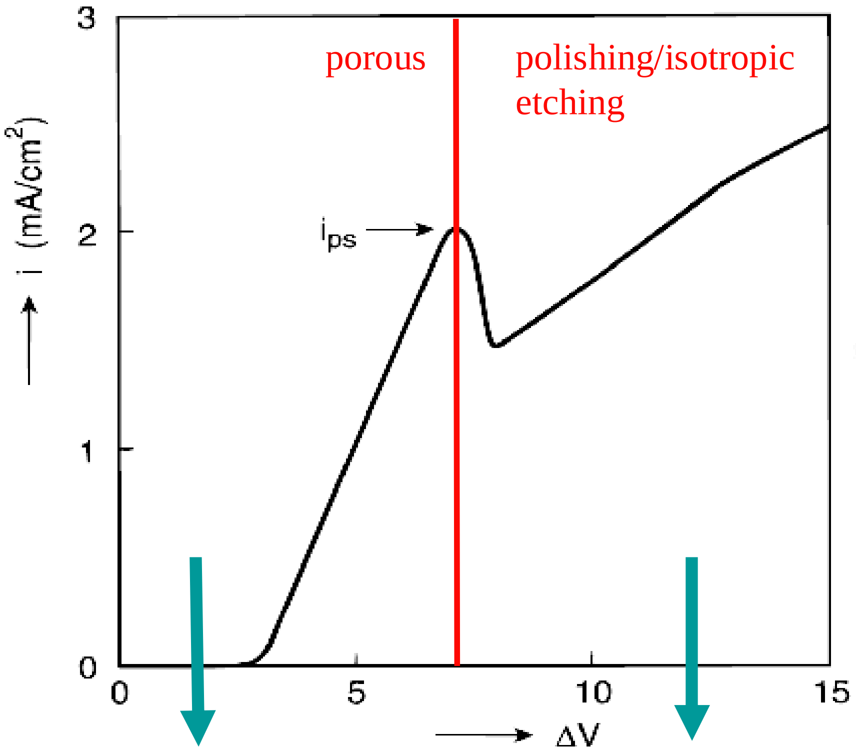
Liquid-filled carbon nanotube

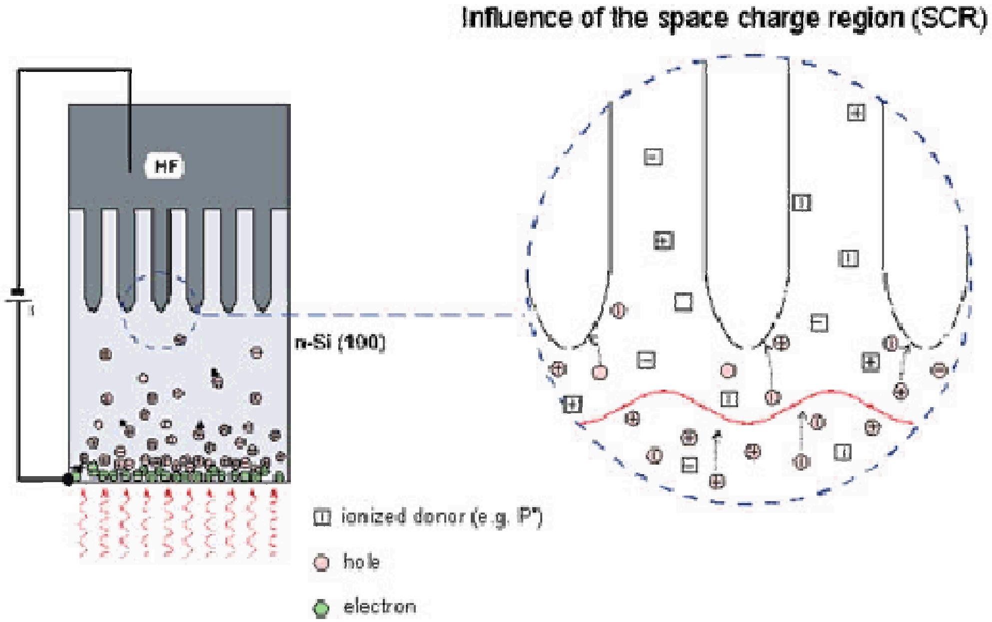


Low magnification TEM micrographs showing a liquid plug in the nanotube.

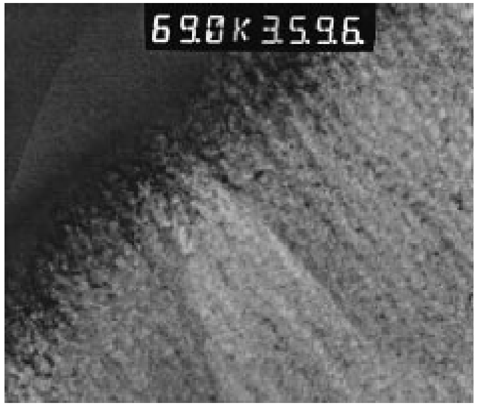
Y. Gogotsi et al.
Chem. Phys. Lett. 365 (2002) 354

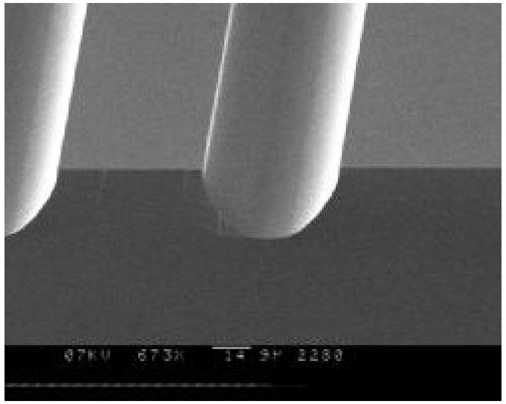
Nanopores by anodization: silicon





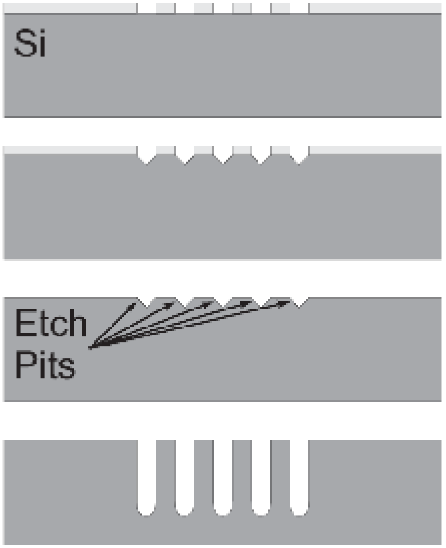
http://www.mpi-halle.mpg.de/~porous_m/Si_pore_growth.html





University of Twente
The Netherlands

Procedure and examples

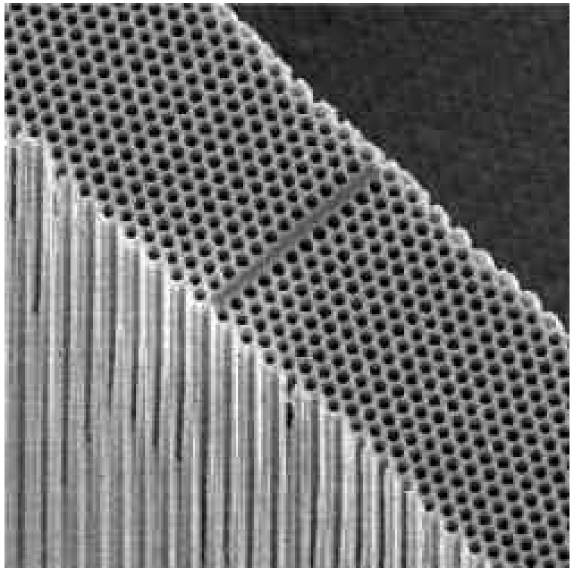


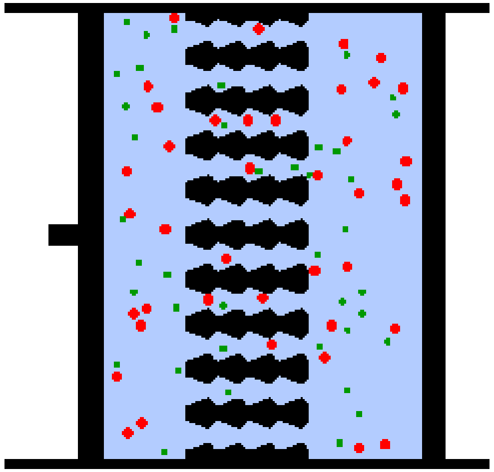
Photolitography

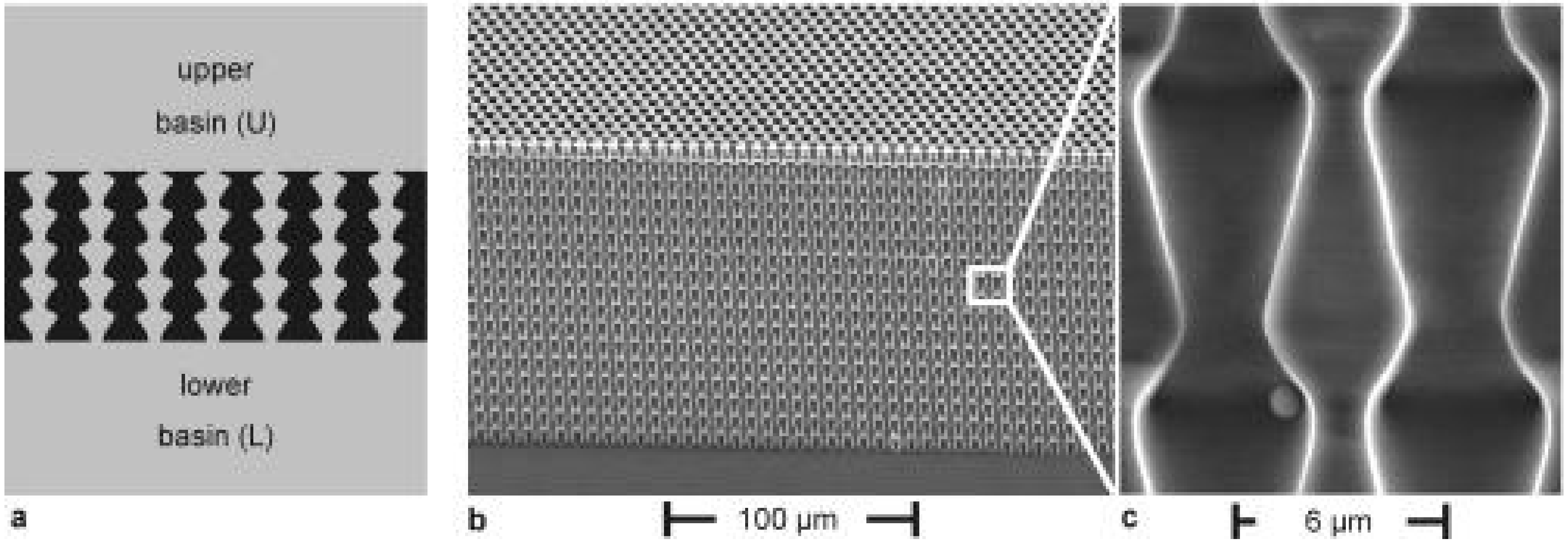
KOH
anisotropic etch

Mask removal

Macroporous
anodization

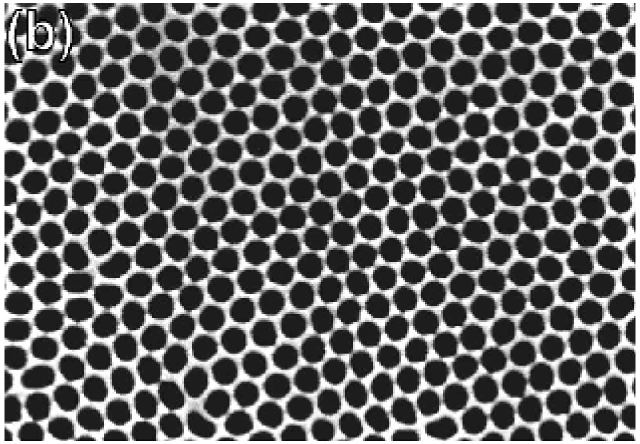


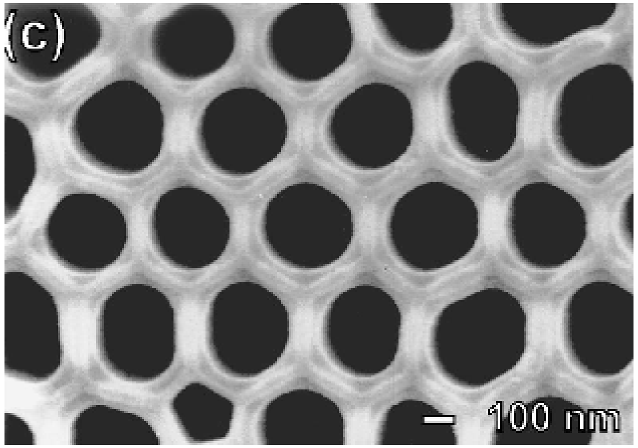


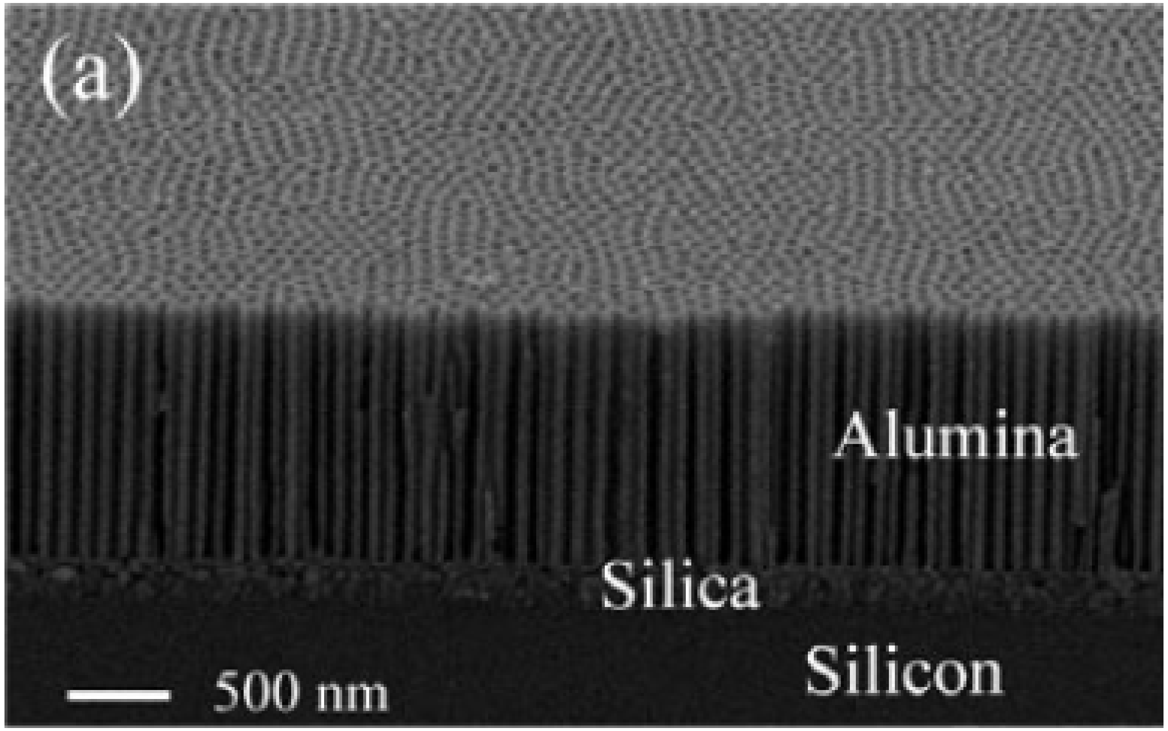


Asymmetric pores in a silicon membrane acting as massively parallel brownian ratchets,
S. Matthias & F. Müller, Nature 424, 53-57 (2003)

Self-organization of pores in anodization of aluminum





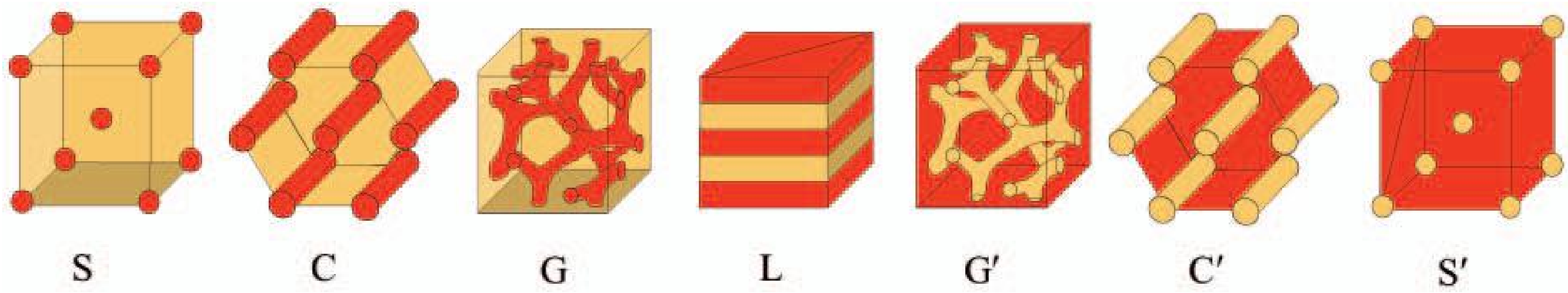


Self-organization: mechanical stress induced, see A.-P. Li e.a., J. Appl. Phys. 84, 1998, p. 6023

Cross-section picture: A. Cai e.a., Nanotechnology 13, 2002, p. 627

http://www.mpi-halle.mpg.de/~porous_m/Si_pore_growth.html

Self-assembly in block co-polymers



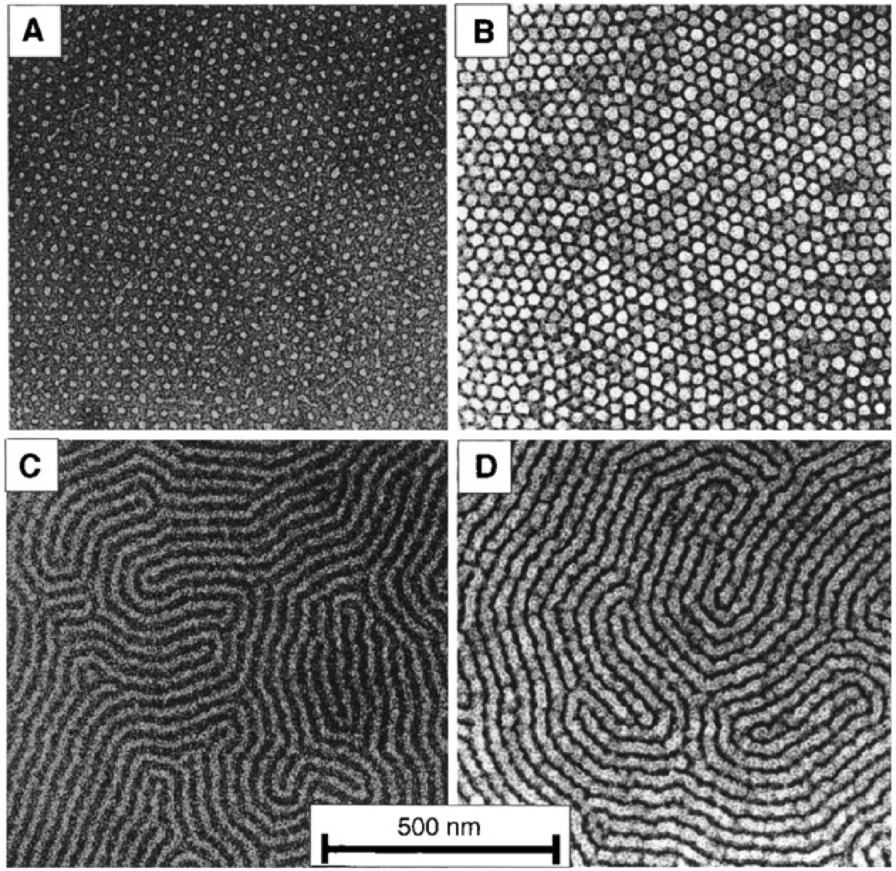
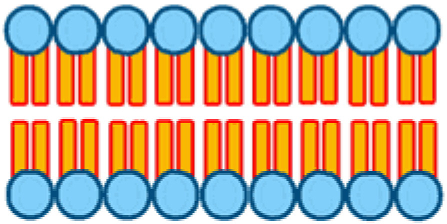


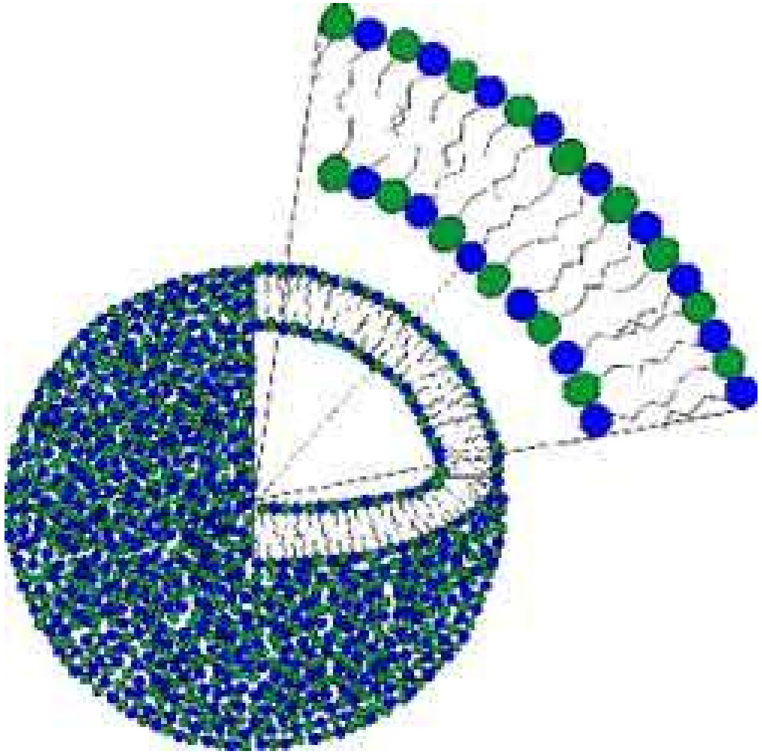
Diagram of microdomain morphologies of diblock copolymers, for varying volume fraction of components. Morphologies range from spherical (S) to cylindrical (C) to gyroid (G) to lamellar (L). The molecular weight of the block copolymer dictates the size of the microdomains, typically 10 nm. From C.J. Hawker e.a., MRS Bull. Dec. 2005, p.952

Examples from M. Park e.a. Science 276, 1997, p. 1401

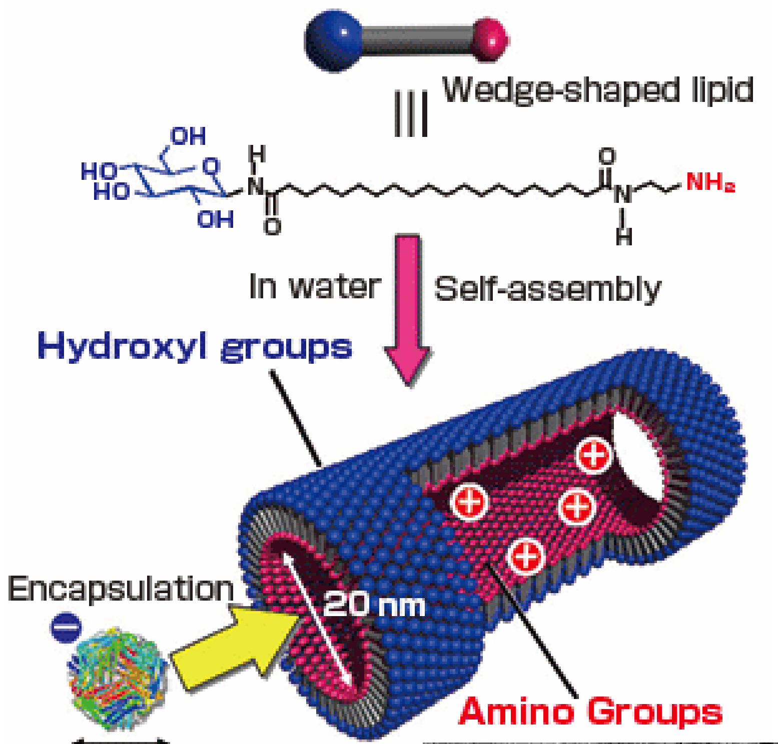
Self-assembly of lipids

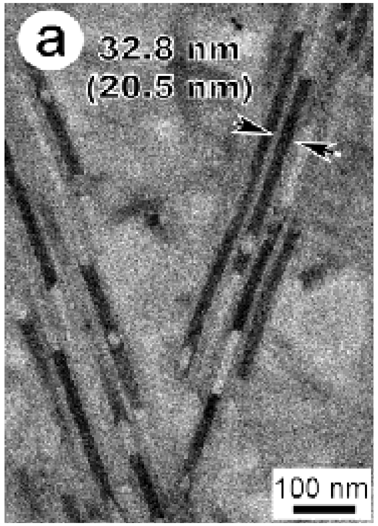


hydrophilic head
hydrophobic tail
forms lipid bilayer (membrane)



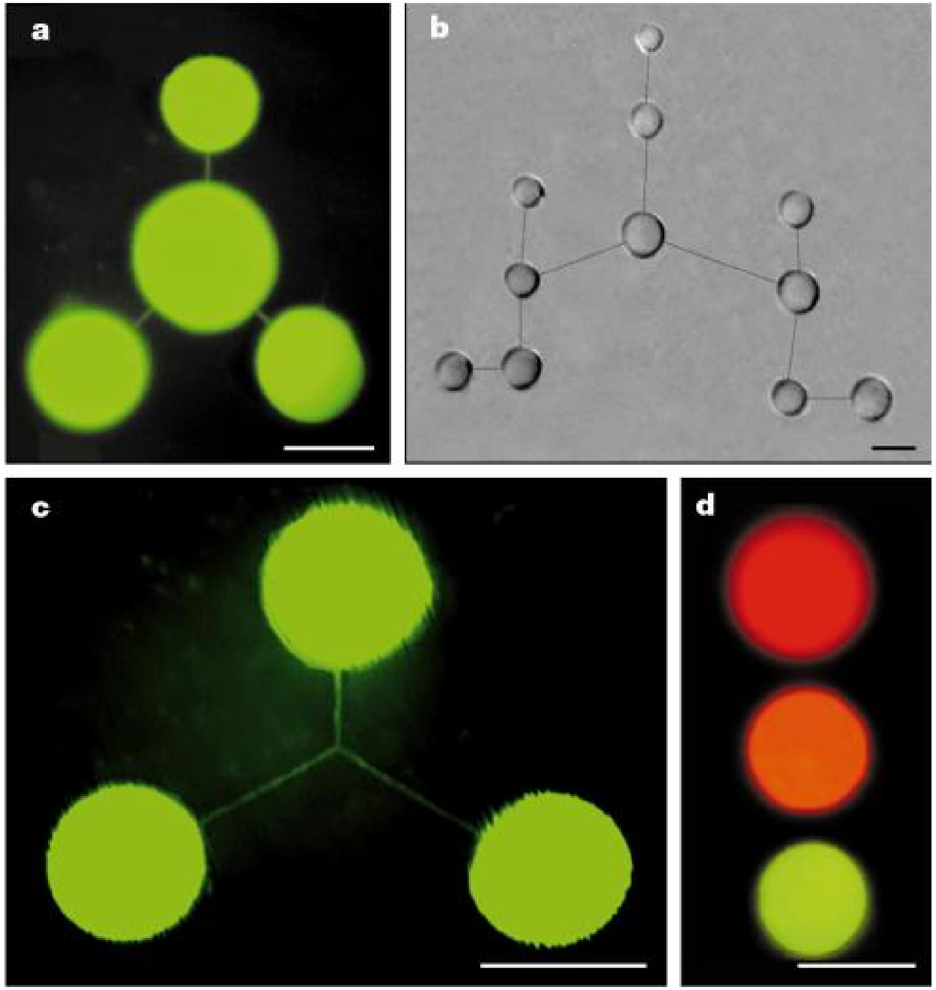
lipid vesicle



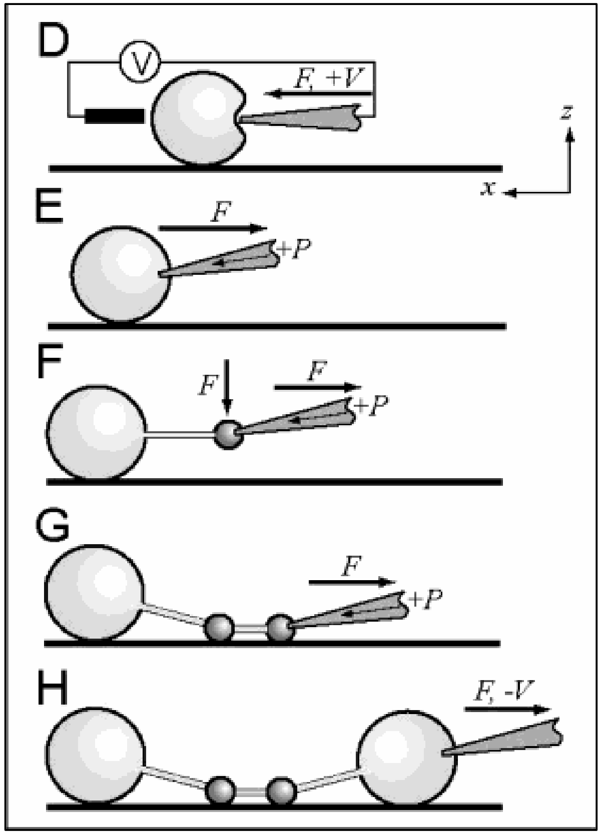


M. Masuda & T. Shimizu, Lipid nanotubes and microtubes, Langmuir 20, 2004, p.5969

Lipid vesicles and nanotubes



Microscopic liposome networks, filled with fluorescent dyes. Scale bars 10 μm.
A. Karlsson e.a., Nature 409, 2001,150

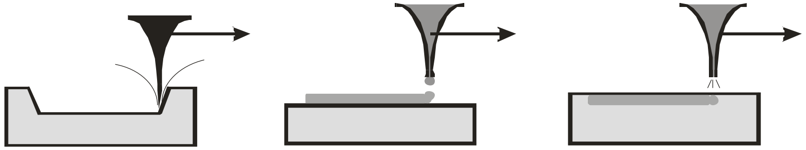


Formation of nanotube-vesicle networks. vesicle: 5 to 30 μm diameter, separation distance: 10 and 100 μm, nanotube diameter: 100-300 nm.

A. Karlsson e.a. Anal. Chem. 75, 2003, p.2529

Summary fabrication methods

WRITING



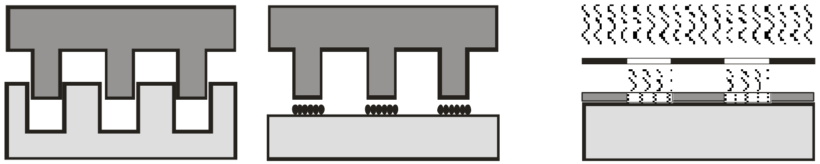
remove
(cut)

add
(dispense)

modify
(burn)

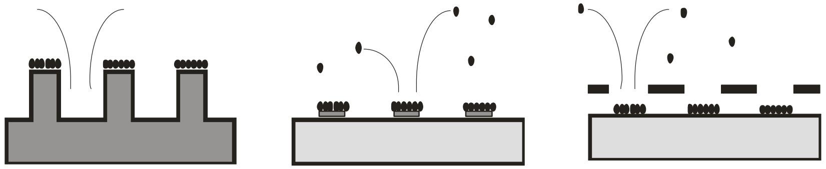
dig - glue -fry

REPLICATION



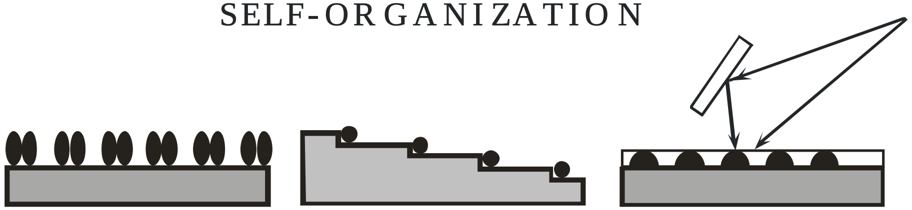
molding / imprinting

modification



material transport

SELF-ORGANIZATION



self-assembly

self-organized
template

interference/
standing wave

photons - atoms - ions - molecules
particles - gels - melts