



**The Abdus Salam
International Centre for Theoretical Physics**



2037-21

Introduction to Optofluidics

1 - 5 June 2009

Fabrication of Optofluidic devices II

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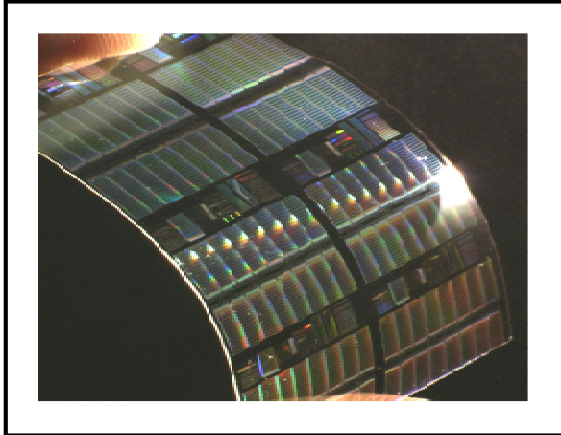
FABRICATION

Massimo Tormen

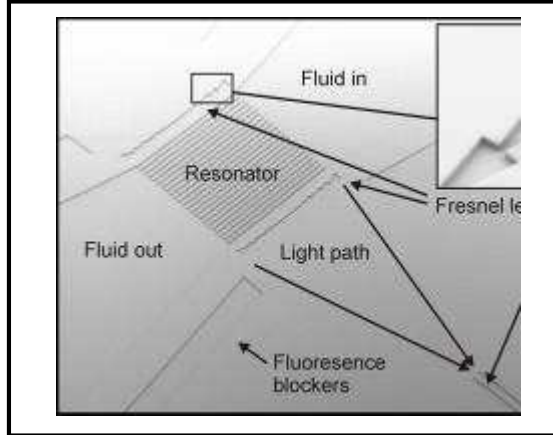
PART II



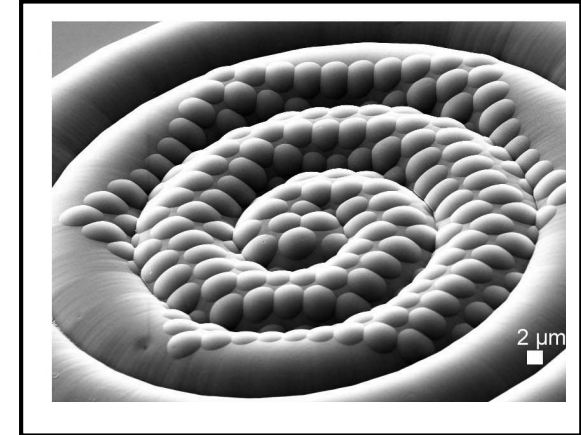
Technology



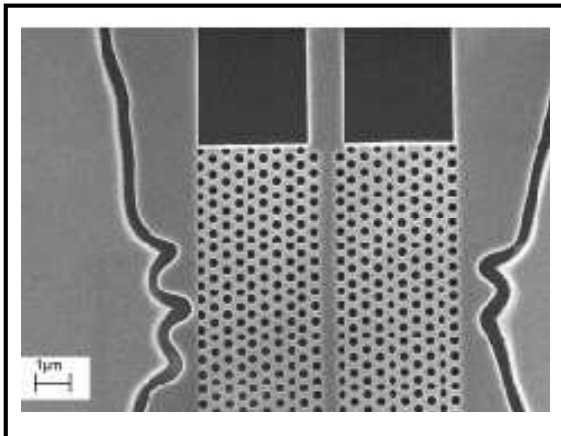
Soft Lithography



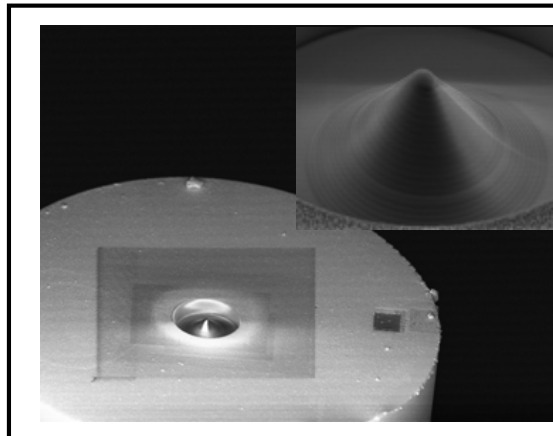
Hot embossing



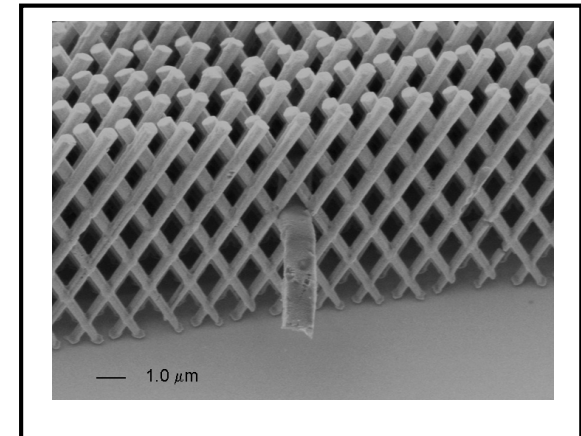
Hybrid approaches



Nanoimprinting



FIB



XRL

Materials & Processes

•Selection of Materials

Mechanical (Young's modulus)
Optical (refraction index)
Thermal (stability)
Chemical (stability)
Wetting (surface energy)
Compatibility with other materials
Compatibility with environment
(cleanroom)



•Selection of the process flow

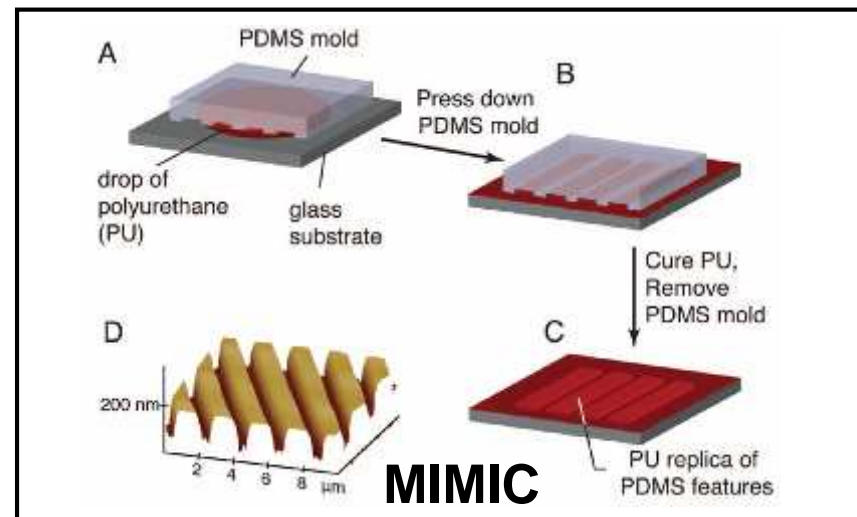
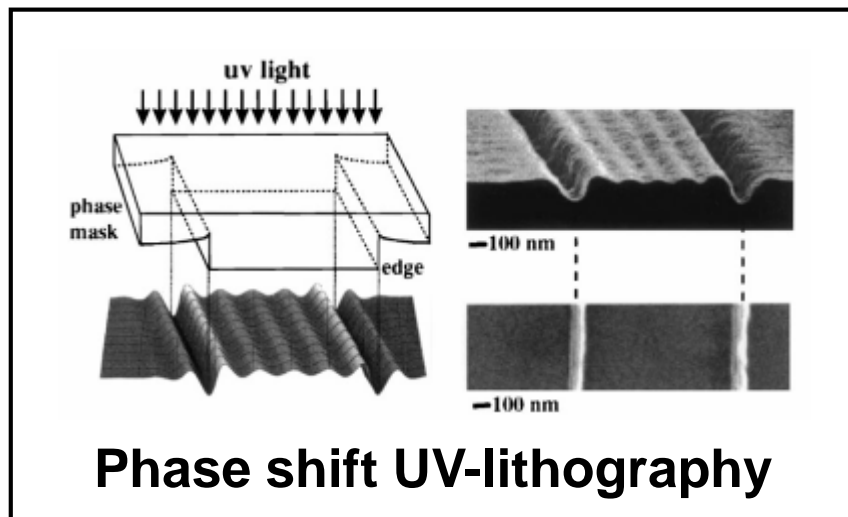
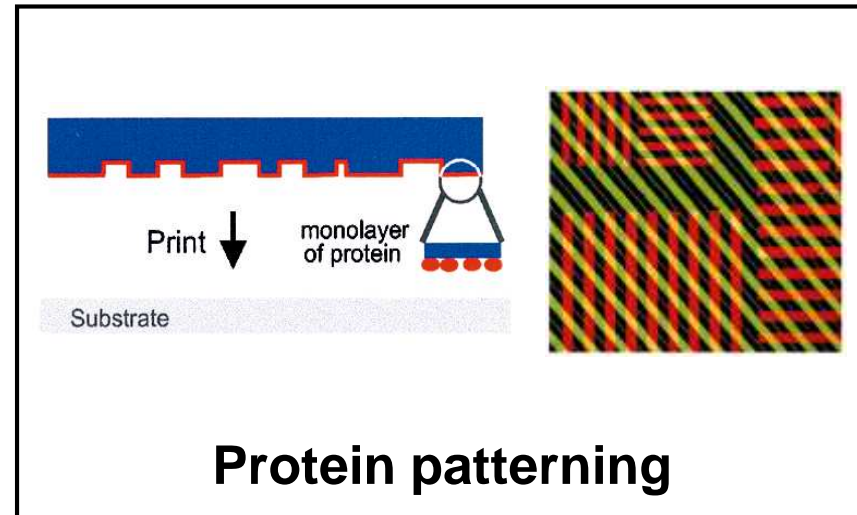
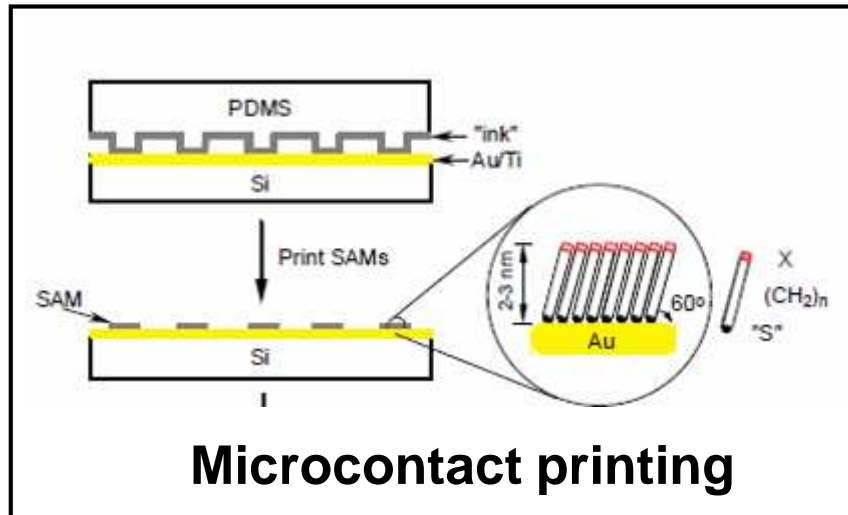
Type of structure
(periodic/aperiodic, 2D/3D...)
Accuracy
Resolution
Aspect ratio
Roughness
Speed (turn-around time)
Sequential/Parallel method
Origination/copying
Direct patterning of functional
material
Cost

Selection of Materials and processes are interdependent

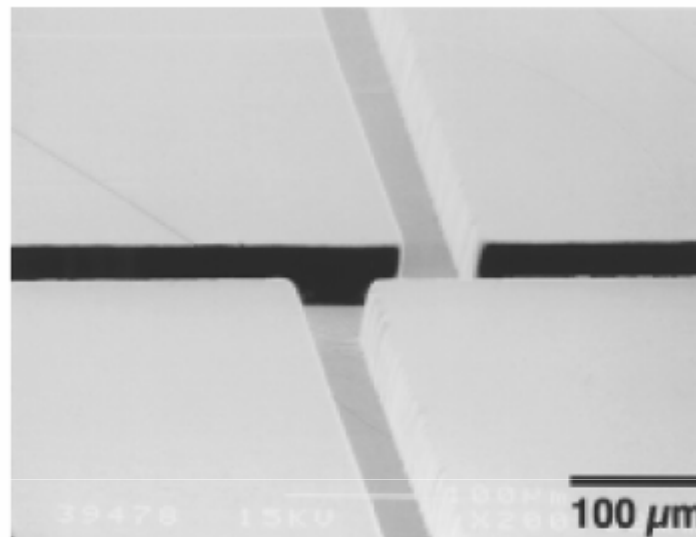
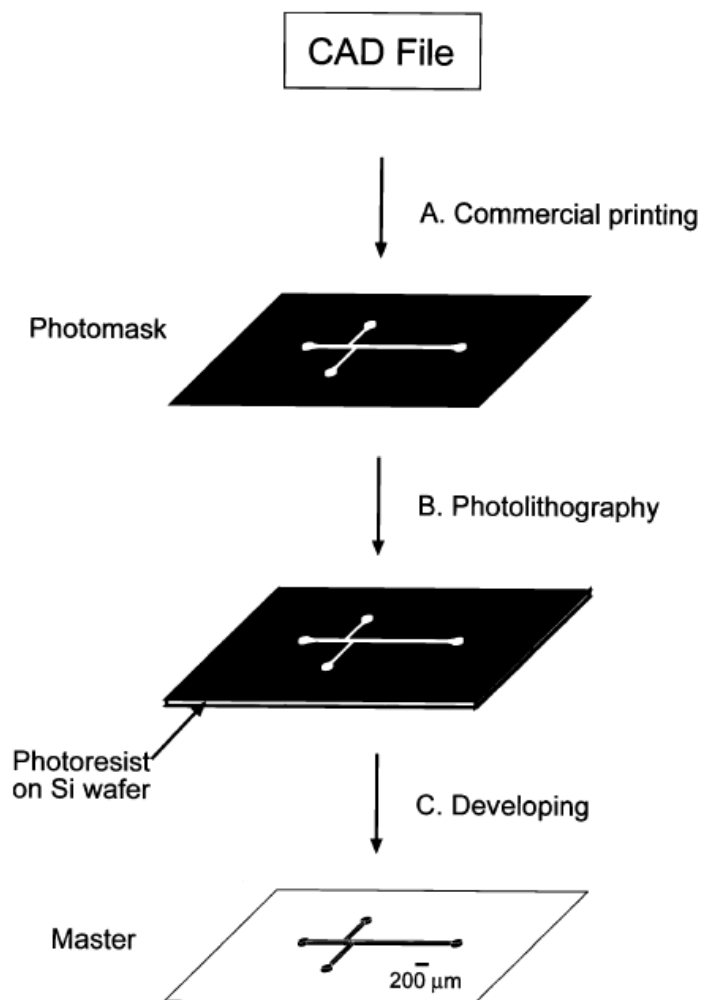
SOFT LITHOGRAPHY

Lithography based on soft stamps

PDMS and Soft Lithography methods



Rapid prototyping for pattern origination



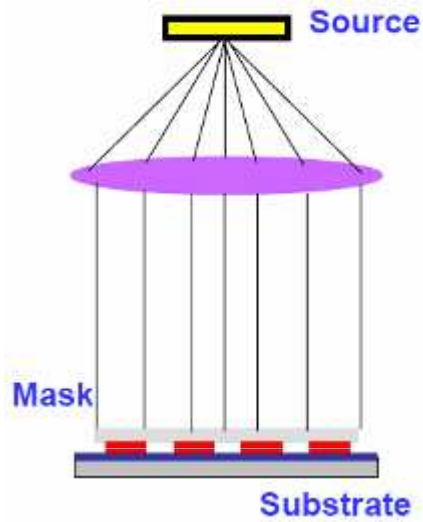
- From the concept to the device 24 h
- Limited resolutions
- Poor accuracy (edge roughness)

Y. Xia and G. M. Whitesides *Angew. Chem. Int. Ed.* **37**, 550, (1998)

UV photolithography

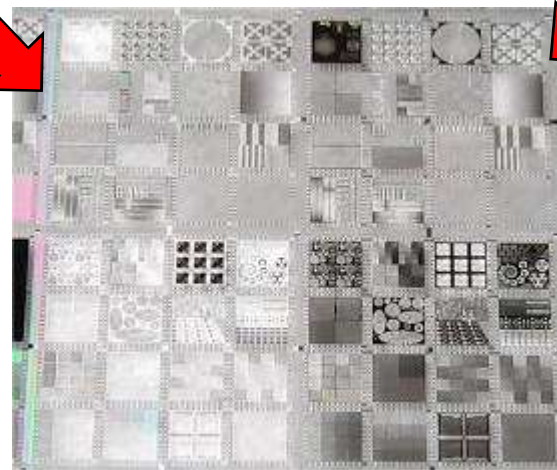


Mask aligner



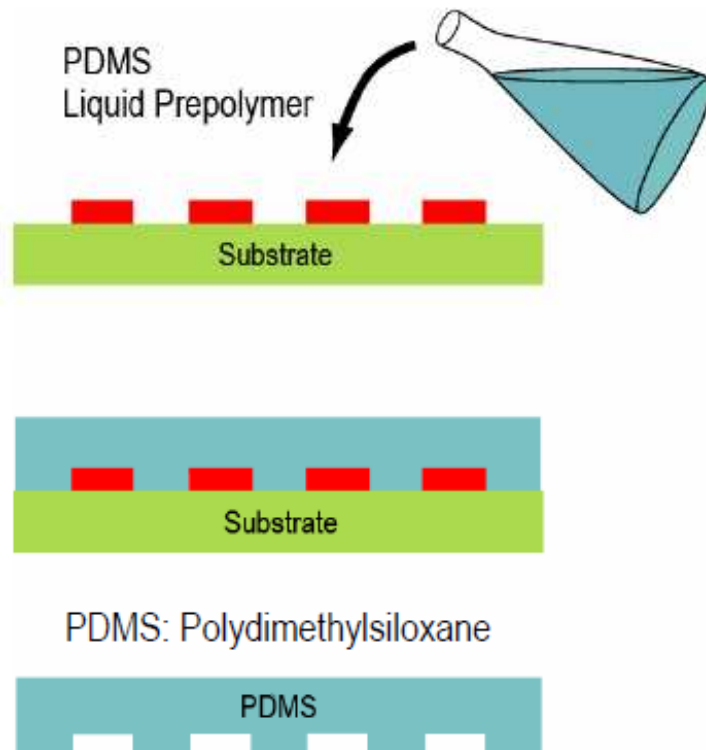
Photomask

Patterned photoresist
=
MASTER



- Requires production of a mask
- Resolution: 1-2 μm
- Sidewall roughness: ~ 100 nm

Casting of PDMS



Mixing components, and degassing in low vacuum.

Liquid precursor is poured onto substrate and master.

Prepolymer fills the cavities.

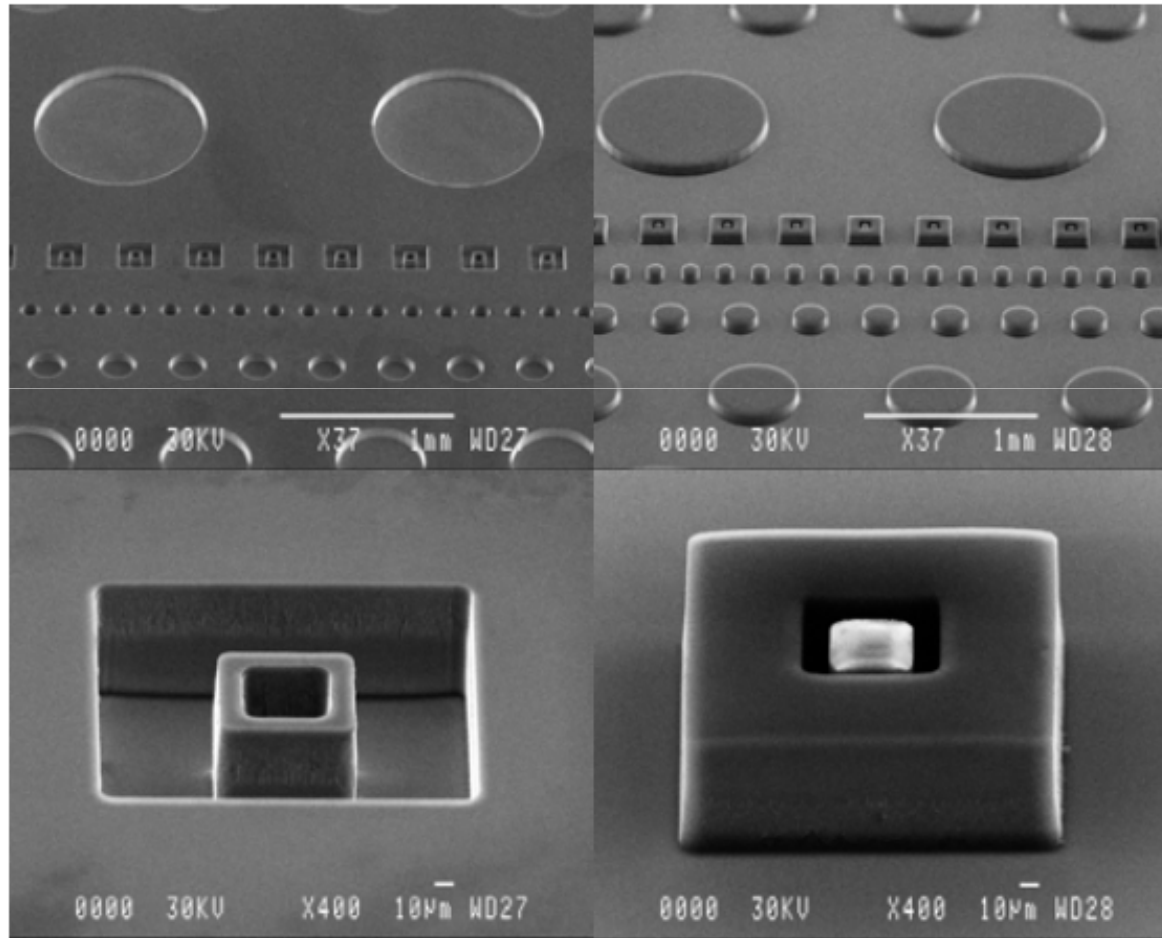
Cure (thermally or UV).

Peeling-off from the master.

Casting of curable polymers

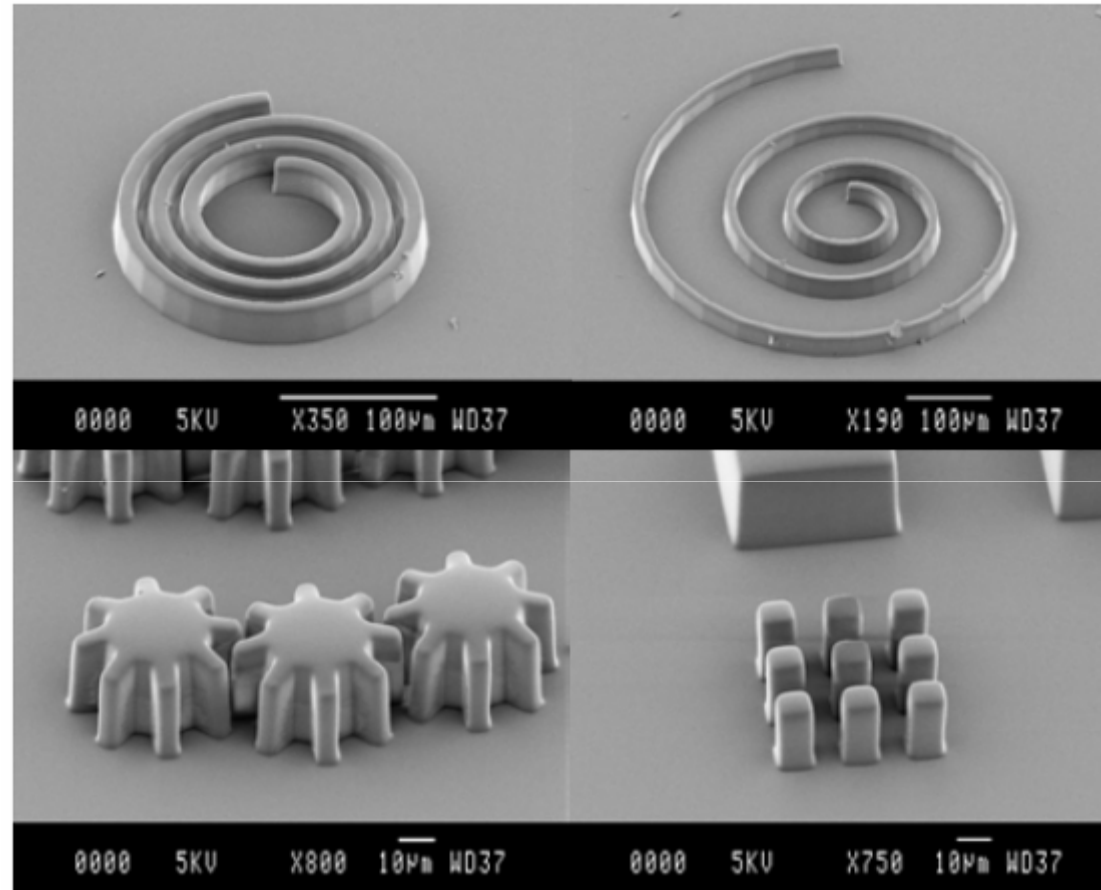
Master

PDMS replica



Source: C. Vieu, LAAS, CNRS, Toulouse, France.

Casting of curable polymers: PDMS

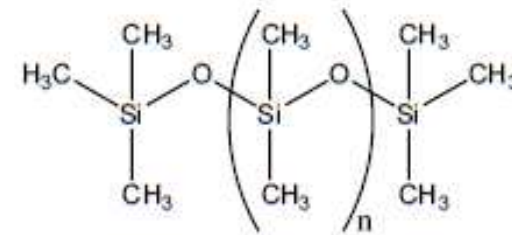


Microstructures fabricated by casting PDMS onto a master with structures made of photoresist

Source: C. Vieu, LAAS, CNRS, Toulouse, France.

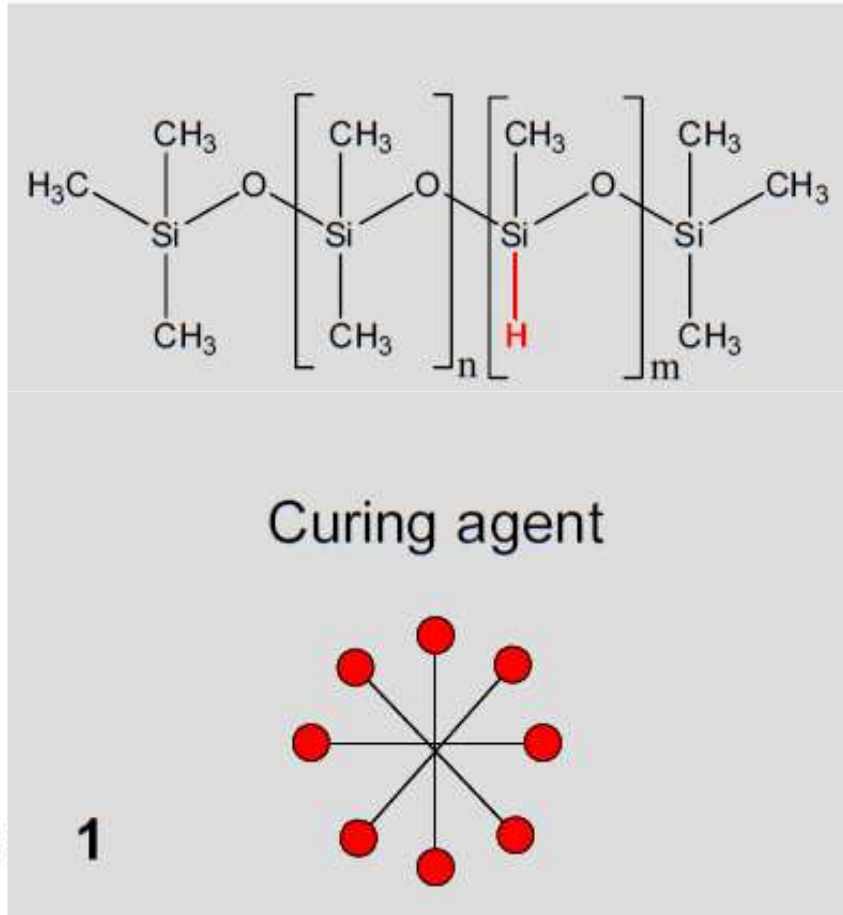
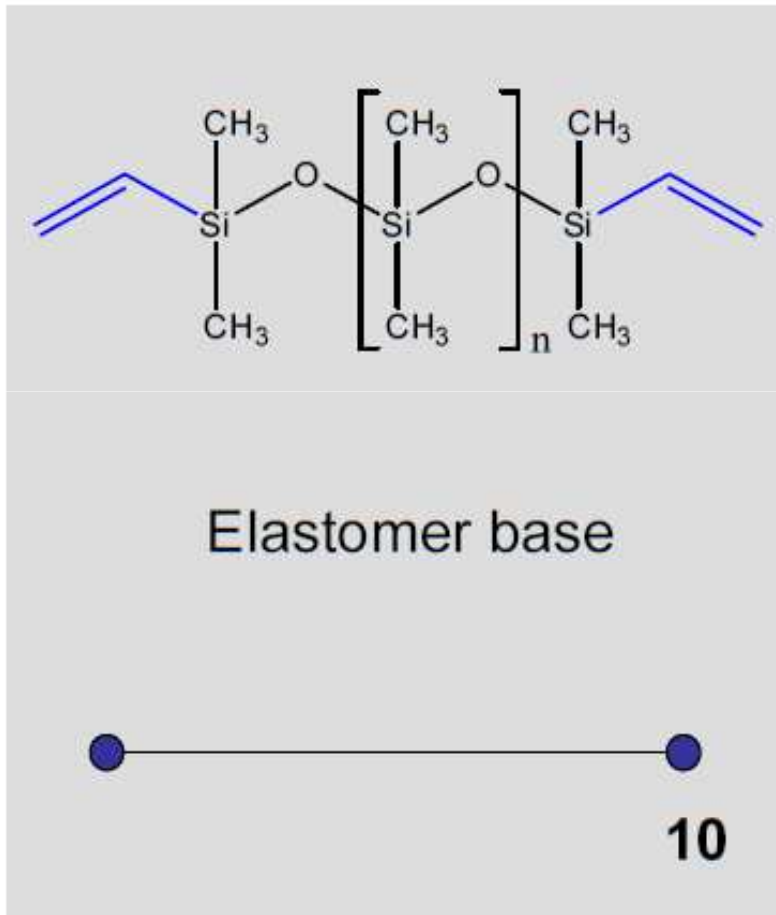
Poly(dimethylsiloxane) as material of choice for microfluidic

- Liquid prepolymers ⇒ easy molding
- Low surface energy ⇒ reliable replication
- Addition cure ⇒ low chemical shrink
- High elasticity ⇒ conformal contact /good print reproducibility
- Low T_g ⇒ wide range of conditions
- Transparent for UV/VIS ⇒ combine with photolithography
- Low Mw residues ⇒ traces of PDMS are always transferred as well



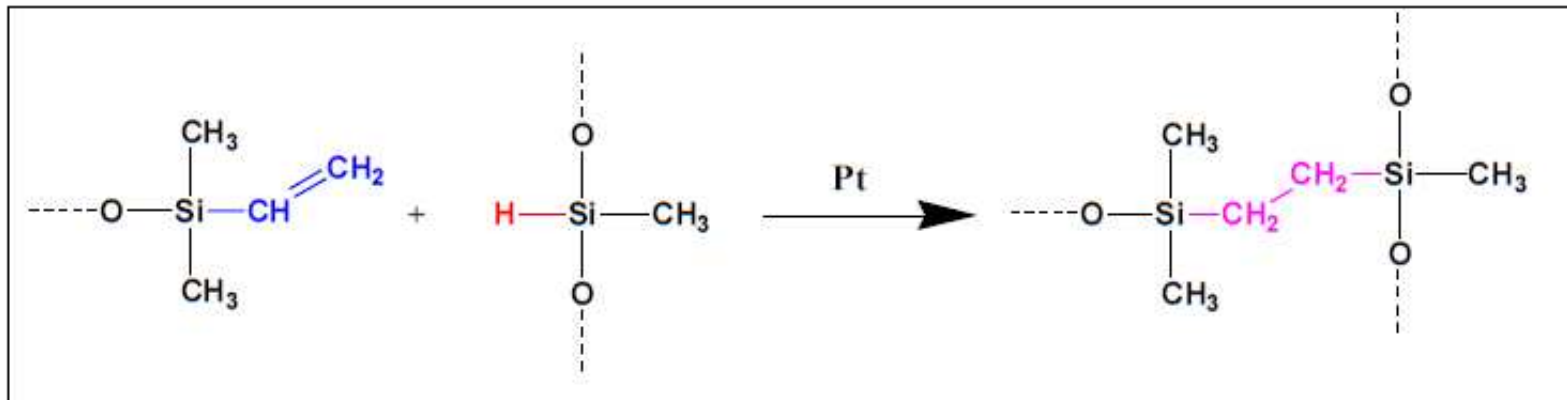
Courtesy: Heiko Wolf, IBM

PDMS prepolymers (Sylgard 184)

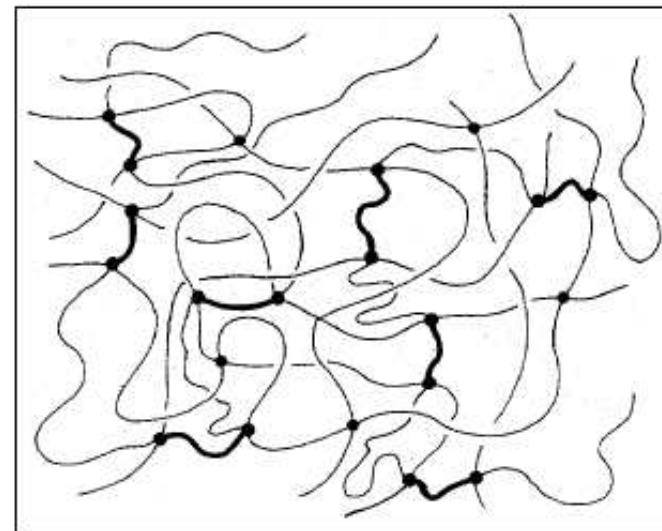


Courtesy: Heiko Wolf, IBM

Curing of Sylgard

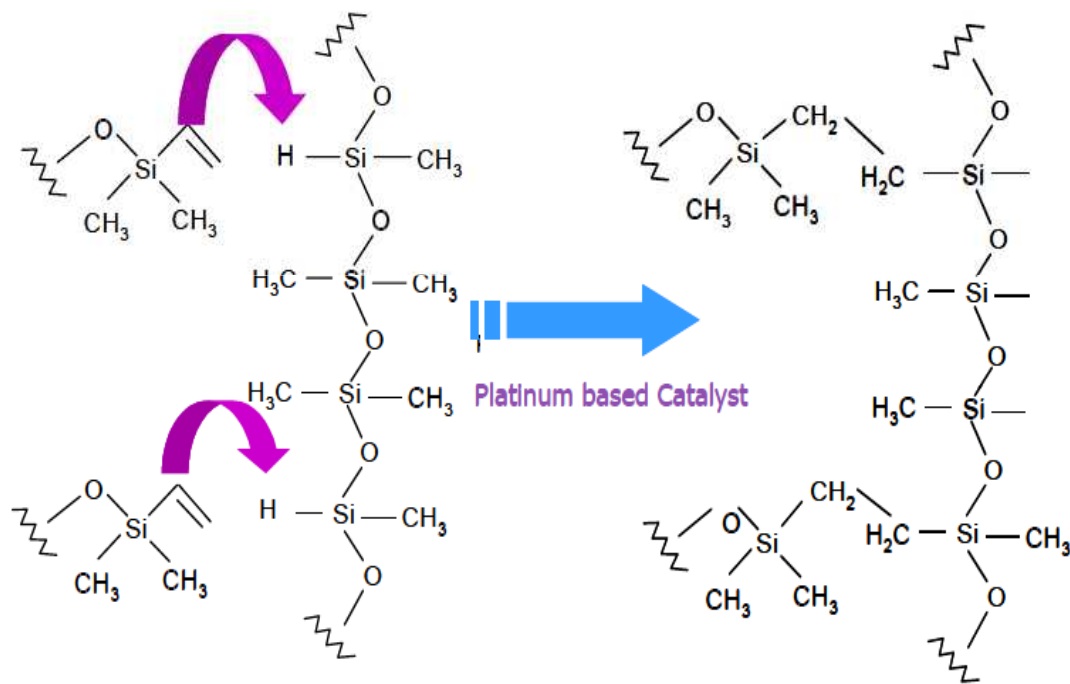


Sylgard 184™ by Dow Corning

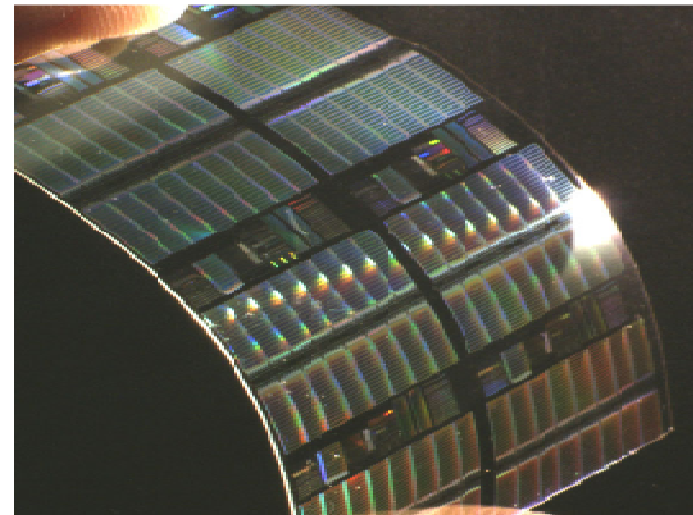


Courtesy: Heiko Wolf, IBM

Crosslinking: formation of a 3D network

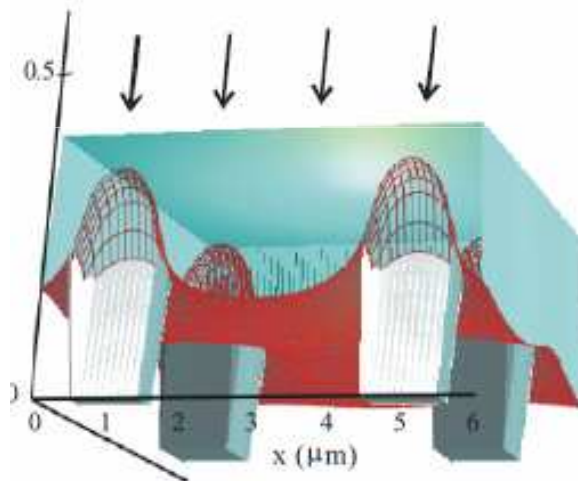


Cross-linking reaction of PDMS precursors

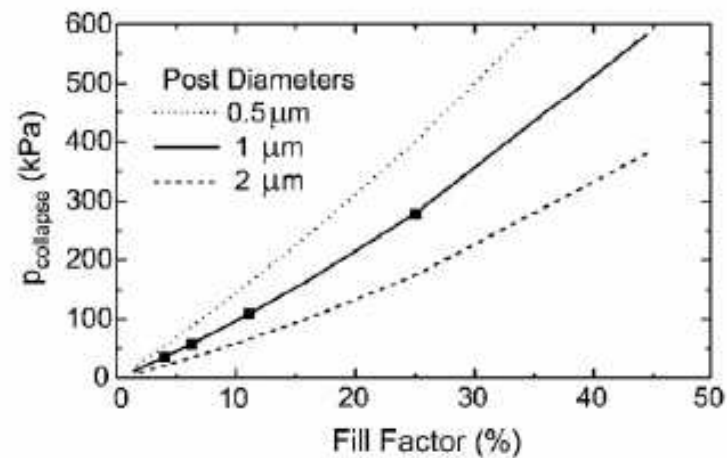


Problems: sagging of unsupported large areas

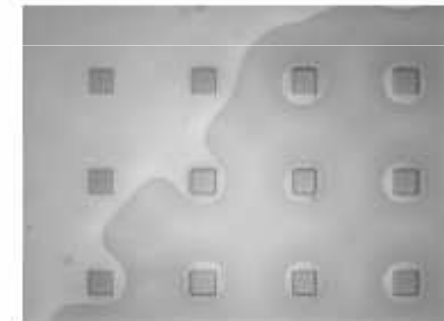
- High modulus PDMS ensures mechanical stability.
- The backplane reduces sagging and improves accuracy.



Deformation of 1 μm wide and 0.45 μm high posts by an external pressure of 40 kPa.



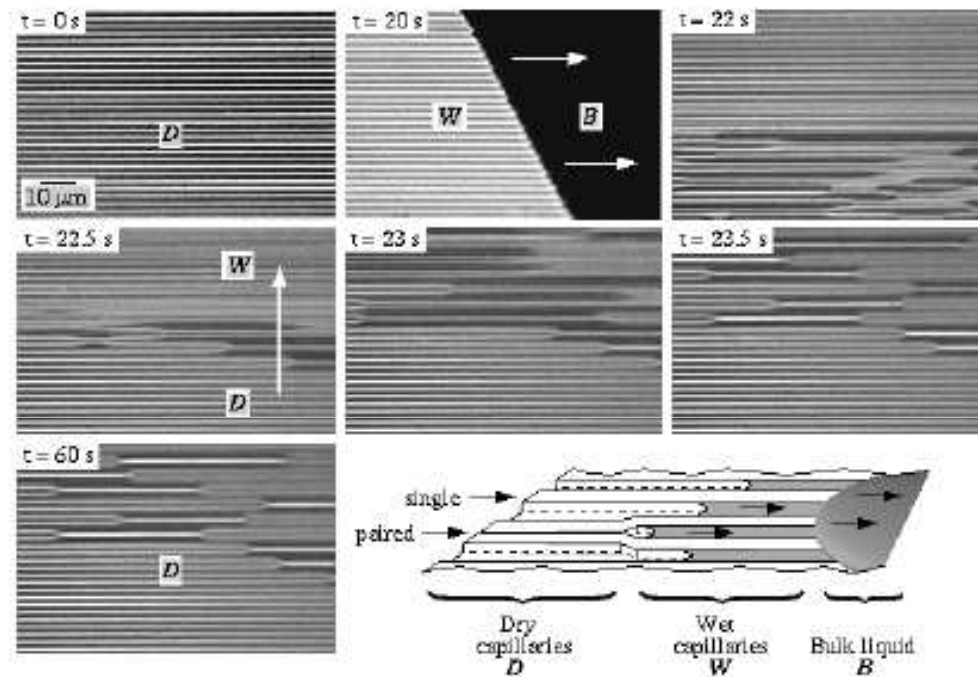
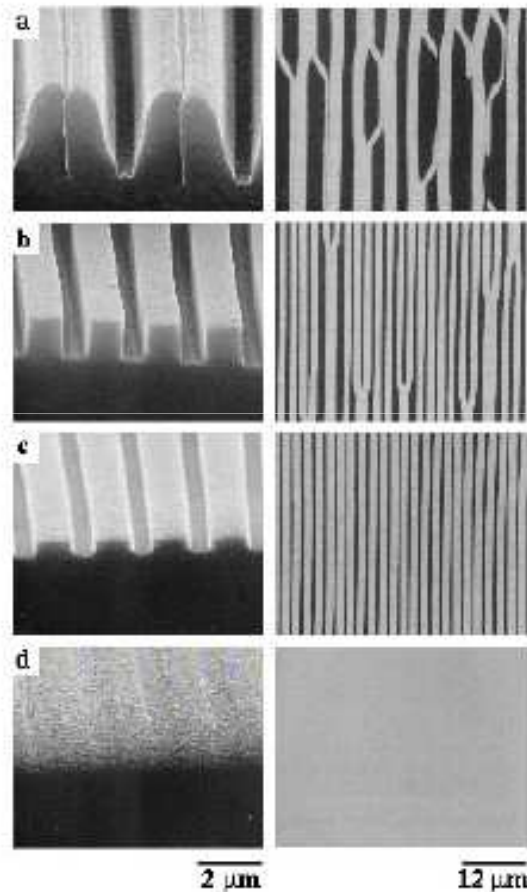
Pressure for onset of collapse as function of post size and fill factor.



Optical image of a collapsed stamp

Courtesy: Heiko Wolf, IBM

Stability of fine PDMS structures



- Elastomer structures with high aspect ratios collapse on demolding.

Courtesy: Heiko Wolf, IBM

Hard PDMS elastomers for high resolution applications

PDMS with higher Young's modulus can be obtained by increasing the number of crosslinks.

Practical guideline:

Add the catalyst to the catalyst to the vinyl component (not to the hydrosilyl component)

Catalysts and vinyl component mixtures are stable (can be stored at room temperature under N₂ or Ar).

The last step is adding the hydrosilyl component (after that the crosslinking reaction starts).

The image shows chemical structures of PDMS chains with vinyl and hydrosilyl groups, and a photograph of the components used for synthesis. The photograph includes a large bottle of VDT 731, a small bottle of HMS 301, a vial of SIP 6831.1, and a jar of VQM 135. Labels indicate 'catalyst' for SIP 6831.1 and 'filler' for VQM 135. The text 'all chemicals from ABCR, Karlsruhe' is also present.

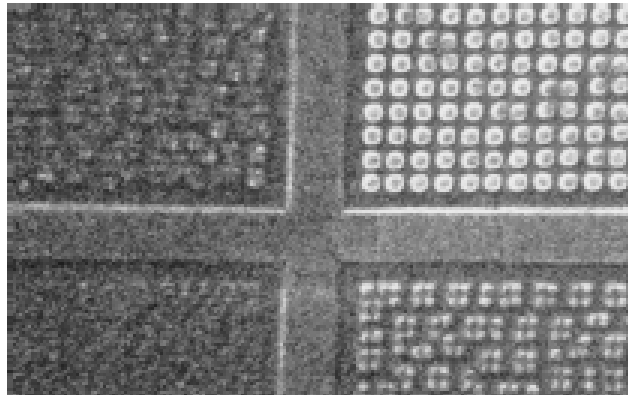
all chemicals from
ABCR, Karlsruhe


VDT 731	HMS 301	SIP 6831.1	VQM 135
34 g	10 g	12 - 25 µl	5 g (optional)

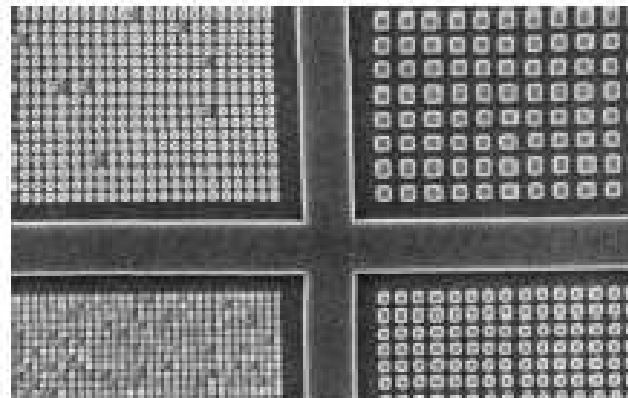
www.abcr.de


Courtesy: Heiko Wolf, IBM

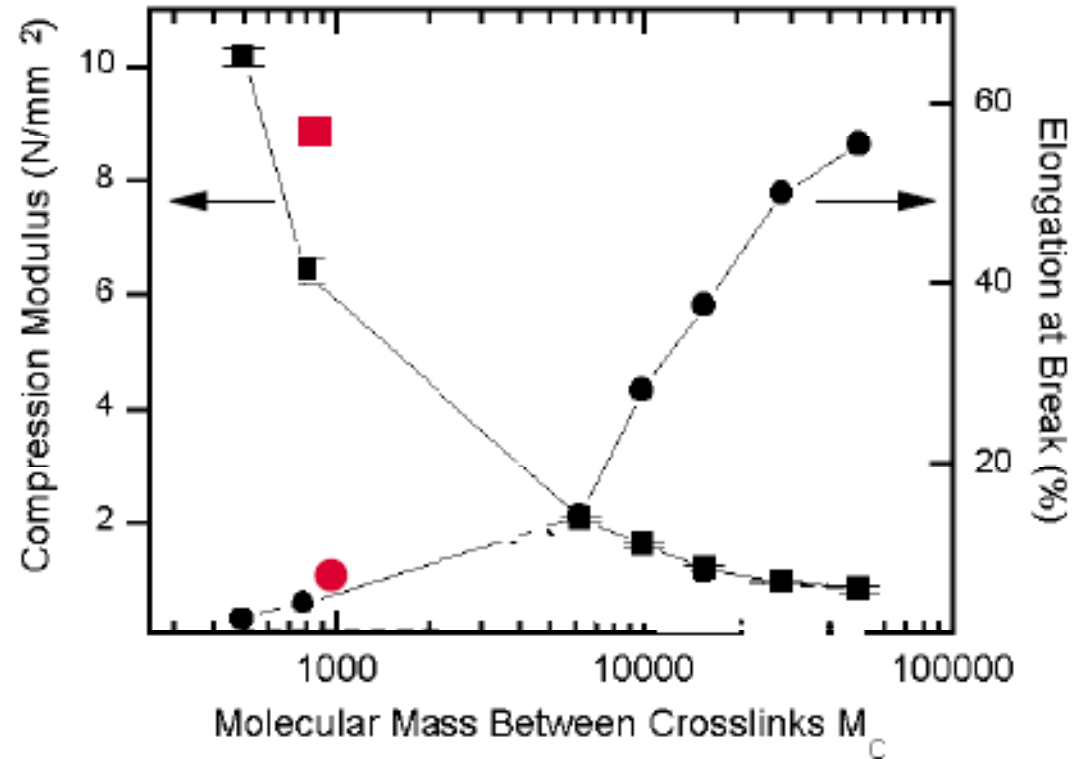
Hard PDMS elastomers for high resolution applications



Sylgard 184; $E=3$ MPa 



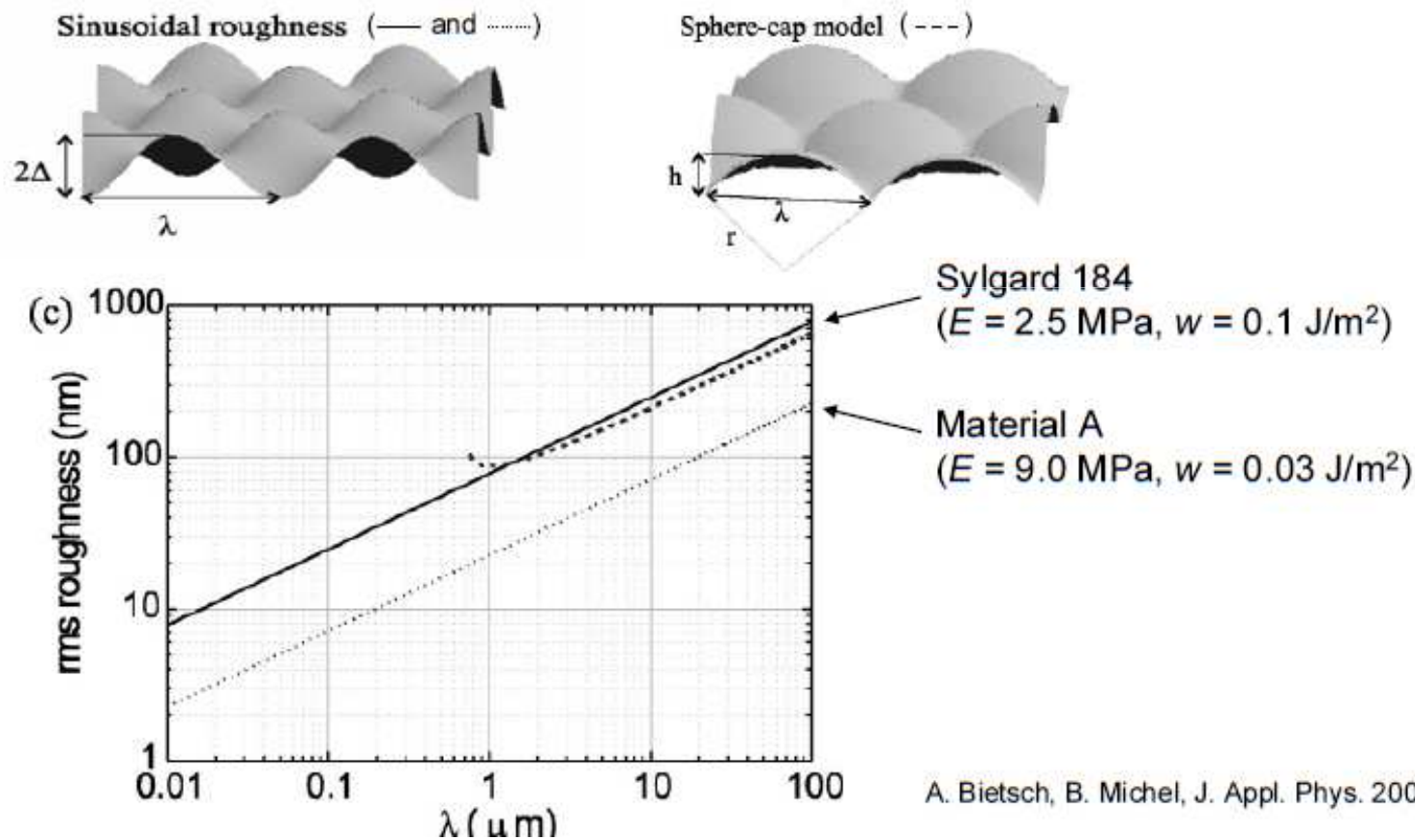
Hard PDMS; $E=10$ MPa 



Courtesy: Heiko Wolf, IBM

Reversible water-proof sealing with PDMS

- *Low modulus of PDMS allows to accommodate for micro roughness.*



Courtesy: Heiko Wolf, IBM

Sealing techniques with PDMS

In MEMS technology sealing glass or silicon by anodic bonding (at high temperatures, pressures, voltages).

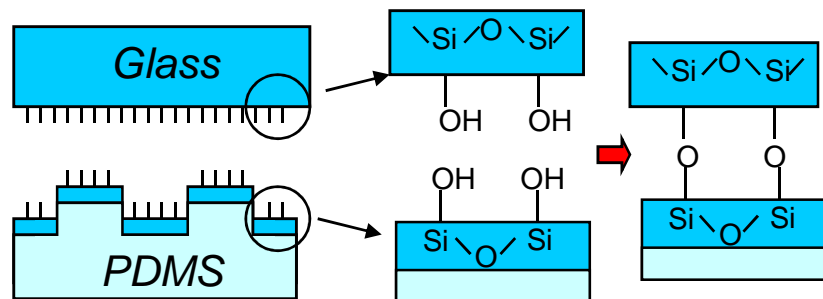
PDMS can be bonded to PDMS itself or glass reversibly or irreversibly.

Reversible sealing

- By simple contact, relying on the -PDMS compliance
- Adhesion forces (weak interaction)

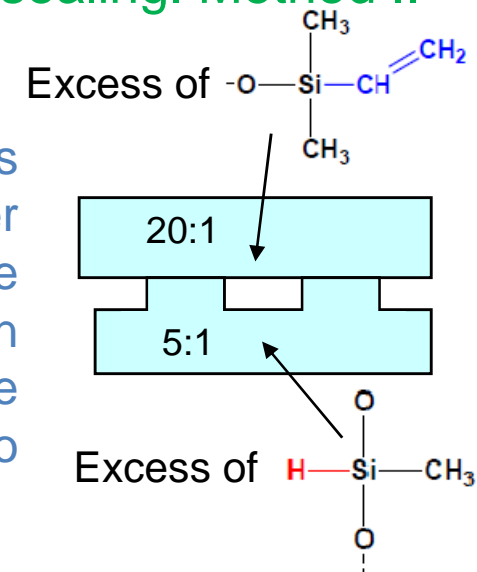
Irreversible sealing. Method I

- Formation of Si-OH group on PDMS and glass by oxygen plasma
- Covalent O-Si-O-bonds with oxidized PDMS upon contact

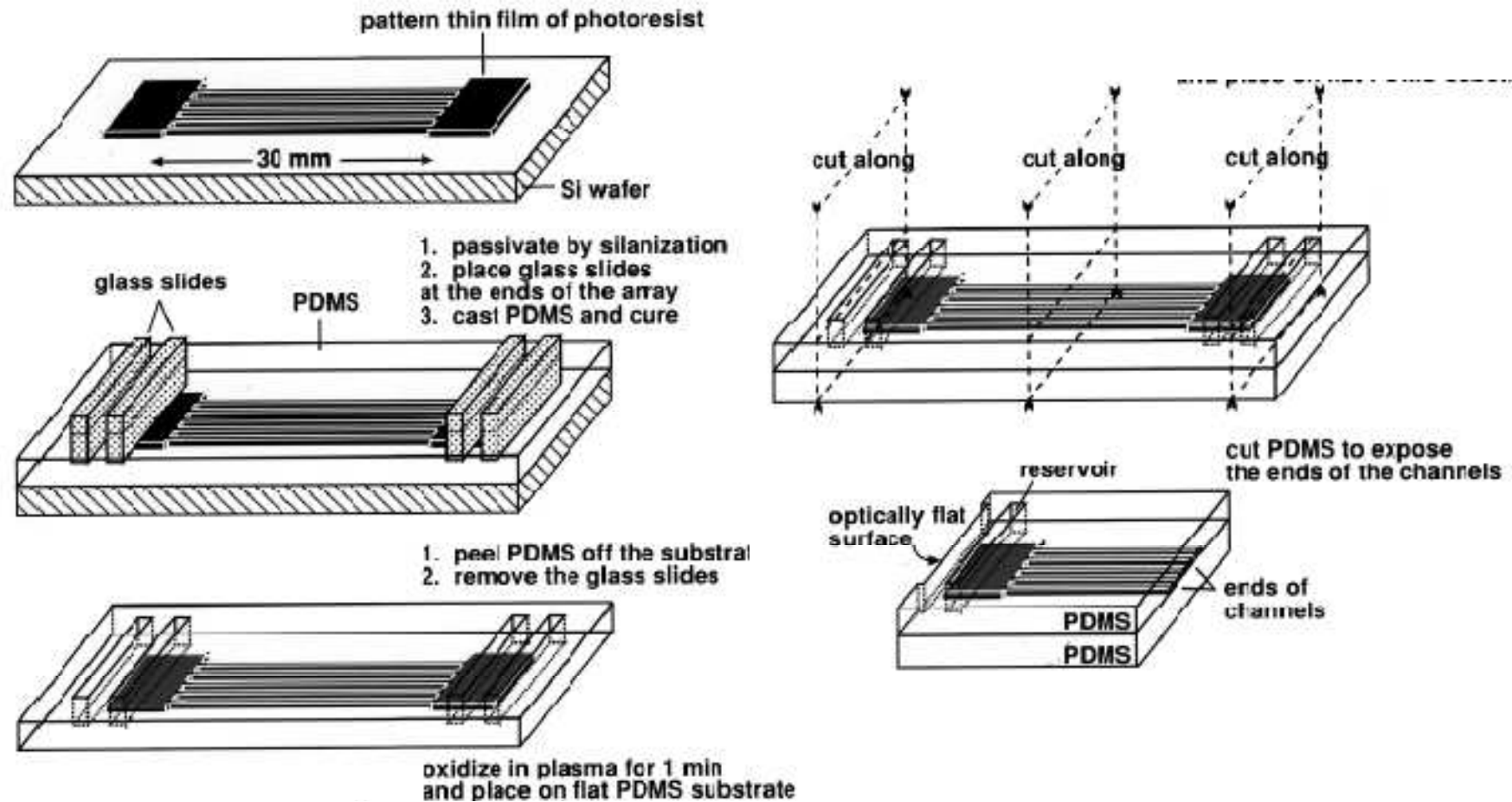


Irreversible sealing. Method II

- Add an excess of the monomer base to one slab and an excess of the curing agent to the other.



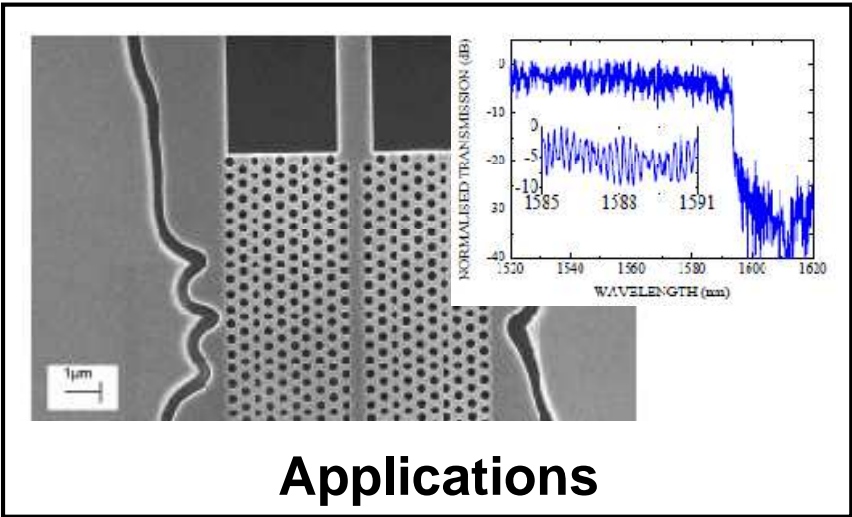
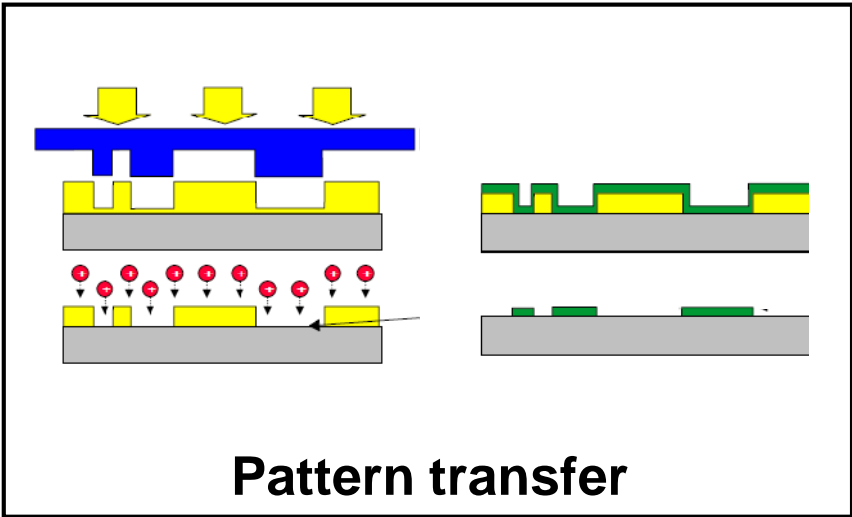
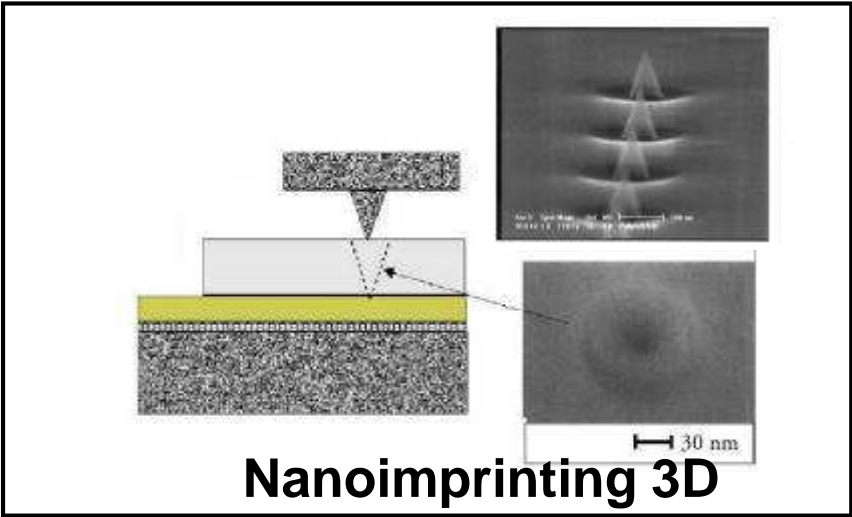
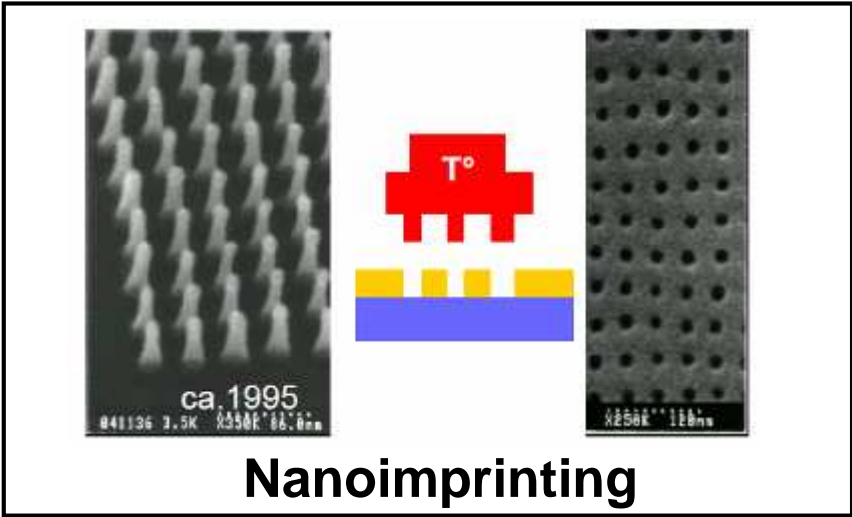
Liquid core waveguides with PDMS (1999)



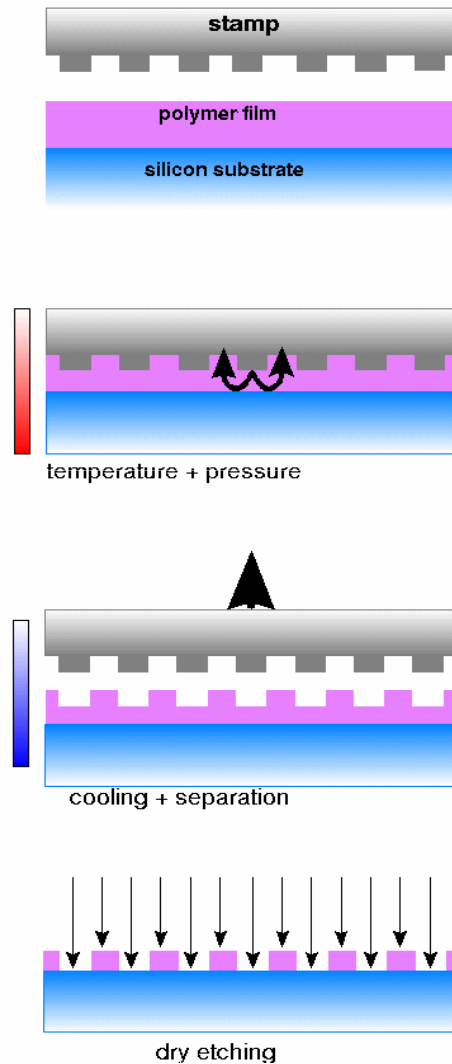
Schueller Adv. Mater. 11, 37 (1999)

NANOIMPRINT LITHOGRAPHY (NIL)

Nanoimprint lithography



Nanoimprint lithography (NIL)



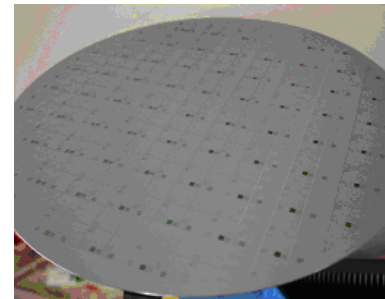
IMPRINT PROCESS:

1. Bring stamp & sample into contact
2. Heat to $T > T_g$
3. Apply pressure
4. Cool down
5. Separation at $T < T_g$
6. RIE (oxygen plasma) to remove residual layer
7. Lift off or pattern transfer by RIE or use printed functional polymer film.

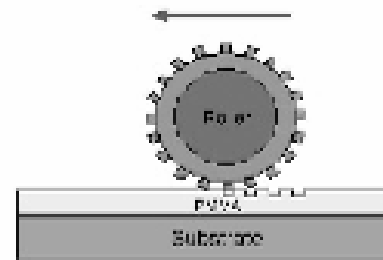
Relatively simple process, min feature size is ca.10 nm, low cost, scalable to wafer size, good throughput, 3D ...

Main Features on NIL

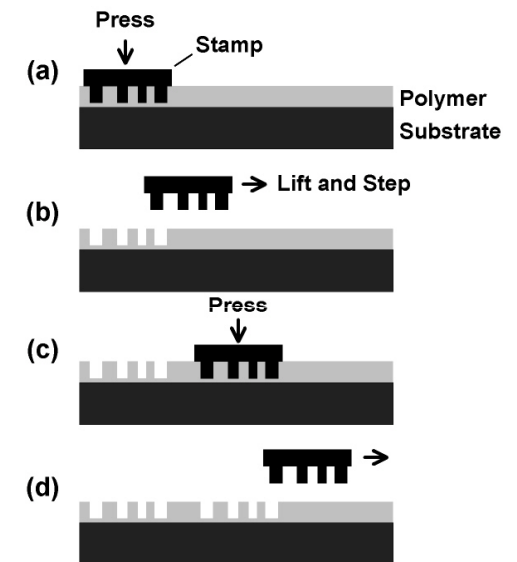
- Can be implemented at low cost in laboratories
- Excellent properties as 2D and 3D patterning technique
- High resolution
- Full wafer, Step & Repeat, or Roll to Roll
- Throughput (good for research, insufficient for production)
- Low cost



Full wafer



Roll To Roll



Step & Repeat

TOOLS for NIL



Hydraulic press



Press by SPECAC



Press by Weber



S.E.T. Step&Repeat NIL tool



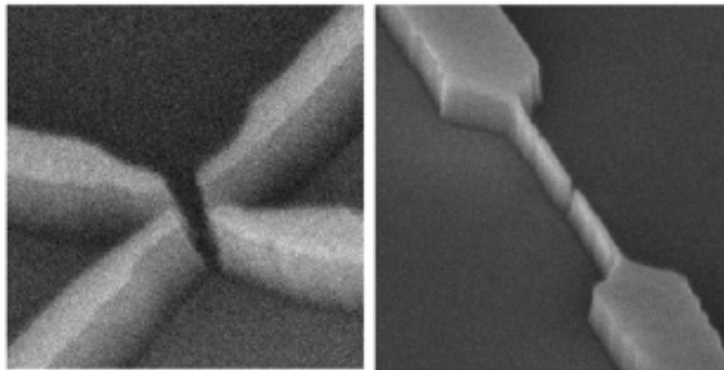
Tool for UV-NIL by Molecular Imprints

Resolution does not depend on the tool used. Even with very basic tool resolution of <math><10\text{ nm}</math> can be obtained.

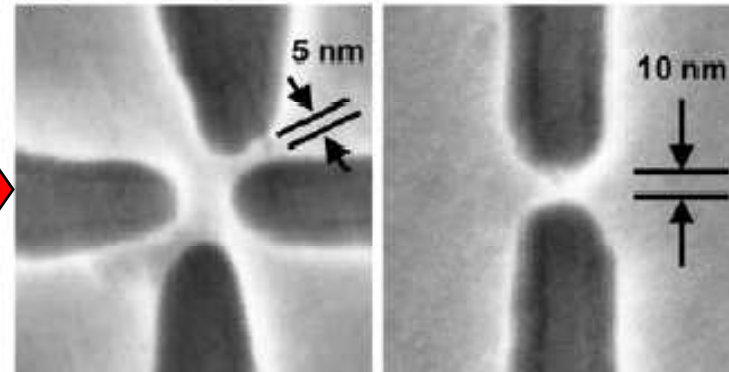
Uniformity, throughput, defectivity, alignment, depend instead on the tool (and on the environment).

Nanoimprint lithography (NIL)

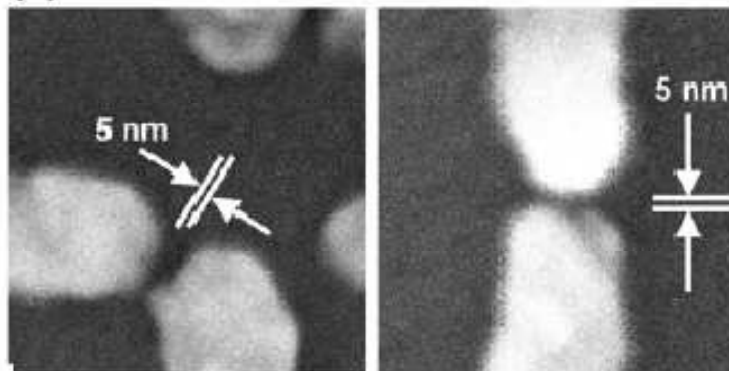
(a) SiO₂ NIL Mold



(b) NIL Polymer Imprint



(c) Au 5 nm Contacts

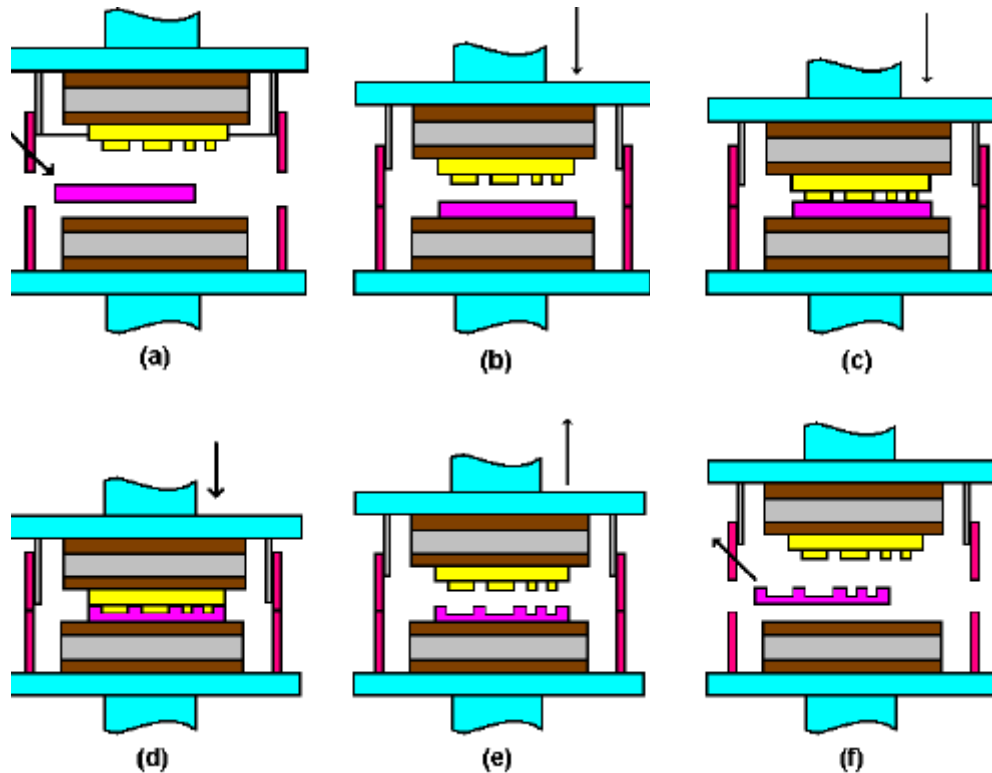


Austin et al. *Nanotechnology*, (2003).

General references:

Chou, S. Y.; Krauss, P. R.; Renstrom, P.J. *Science* **1996**, *272*, 85
Reviews: Guo, L. J. *J. Phys. D, Appl. Phys.* **2004**, *37*, R123; C. M. Sotomayor Torres et al. *Mater. Sci. Eng. C* **2003**, *23*, 23; C. M. Sotomayor Torres, Ed. *Alternative Lithography*, 2003, Kluwer Academic, NY

Hot embossing



WHY HOT EMBOSSING?

Low-cost method for Volume production

- Raw materials are cheap
- Manufacturing is simple (batch replication)

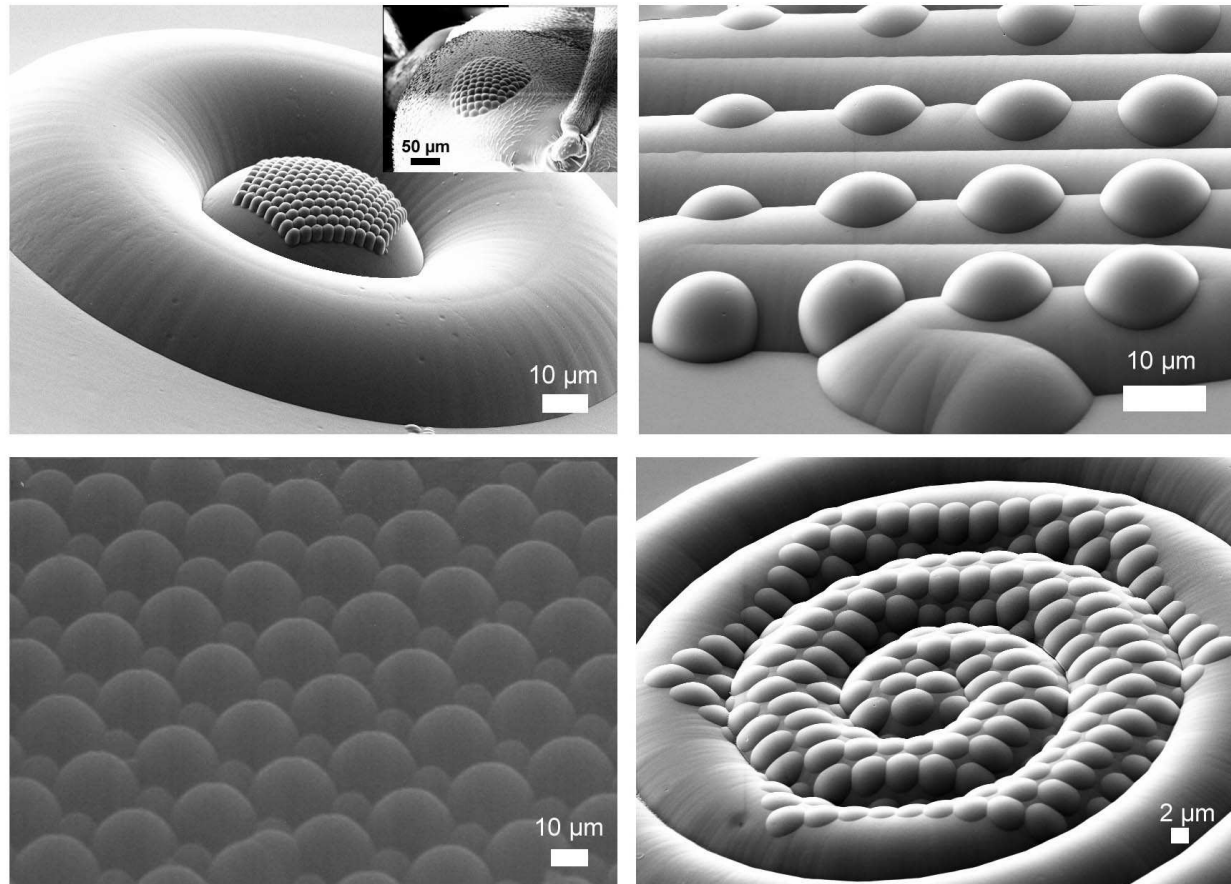
Extremely precise

- Resolution and accuracy in the nm range
- Reproduce 3D profiles



CD and DVD are produced by hot embossing (or injection molding).

Hot embossing of complex microoptics

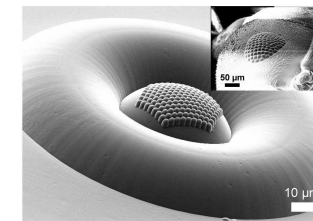


NaPa
Emerging Nanopatterning Methods

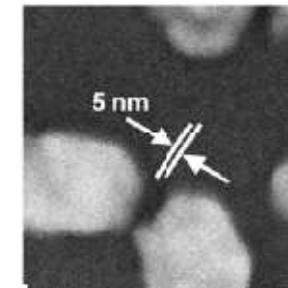
Nanoimprinting vs Hot embossing

What is the difference between Nanoimprint Lithography and Hot Embossing?

In the Hot Embossing process the relief is produced on a “bulk” polymer ($\gg 10 \mu\text{m}$) . The polymer structure enters as it is in the assembled device.

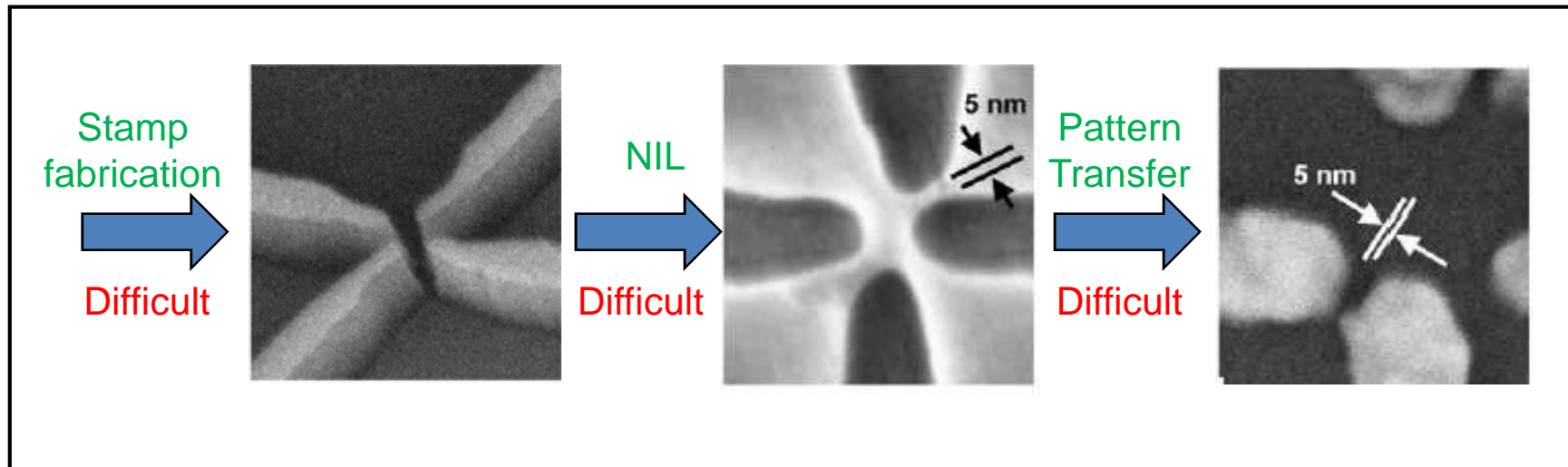
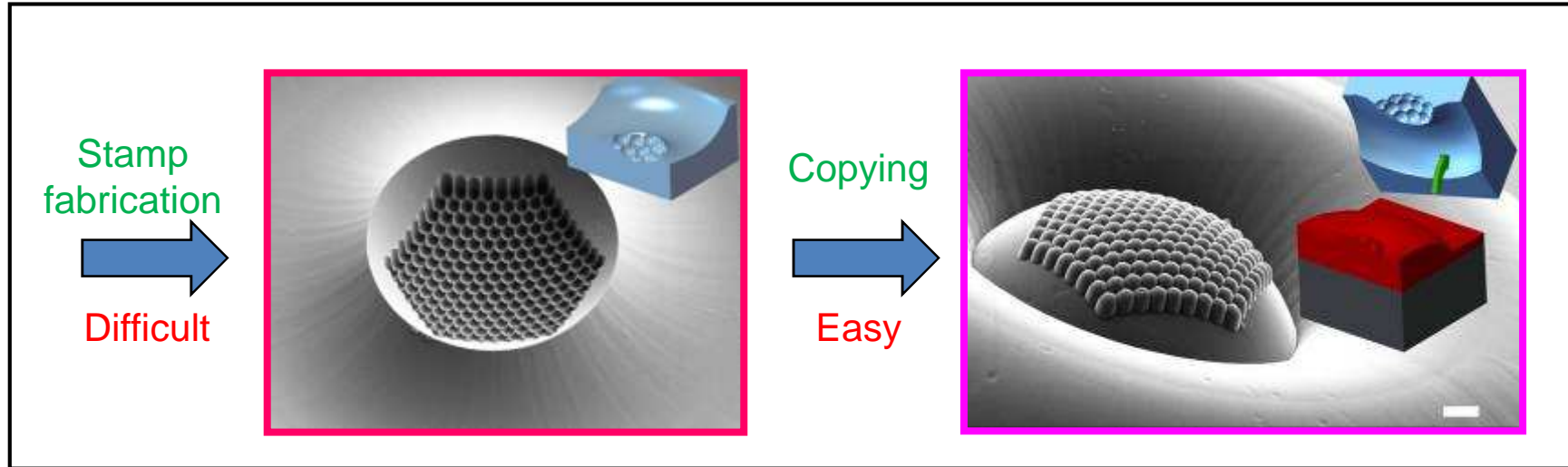


In NIL the relief is produced on a thin ($\sim 100 \text{ nm}$) sacrificial film that it is used for pattern transfer onto the substrate either by additive or subtractive methods.

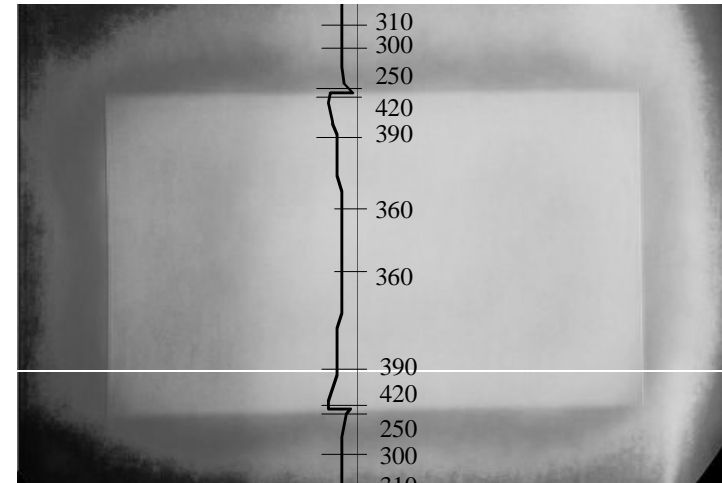
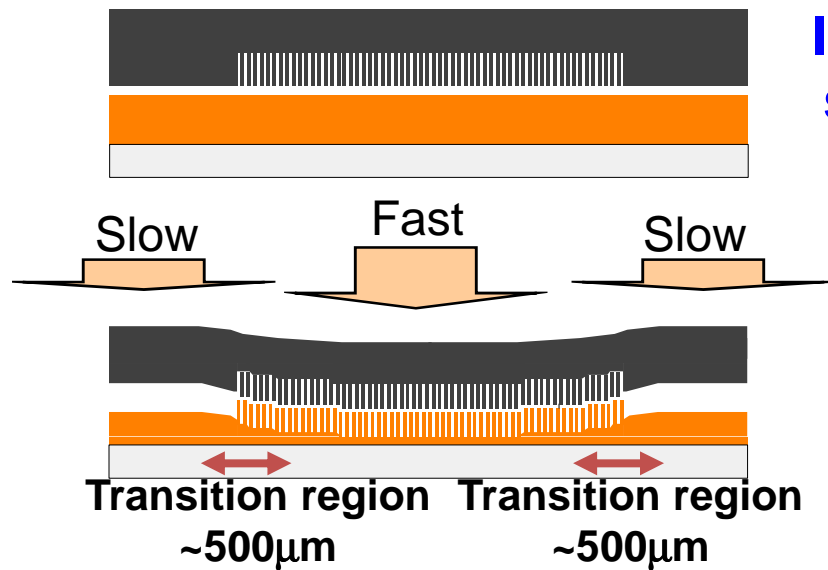


Critical step in NIL: obtain a very thin ($\sim 10 \text{ nm}$) and uniform residual layer. This requires process optimization, and is a prerequisite for a successful pattern transfer.

Nanoimprinting vs Hot embossing

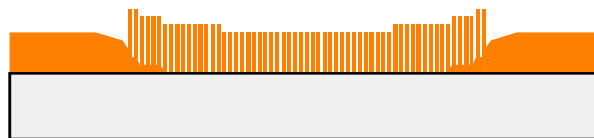


Copying of Large Area Grating Stamps

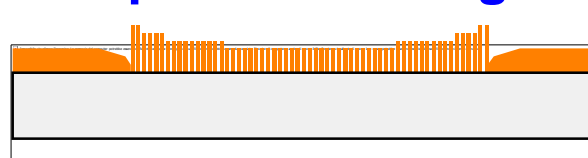


$h_{f,1}=310\text{nm}$, $h_{f,1}(\text{theory})=316\text{nm}$
 $h_{f,2}=200\text{nm}$, $h_{f,2}(\text{theory})=240\text{nm}$,

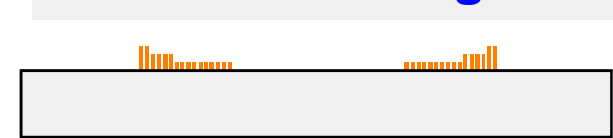
Under-thinning



Optimal thinning



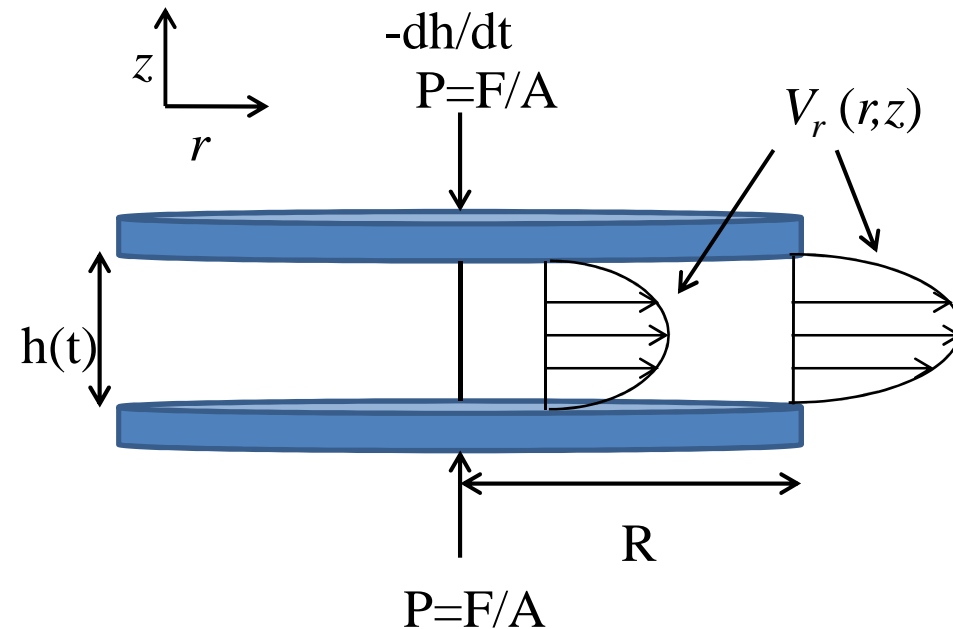
Over-thinning



Simple model for residual layer estimation

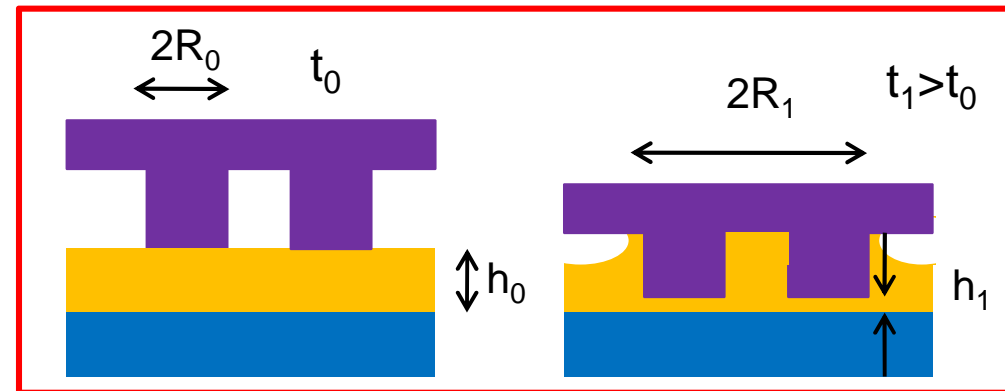
Stefan equation

$$F = -\frac{3\pi R^4}{2h(t)^3} \frac{dh}{dt} \eta_0$$

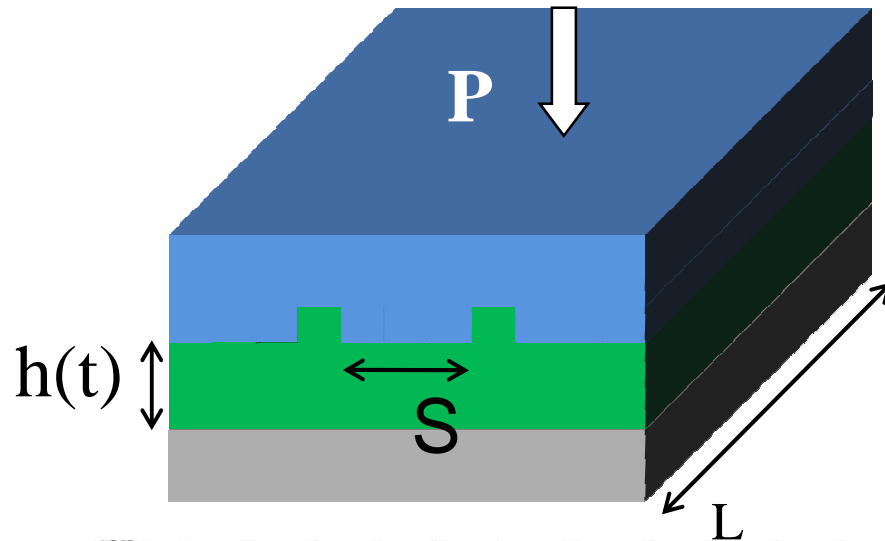


During the process

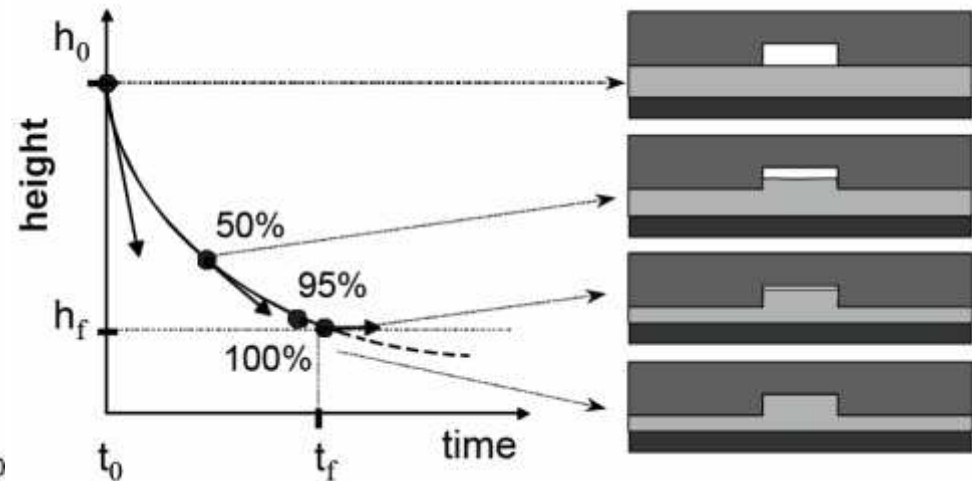
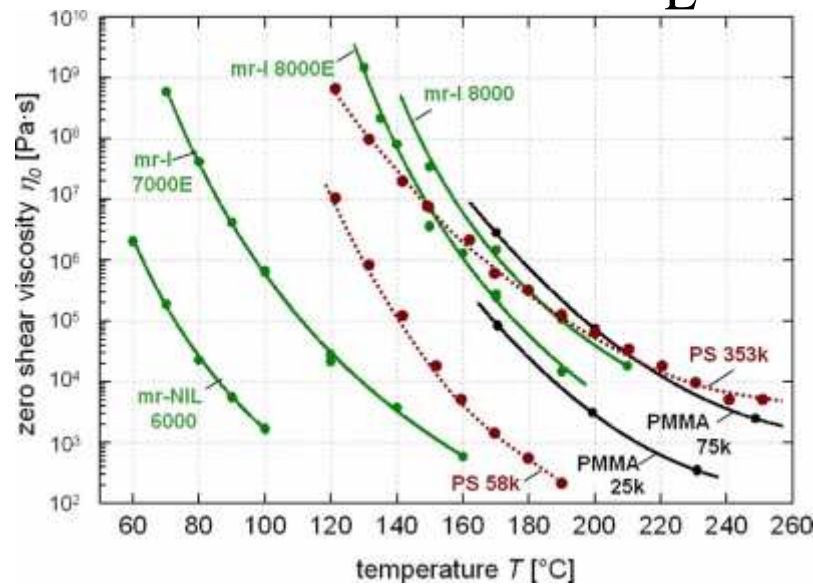
- The residual thickness h decreases
- The effective size of the structure R increases (when the cavity are filled)
- The force F diverges



Residual layer

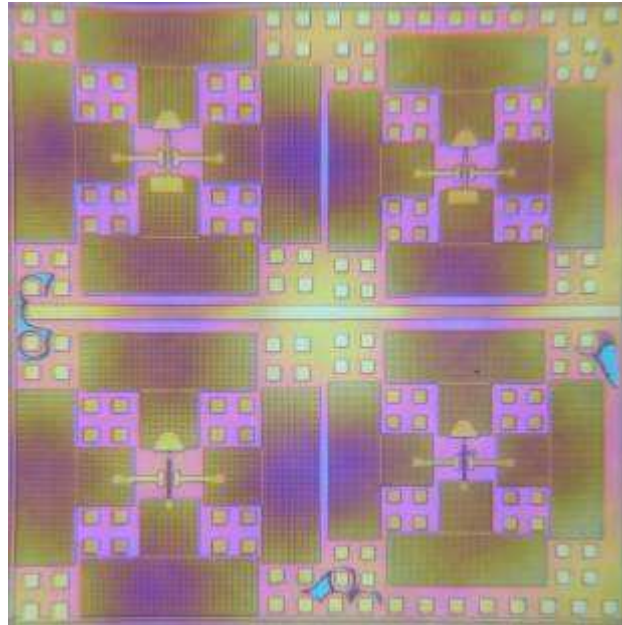


$$t_f = \frac{\eta_0 s^2}{2p} \left(\frac{1}{h_f^2} - \frac{1}{h_0^2} \right)$$



Simulation and experiments on residual layer

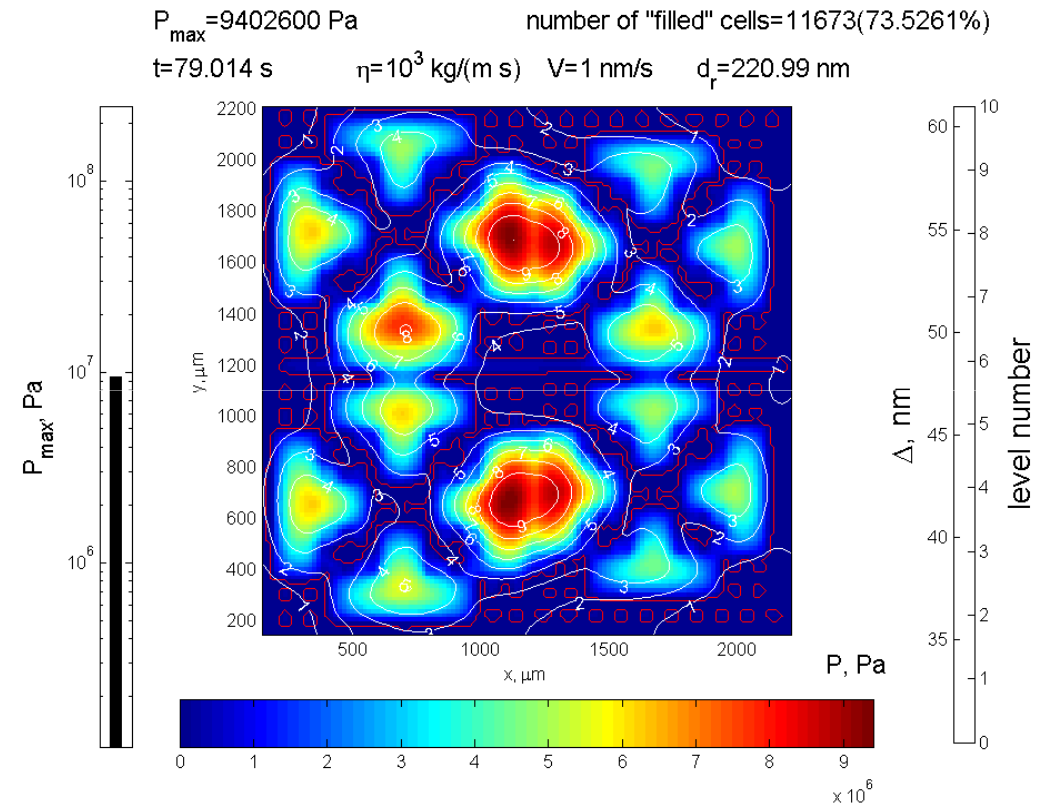
Experiment



Micrograph of imprinted structure (different colors correspond to different thickness; the violet correspond to areas with thicker residual layer).

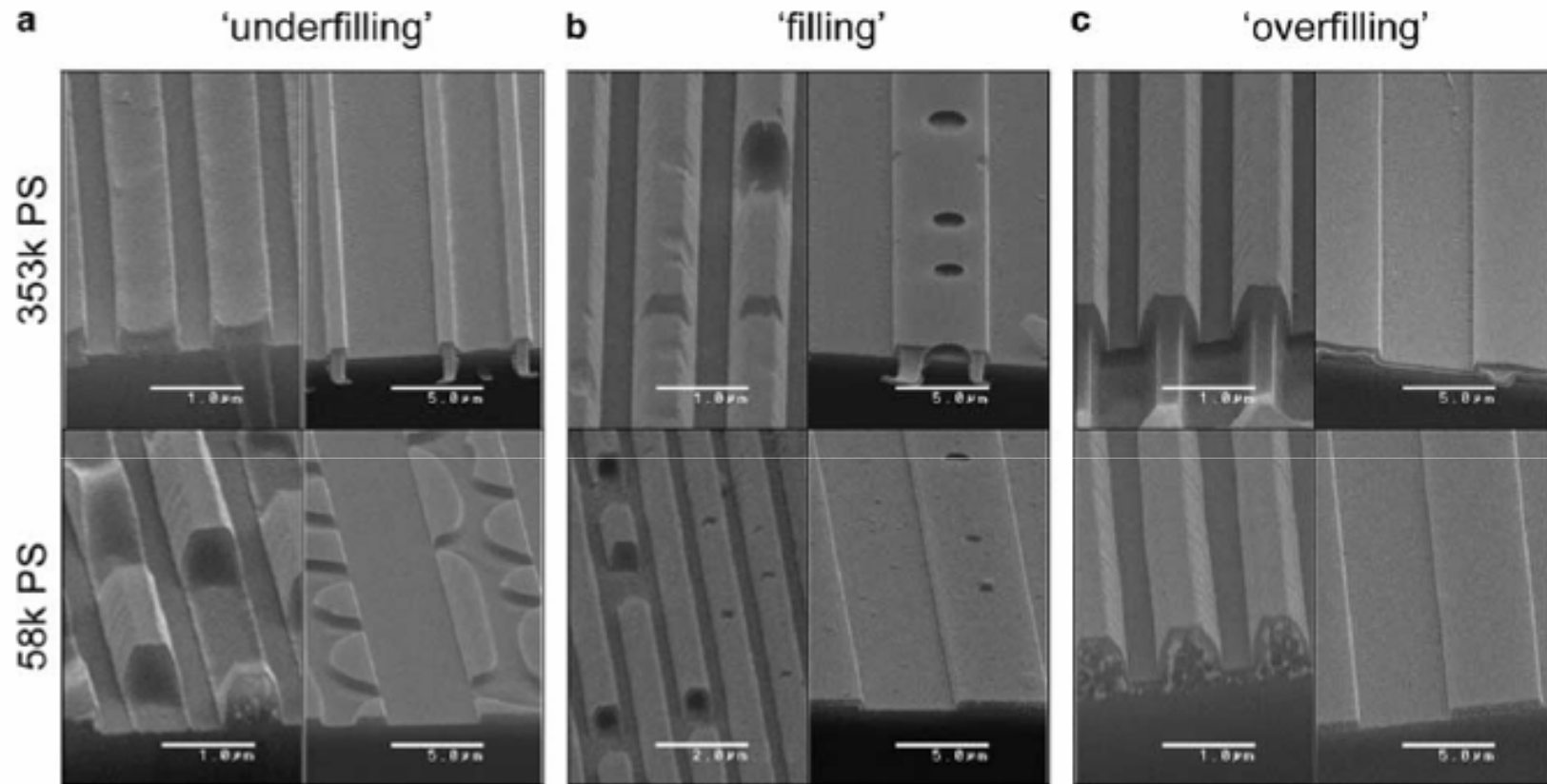
The pressure distribution is the correspondence of areas of high pressure in the simulation to areas of high residual layer thickness in the imprint experiment (see figures).

Simulation



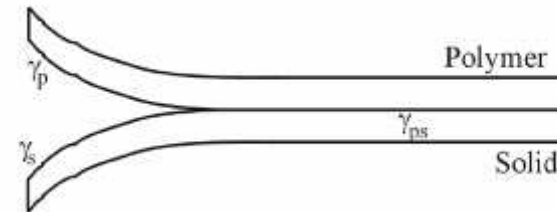
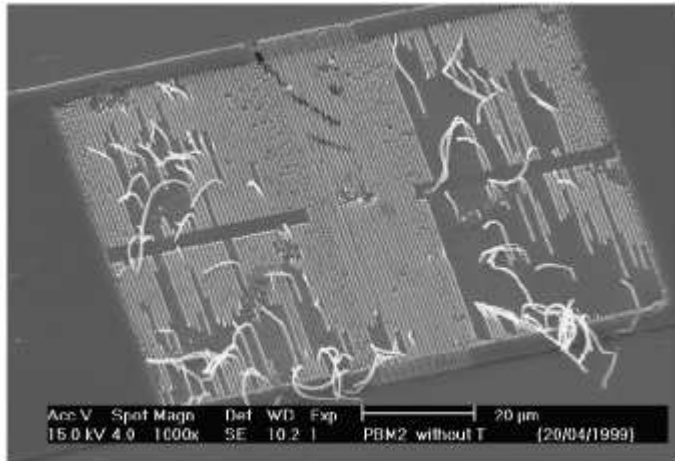
Simulated pressure **P** and elastic displacement Δ distributions (for the calculation elastic properties of single-crystalline silicon were used). Red lines show the position of the boundary between "unfilled" and "filled" regions. Numbered white level lines indicate elastic displacement values (see right scale in the figure).

Optimal polymer thickness



H. Schulz et al. Microelectronic Engineering 83 (2006) 259

When stamp release fails



Adhesion energy

Polymer ripped away during stamp release due to strong adhesion and large surface area of contact.

The finer the nanostructures the worst the problem.

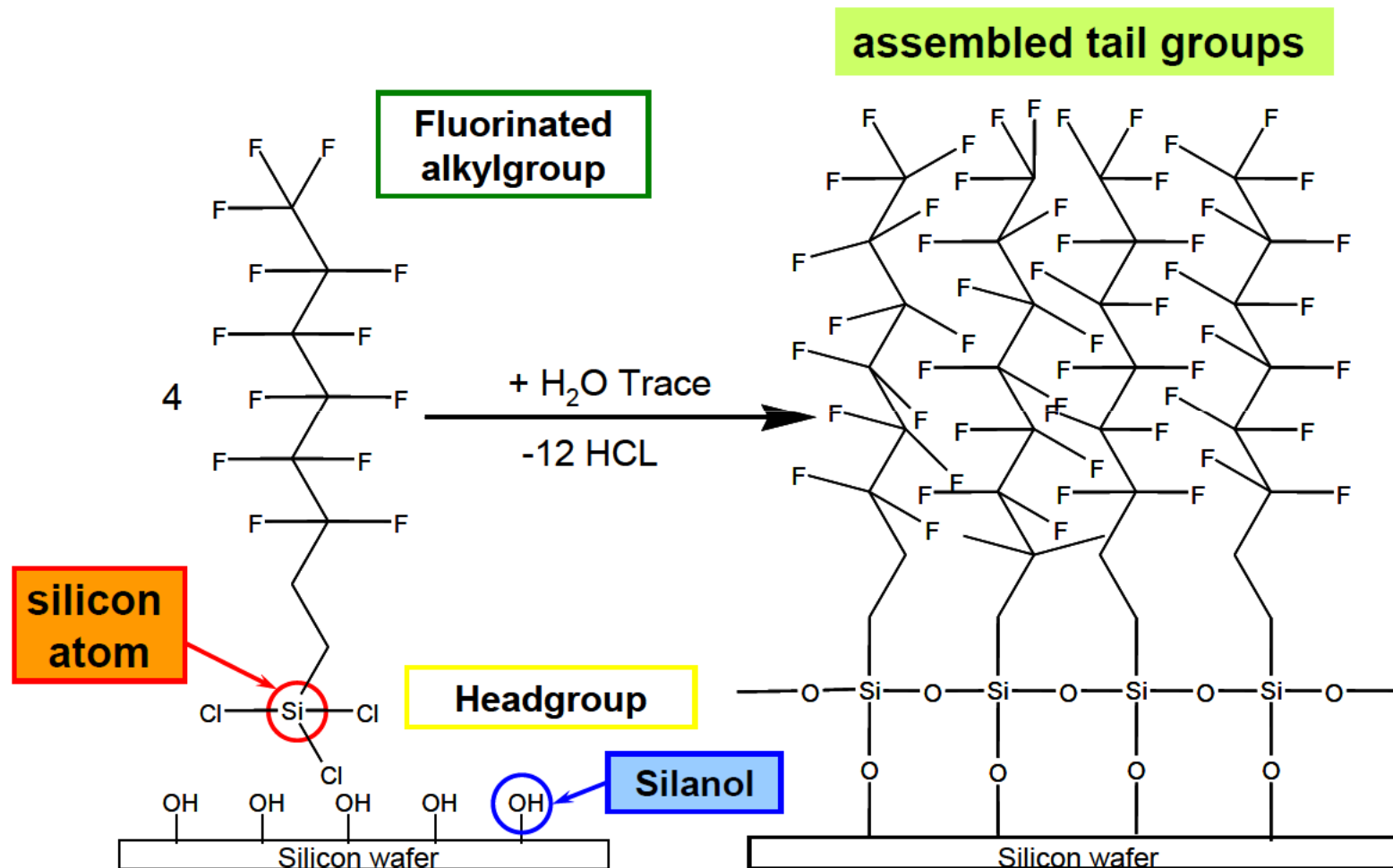
Favorable for stamp release

Unfavorable for stamp release



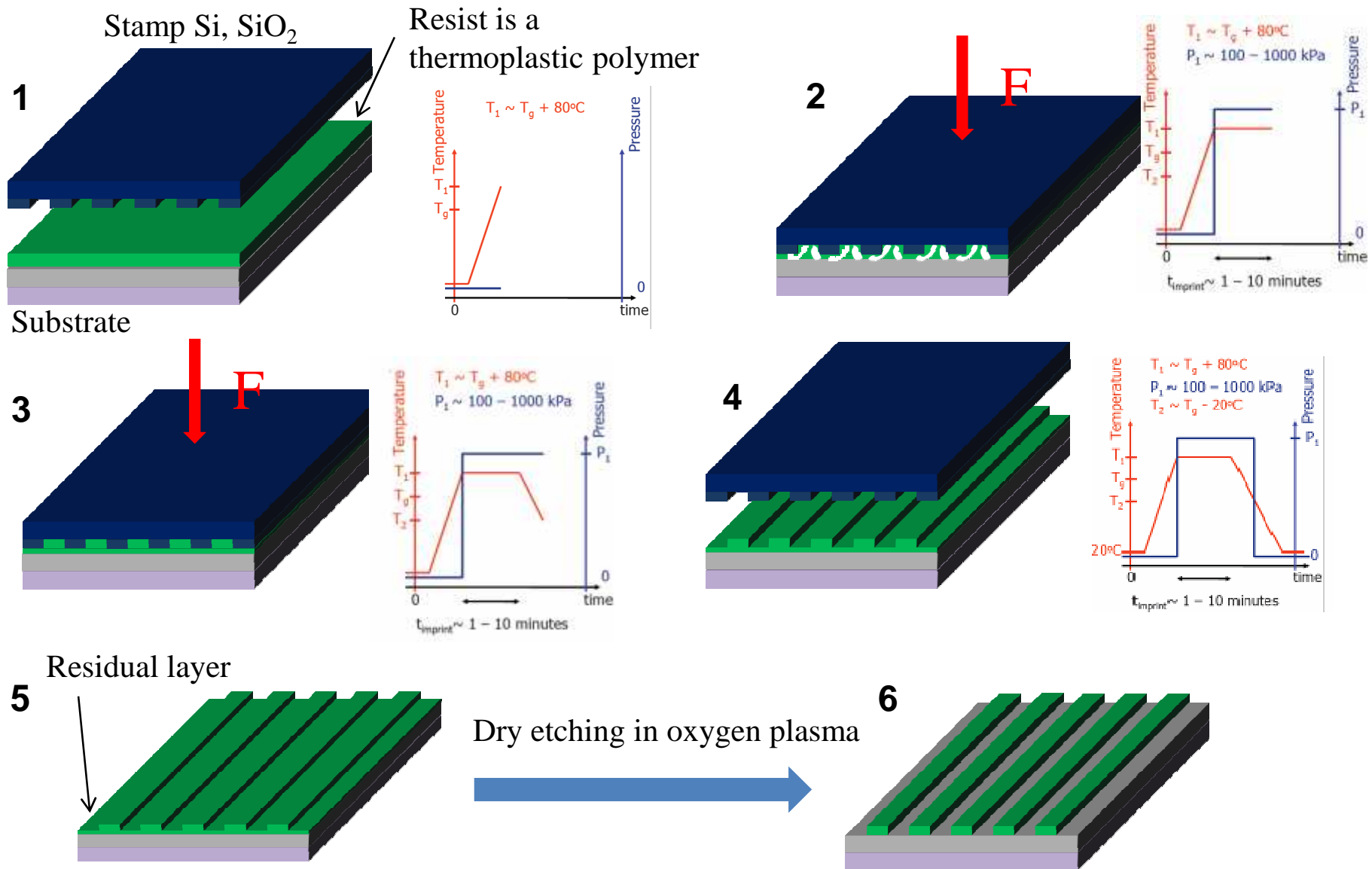
Different contact angles for water on structured (linear grating $\Lambda=600\text{nm}, d=200\text{nm}$) and unstructured, plasma treated and silanated surfaces (TFS tridecafluoro-trichlorosilane)

Fluorinated organosilane as molecular anti-adhesive layer



Courtesy: Helmut Schiff, PSI

NanoImprint Lithography (NIL) process



Related Processes: Laser Assisted NIL

- 50 ps laser ($\lambda=308$ nm) pulse (~ 0.4 J/cm²)
- Quartz template
- 2.5x2.5 mm² spot size

Real time monitoring of nanosecond imprint process

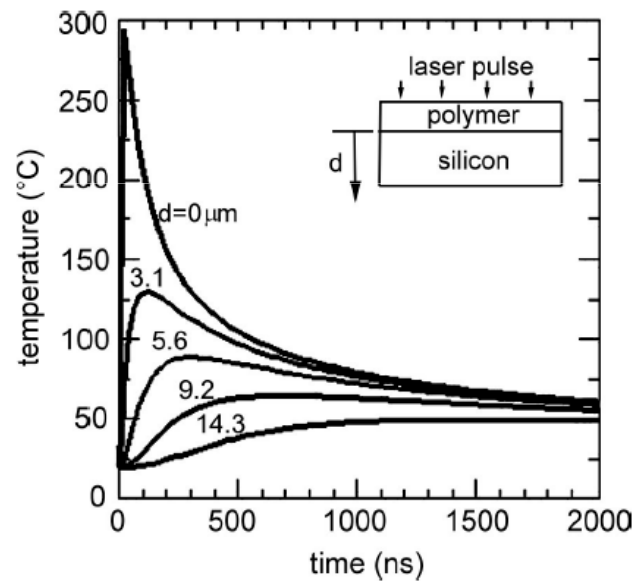
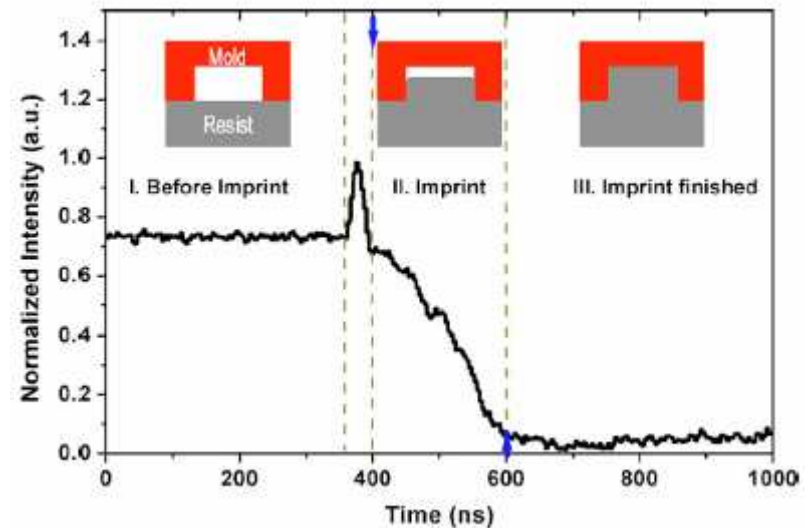
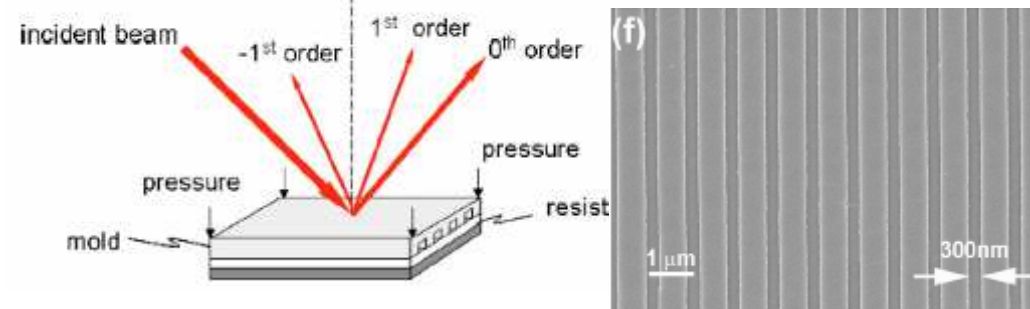
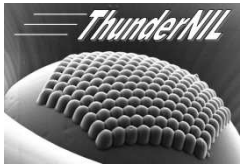


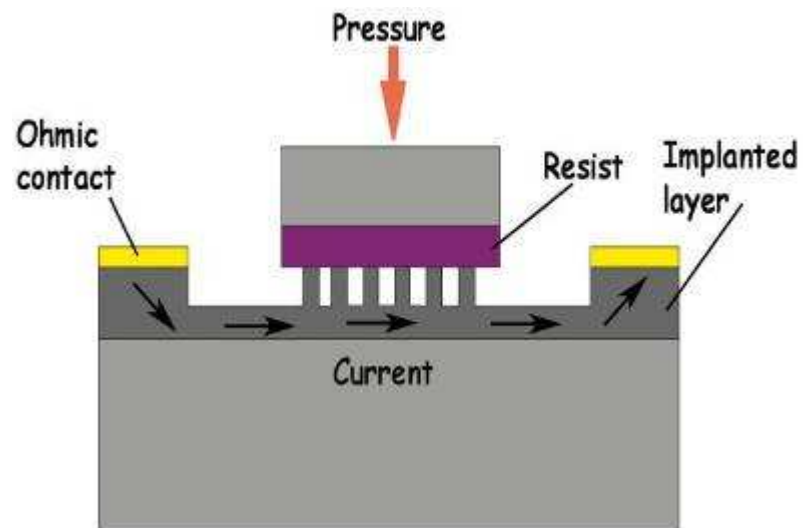
FIG. 5. Simulation results of temperature evolution in the surface layer of a Si substrate after the incidence of a single laser pulse (0.4 J/cm²). Each curve represents the temperature as a function of time at different distances from the Si surface. The inset shows the model geometry in which we assume a 200 nm polymer film on a 500 μm Si substrate.





ThunderNIL working principle

Stamp with integrated heater

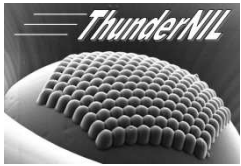


Intense current pulse flowing as a uniform sheet under the patterned surface of the stamp

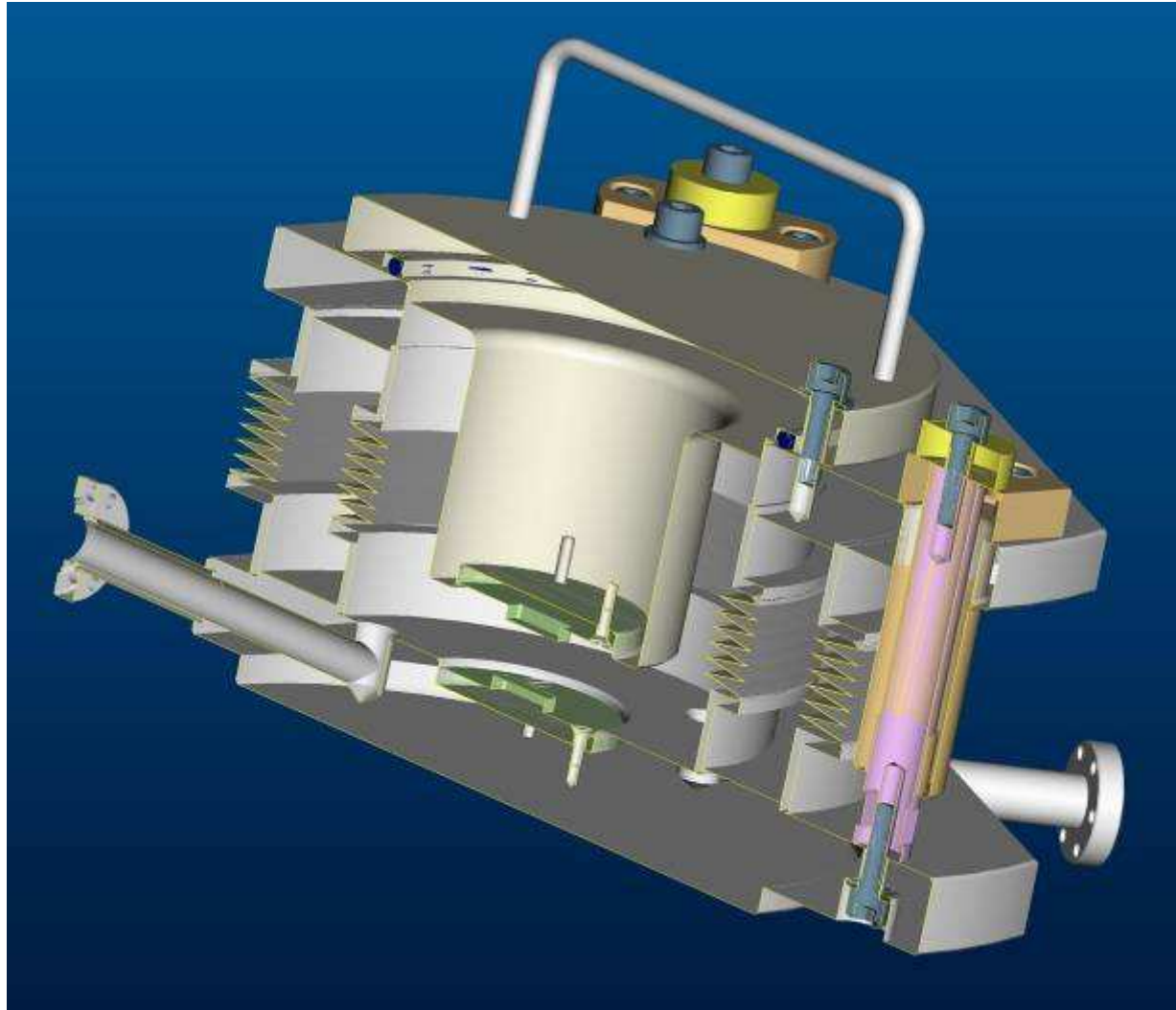
Nanoimprinted grating in 100 μs

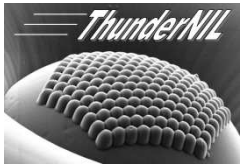


Grating of 250nm L/S imprinted on $>1 \text{ cm}^2$

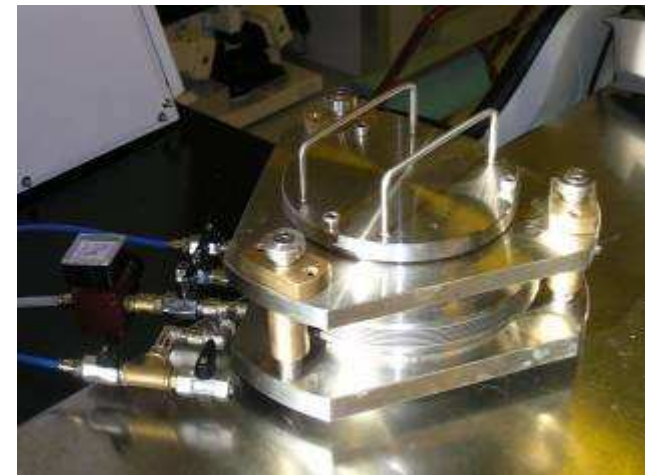
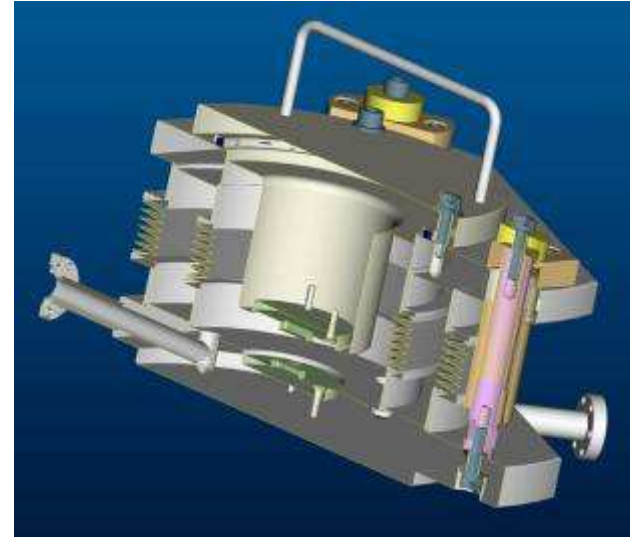


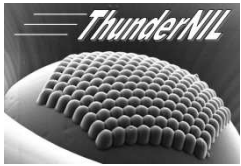
Equipment for ThunderNIL - Prototype



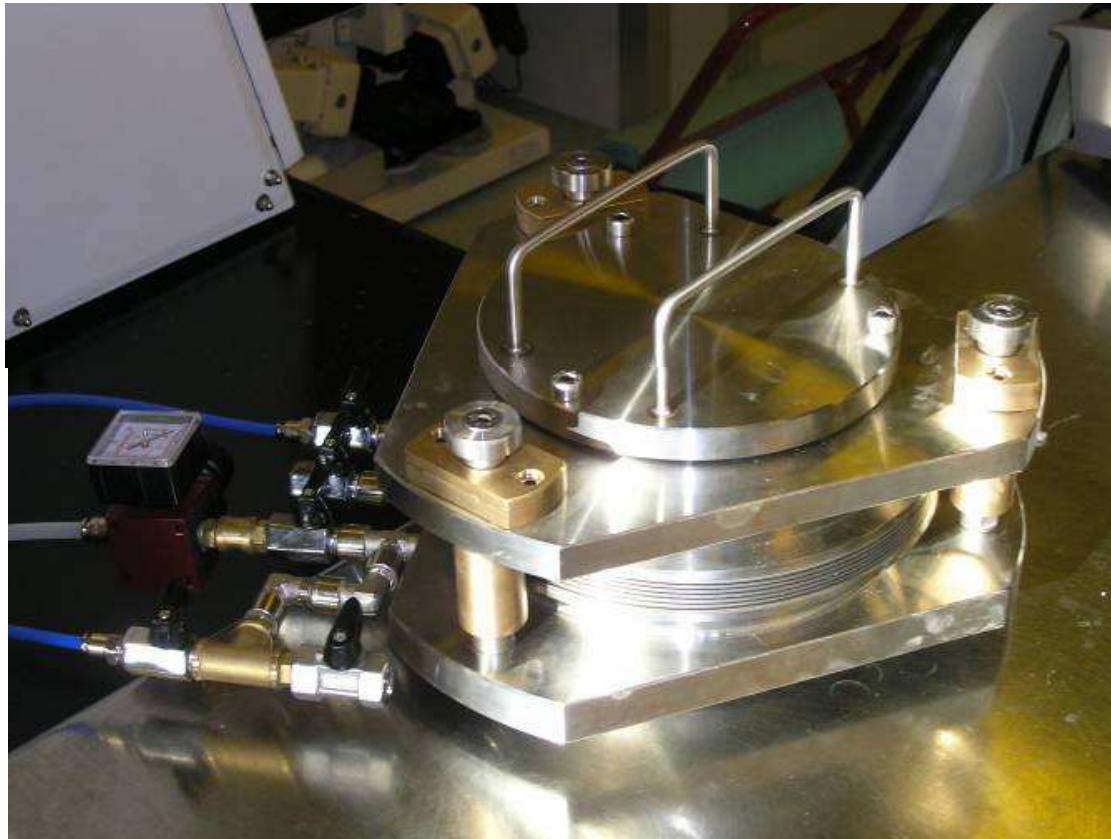
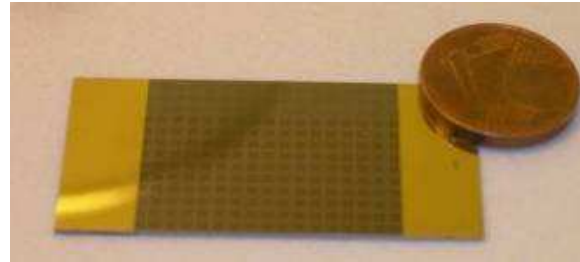


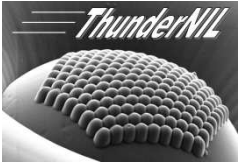
Equipment for ThunderNIL - Prototype





Equipment for ThunderNIL - Prototype





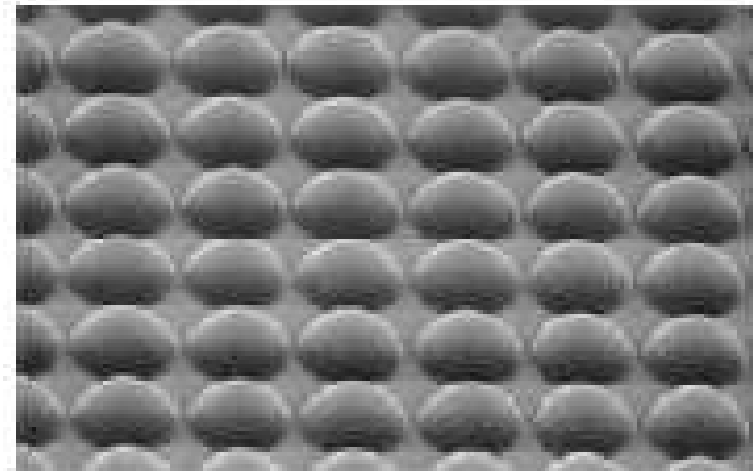
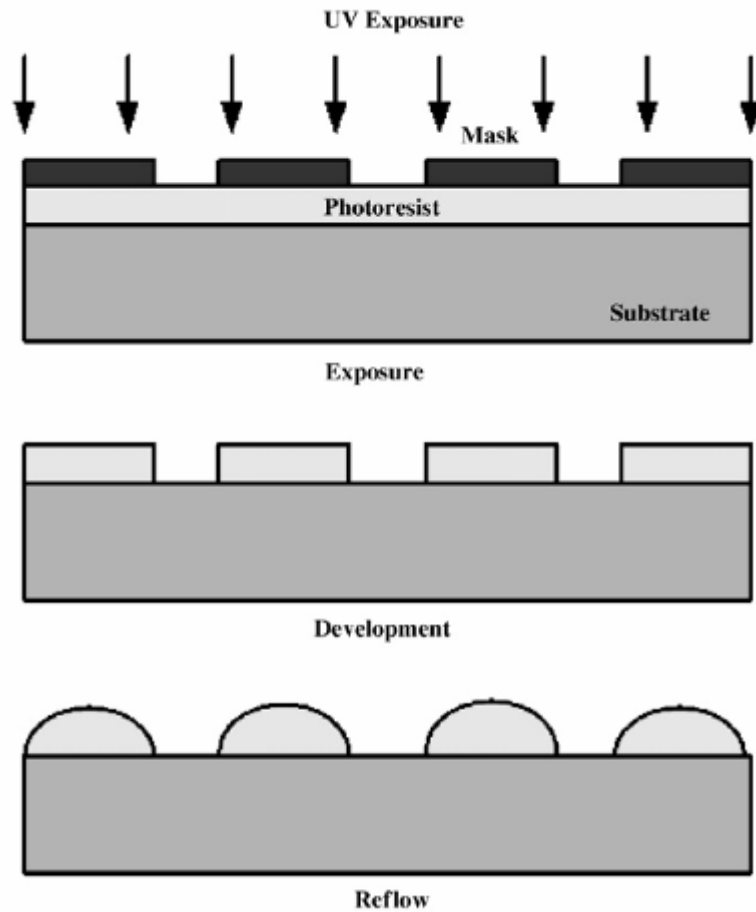
Competitive advantages

- Thermal cycle much faster
 - Heat is provided by the stamp, not by hot plates



- High potential throughput (>1000 substrates/hour)
- Energy saving (>1000 J/cm² → 1 J/cm²)
- Reduced effects of thermal expansion
 - Improved alignment capability

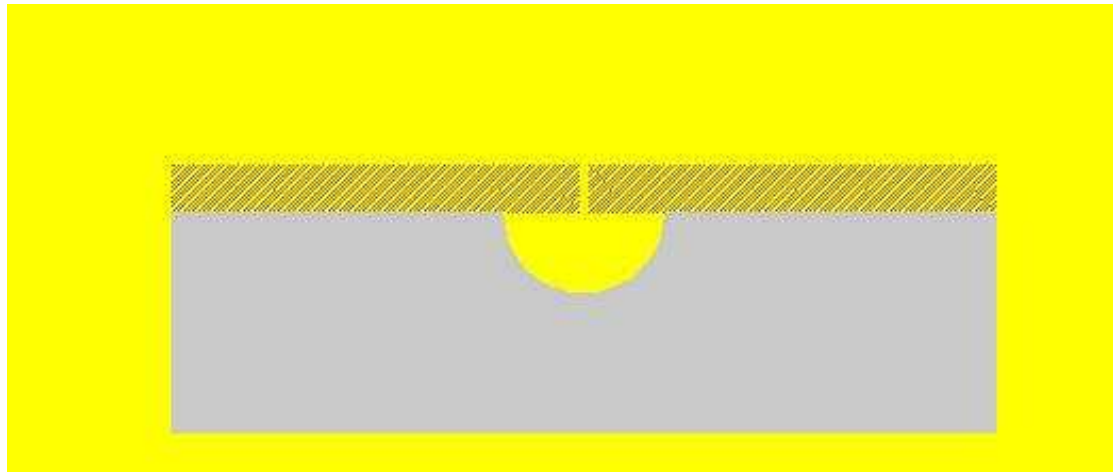
Microlenses by Polymer Reflow technique



AN EFFECTIVE TECHNIQUE FOR MAKING MICROLENSES



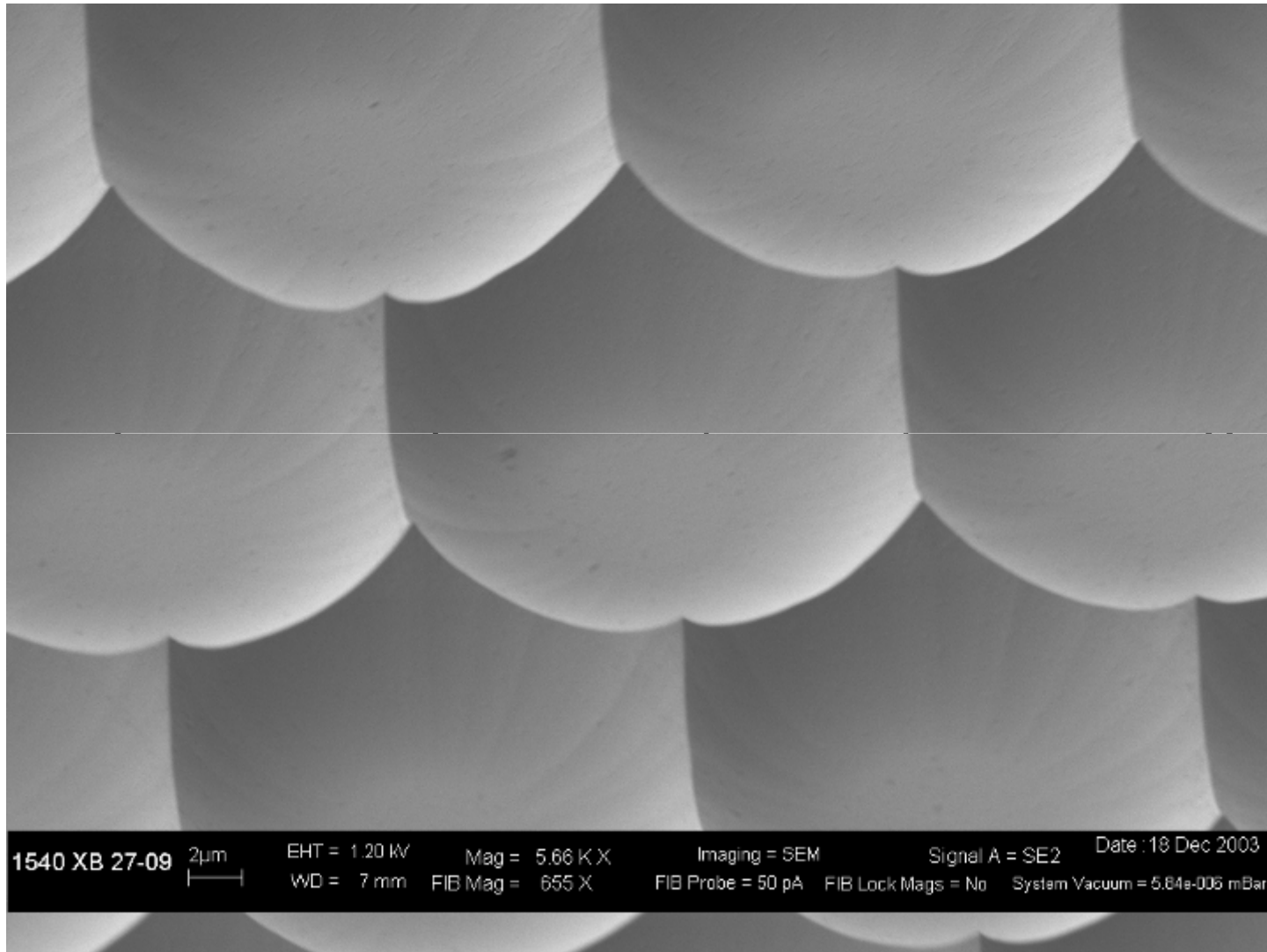
“Exploiting” Natural geometries



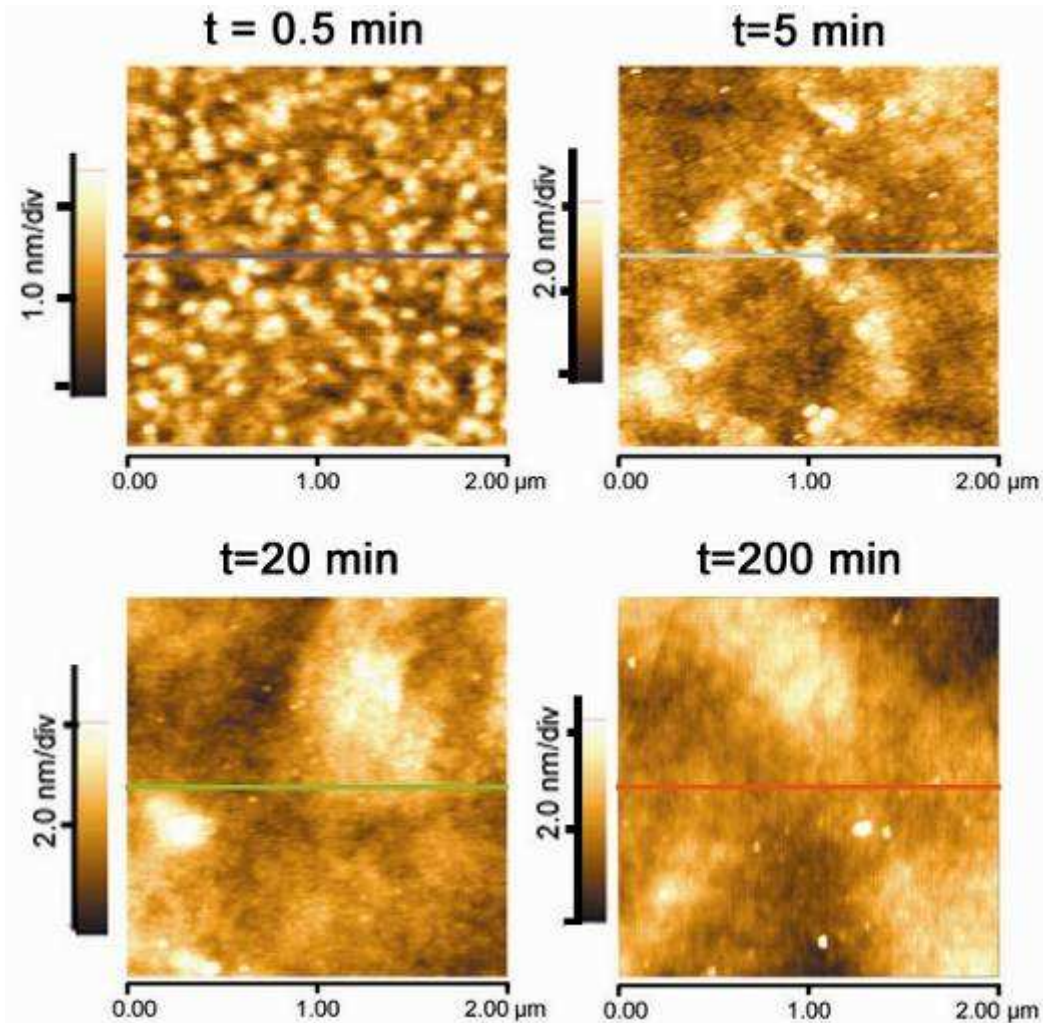
*The book of Nature is written in the
characters of the geometry.*

Galileo Galilei

Isotropic etching of quartz

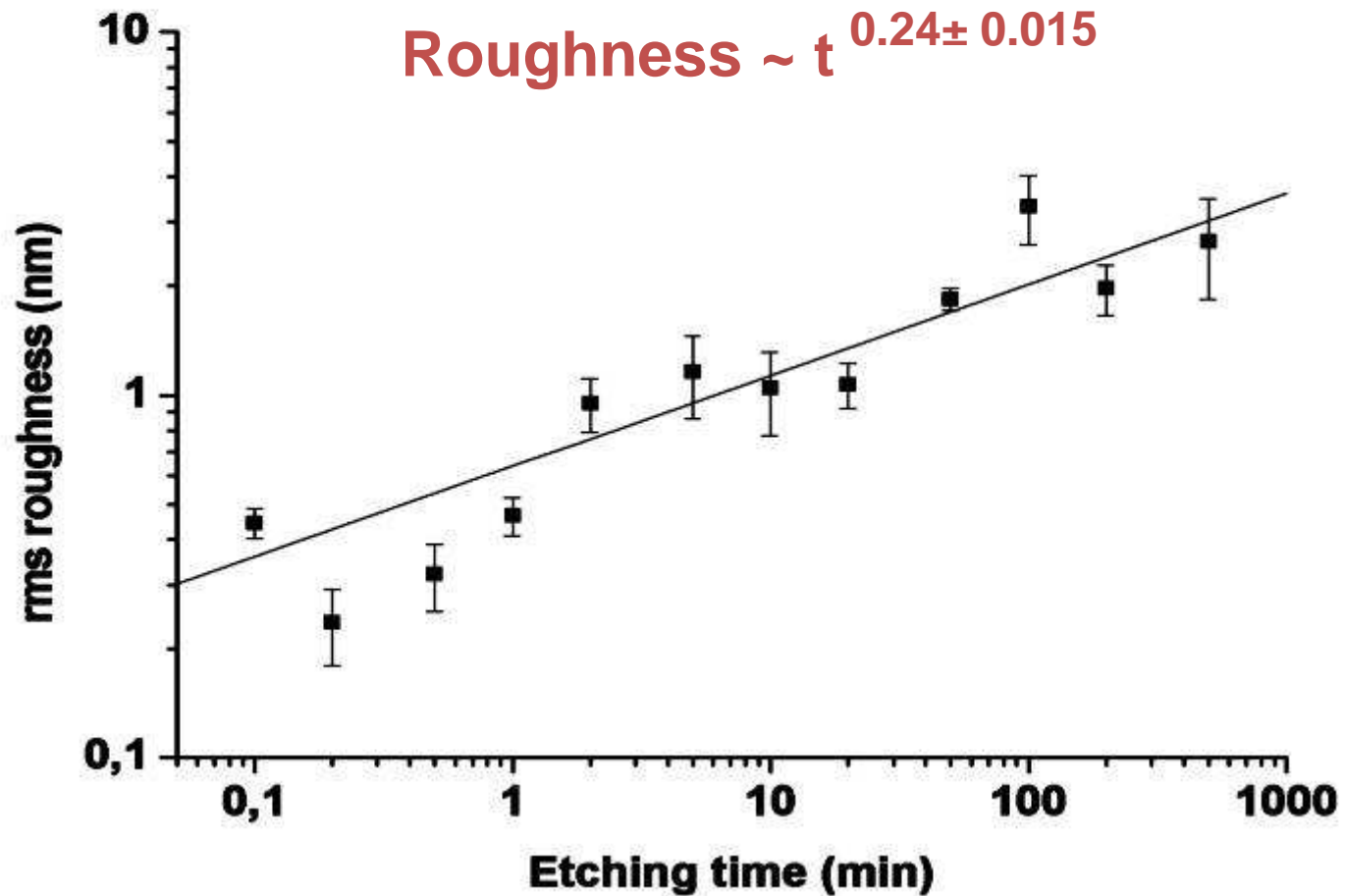


Roughness vs. etching time by AFM



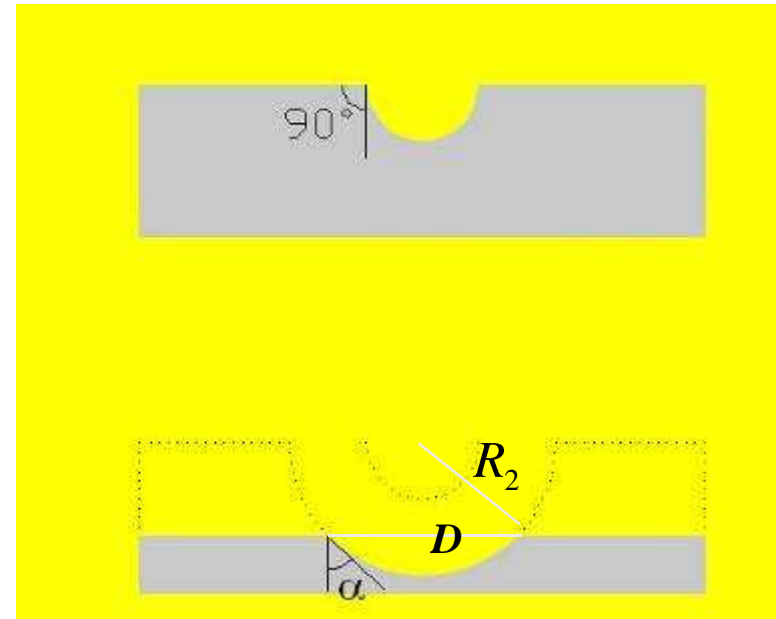
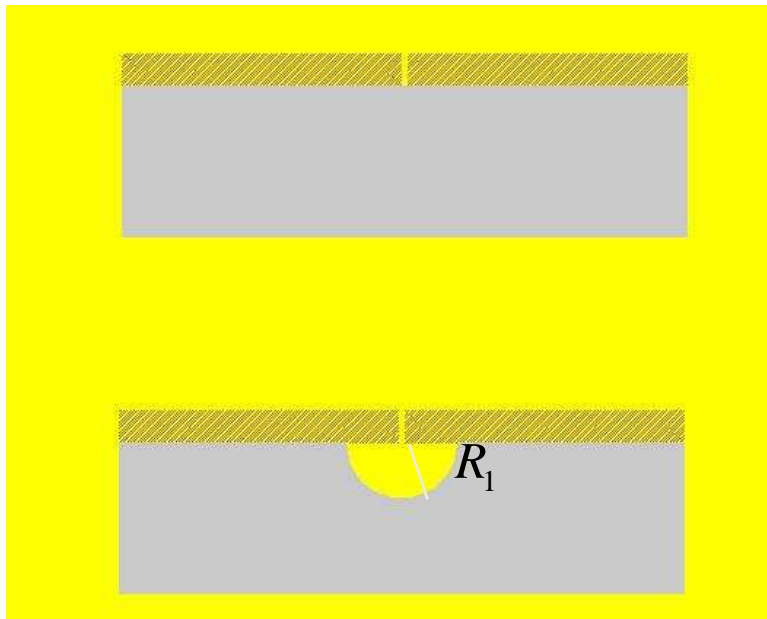
Etching rate 0.6 μm/min (HF 39.5%)

Roughness vs. etching time by AFM

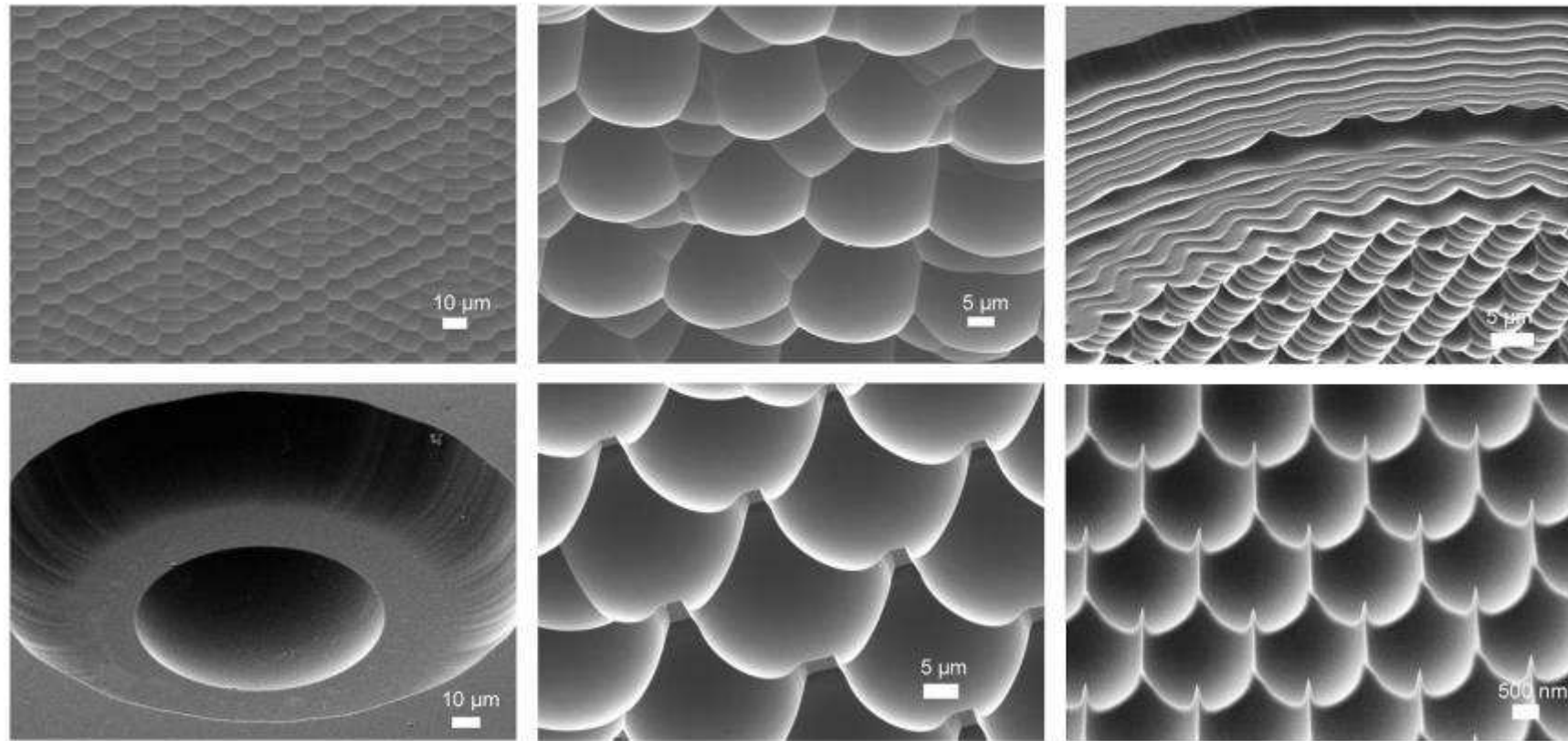


Etching rate 0.6 $\mu\text{m}/\text{min}$ (HF 39.5%)

Controlling curvature & diameter

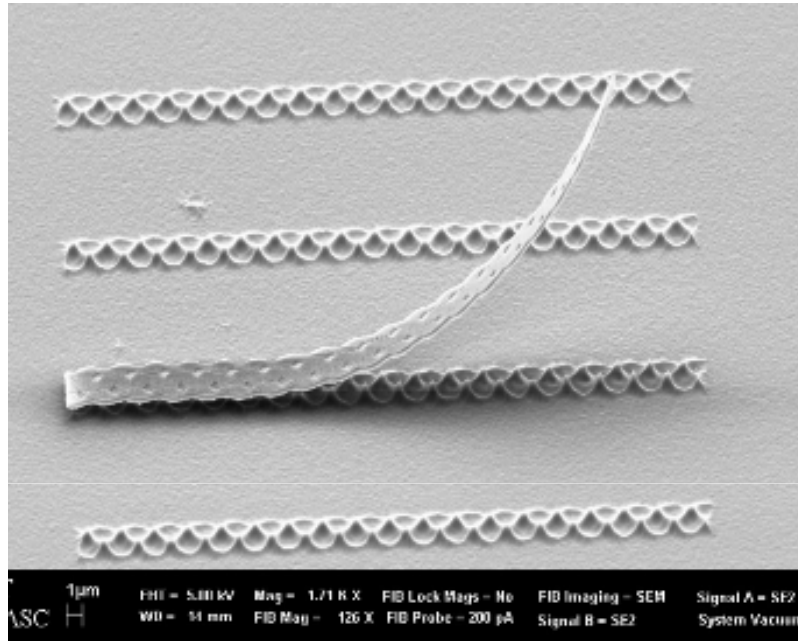


Large area 3D patterning

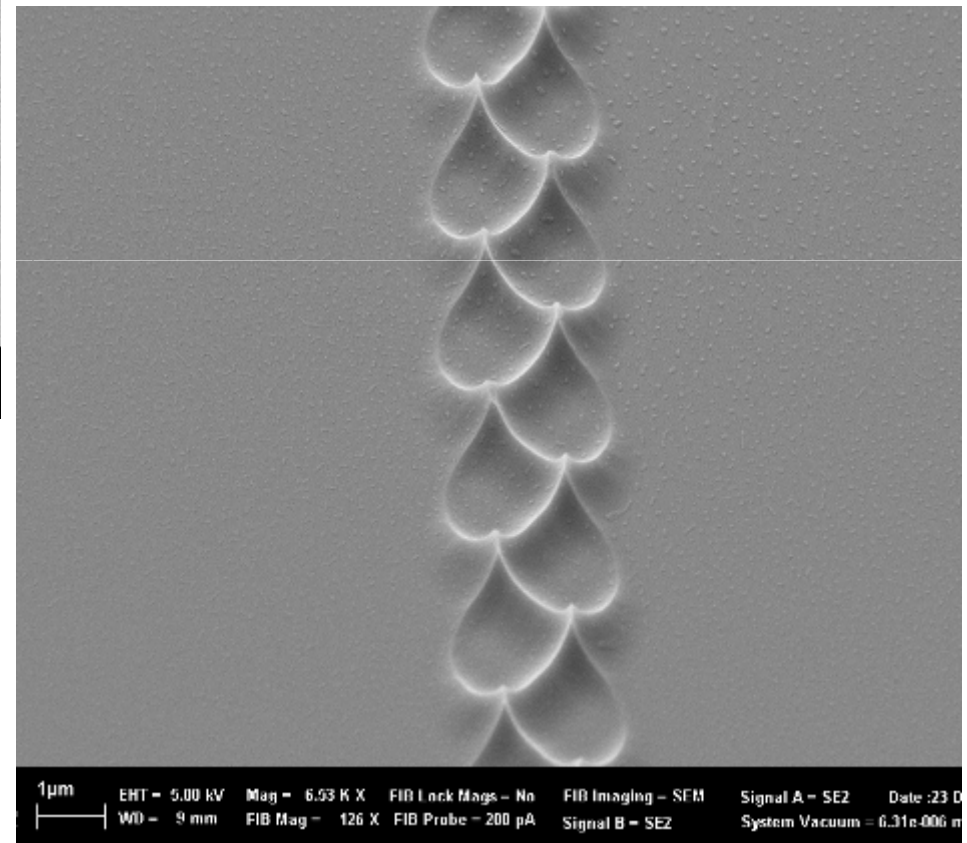


2 cm² written in few hours by EBL

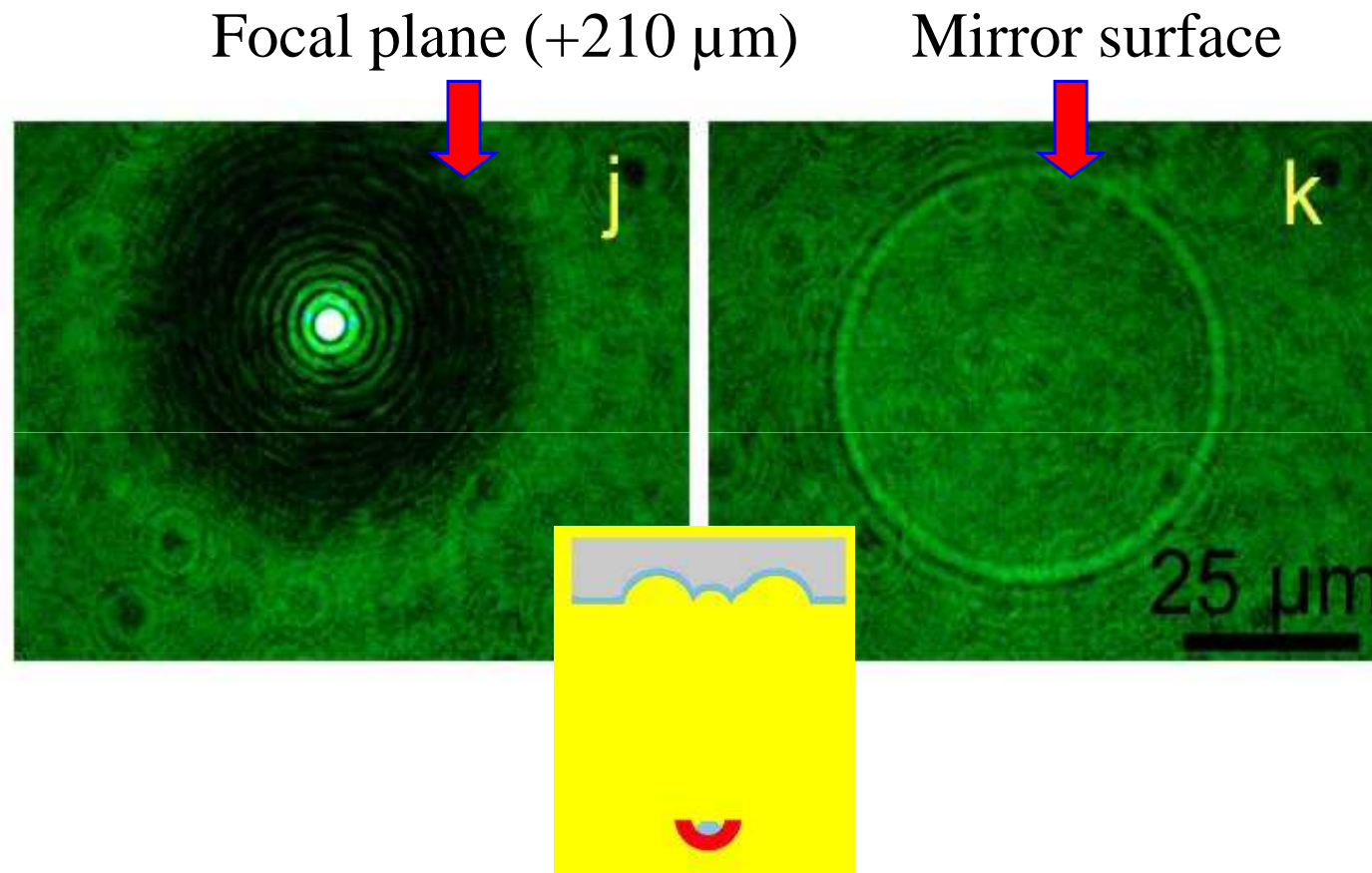
High resolution patterning of curves in 3D



- Design a 2D pattern in order for the edges to define given curves in 3D.
- Sub-100 nm resolution



Micromirrors



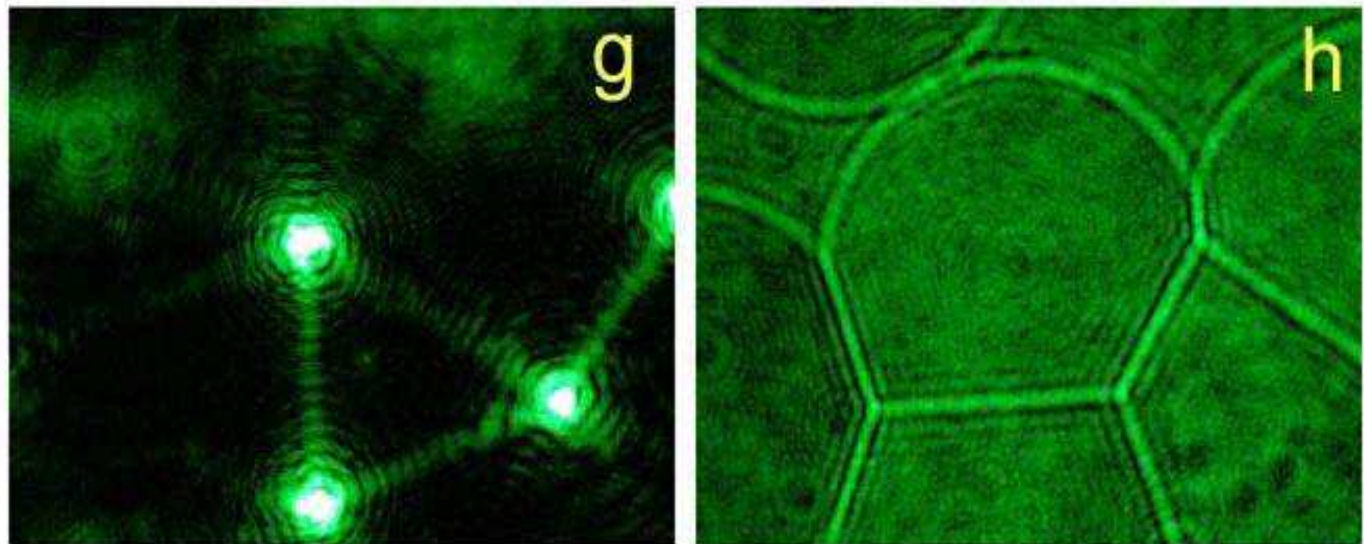
*Optical images of a spherical micromirror ($R=420 \mu\text{m}$,
 $D= 54 \mu\text{m}$) illuminated by an argon laser ($\lambda= 514.5 \text{ nm}$).*

Micromirrors

Focal plane (+210 μm)

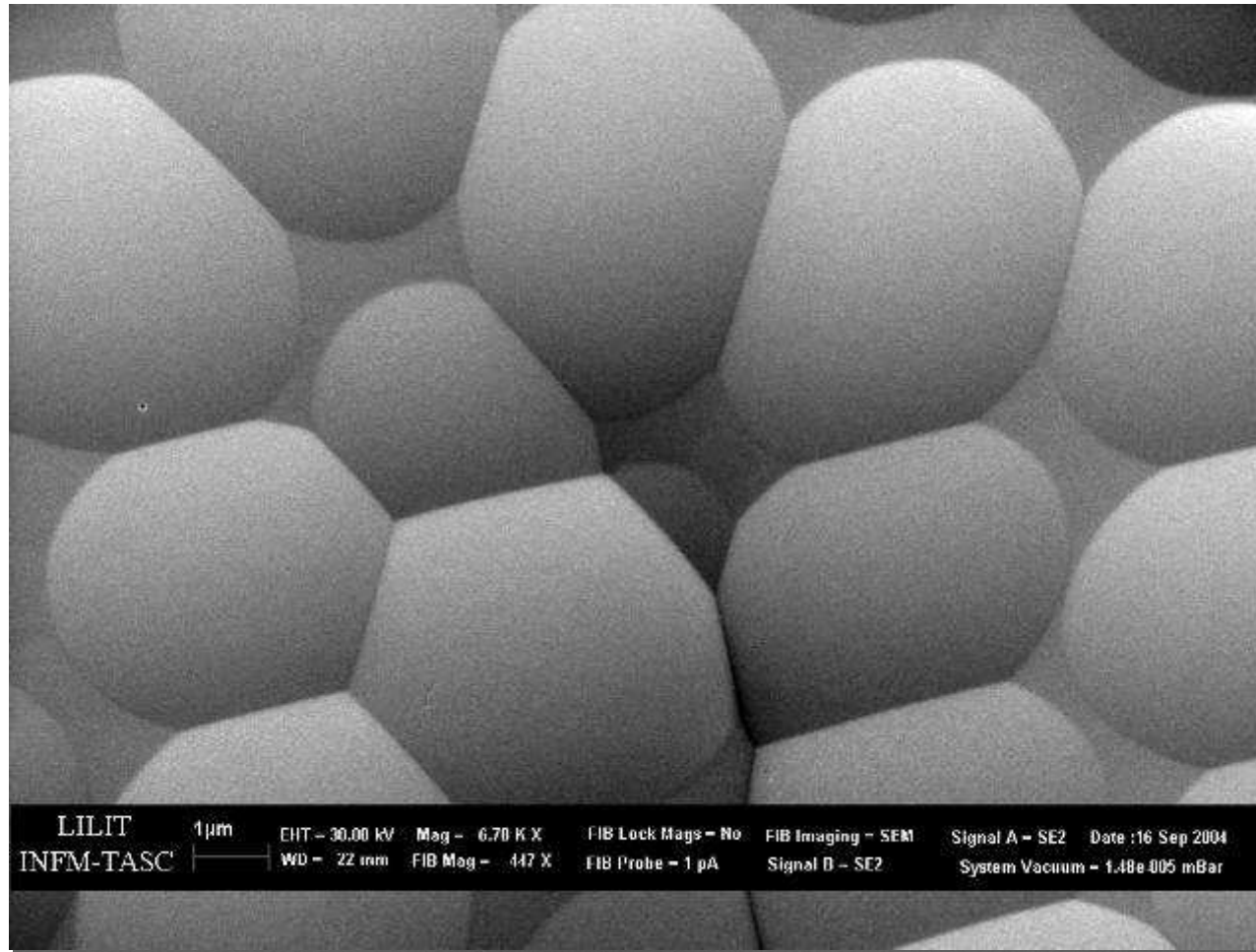


Mirror surface



Images of an arbitrary arrangement of intersecting spherical micromirrors ($R=420 \mu\text{m}$) illuminated by an argon laser ($\lambda= 514.5 \text{ nm}$).

Complex refractive optics



Optical Performances

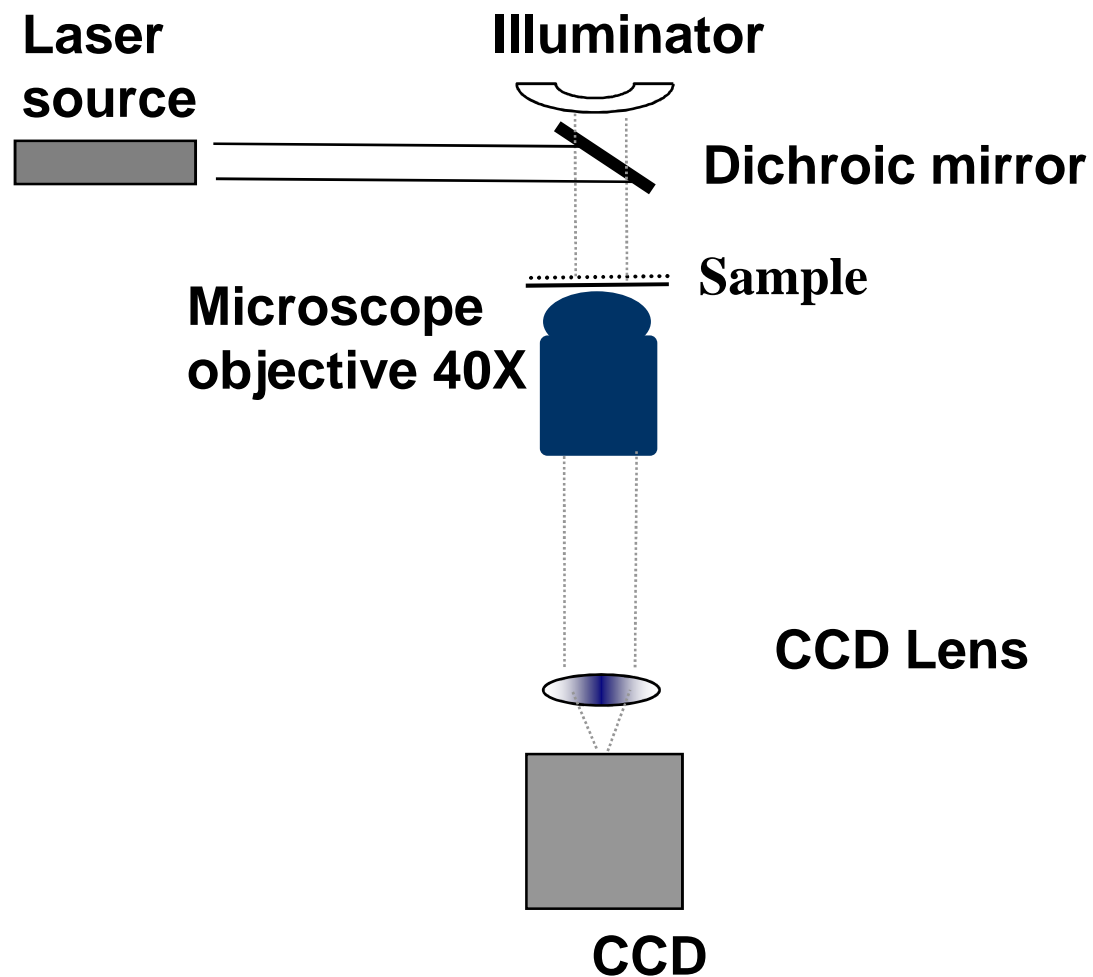
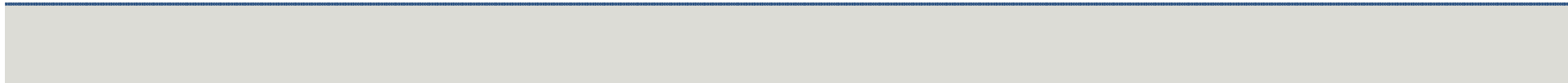
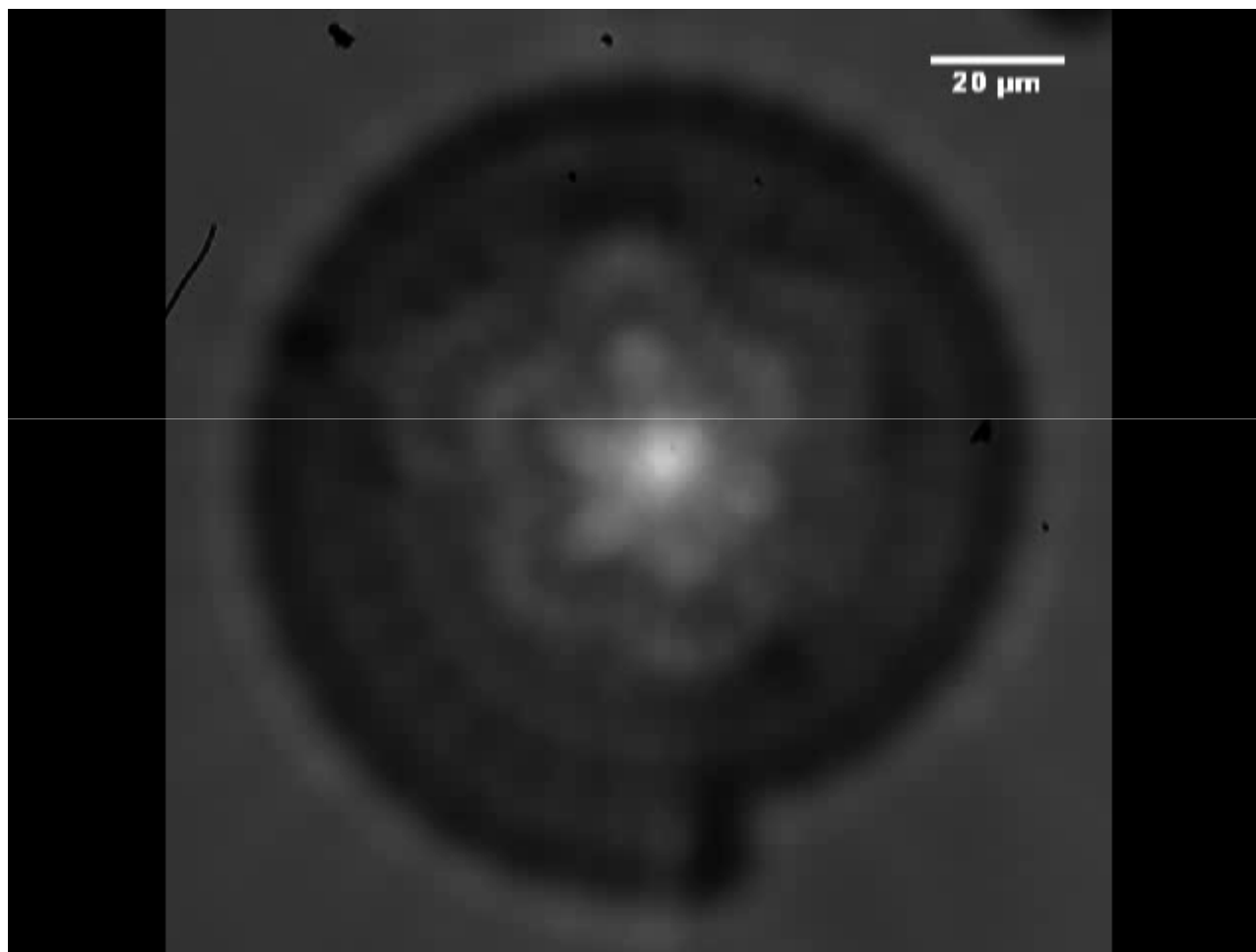


Image at different planes



Natural compound eyes

- Examples of complex refractive optics in the nature
- The compound eyes of the insects
 - Limited weight
 - Reduced space
 - Low metabolic consumption
- Ommatidia



Thousands of lenses in the dragonfly eyes

Artificial compound eyes

