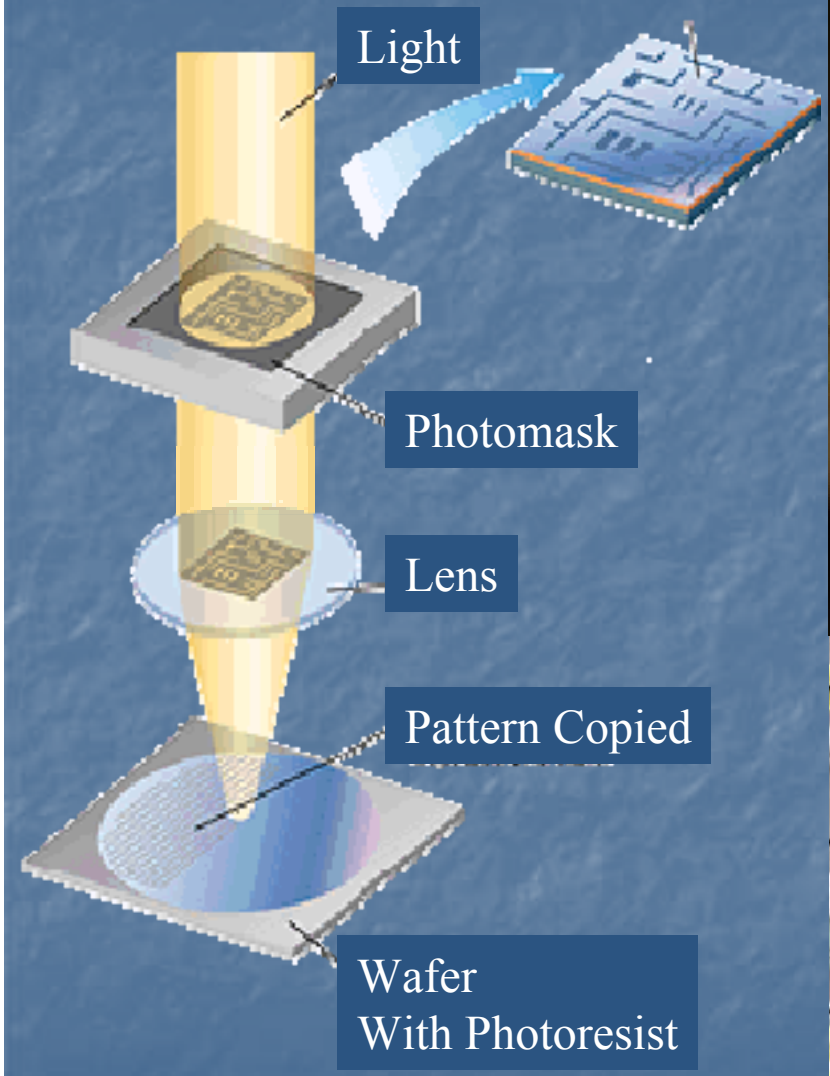
An introduction to Soft Lithography

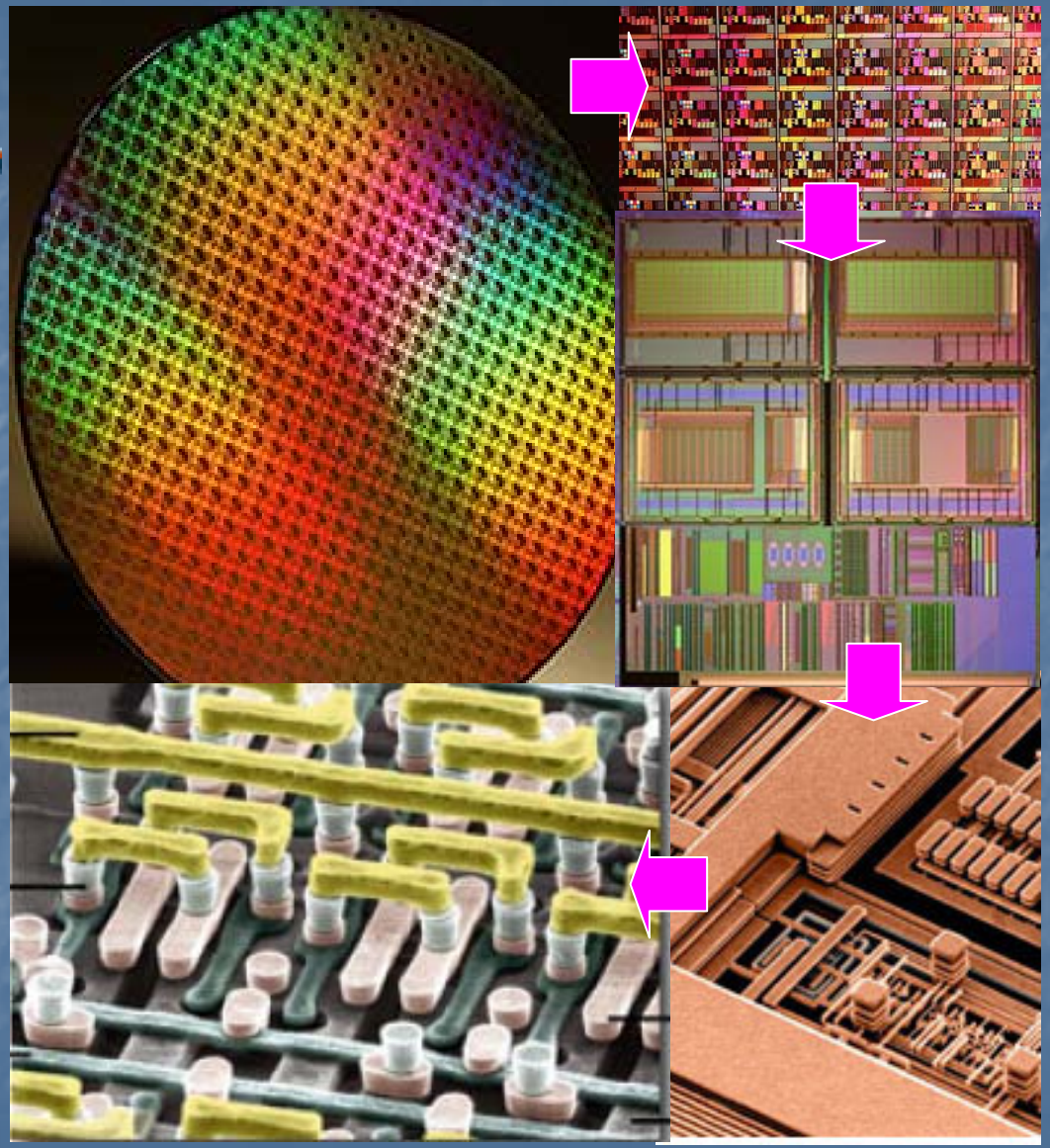
Marco Salerno

Outline

- current micro/nano-fabrication scenario
- key definitions & concepts
- list of different techniques
- fields of applications, examples

The common way: Si & Photolithography

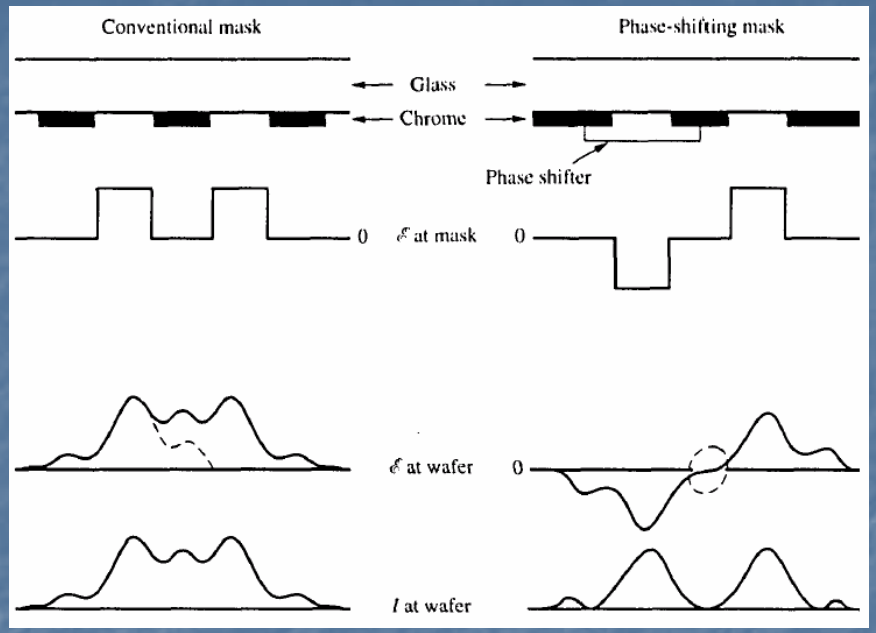




www.just2good.co.uk/ cpuSilicon.htm

http://www-306.ibm.com/chips/gallery/

Pushed to the limit: Phase-shift Photolithography

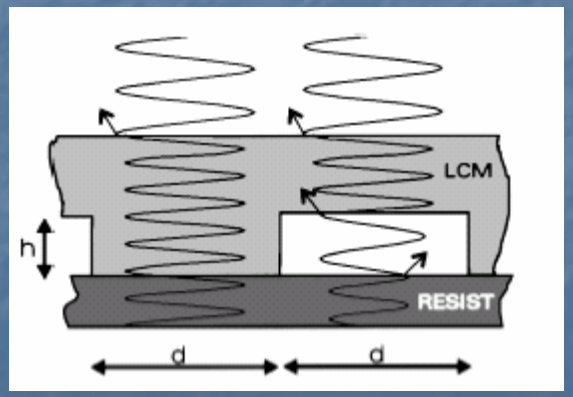


$\Delta\varphi = k\,\Delta s = k\,n\,\Delta l = \pi$

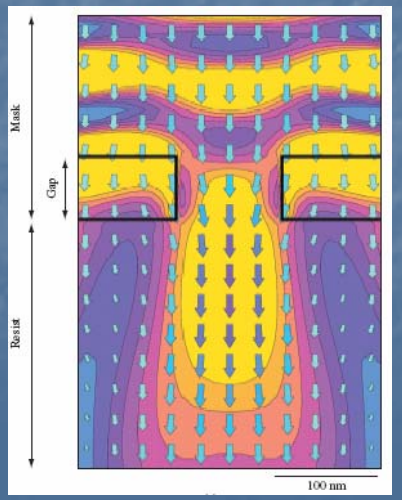
Rogers, …, Whitesides,
Appl. Phys. Lett. **1997**, *70*, 2658 :

90 nm linewidth demonstrated

doubled contrast
→ +25 to +100% resolution



Michel, B.; Bernard, A., et al.
IBM J. Res. & Dev. **2001**, *45*, 697-717.



A long story…

you already know about Moore Law !

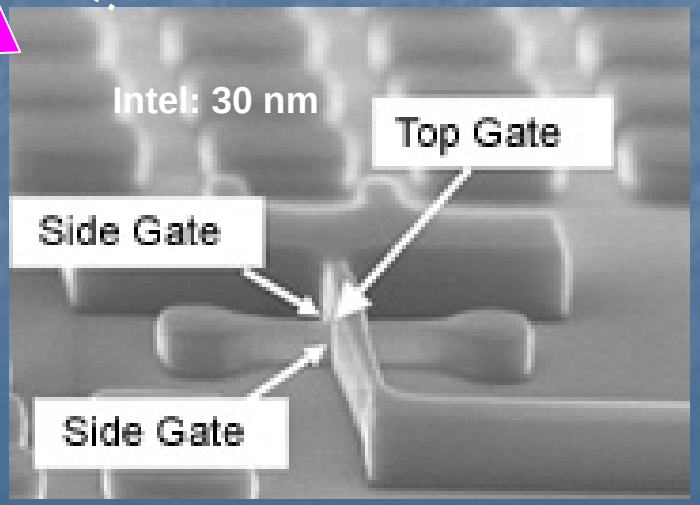
$$d(t) = d_0\ 2^{-t/3}$$
$$N(t) \sim 1/A_{unit} \sim 1/d^2 = (1/d_0^2)2^{2t/3}$$

best consumer gate length in production: ~65 nm

absolute better result: 20-30 nm

in ~6 decades…

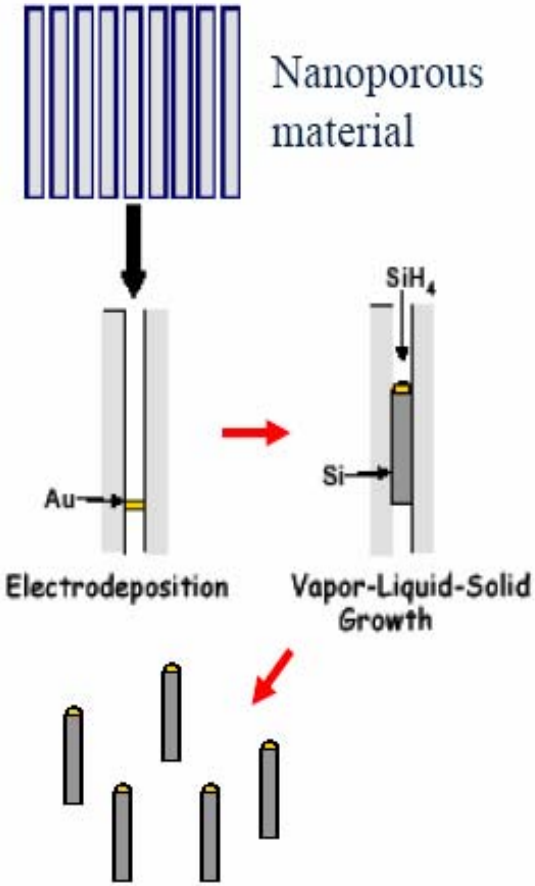
Year	Lithographic method	Resolution [nm]	Bits (DRAM)
	Photolithography (λ[nm])		
1992	UV (436), *g* line of Hg lamp	500	16 M
1995	UV (365), *i* line of Hg lamp	350	64 M
1998	DUV (248), KrF excimer laser	250	256 M
2001	DUV (193), ArF excimer laser	180	1 G
2004	DUV (157), F_2 excimer laser	120	4 G
2007	DUV (126), dimer discharge from an argon laser	100	16 G
2010	*Advanced lithography* extreme UV (EUV, 13 nm) soft X-ray (6–40 nm) focused ion beam (FIB) electron-beam writing proximal-probe methods	< 100[c]	> 16 G



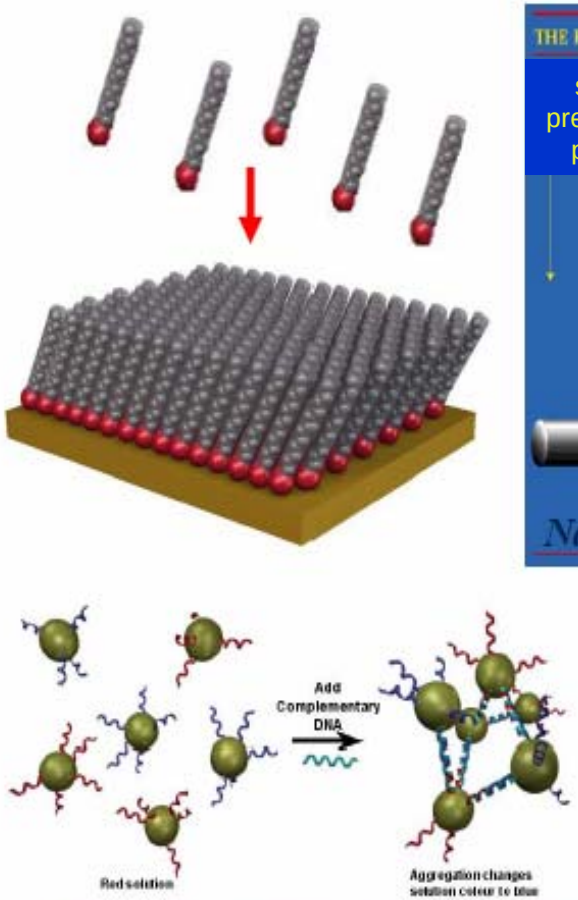
"Bottom-up" Nanofabrication

Several process approaches exist including:

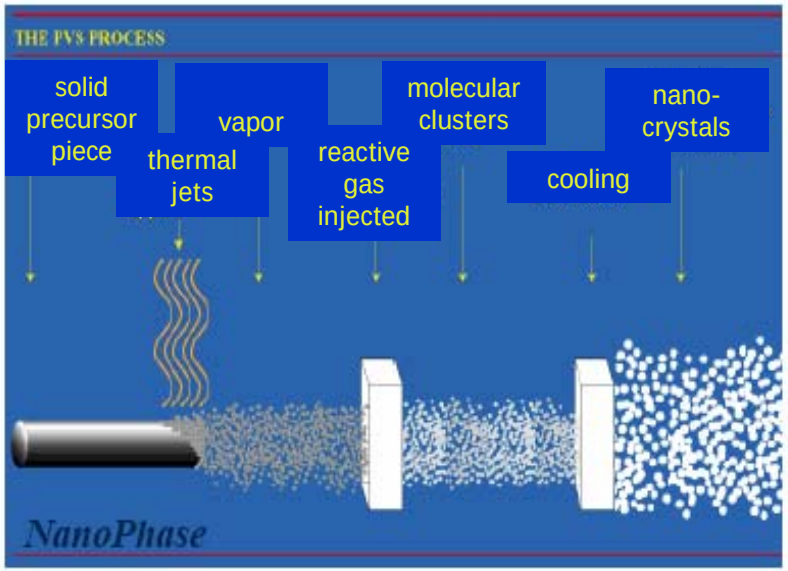
Templated growth



Self assembly



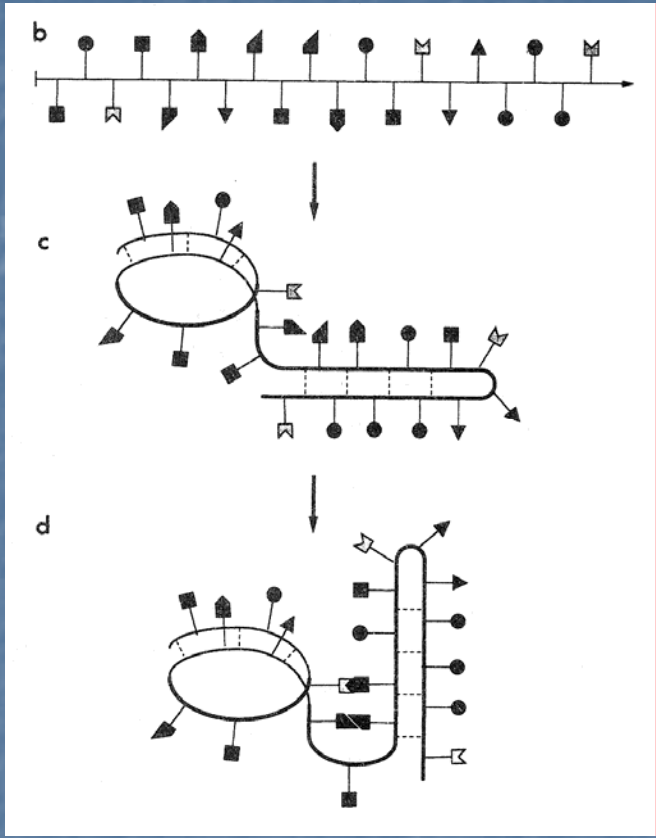
Physical Vapor Synthesis



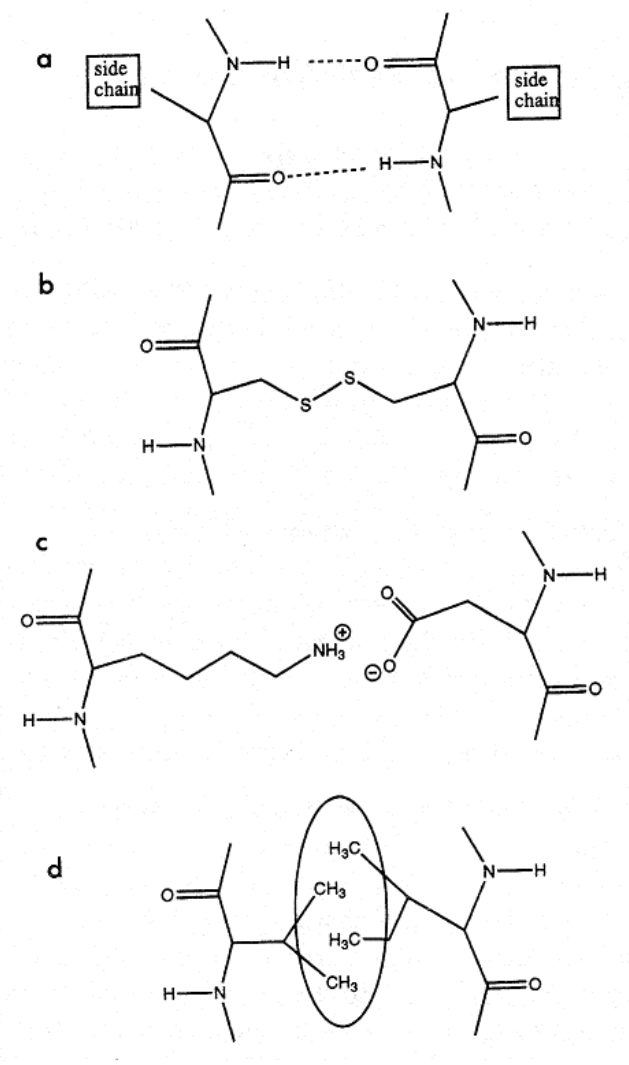
Produces 8nm-75nm particles in a wide variety of materials

Redwing, et. al., PSU Letsinger et al., *Angew. Chem. Int. Ed.* **2001**, *40*, 2909.

Masterpieces of weak interactions



variety of side chains
(from e.g. single H Glycine
to double-ring Tryptophane)
→ the chain curls up:
secondary & tertiary structure:
protein folding



- H bond
- electrostatic attraction between polar molecules (salt bridges)
- vdW between negative e clouds of one atom & positive nuclei of another
- hydrophobic interactions

- disulfide bond: covalent, but easily formed/broken in physiological conditions (helps stabilize 3D cell structure)

Self- assembling

definition: spontaneous organization of molecules (opbjects) into stable, well-defined structures by non-covalent forces

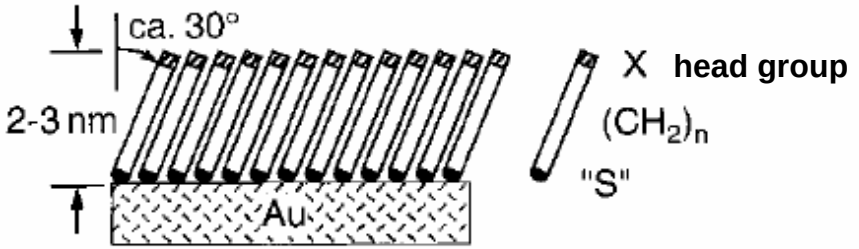
driving force: thermodynamic equilibrium

final structure: determined by the subunits

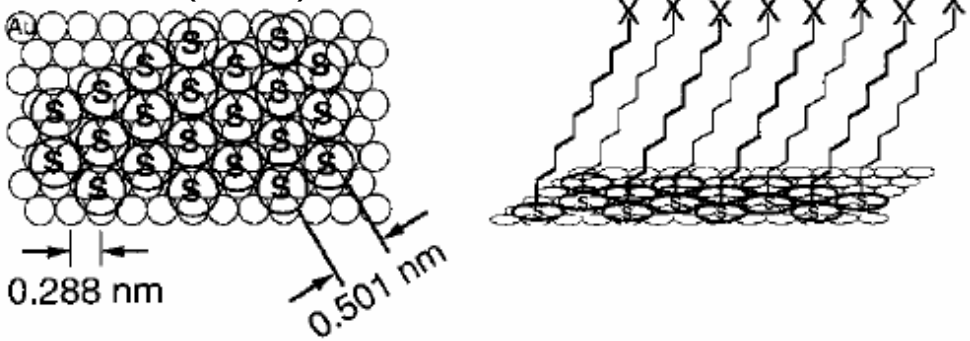
in 3D world of biology: folding of proteins, formation of DNA helix, ...

Self Assembled Monolayers

$$X(CH_2)_nSH + Au^0 \longrightarrow X(CH_2)_nS^-Au^I + 1/2\ H_2$$



(√3x√3)R30° structure



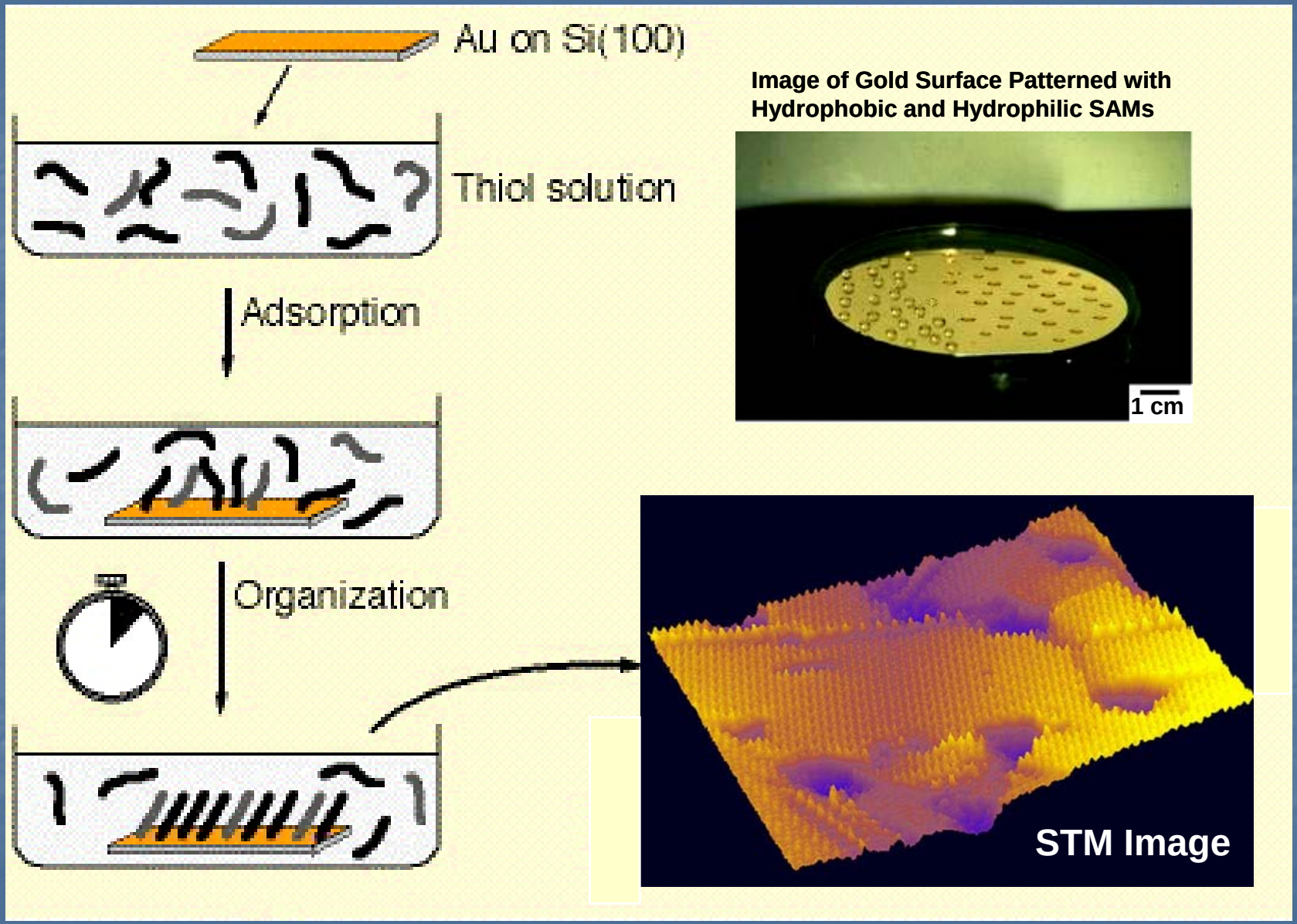
chemisorption and self-organization of long-chain organic molecules on flat substrates

alkanethiolates $CH_3(CH_2)_nS^-$

Au (111)

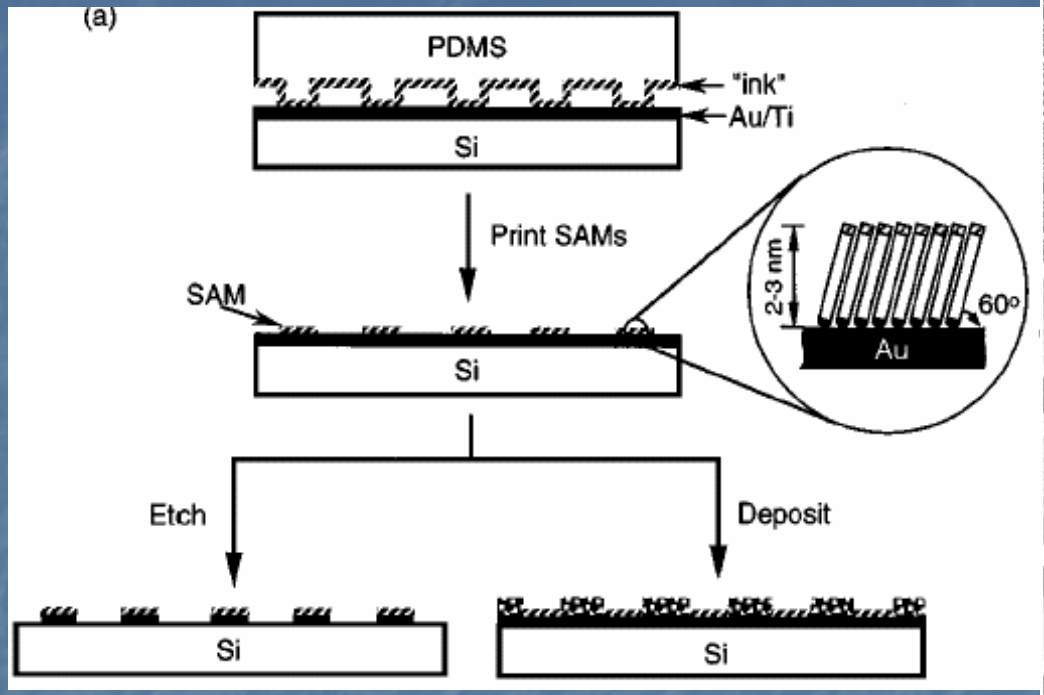
Laibinis, Whitesides, et al. JACS 1991, 113, 152

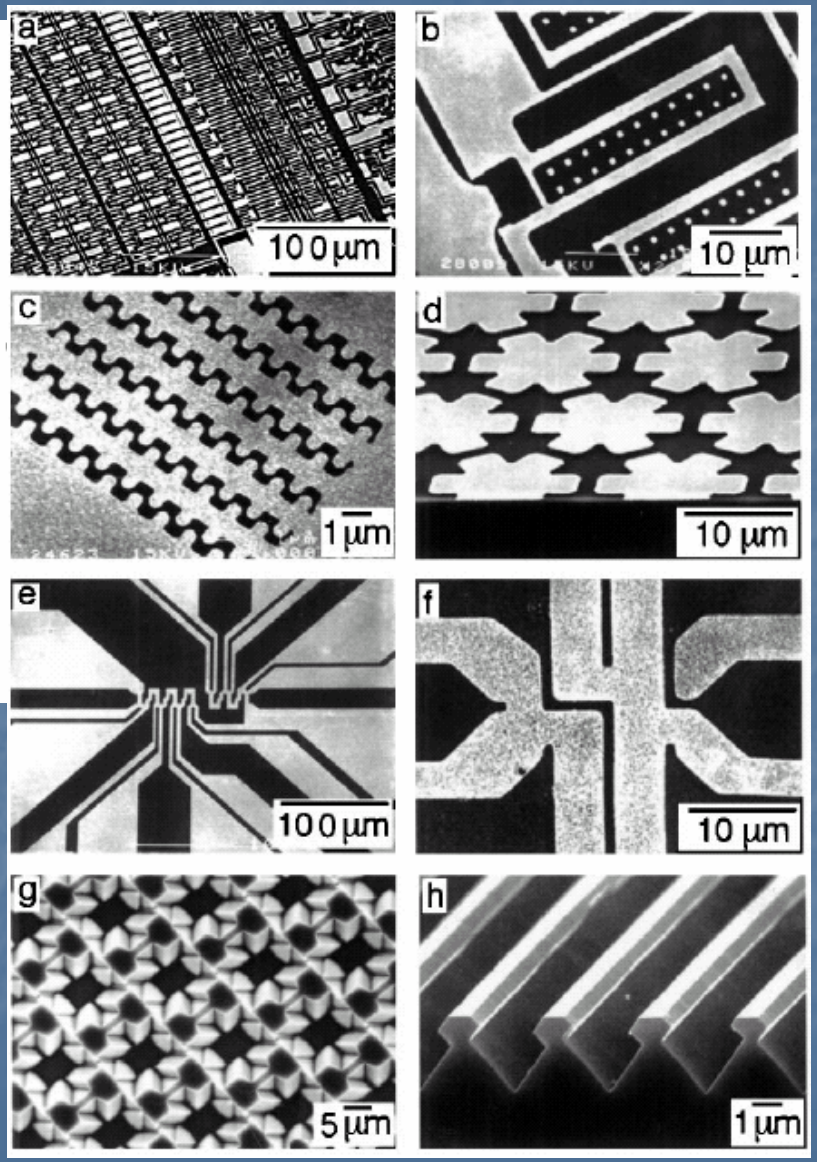
How to obtain SAMs

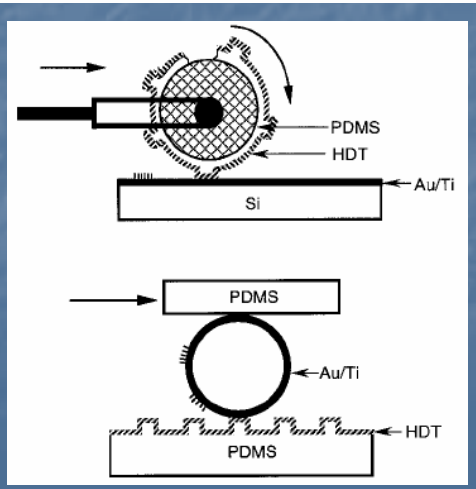


Xia, Y.; Whitesides, G. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 550.
Michel, B.; Bernard, A., et al. *IBM J. Res. & Dev.* **2001**, *45*, 697.

Microcontact Printing







a-c: Silver,
e: Gold,
f: copper

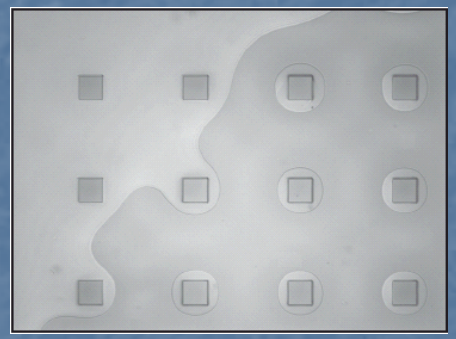
a, b: rolling stamp

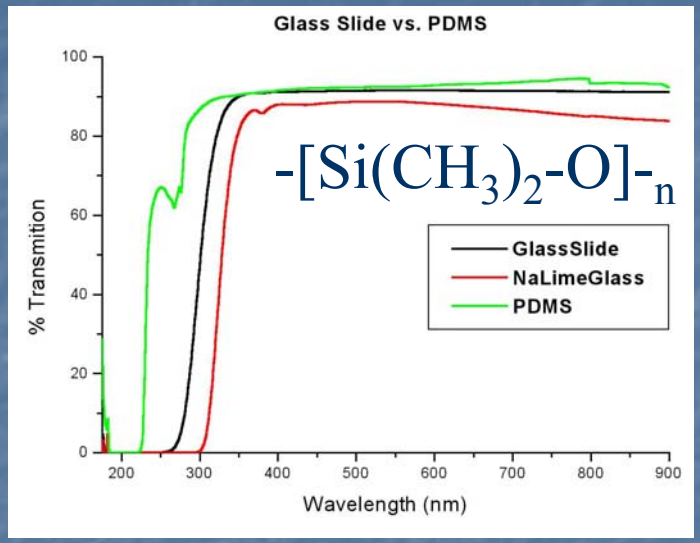
g, h: metal as etch mask for silicon

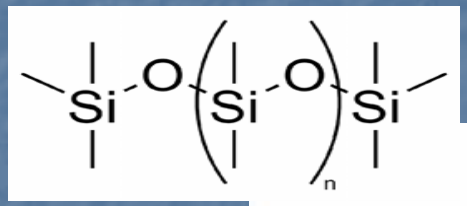
Xia, Y.; Whitesides, G. M. *Ann. Rev. Mater. Sci* **1998**, *28*, 153.

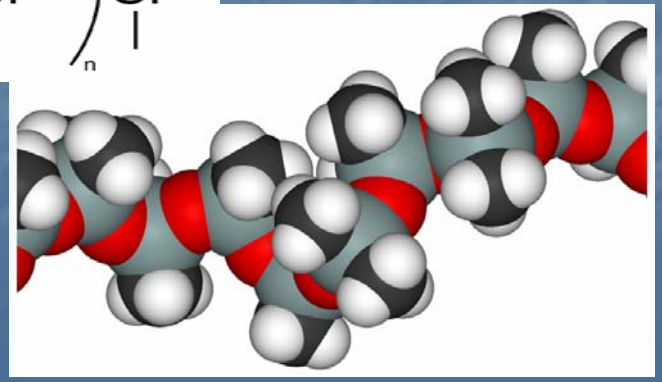
The Core Material of Soft Lithography

Poly(dimethyl-siloxane)



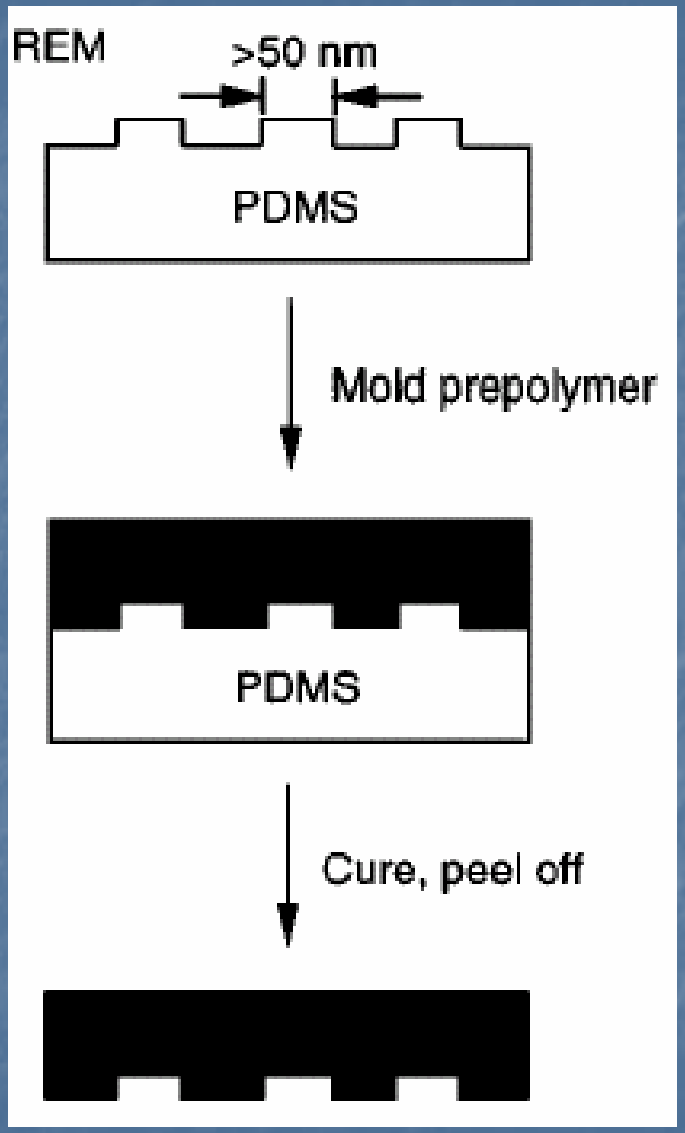


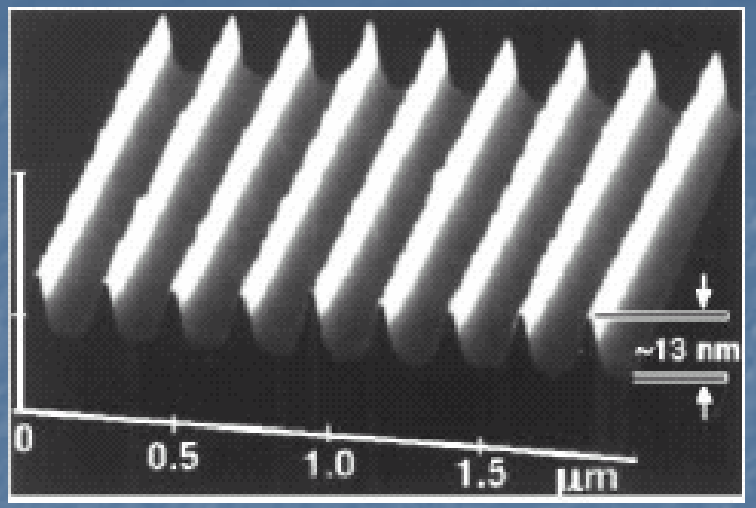




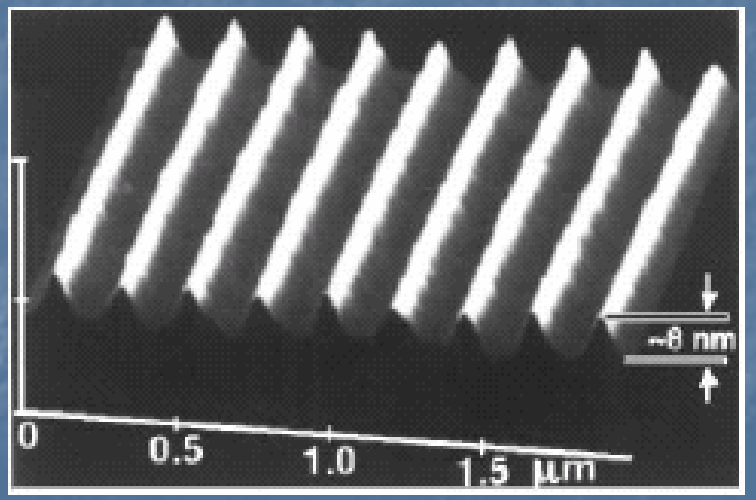
- Transparent
- Low Thermal Expansion
- Chemically Inert
- Environmentally Safe
- Reusable for patterning
- Best Resolution: 2-10 nm

oldest & easiest Soft Litho: Replica Molding (ReM)





PDMS master



PU mold

Xia, Y.; Whitesides, G. M. *Ann. Rev. Mater. Sci* **1998**, *28*, 153.

Masters & Molds / Stamps

Master fabrication:

E-Beam FIB

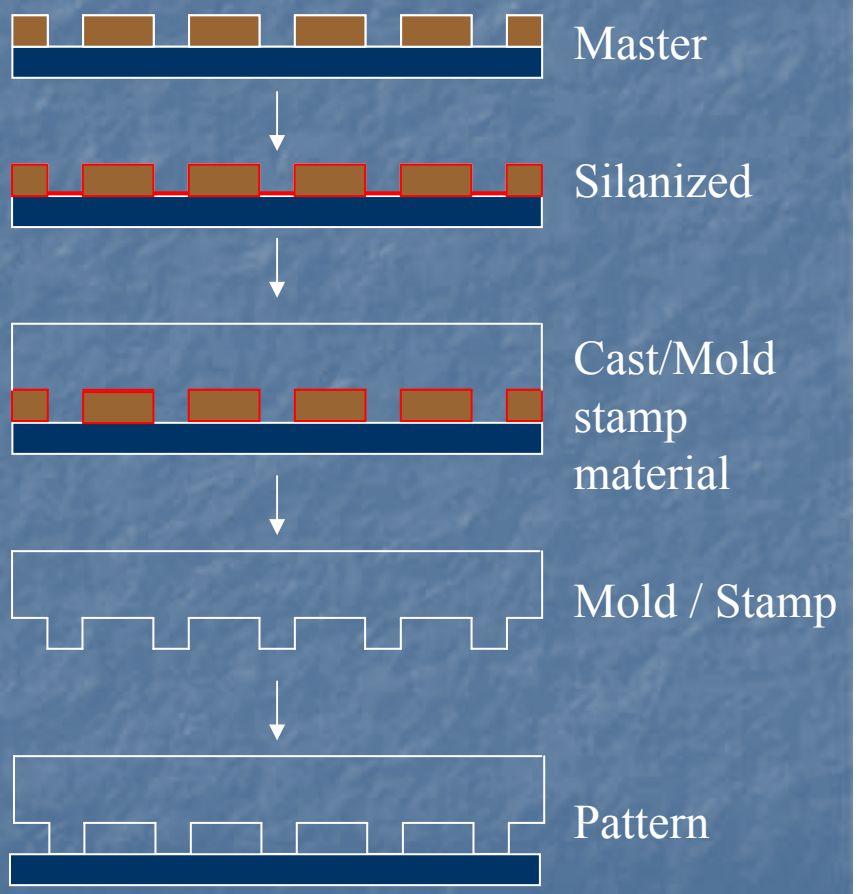
Photolithography Micromachining

Holography SPM lithography

Mold / Stamp fabrication:

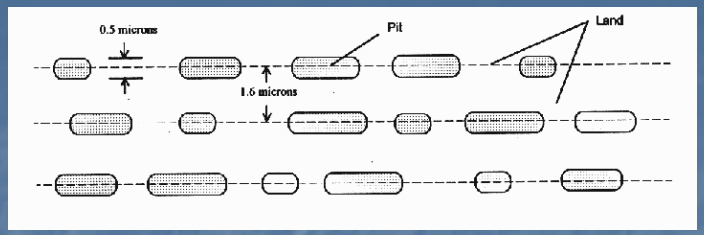
Replica molding

Advantages:
- keep Master safe
- tune material to application: PDMS, PC, …



Rapid Prototyping

CD micro-imprinting: Soft Litho ante litteram

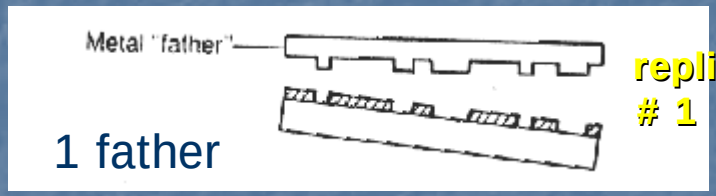


top-view
of the pits

K. Pohlmann, The Compact Disk Handbook, A-R Editions, 1992

photo
lithography

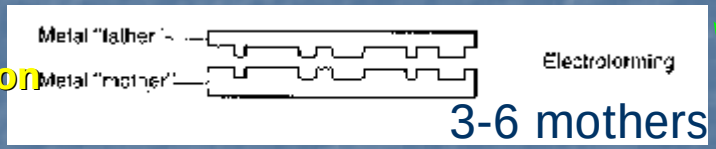
1 master



1 father

replication
1

replication
#2

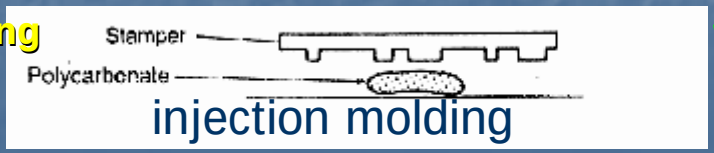


3-6 mothers

3-6 sons (stampers)

replication
3

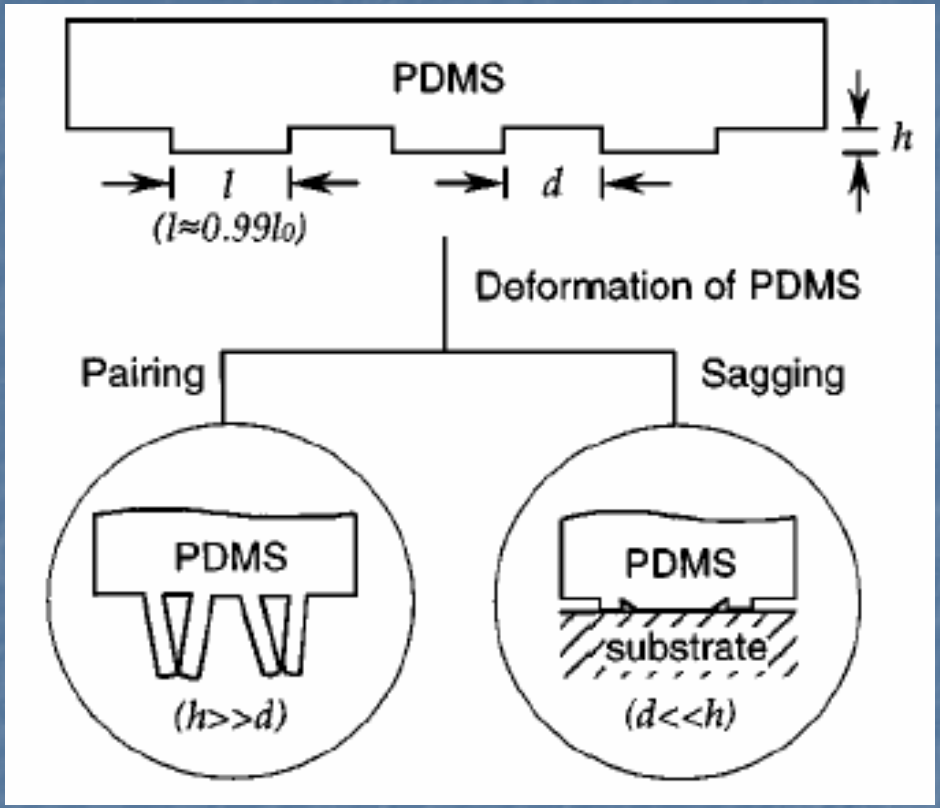
embossing



injection molding

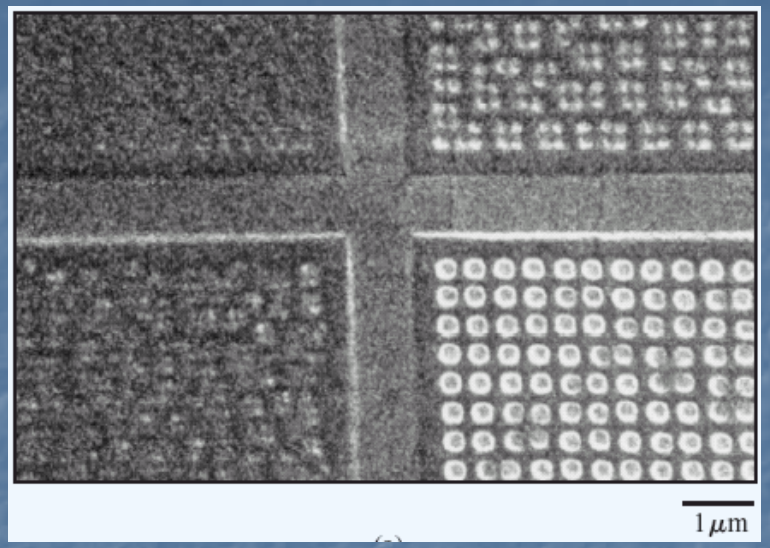
50-100 nm Al or Ag (Au)
10-30 μm acrylic

μ-contact printing problems

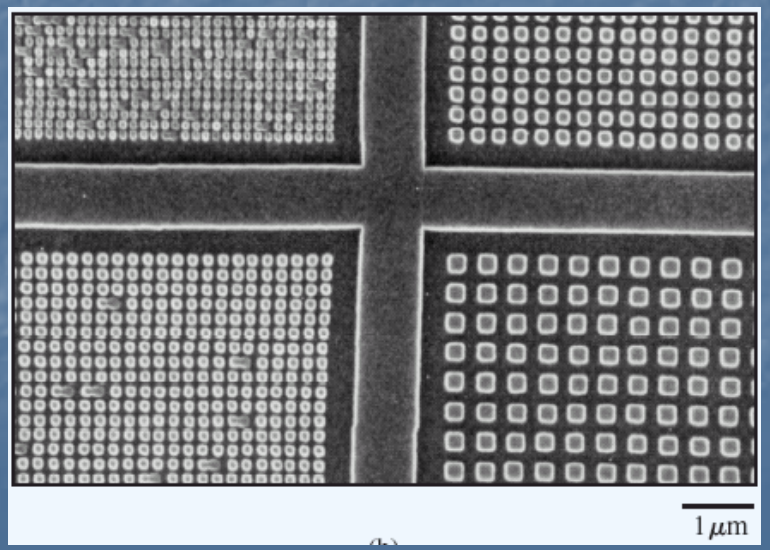


(h/l) range is 2.0-0.2 d≥20h

d (.2-20 μm); h (.5-200 μm); l (0.5-200 μm)



Sylgard 184



h-PDMS

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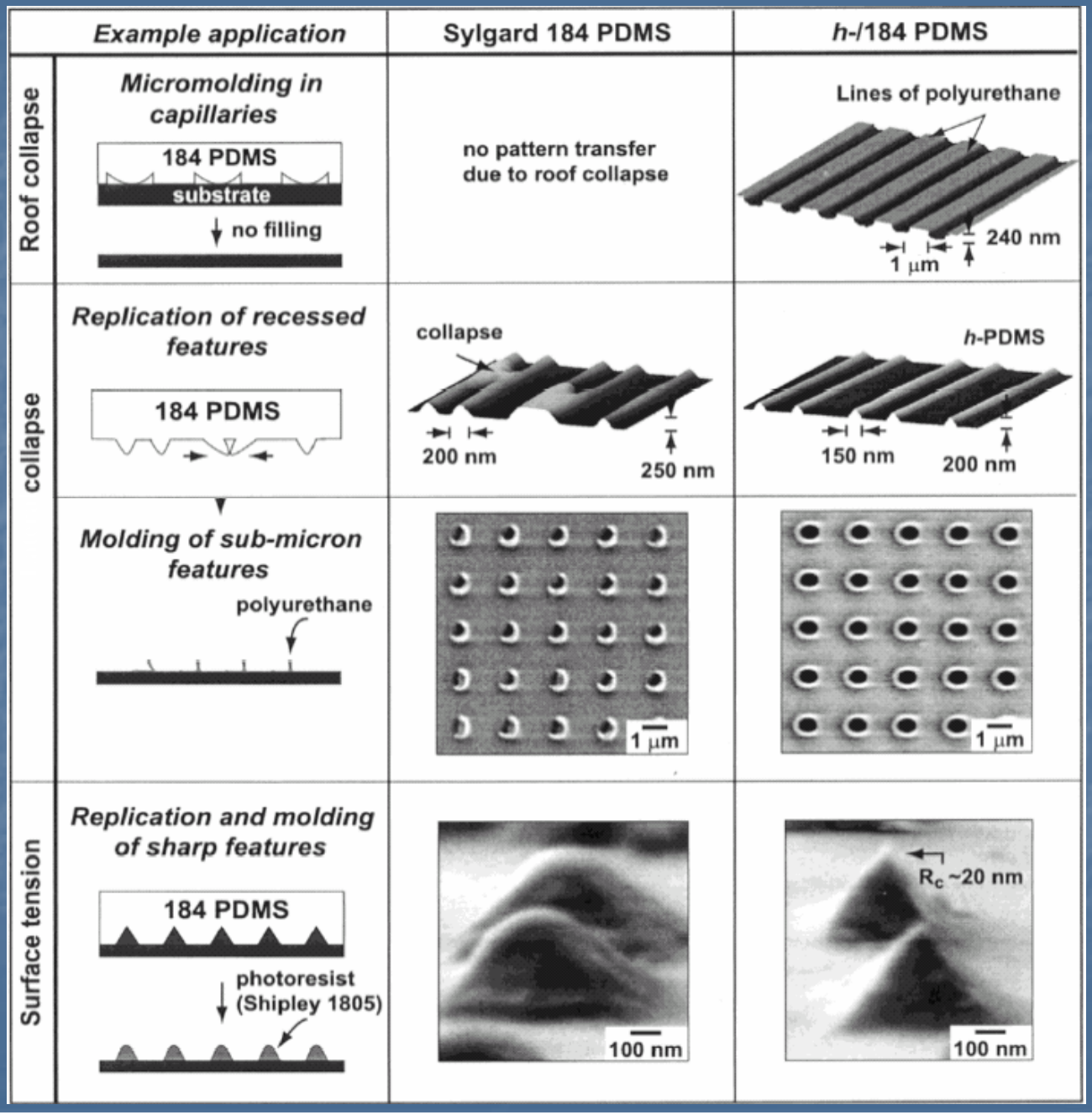
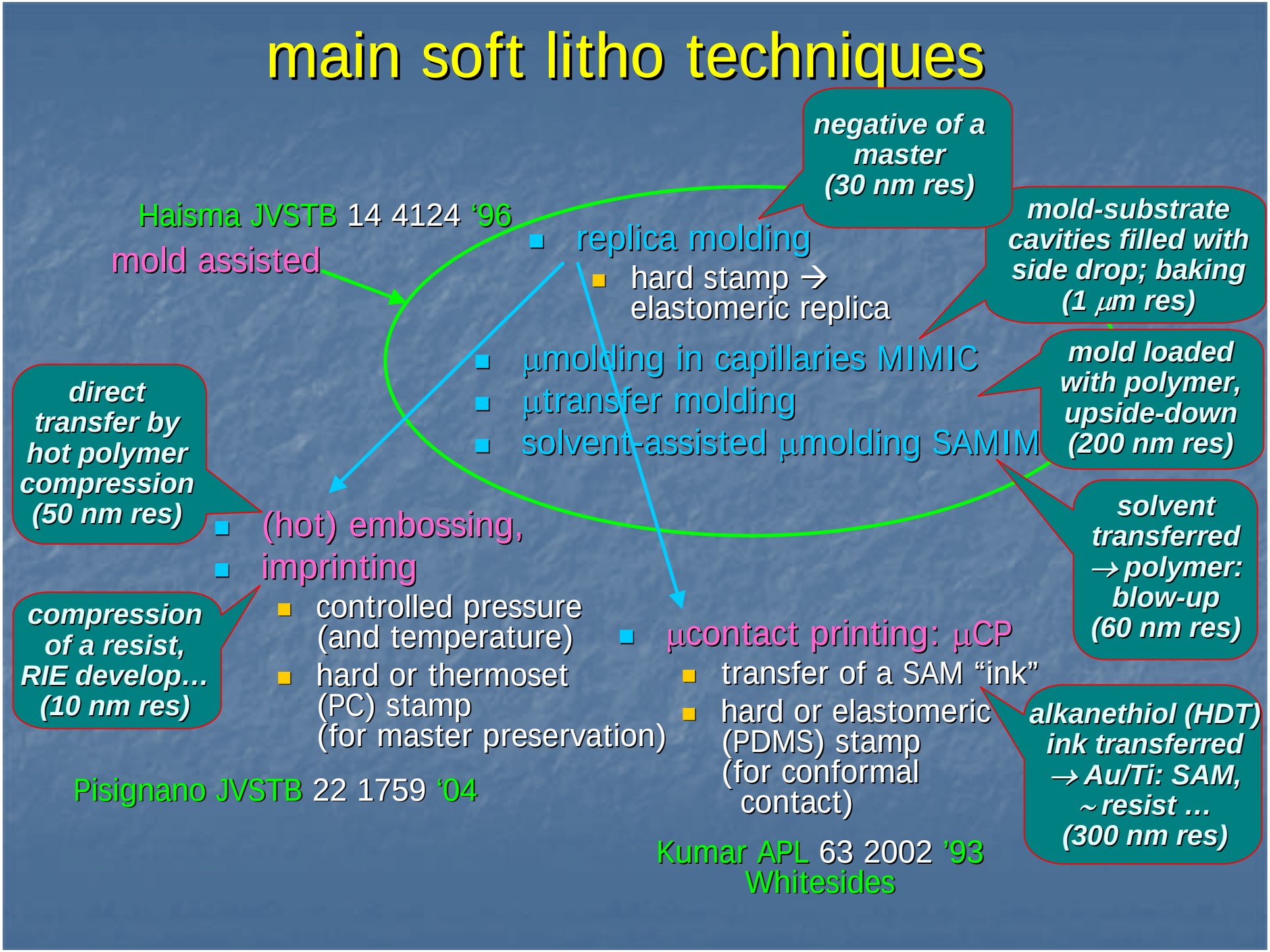
Improved Materials

Odom, T. W. et al. *Langmuir* **2002**, *18*, 5314.

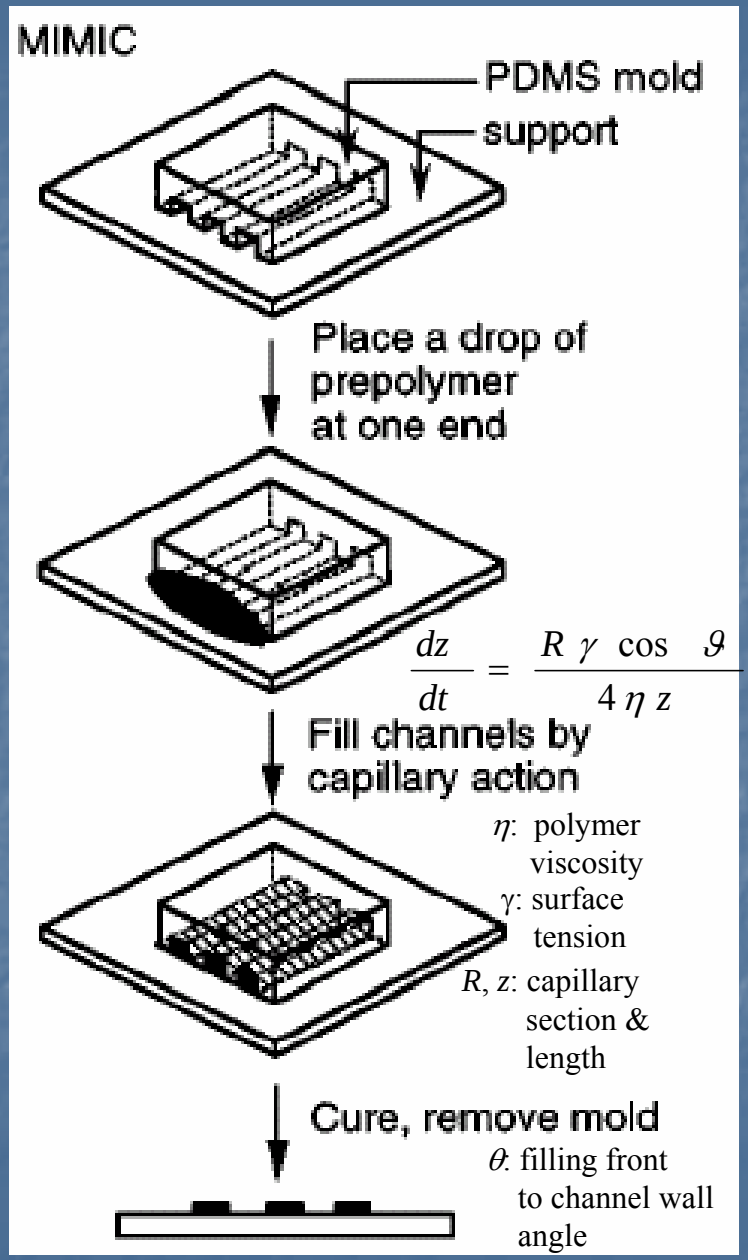


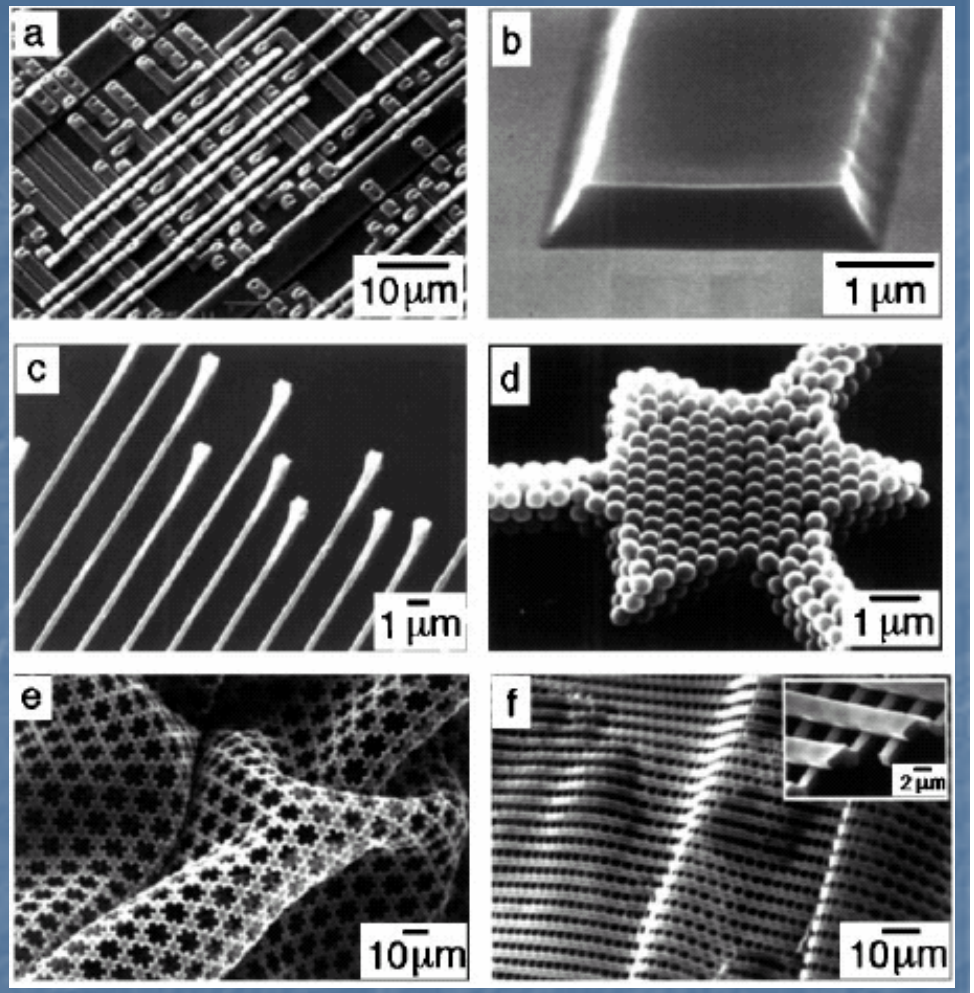
hard PDMS, E_{Young}: ~2→~2000 MPa

main soft litho techniques



MicroMolding in Capillaries (MiMIC)





a: PU on Si
b: polyaniline
c: ZrO_2
d; polystryene colloids
e+f: free standing PU

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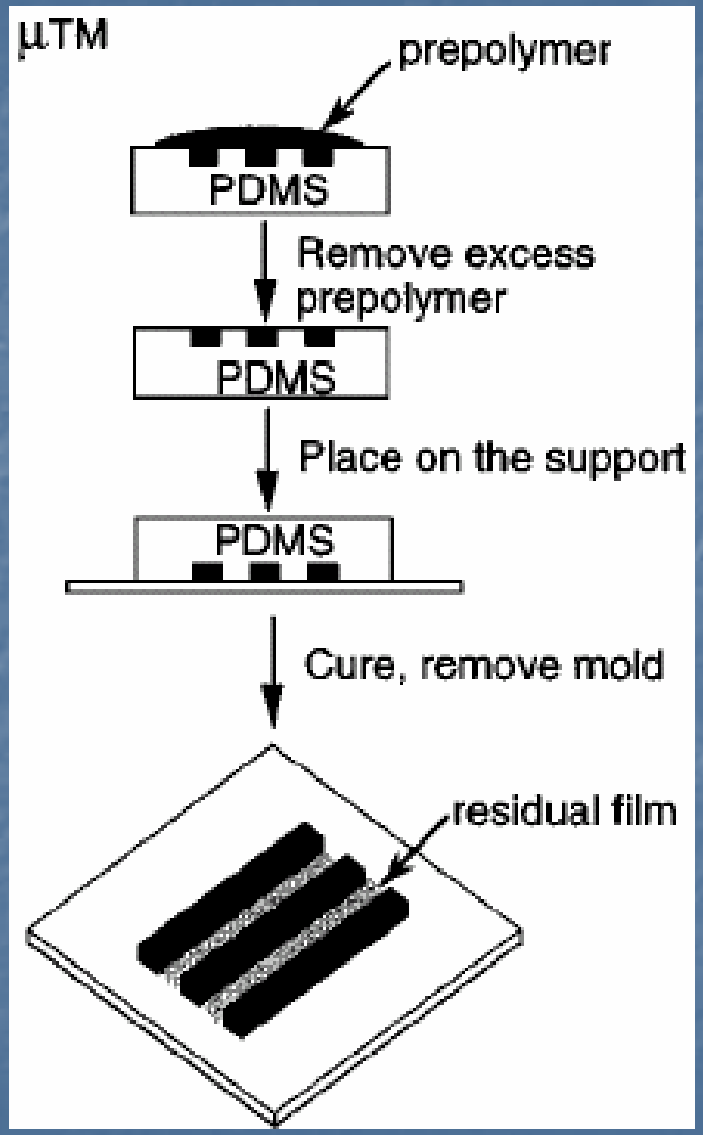
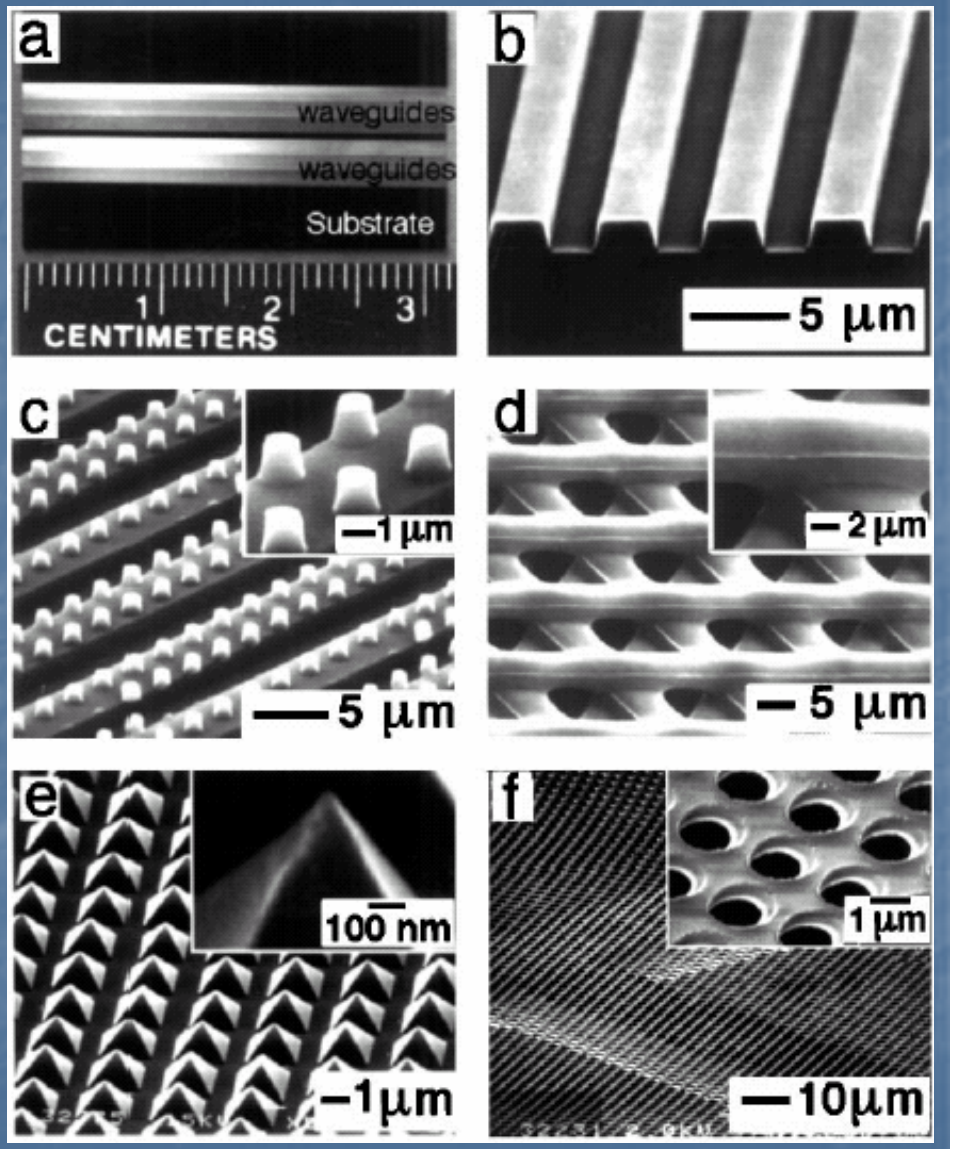
MicroTransfer Molding (µTM)





a+b: PU c+d: epoxy e+f: solgel

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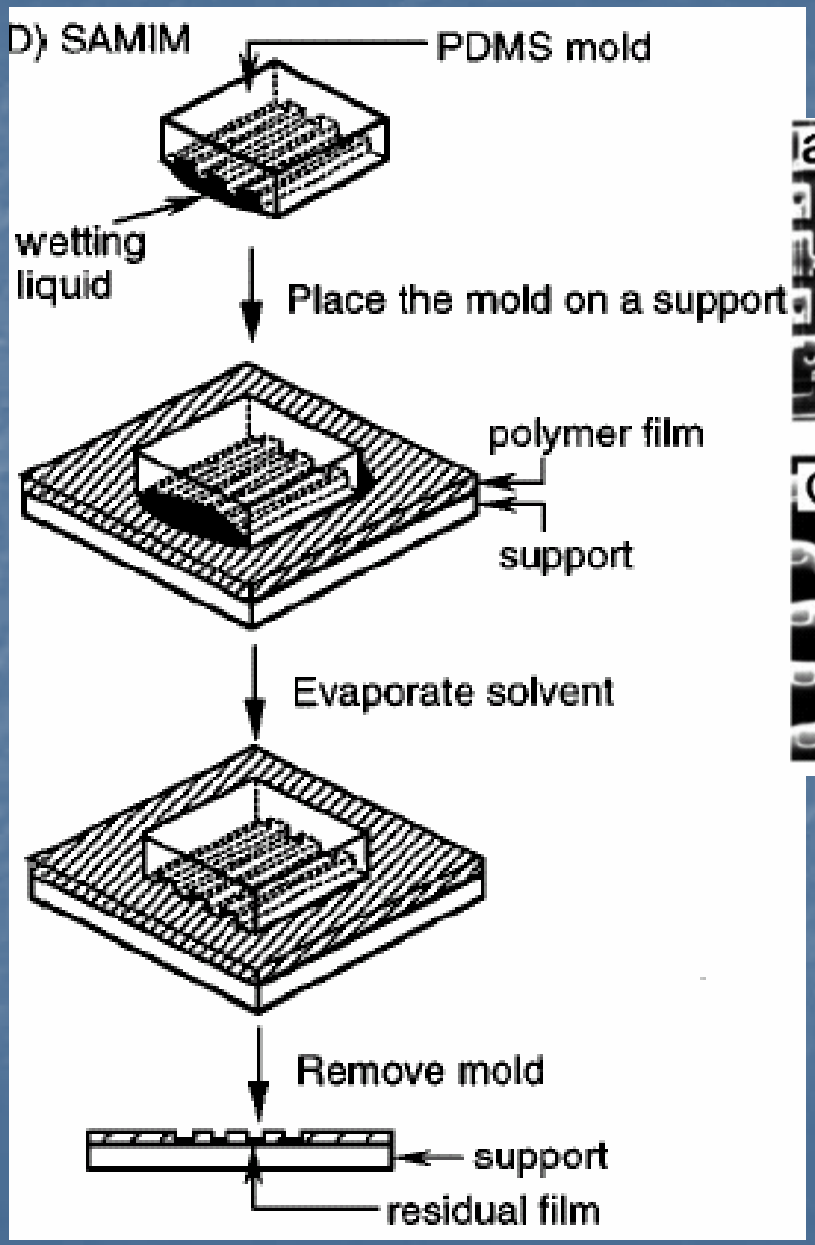
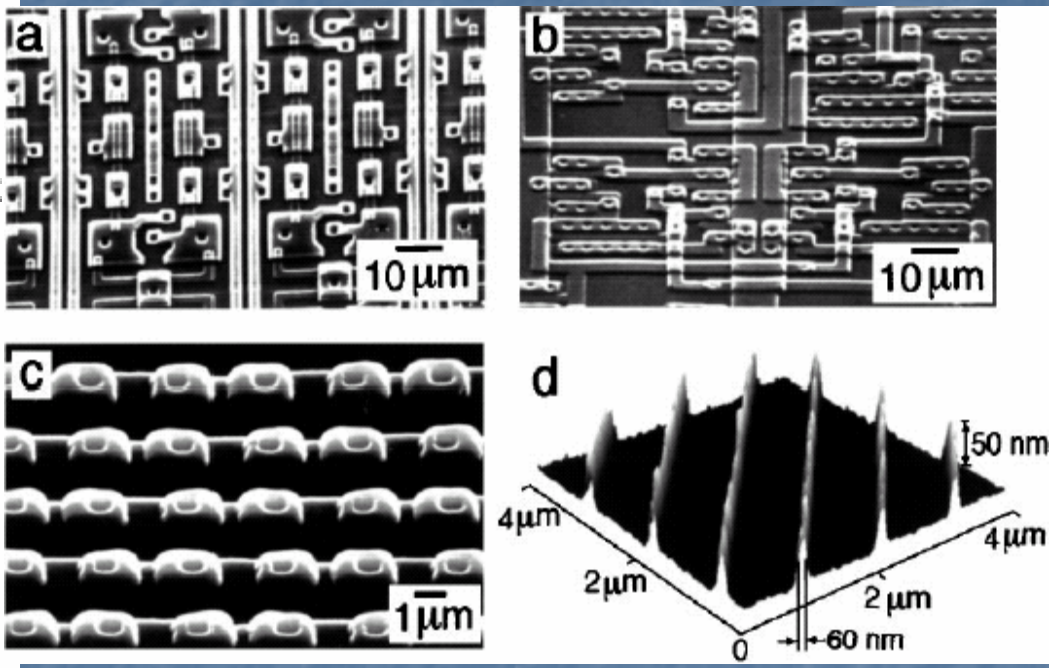
Solvent Assisted MicroMolding (SAMiM)





photoresist on
a: SiO_2
b: polystrene
c: ABS

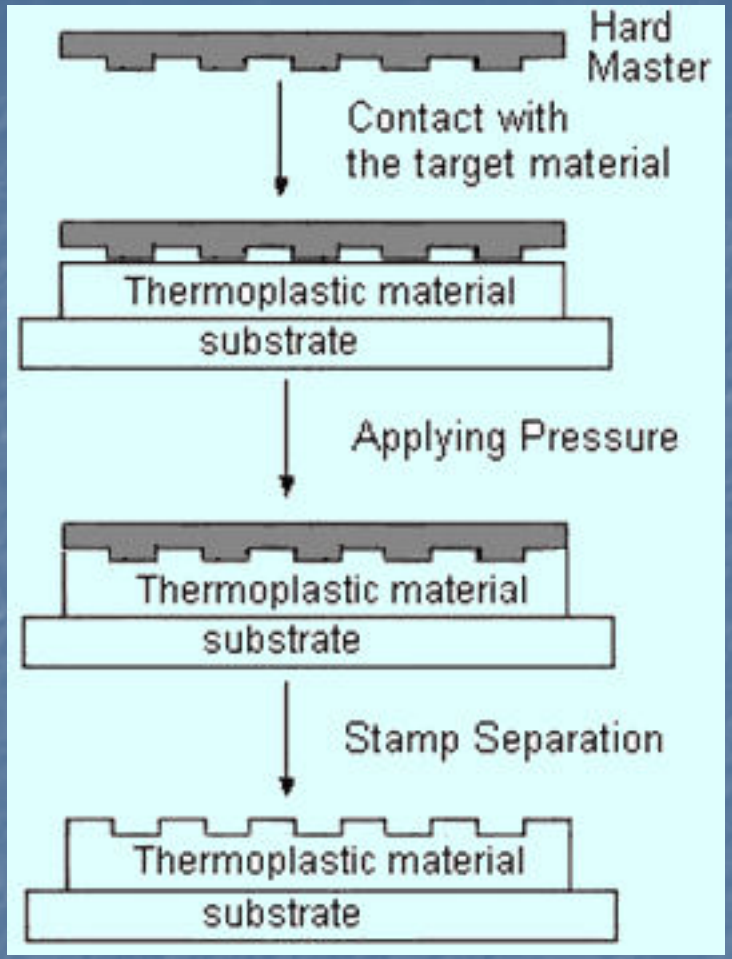
Xia, Y.; Whitesides, G. M. *Ann. Rev. Mater. Sci* **1998**, *28*, 153.

NIL (or HEL)

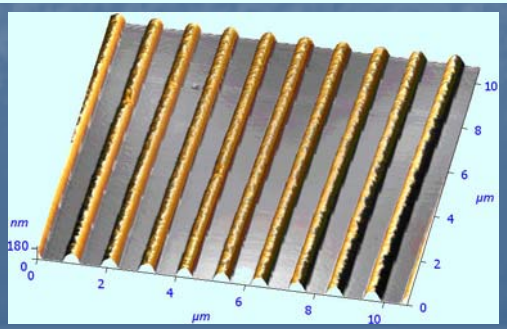
in PMMA (T_g~105 °C):

NIL: patented technique (1998 US) by Chou
APL 67 3114 '95, Science 272 85 '96
~200 °C, ~130 bar <~1900 psi
holes 25 nm diam., 120 nm period
trenches 60 nm width, 100 nm depth
lines 50 nm width, 175 nm gap, 150 nm height
a.r.=3 collapsed

HEL: by Jaszewski
μeE 41/42 575 '98
MW 25k-500k
thickness 50-300 nm
130-160 °C, 20-100 bar, few minutes



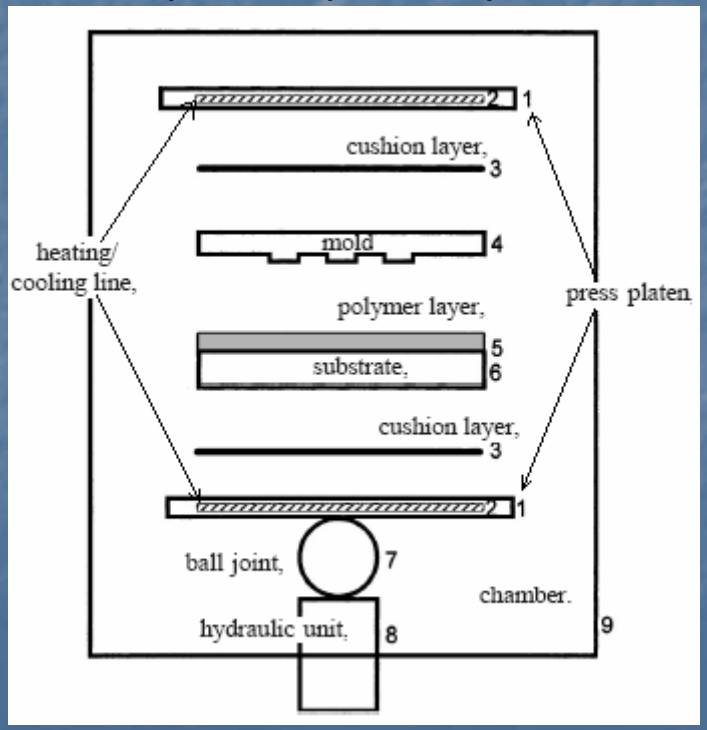
+ transfer of 20 nm dots/lines into Ni on Au substrate demonstrated (better than EBL!)
- master-target separation (use OTS)
- imprinted film residual layer on the substrate



Pressing tool

- "home-made" or professional (isobaric demolding)
- usually fast heating/cooling not necessary
  (some 10 minutes, but also: shock cooldown by liquid N_2!)
- usually vacuum not necessary (but helps remove air bubbles and water vapor from interface)

- large areas
  - ball-joint for parallelism
  - cushion layers against unflatness
    (uneven pressure)

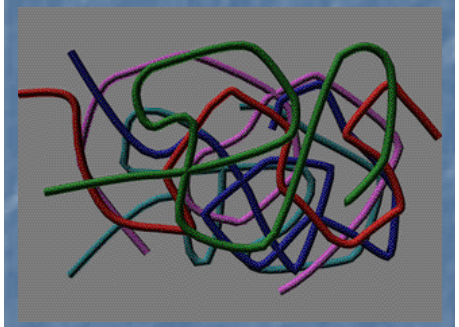


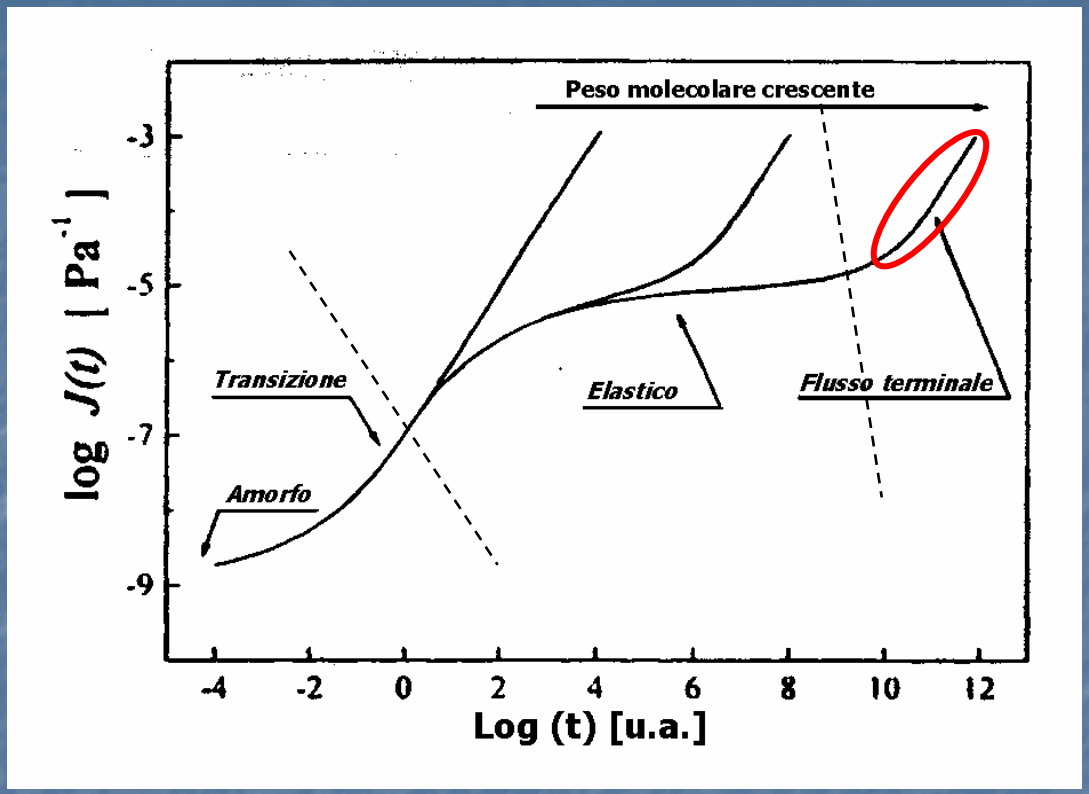
Obducat "Eitre2"

(Nanonex, Suss Microtech, ...)

Elastic regimes in time on compression

compliance J:
~1/E,
adaptation to
mechanical stress





viscous fluid:
imprinting regime

similar to phase transition :
3 regimes of reaction

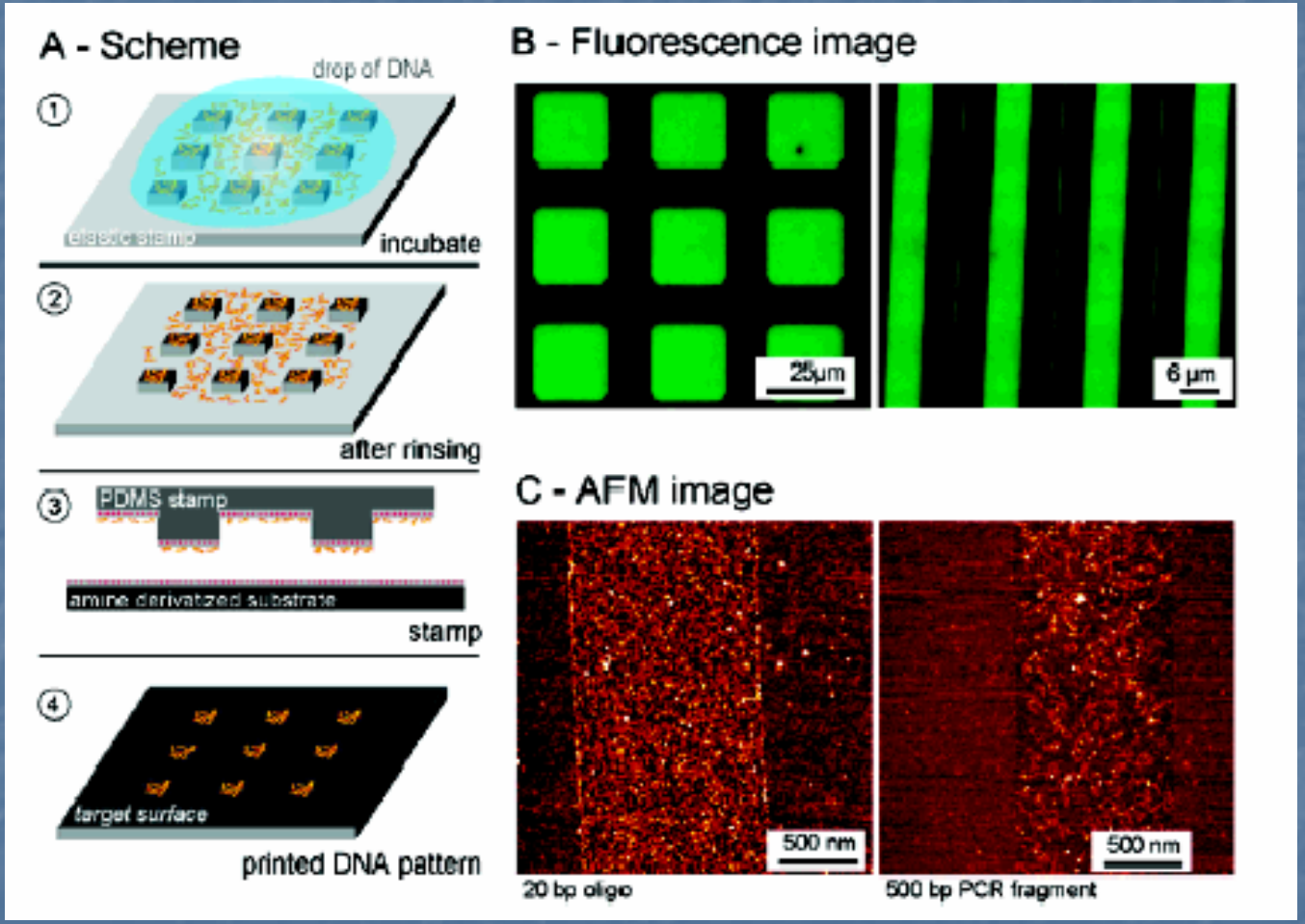
since the difference in time scales is of orders of magnitude,

to observe the different regimes one has to **operate on T**

$MW \rightleftharpoons \tau_C \rightleftharpoons T_g$

thermoplastic behaviour of polymers depends mainly on MW

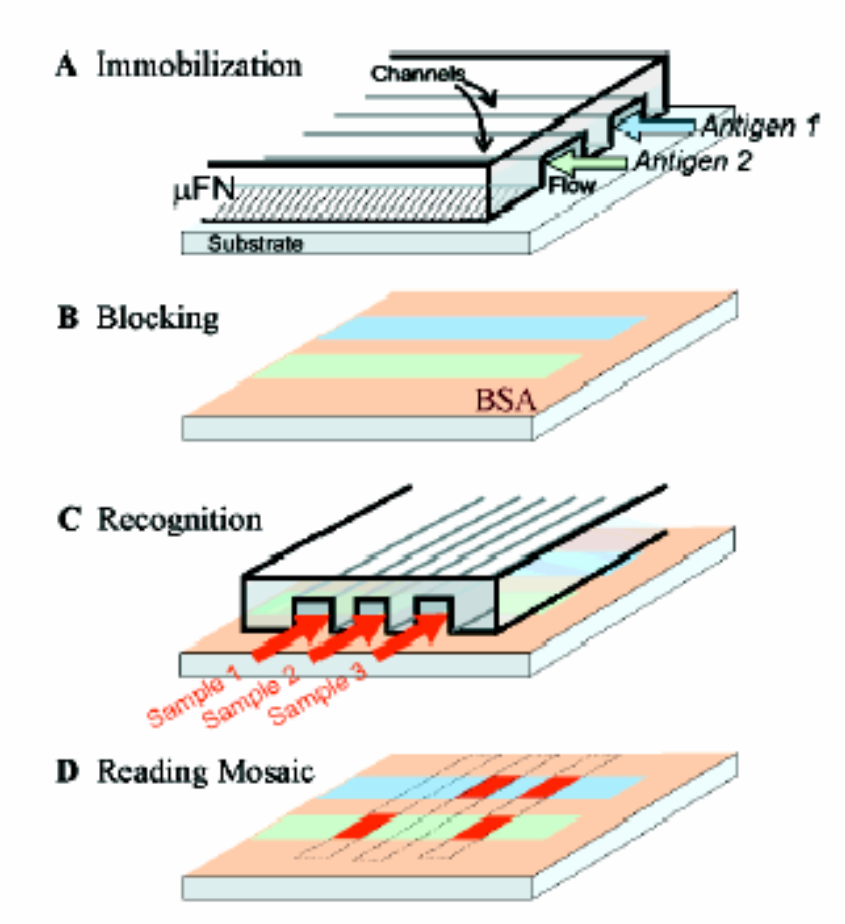
Microcontact Printing DNA, Proteins

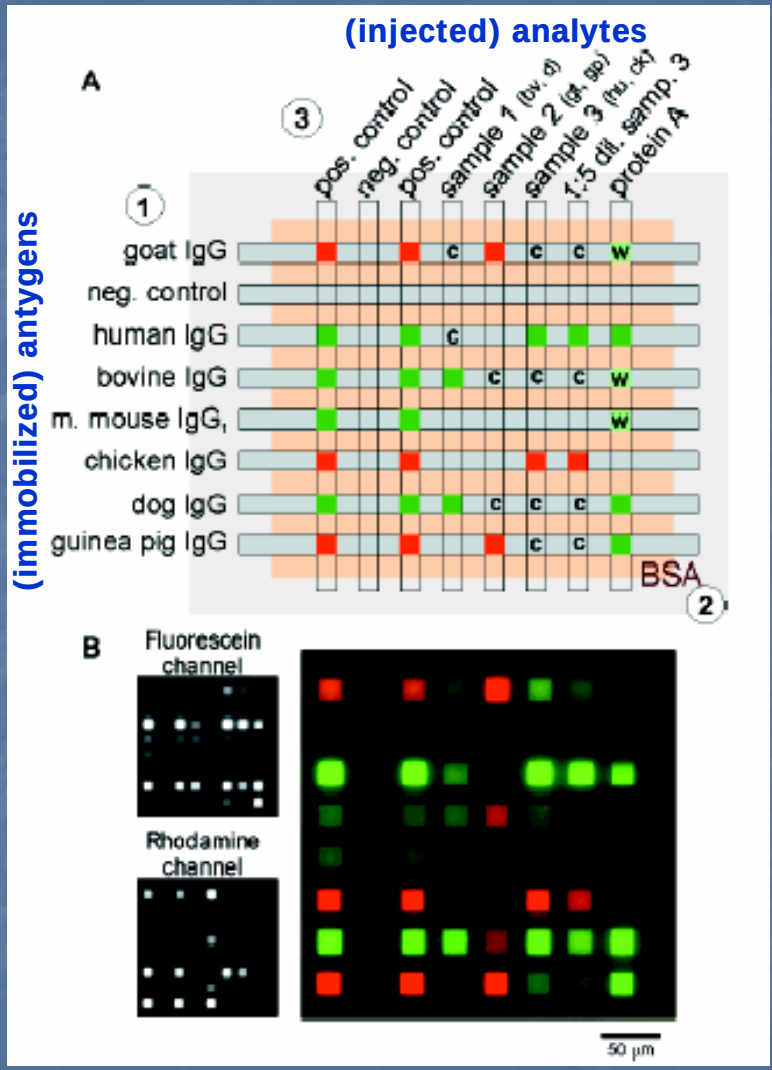


S.A. Lange, V. Benes, D.P. Kern, J.K.H. Horber, A. Bernard, *Anal. Chem.* **2004**, 76, 1641.

H. Wolf et al. *IBM Journal of Research & Development*. **2001**, 45, 697.

Mosaic Immunoassays

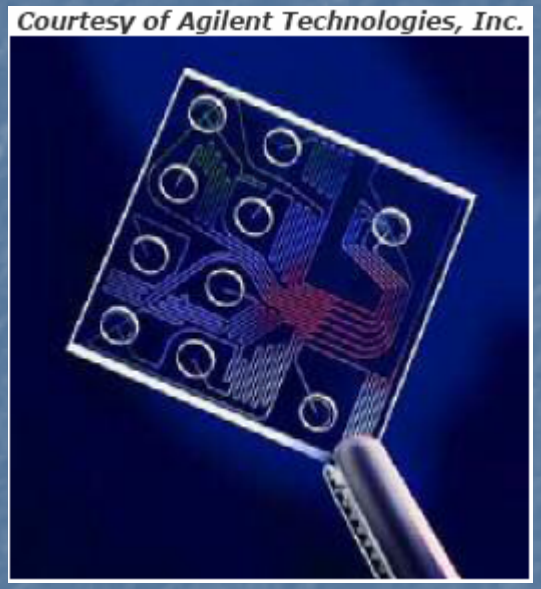




A. Bernard, B. Michel, E. Delamarche, *Anal. Chem.* **2001**, 73, 8

→ *economy of reagents and time*

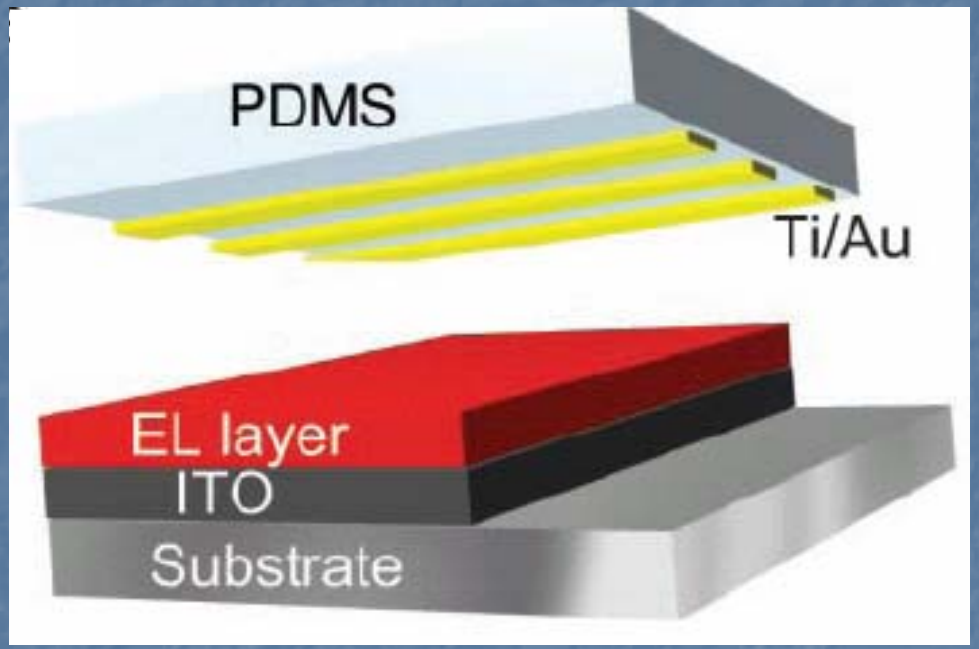
Lab on a Chip



- goal: to automate & speed up lab analysis normally made by humans
- miniaturized means portable & disposable (health care, terrorist attack reply, ...)
- no conducting wires as in electronic relatives
- → channels, to be designed 3D
- no pumps/valves, but by V:
- electrophoresis: moves ions in the fluids (different speed for different mass)
- electro-osmosis: works on thin layers of ions at the wall interface, & moves all column
- Affymetrix's "GeneChip", Agilent's "LabChip"

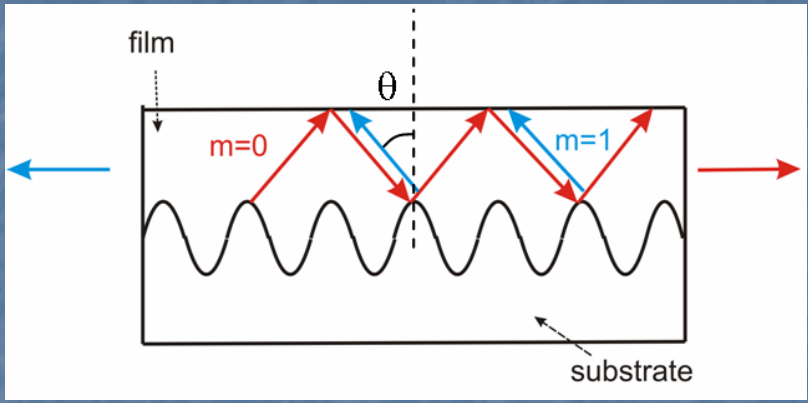
Organic Light Emitting Diodes

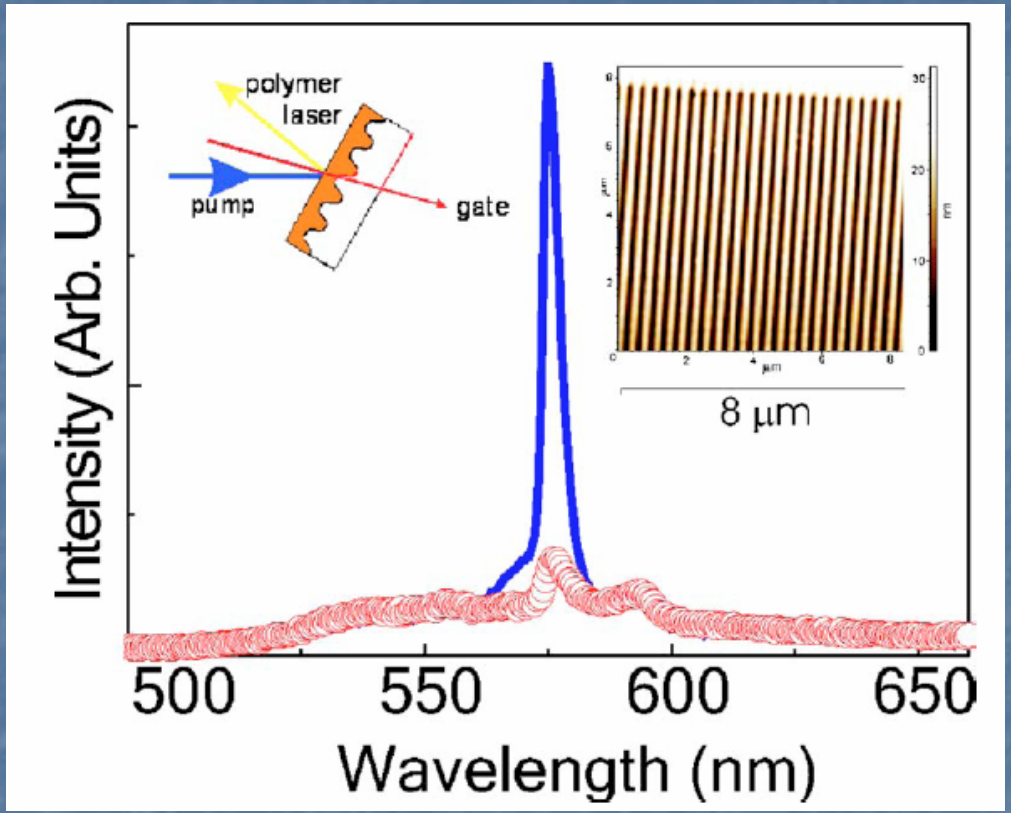
- Soft contact lamination provides a means for establishing electrical contacts at room temperature in ambient conditions
- Applications:
  - Conformable light sources
  - Nanoscale optoelectronics

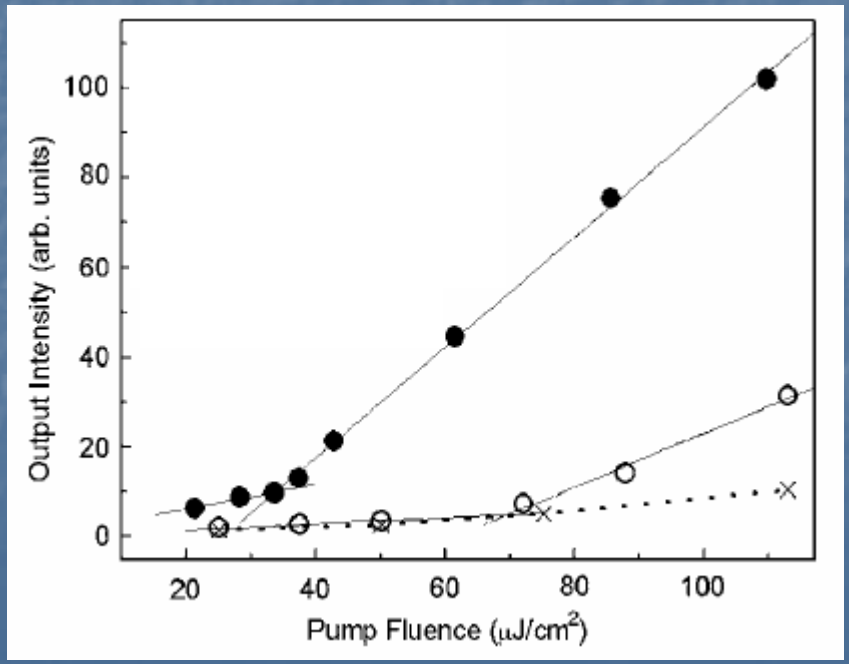


Lee, T., *et.al.,PNAS* **2004**, *101*, 429.

Distributed Feedback Lasers

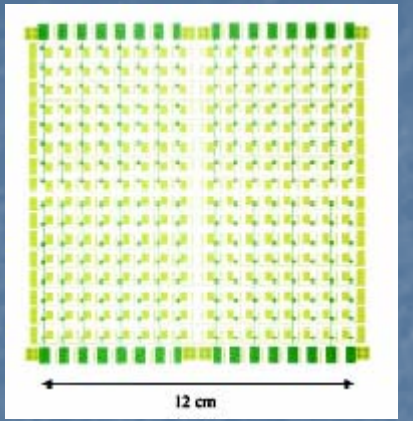


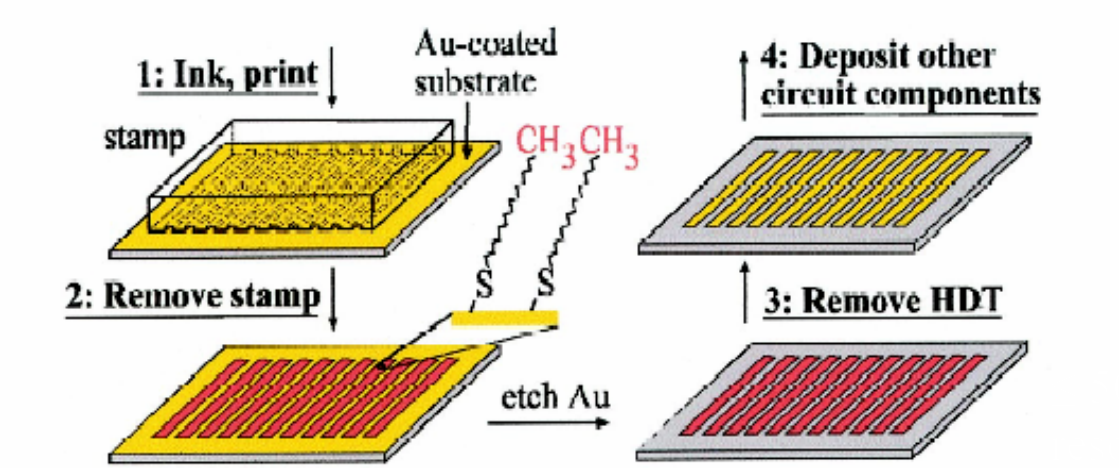




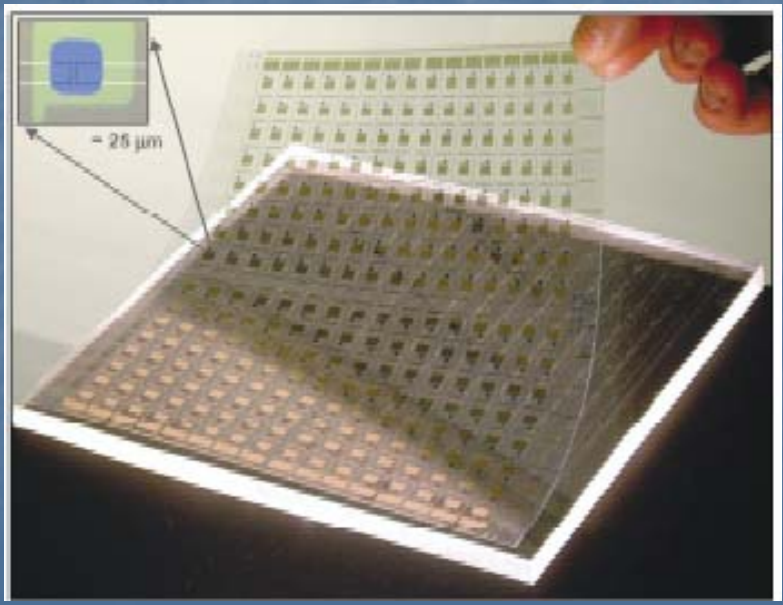
- hot embossing (NIL) or even RT embossing (for low MW active materials, olygomers)
- planarization of patterned (quartz) substrate (lower n contrast i.e. higher lasing threshold)

μ-contact Printing made Electronic Paper





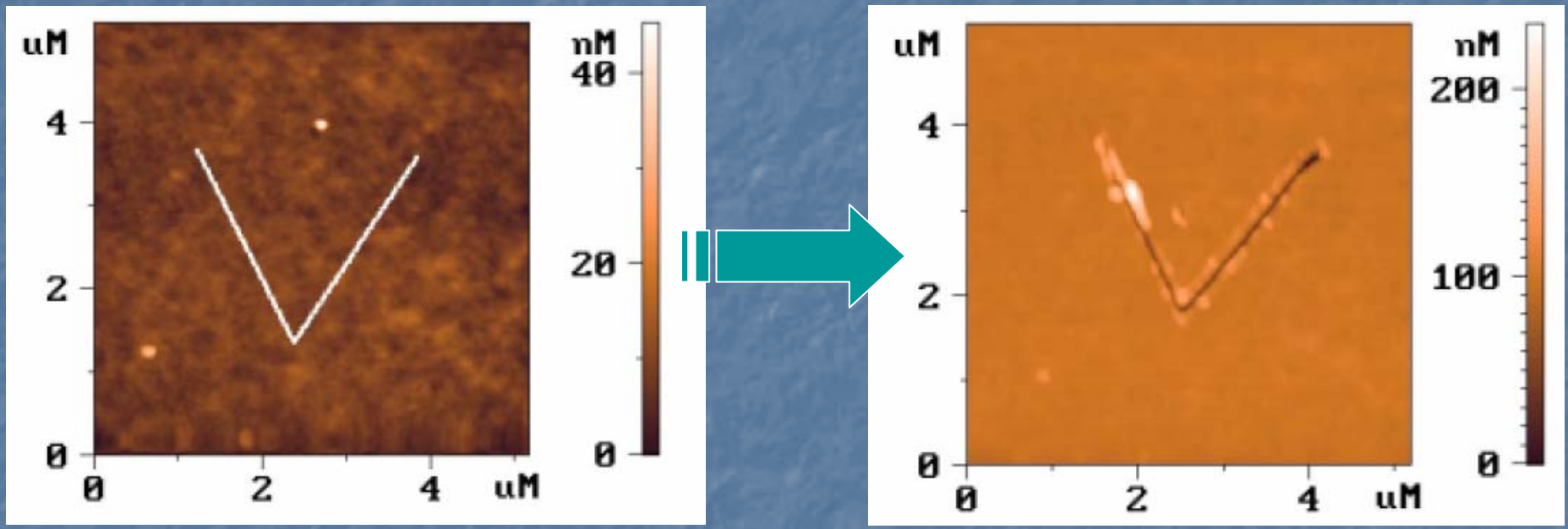
0 nm
olution



Dodabalapur, A.et.al. *Appl. Phys. Lett.* **1998**, *73*, 142-144.
Rogers, J. A. et. al. *Proc. Nat. Acad. Sci. USA* **2001**, *98*, 4835-4840.

AFM “lithography”

vector scan ploughing

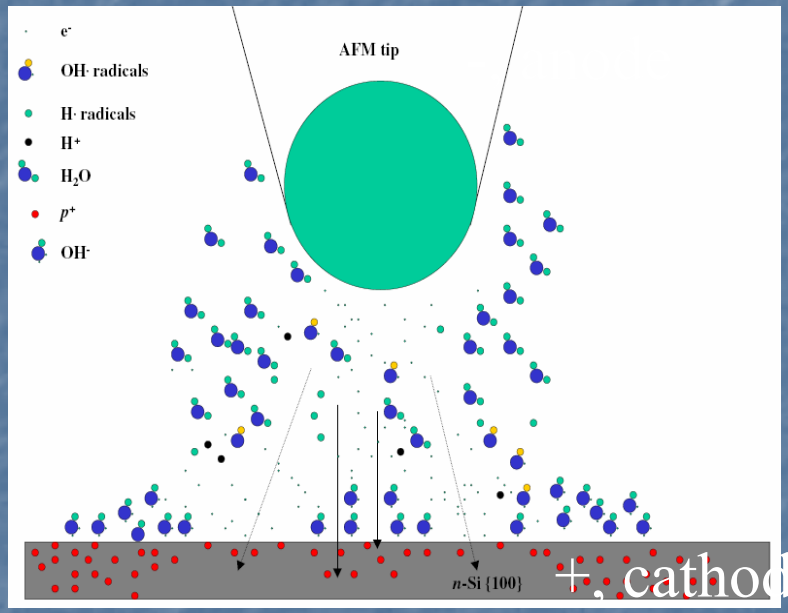


- subtractive
- hardly uniform (dragged matter!)
- convolution effects (edge ripples)

AFM Local Anodic Oxidation

in air we have adsorbed water at the surfaces
→ electrically induced chemical transformation

$V_{tip} < V_{sample}$

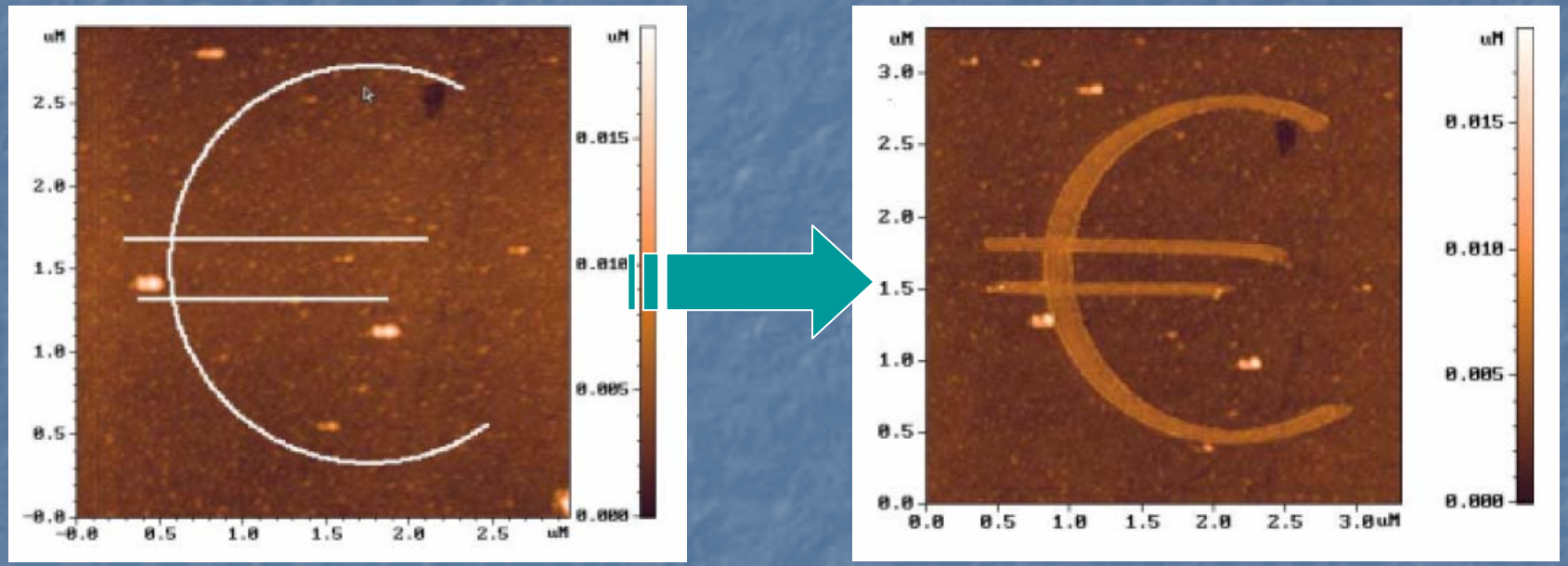


at tip: $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$
at Si: $Si + 2OH^- - 4e^- \rightarrow SiO_2 + 2H^+$
net EC reaction: Si oxidation

- conducting levers (e.g. Pt coated)
- conducting substrates (e.g. doped Si, thin Ti or GaAs)

- T-AFM imaging with low A
- pulsed electrical bias

lithographic vector scan in Anodic Voltage lithography



- additive
- less edge problems
- large convolution broadening (meniscus)

AFM Dip Pen Nanolithography

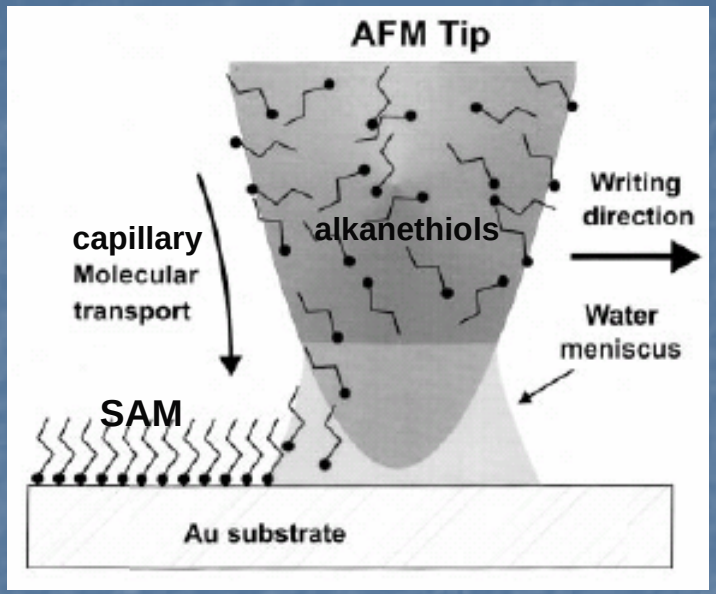
Piner Mirkin
Sci.'99 283, 661

problem of shear force due to adhesion

↓

useful tool

meniscus size : function of RH%, tip area



"paper"- "ink"
chemical affinity required

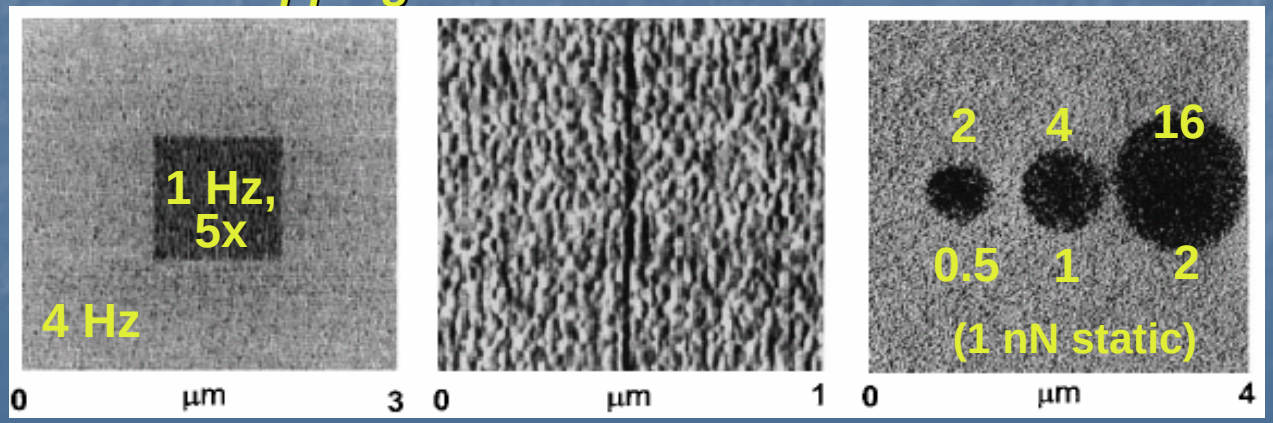
(tip="nib")

~ μ-contact printing
// → Σ

- slow
+ selective writing
(after imaging)
+ no resist litho

after 1 min dipping in acetonitrile sol of OctaDecaneThiol :

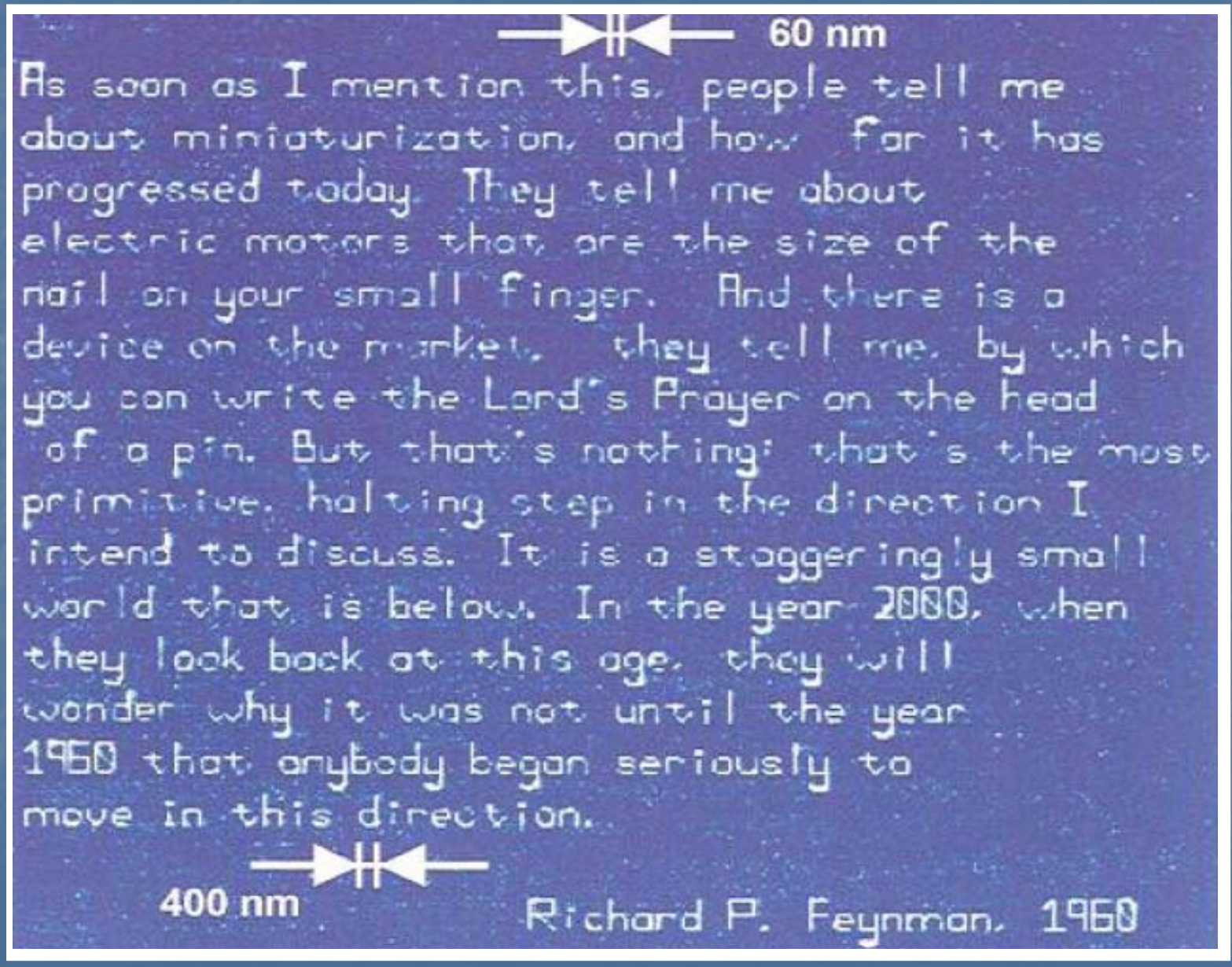
LFM :



: t/min

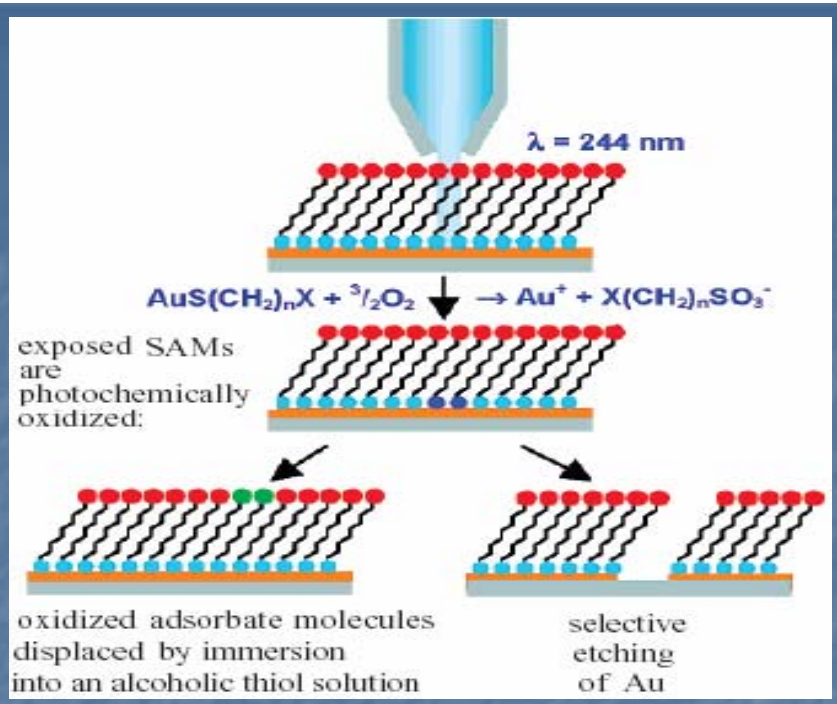
: ∅/μm

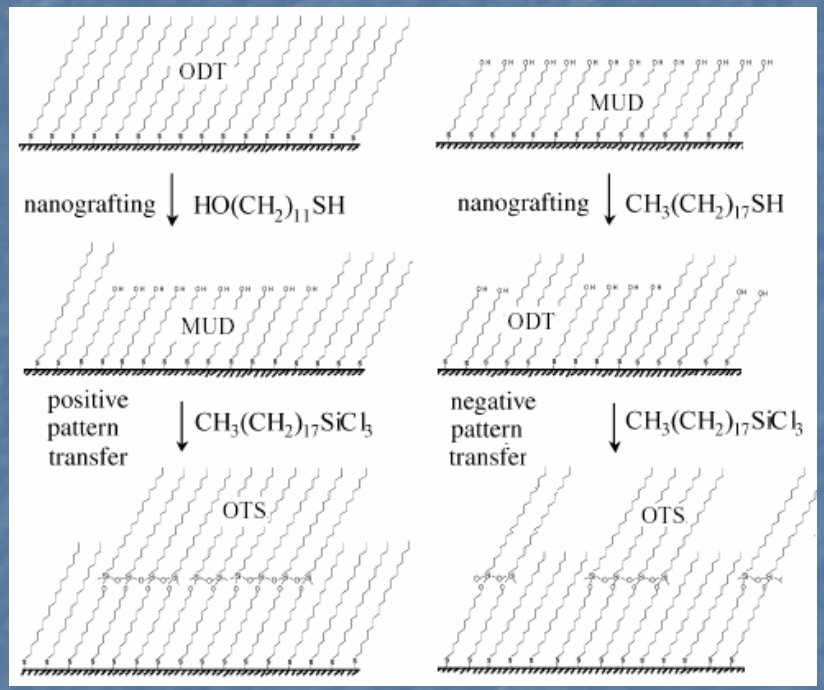
The founding speech of nanotechnology



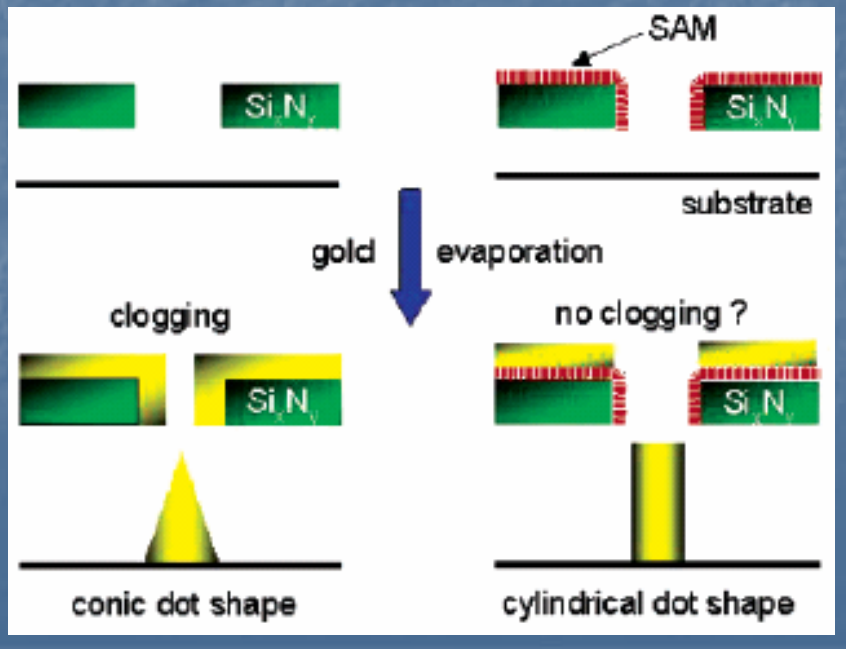
et cetera . . .

SNOM Photolitho (SNFP) :

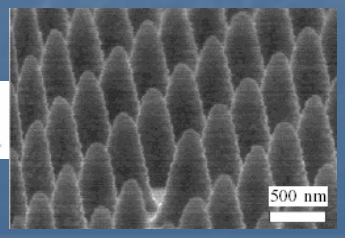




: AFM Nanografting

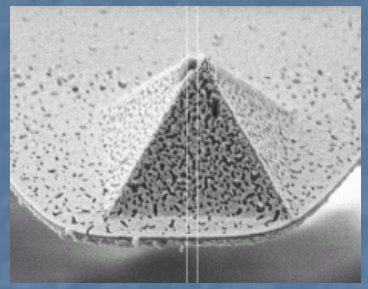


Nanostencil :

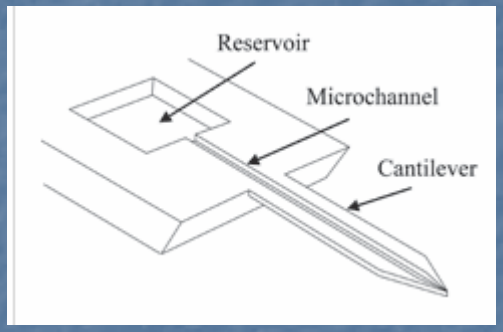


Au dots (1 μm high) by evaporation through a CF−Si(OEt)$_3$-coated stencil

Fountain Pen Nanolithography



by FIB milling… ('93)



commercial product ('07)

BIOFORCE NANOSCIENCES

Nano eNabler™ System

Benchtop Molecular Printer

Technology

Principle: The Nano eNabler™ system is a multifunctional surface patterning platform for dispensing attoliter to femtoliter volumes of biomolecules, nanoparticles and other liquids onto a wide variety of surfaces.

Technical characteristics: Prints spots and lines from 1 to 30 microns, 100msec printing cycle, 20 nm stage resolution, 50 mm XY travel, multiplexing ability.

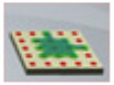
Benefits: Faster and more flexible than conventional technologies; no clogging or misalignment problems, multiplexing ability.

Design. Print. Publish. *Repeat.*

Applications

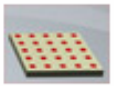
The Nano eNabler™ system allows the deposition of minute quantities of liquids at defined locations with high spatial accuracy and high speed.

The technology opens doors for innovation in various fields of biotechnology, nanotechnology and medicine.

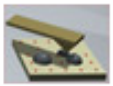


Cell patterning
Direct cell growth and interactions

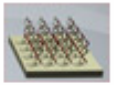
Biosensor functionalization Create novel sensors and devices



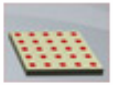
Biomarker screening
From as few as 4 cells



Virus detection
Fast, sensitive non-destructive



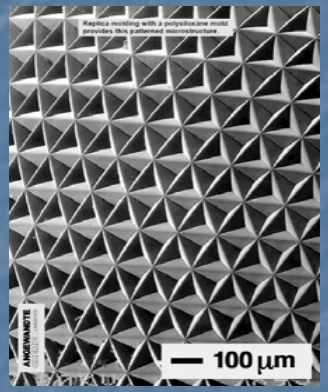
Drug discovery
Fast HTS through multiplexing



Small volume bioassays
Data from 1 µl samples

“Soft” lithography in short

Xia, Whitesides
Angew.Chem.Int.Ed.
37 550 ‘98



- an organic material is used as target, stamp or mold to transfer the pattern
- no radiation

usually additive,
500 μm - 10 nm res

+ no radiation damage,
no diffraction, scattering, etc.
+ little chemistry
+ large scope
+ low cost
+ low substrate planarity required
+ new possible combinations of materials:

parallel but :
- low throughput
- slow

- polymer-semiconductor
- organic semicond.-dielectric
- biological material-oxide
- colloid-glass
- ceramic-metal
- polymer-superconductor …

Thank you !