Fabrication of high aspect ratio nanostructures using capillary lithography

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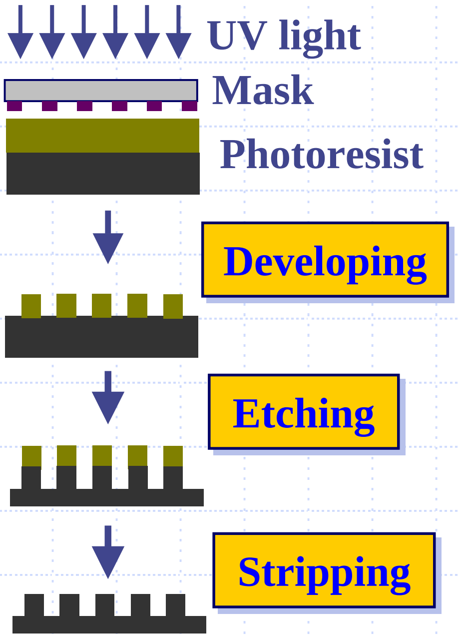
Traditional nanoscale patterning: Photolithography



- Photolithography is fast approaching the diffraction limit:

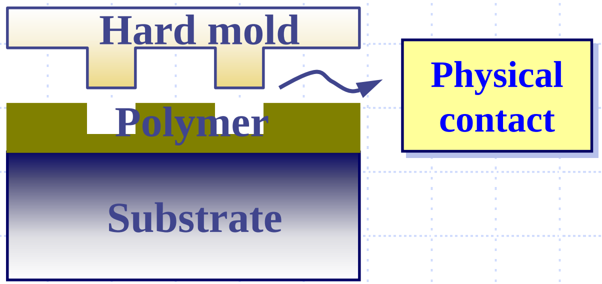
  Current consensus: Not applicable to feature sizes smaller than 100nm

  Even if possible, economically unbearable

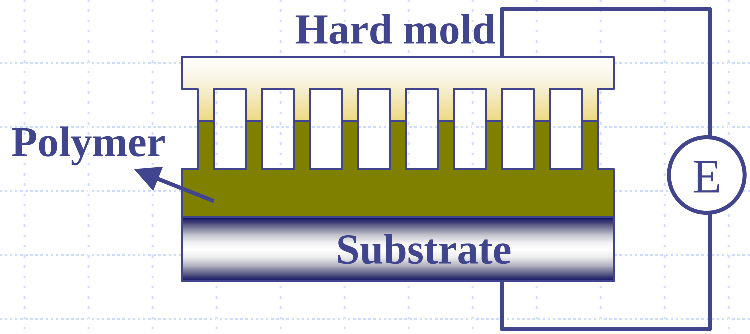
  Alternative: Deep UV lithography, E-beam lithography

Other unconventional top-down methods

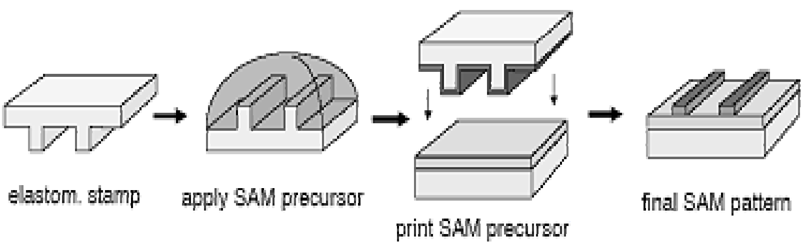
Nanoimprint lithography
(Chou et al., Science, 1996)



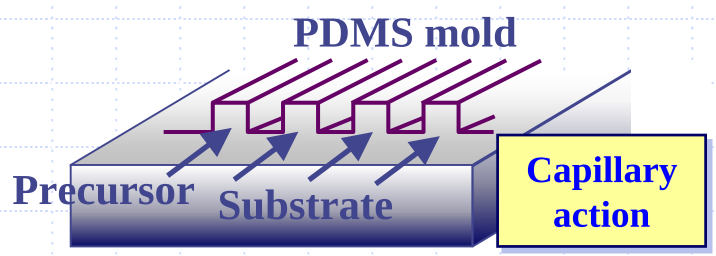
Electrically induced structure formation
(Schäffer et al., Nature, 2000)



Micro/nanocontact printing
(Whitesides et al., JACS, 1992)



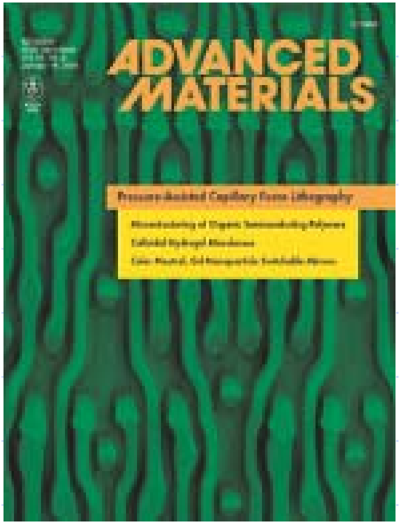
Micromolding in capillaries
(Whitesides et al., Nature, 1995)

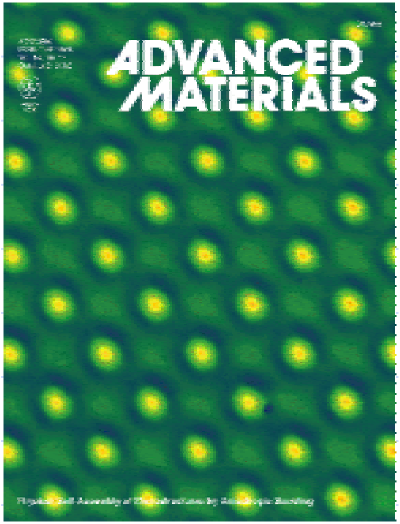


❑ Origin of imprint and soft lithography?

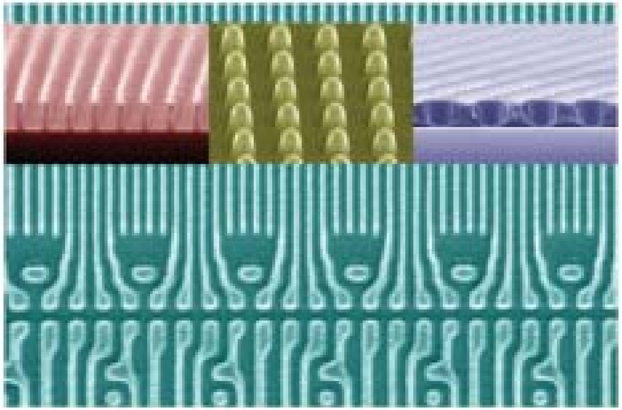
➢ The world's first printed masterpiece called "직지심경" was invented in Korea in the early 11th century, which precedes that of Germany by more than 200 years!

Capillary Lithography
(모세관 리소그라피)

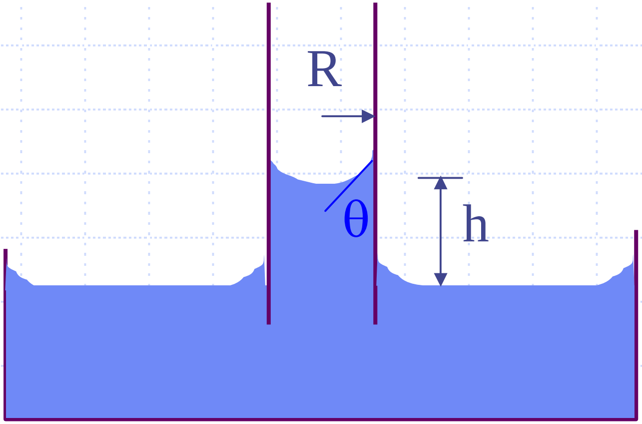


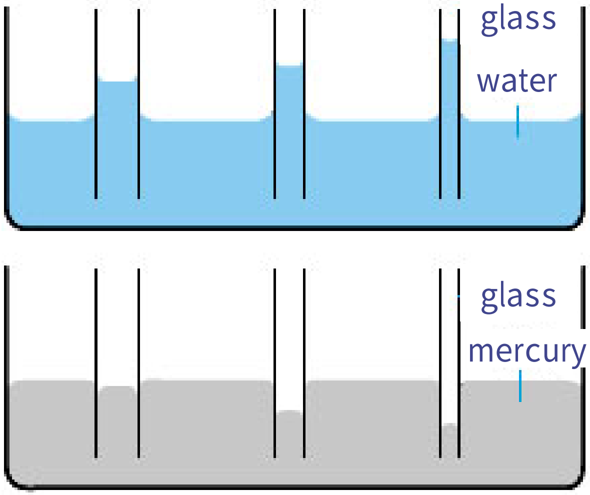


APL cover paper



What is capillarity?





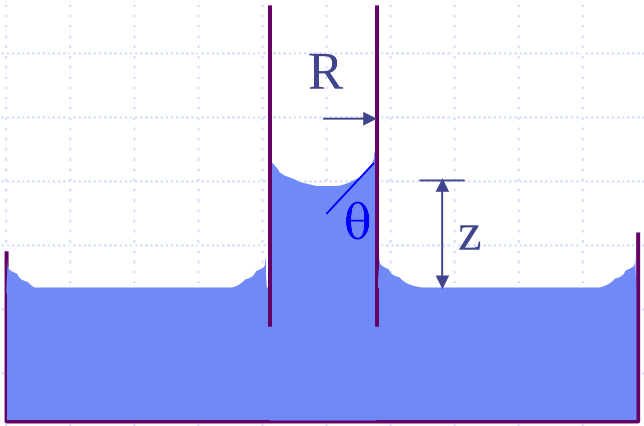
- Young-Laplace equation

$$\Delta P = \frac{2\gamma}{R}\cos\theta,\ h = \frac{2\gamma}{\rho g R}\cos\theta$$

- Laplace pressure vs. Gravity
- Tube size ~ typically on the order of **mm**
- Capillary rise is relatively fast

Capillary kinetics

Assumption: Poiseuille flow (neglect of inertial force)



1. Without gravity (LWR equation)

$$\frac{dz}{dt} = \frac{R\gamma_{LV}\cos\theta}{4\eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4\eta z}$$

R: hydraulic radius
η: viscosity
z(t): capillary movement

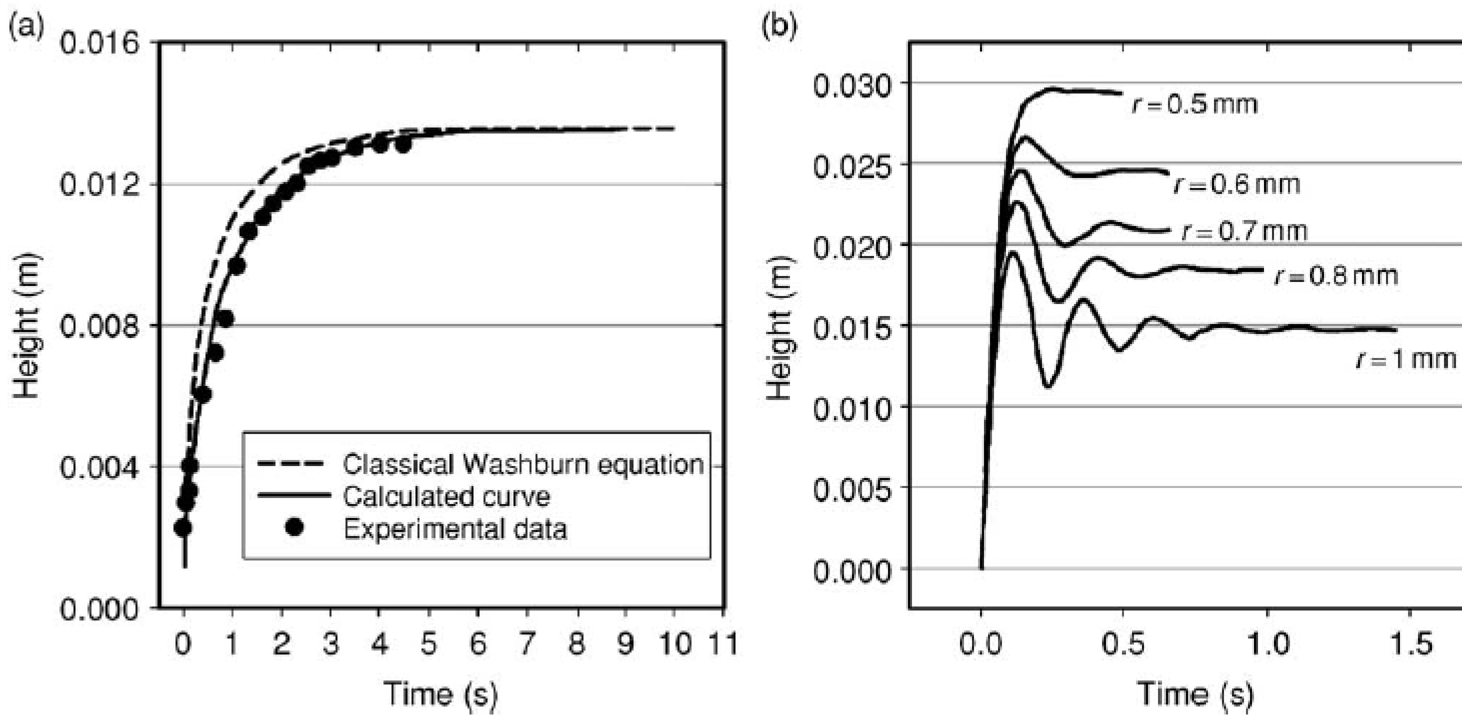
$\longrightarrow$ $z \sim t^{1/2}$

1. With gravity

$$\frac{\rho g R^2}{8\eta} t = z(t) - z_e \ln\left[1 - \frac{z(t)}{z_e}\right]$$

z_e: equilibrium capillary rise
ρ: density
g: gravity coefficient

$\longrightarrow$ Diverges as $z \to z_e$



(a) Silicon oil in glass tube with r = 0.315 mm.
(b) Inertia-induced oscillations

Merits of capillarity (in terms of micro/nanofabrication)

- Familiar and physically well understood
- A natural, spontaneous phenomenon

  ~ no need to apply an external energy or stimulus
- One-step and three dimensional patterning

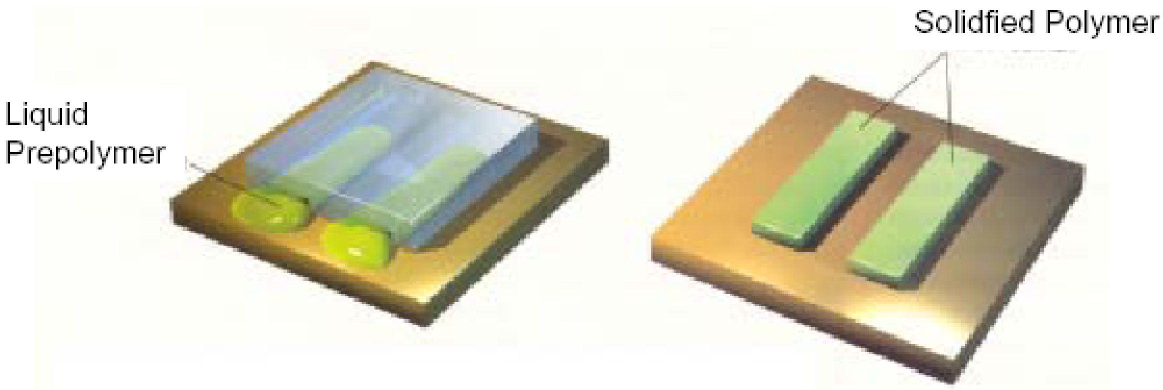
  (cf. photolithography)
- Versatile use

  ~ capillary rise or depression

First introduction of capillary force

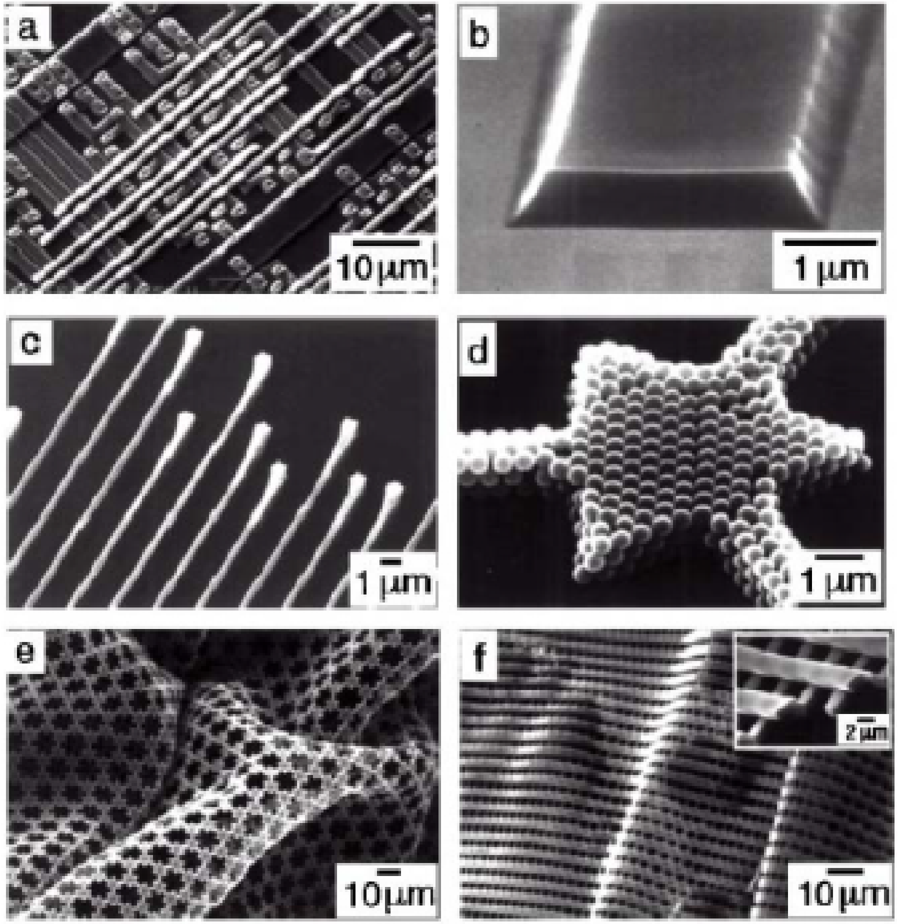
E. Kim, Y. Xia, and G. M. Whitesides, *Nature*, 376, 581 (1995)

MIcroMolding In Capillary (MIMIC)



- PDMS mold is placed on the surface of a substrate and makes conformal contact with that surface
- The relief structure in the mold forms a network of empty channels
- When a low-viscosity liquid prepolymer is placed at the open ends of the network of channels, the liquid spontaneously fills the channels by capillary action.
- After filling the channels and curing the prepolymer into a solid, the PDMS mold is removed, and a network of polymeric material remains on the surface of the substrate

Results of MIMIC



SEM images of microstructures of various materials fabricated using MIMIC:

(*a*) Quasi-three-dimensional structures of PU formed on Si/SiO_2

(*b–d*) Patterned microstructures of polyaniline emeraldine HCl salt, zirconia (ZrO2), and polystyrene beads, respectively, that were fabricated from their solutions or suspensions using MIMIC

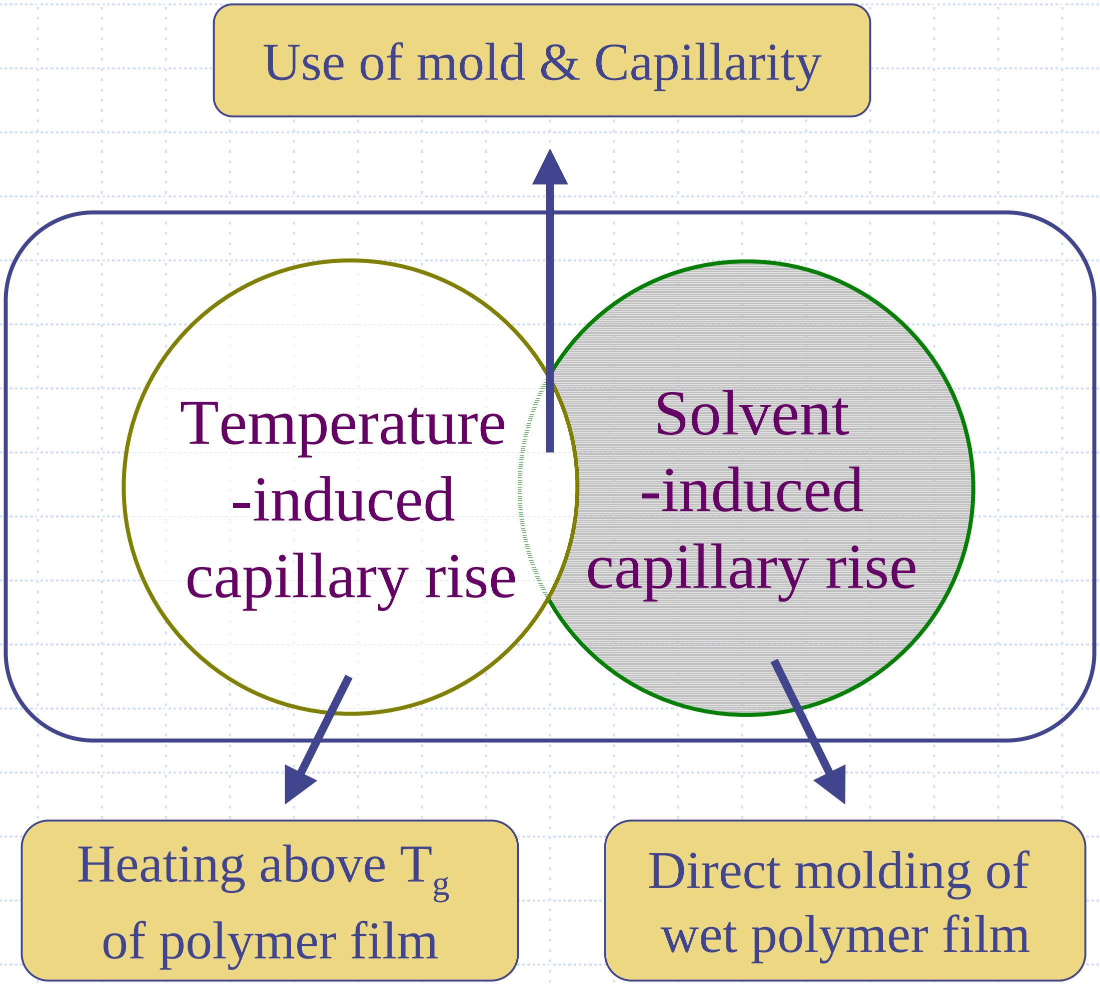
(*e,f*) Free-standing microstructured membranes of polyurethane. The buckling occurred during sample preparation

Limitations of MIMIC

- Low resolution (> ~ 1μm)
- PDMS need to have a network structure inside
- Slow and incomplete patterning (use of vacuum?)
- No capillary action with hydrophilic bio fluids (θ ~ 105º)

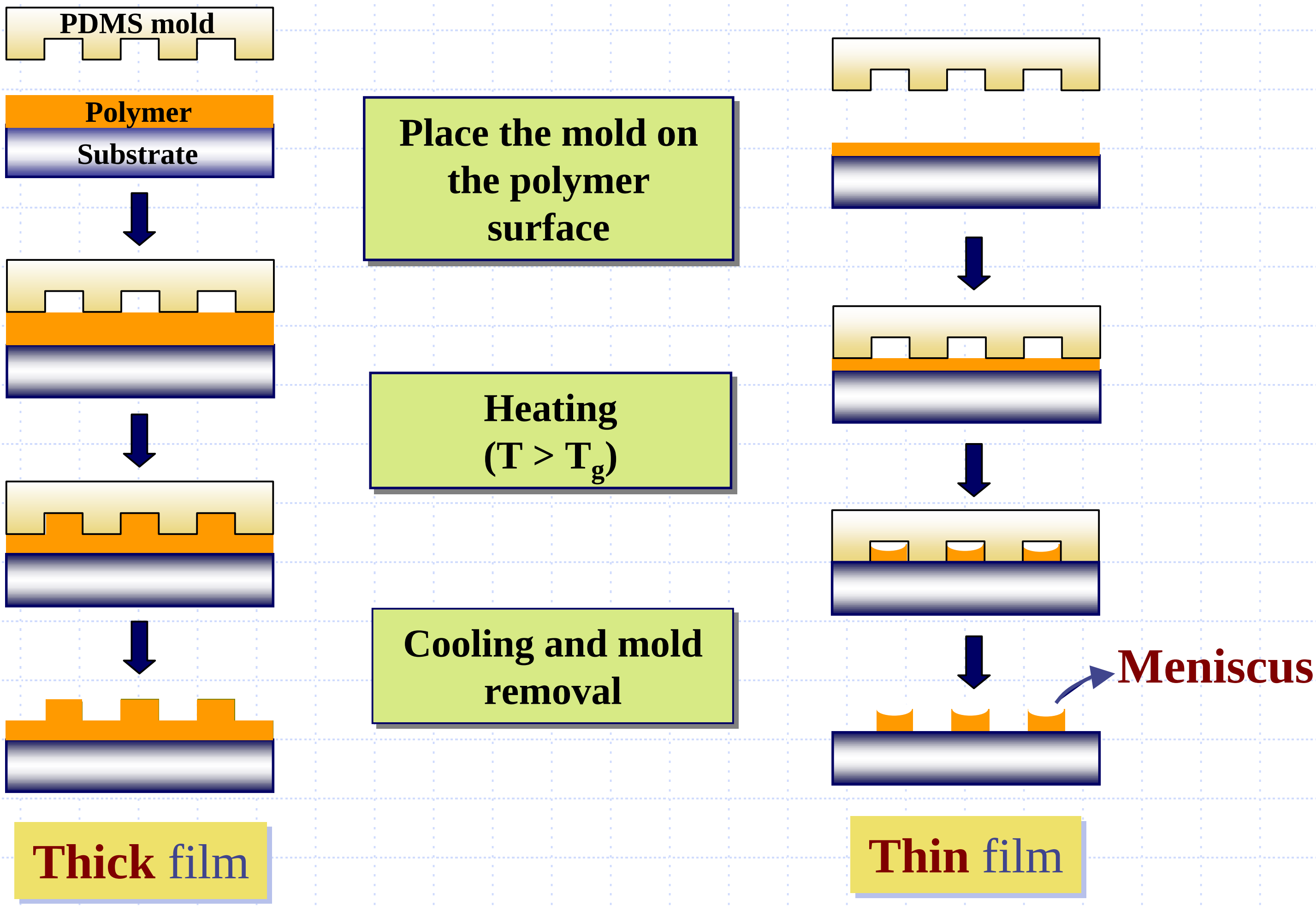
Capillary Lithography

- **How to make an immobile polymer film into a mobile one?**

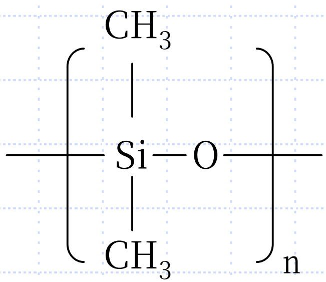


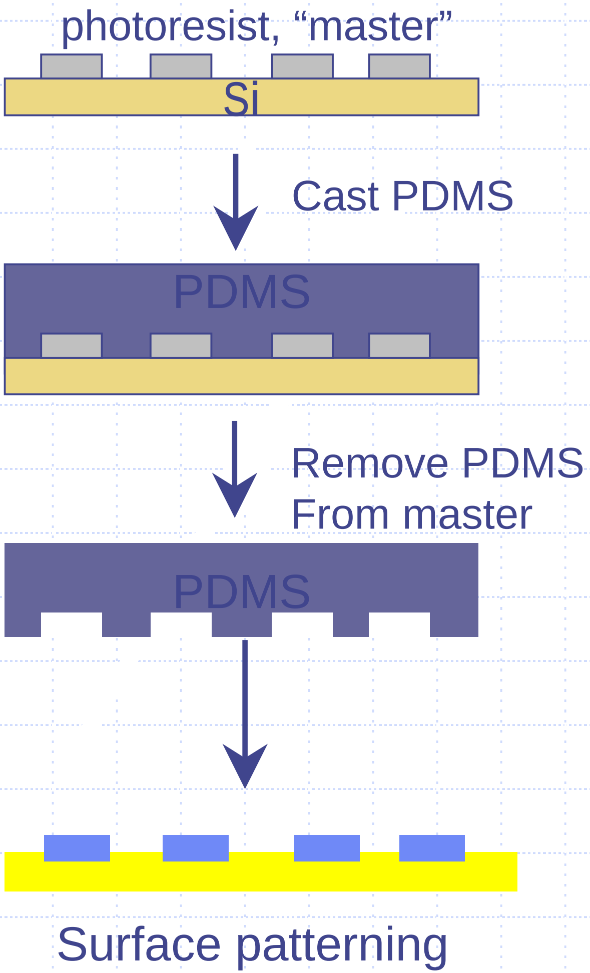
1. Patterning by temperature-directed capillarity

Suh, Kim, and Lee, Adv. Mater. (2001)



Fabrication of polydimethylsiloxane (PDMS) mold





- Base: Curing agent = 10 : 1

- Modulus is tunable depending on the amount of curing agent

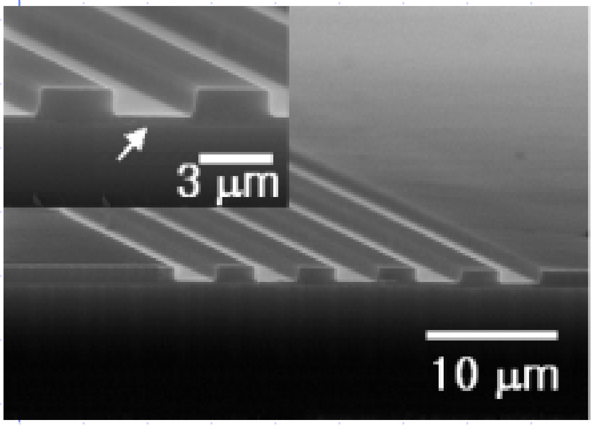
- Young's modulus ~ 3.2 MPa

Why PDMS (Dow Sylgard™ 184 elastomer)?

- Low interfacial free energy (21.6 dyn/cm) and good chemical stability; most molecules or polymers being patterned or molded do not adhere irreversibly to, or react with, the surface of PDMS
- Not hydroscopic so does not swell with humidity
- High gas permeability
- Good thermal stability (up to 186±C in air)
- Prepolymers being molded can be cured thermally
- Optically transparent down to 300 nm; prepolymers being molded can also be cured by UV cross-linking
- Isotropic and homogeneous
- Stamps or molds made from this material can be deformed mechanically to manipulate the patterns and relief structures in their surfaces (22, 37, 38). The
- Durable when used as a stamp (used >50 times over a period of several months without noticeable degradation in performance)
- Interfacial properties can be changed readily either by modifying the prepolymers or by treating the surface with plasma to form siloxane SAMs to give appropriate interfacial interactions with other materials with a wide range of interfacial free energies

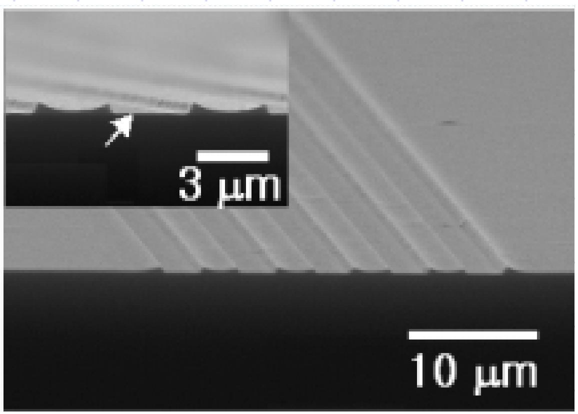
Results

Thick and Thin polymer films



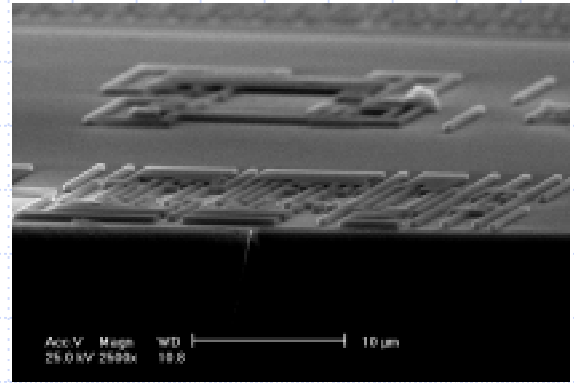
Film thickness: 1.5 µm

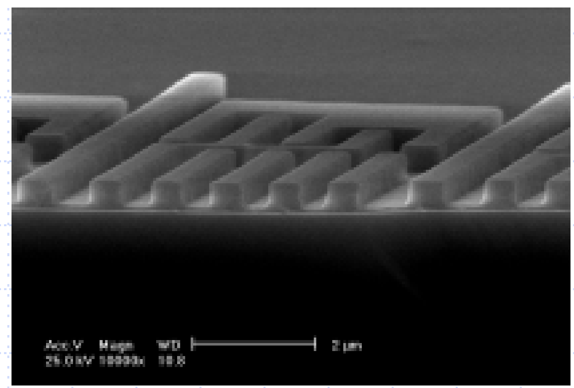
Polystyrene, 130°C, 24 hrs



Film thickness: 180 nm

Complex and Large-area patterning

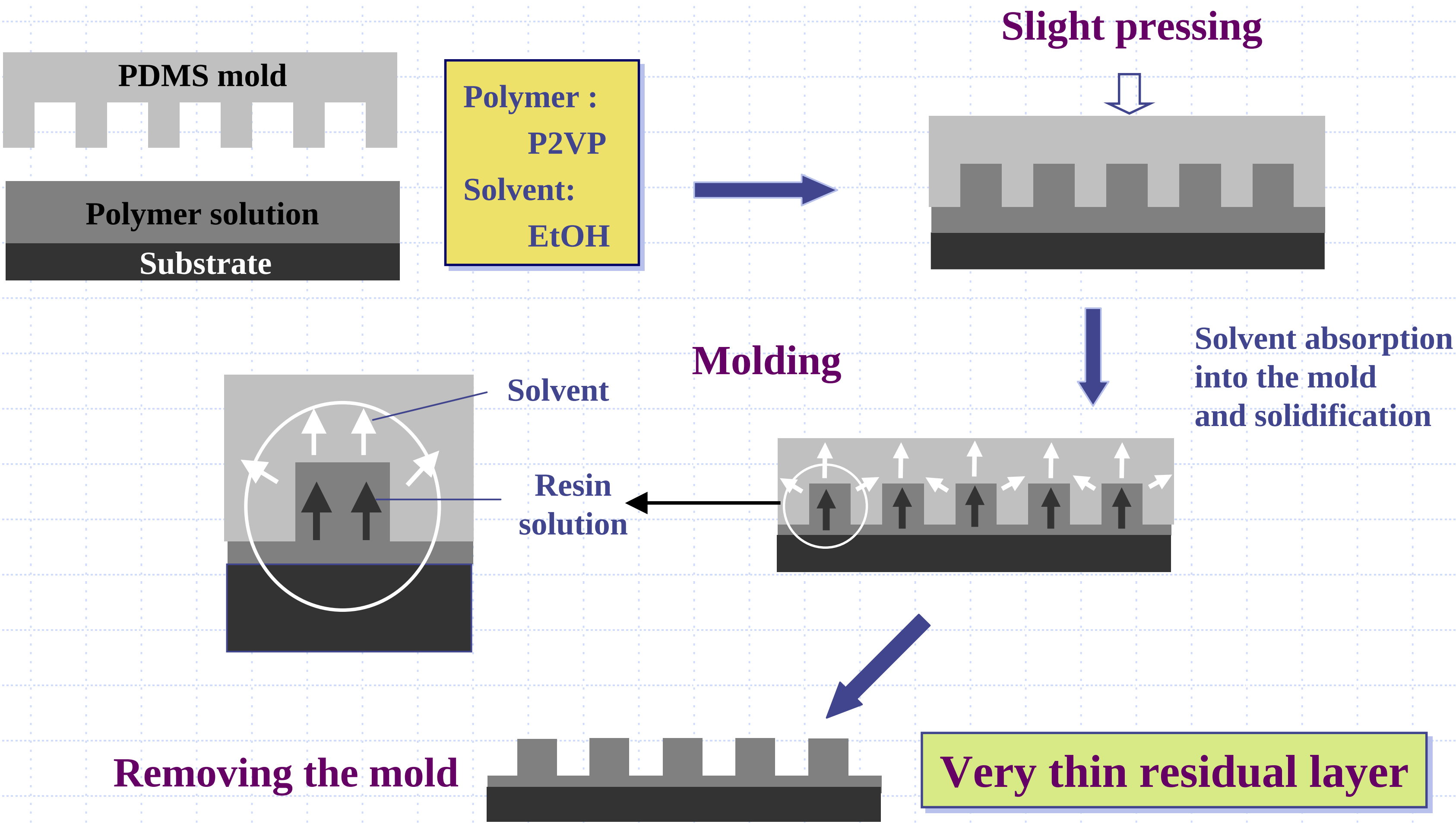




Styrene-Butadiene-Styrene copolymer
120°C, 24hrs

2. Patterning by solvent-directed capillarity

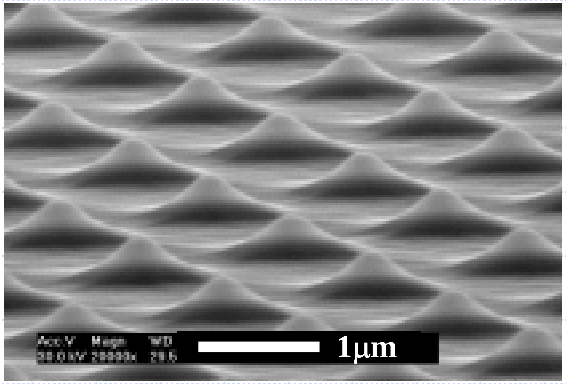
Kim, Suh, and Lee, Appl. Phys. Lett. (2001)



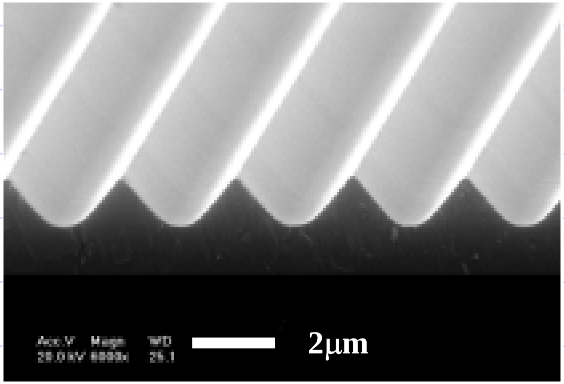
Very thin residual layer

Results

Three-dimensional pattern

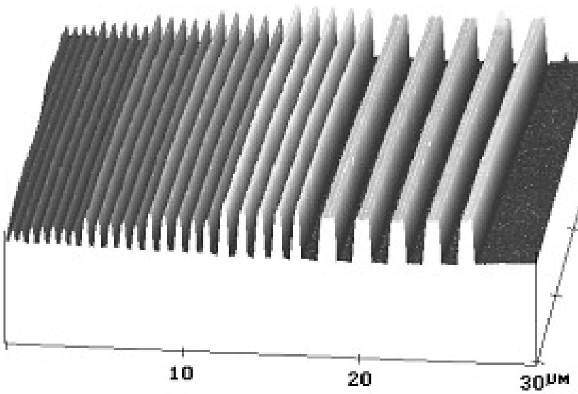


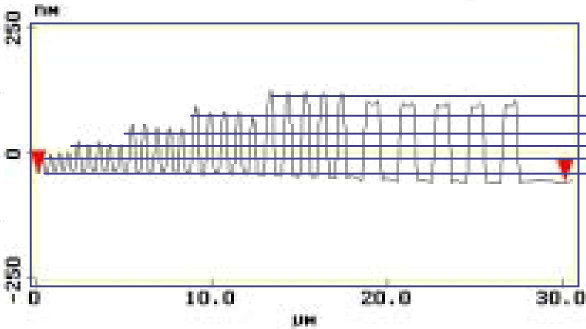
Cone-shaped pattern



Saw-shaped pattern

Multi-level structures





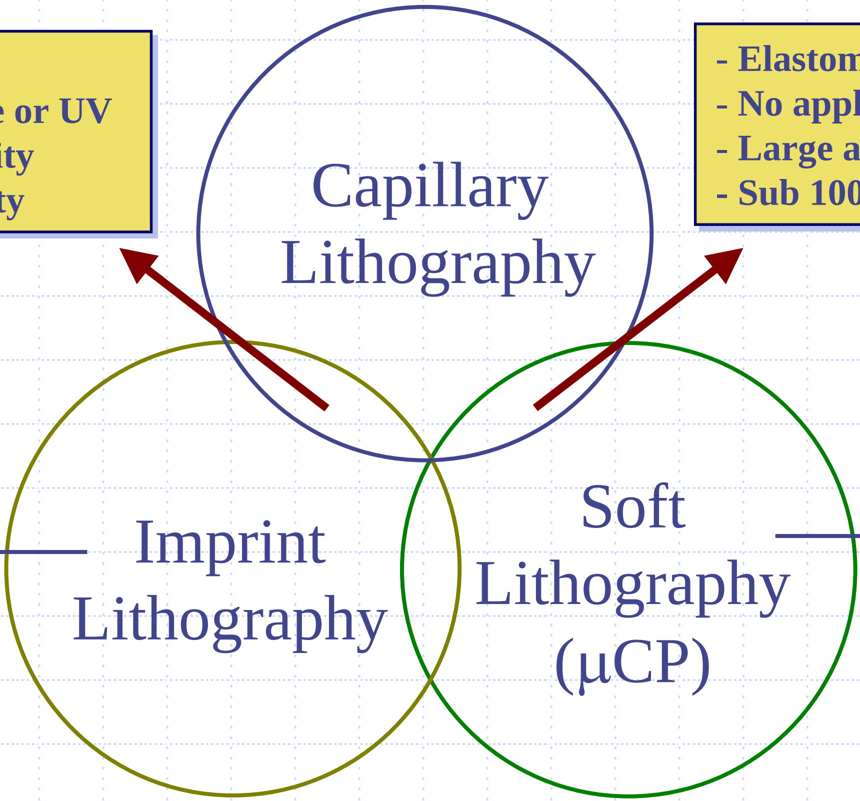
~ 5 levels

One-step processing

Three unconventional lithographies: contact-based

- Molding technique
- Use of temperature or UV
- Good reproducibility
- High pattern fidelity

- Elastomeric stamp
- No application of pressure
- Large area processing
- Sub 100 nm stamp?

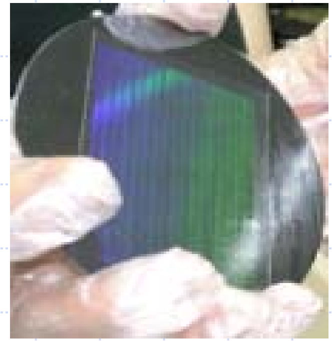
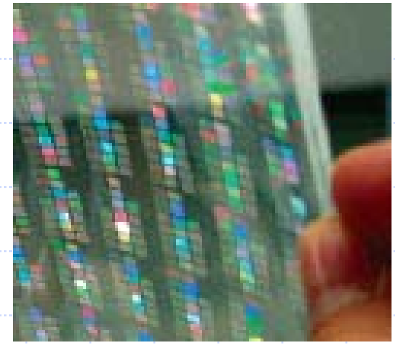
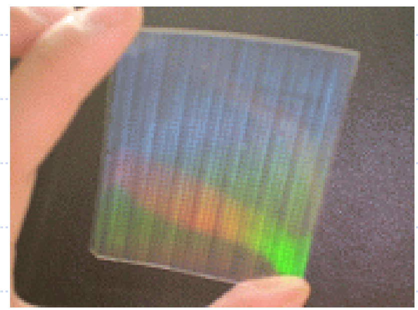


- High pressure
- Residual layer
- Minimum feature size ~ 7 nm

- Direct exposure of substrate
- Poor resolution
- Minimum feature size ~ 50 nm

Change of mold from PDMS to PUA

- Polyurethane acrylate mold **(PUA)**

- Properties
  1. mechanical rigidity
  2. flexibility
  3. small shrinkage (0.7 %)
  4. light transmittance

→ adequately ***hard*** yet ***flexible*** enough for patterning

→ *high resolution & conformal contact*

→ *large area patterning without applying high pressure in nanoscale*

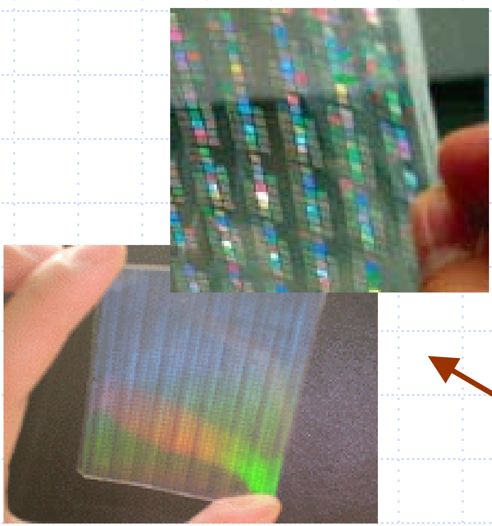
PUA mold

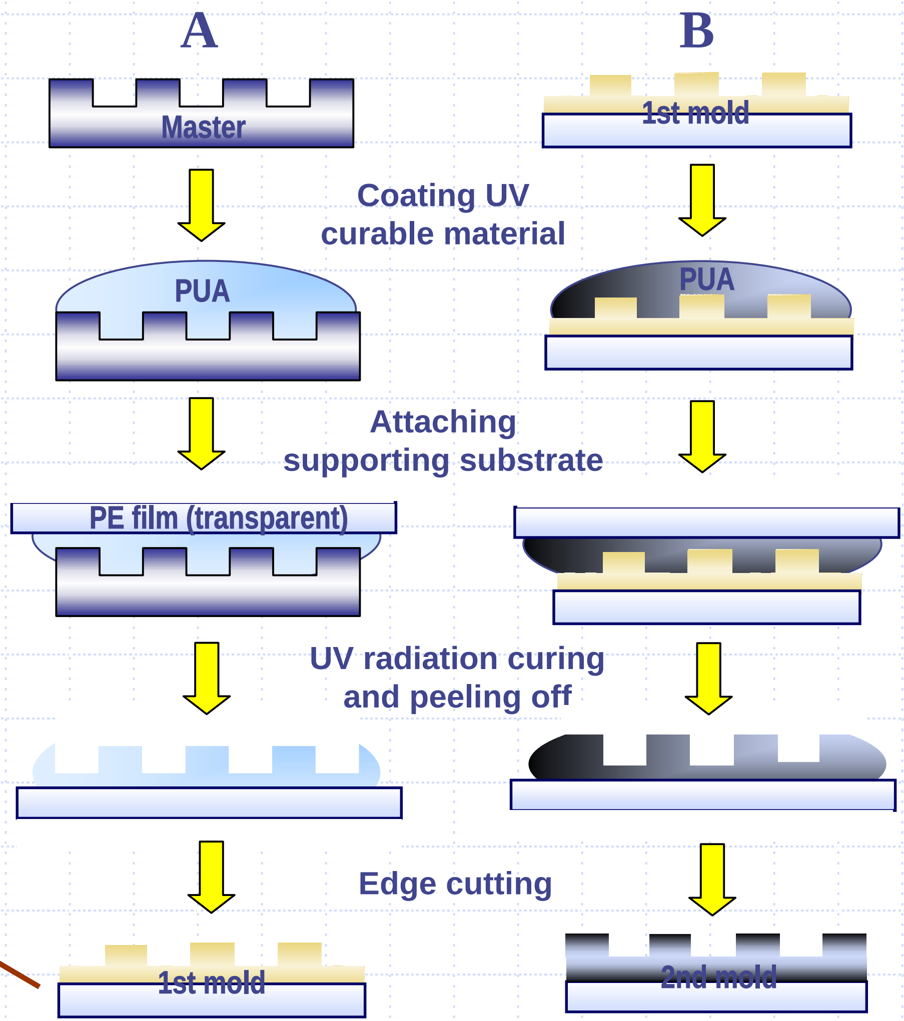
(Self replication)

- Procedure

trapped polymer radicals and remaining unsaturated acrylate in the first replica need to be removed by excessive exposure to UV for self-replication .

-> ***lower the surface energy of PUA mold.***

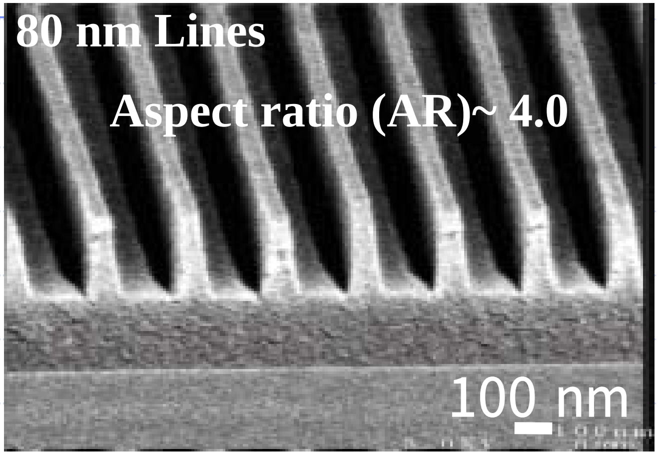


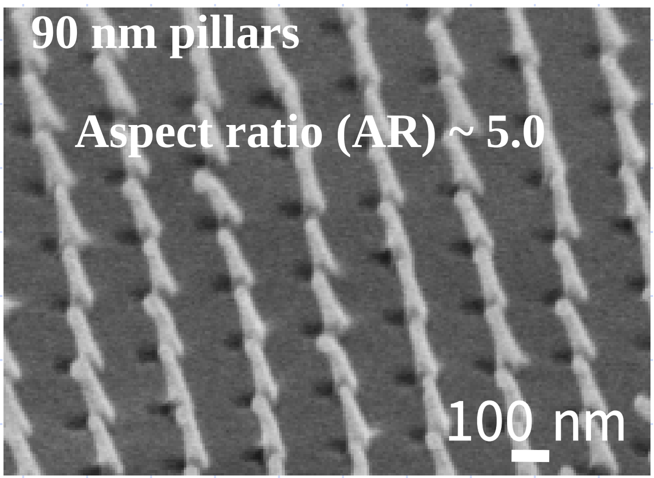


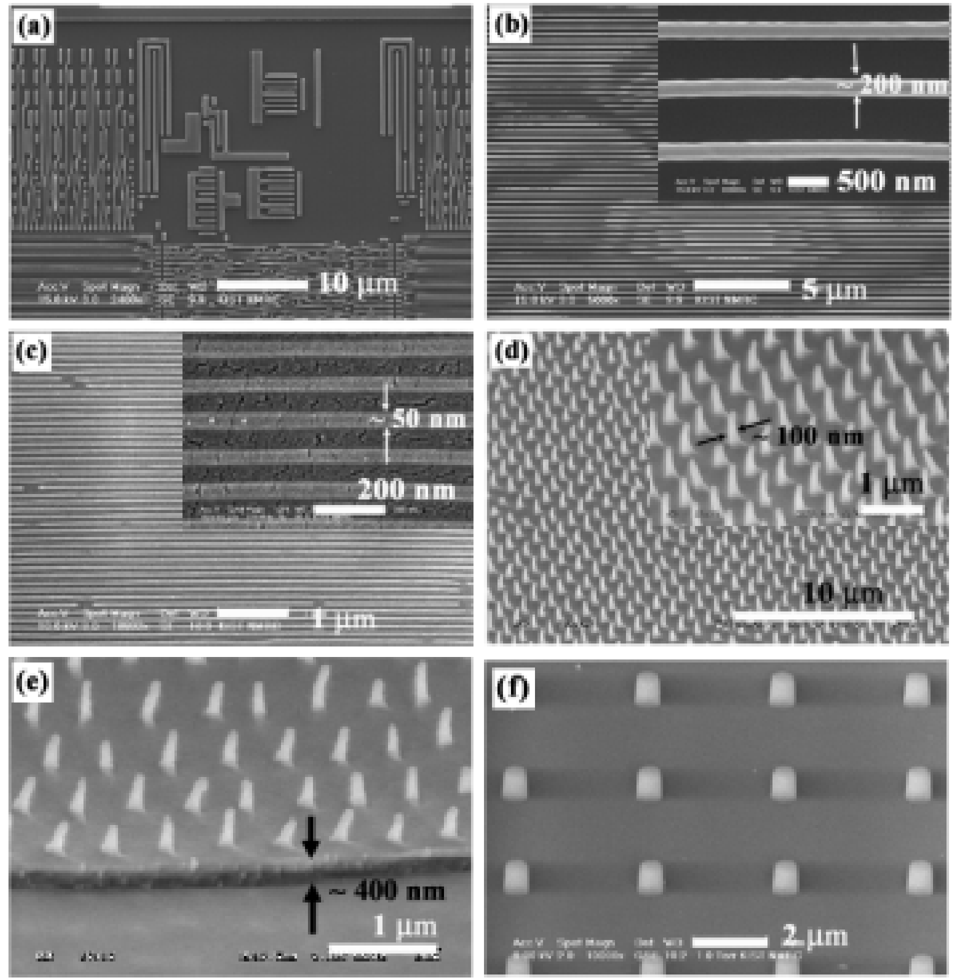
: ***self replication***, very fine structure (less than 100 nm)

"An ultraviolet-curable mold for sub-100 nm lithography", *JACS*, 2004

Results

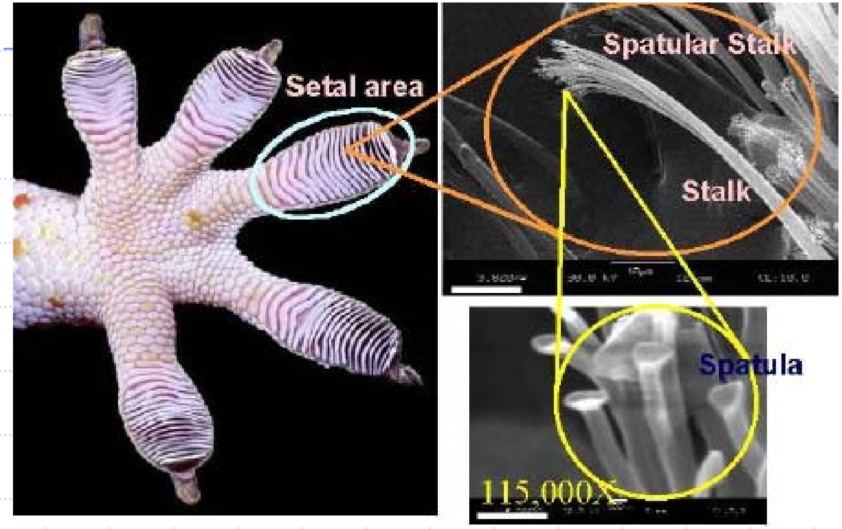

80 nm Lines
Aspect ratio (AR)~ 4.0
100 nm

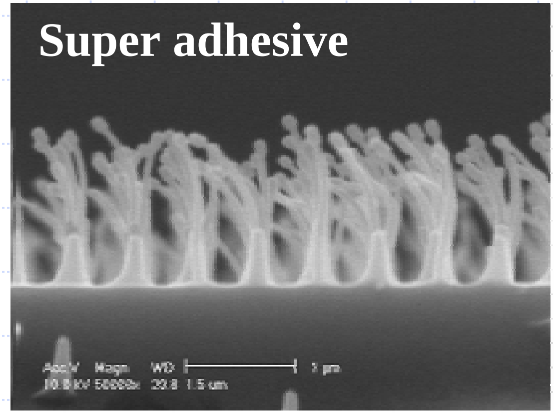

90 nm pillars
Aspect ratio (AR) ~ 5.0
100 nm

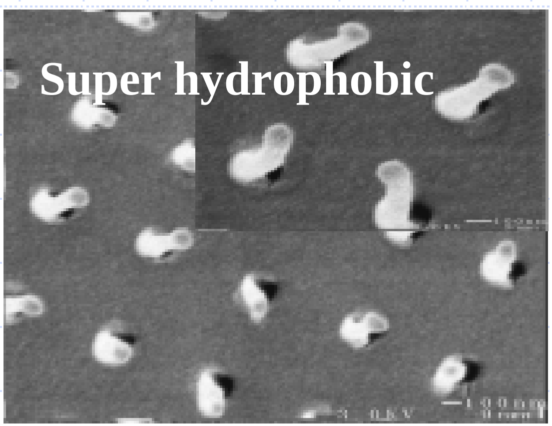

(a)
10 µm
(b)
~ 200 nm
500 nm
5 µm
(c)
~ 50 nm
200 nm
1 µm
(d)
100 nm
1 µm
10 µm
(e)
~ 400 nm
1 µm
(f)
2 µm

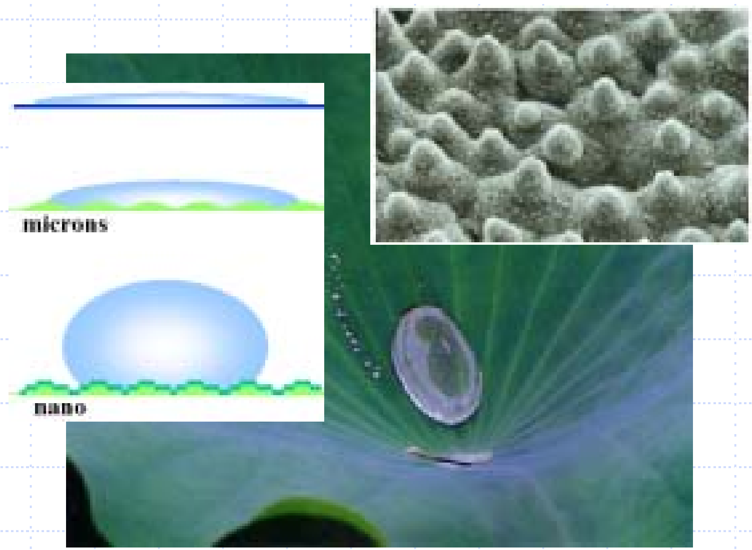
Applications of high AR nanostructures– (1) Biomimetics

Suh et al., Adv. Mater. (2005)



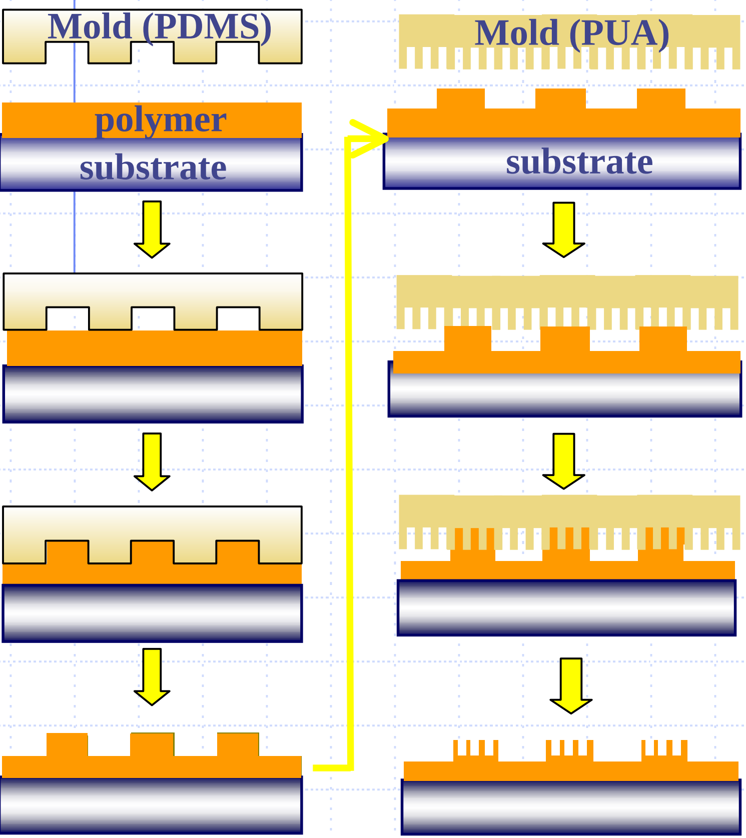


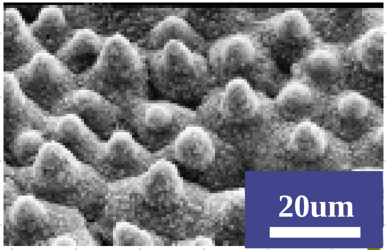


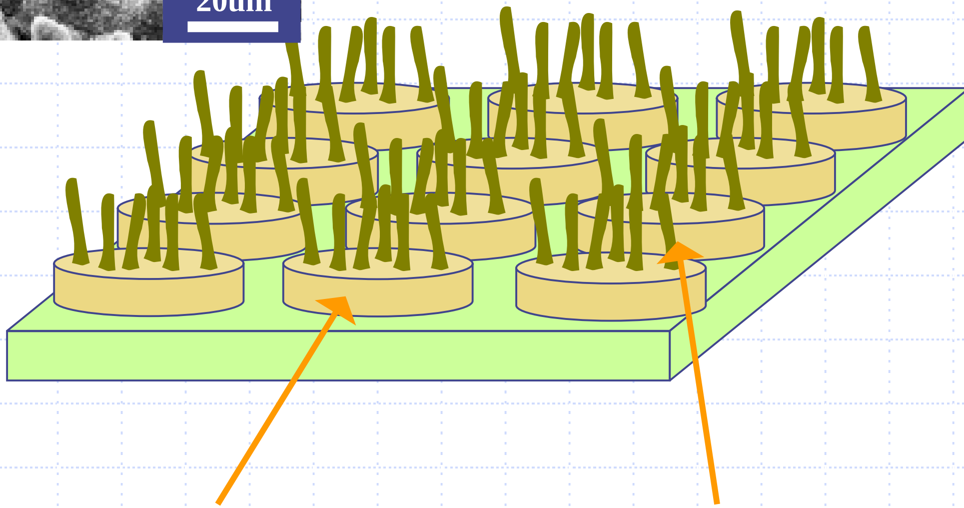


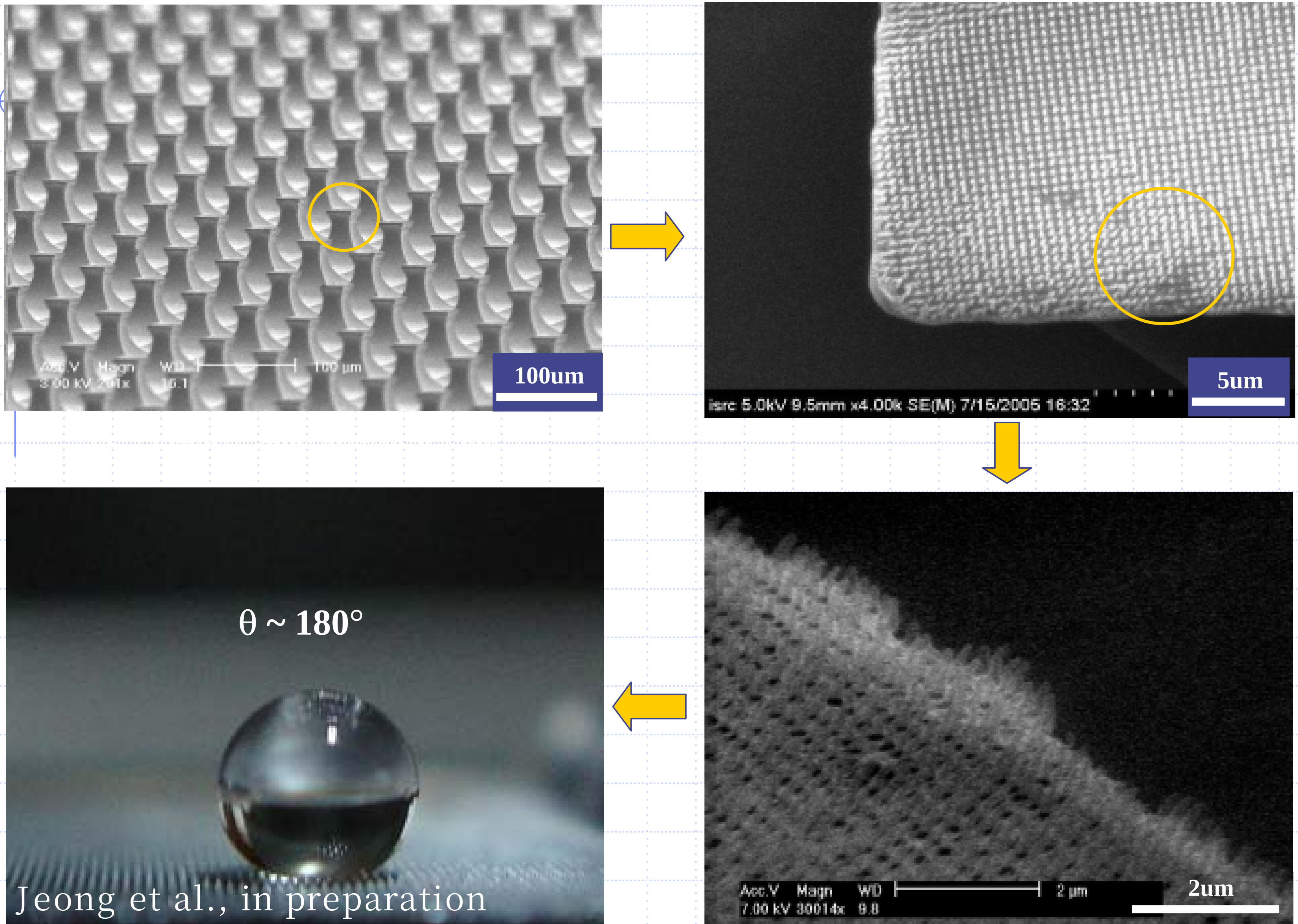
Strategy

Micro+nano structures
using two-step capillary lithography (Nano-turf)







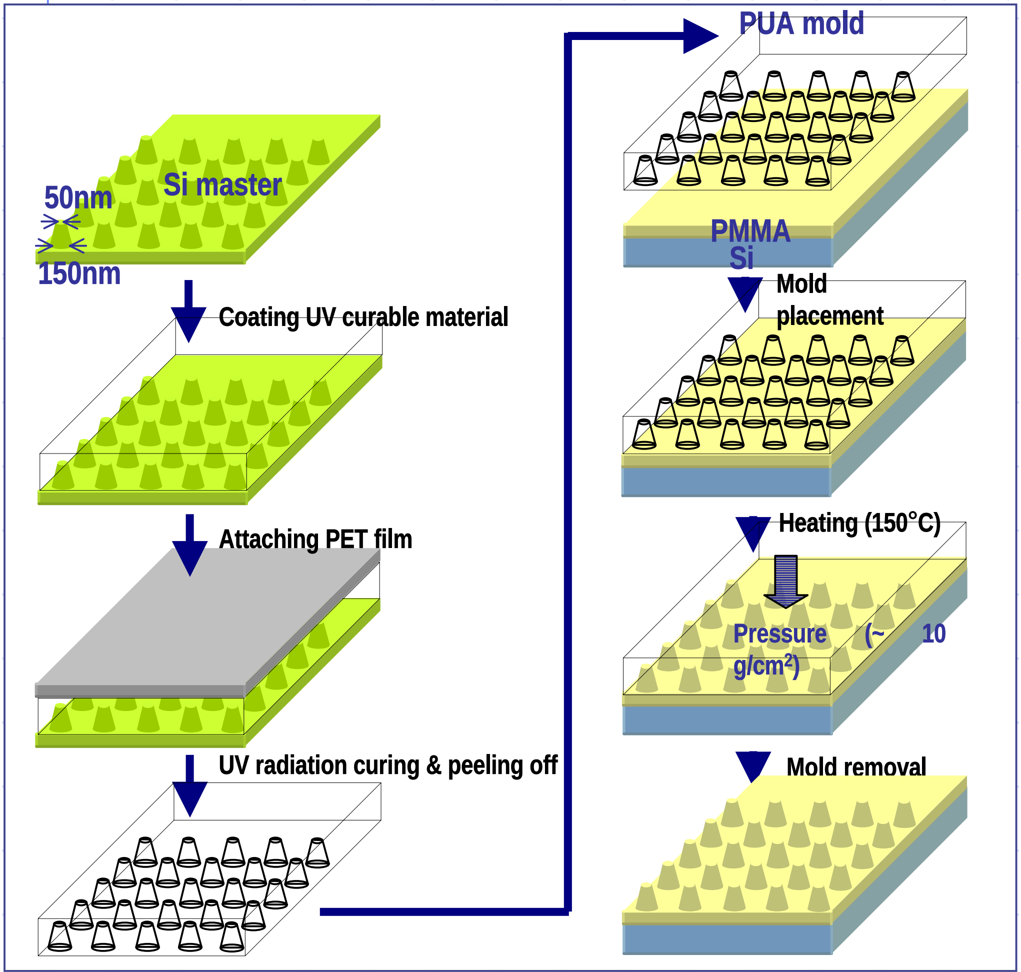


Jeong et al., in preparation

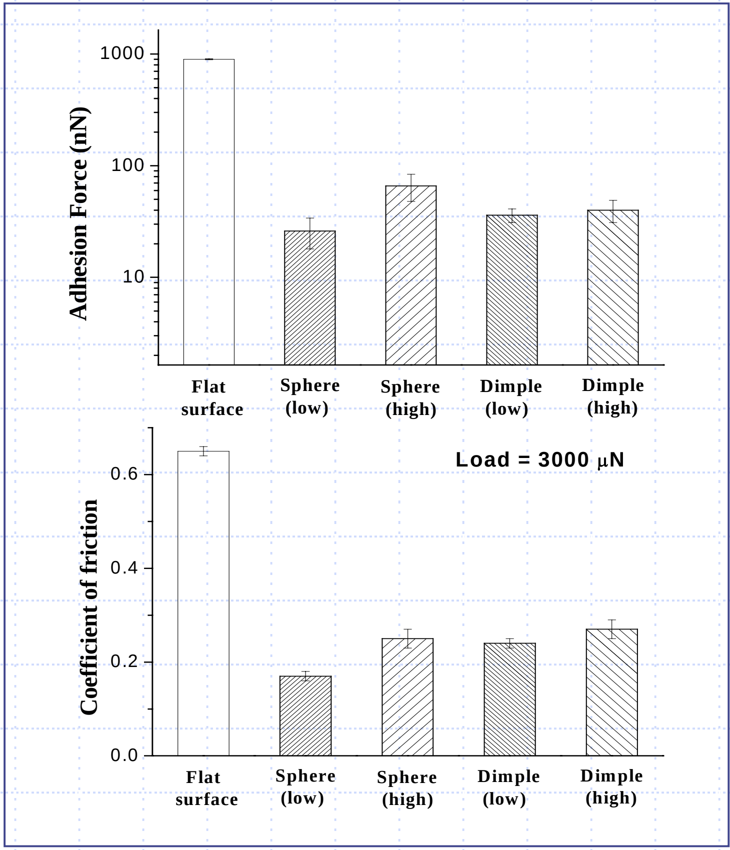
Applications of high AR nanostructures– (2) Nanotribology

- Suh et al., submitted to Applied Physics Letters

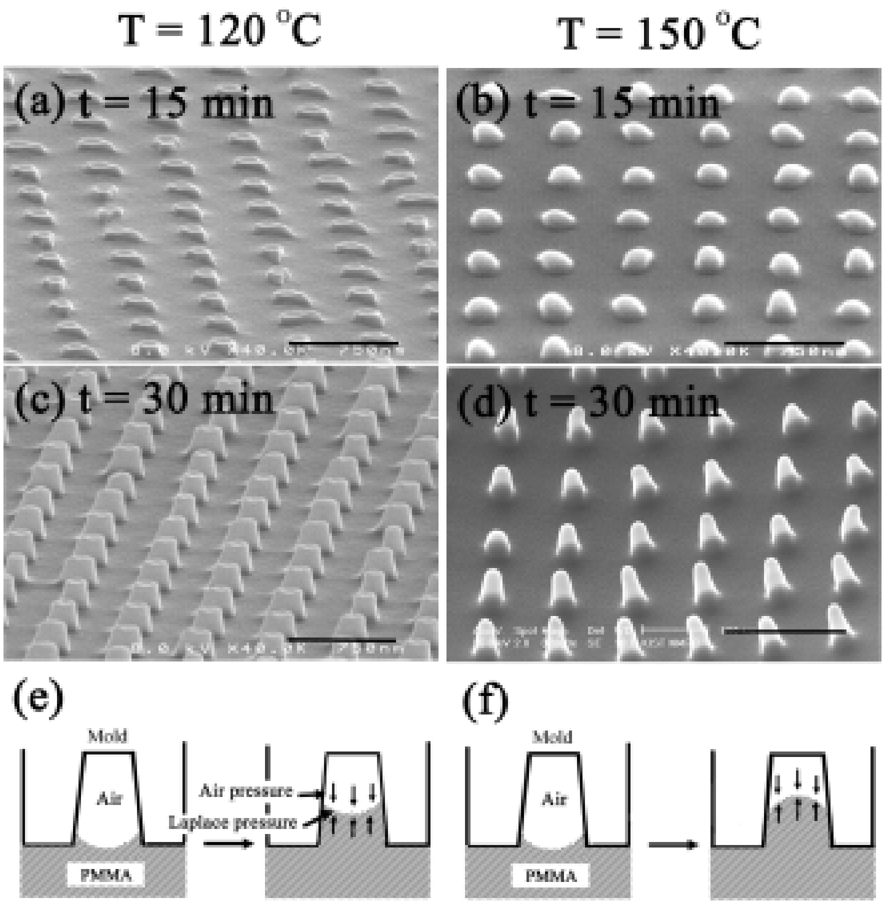
Reduction of adhesive and friction forces by shape-engineering surface nanotopography



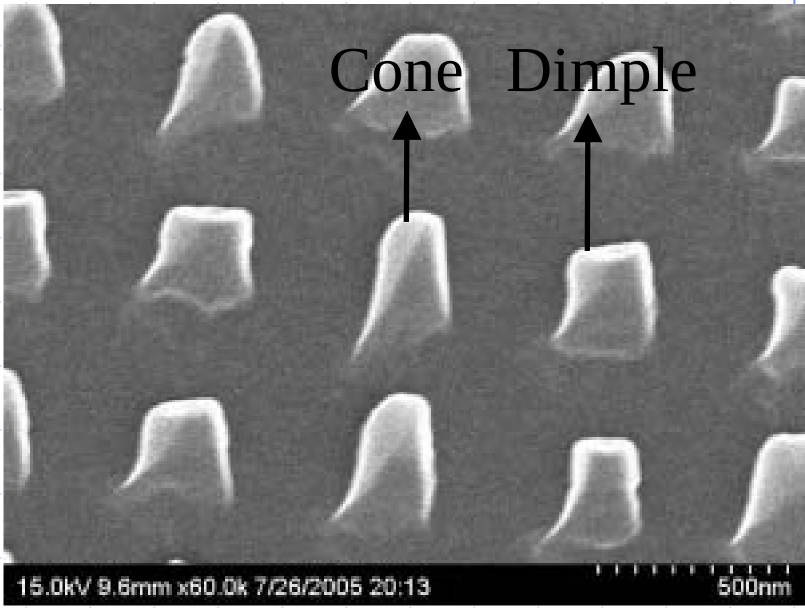
- The nano-structure makes the adhesion and friction be reduced.



SEM images

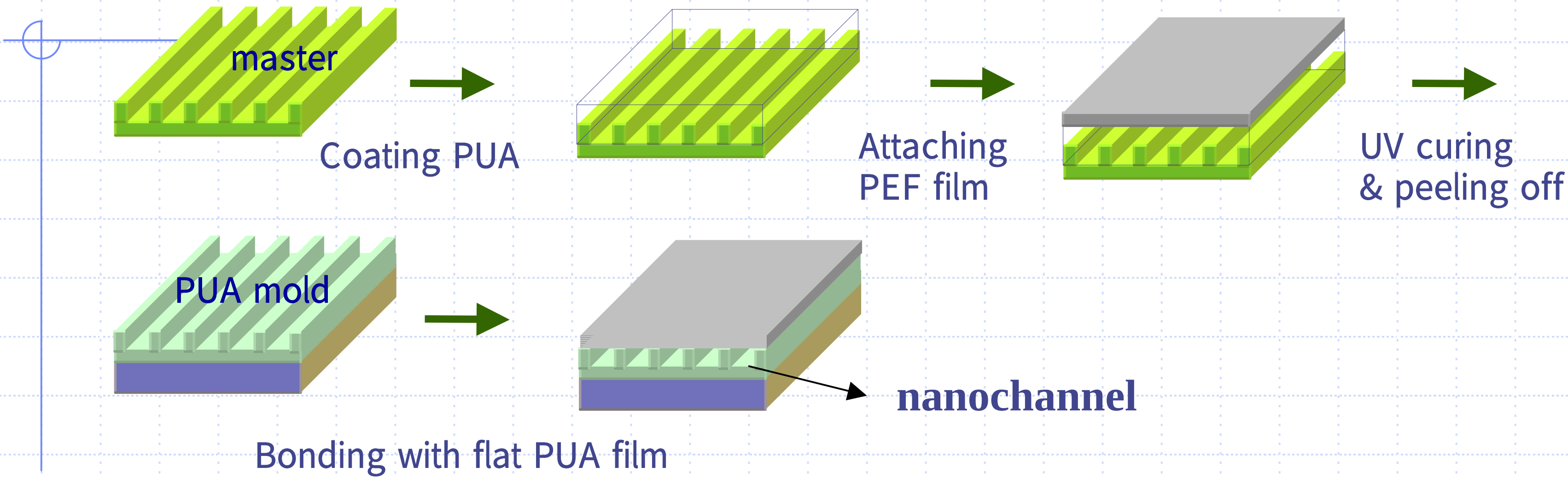


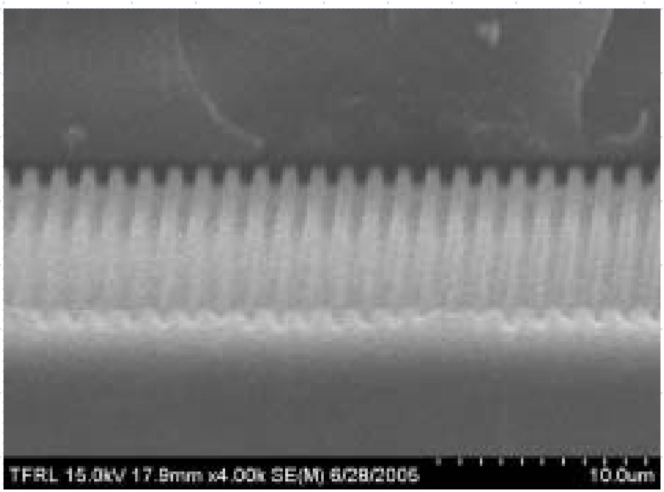
- Tilted SEM images for the two types of nanostructures at different temperatures

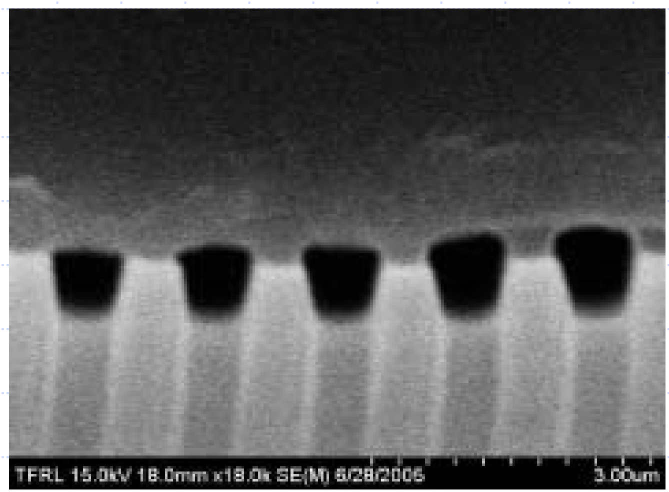


- SEM image for the combination of cones and dimples when annealed at 135°C for 30 min.

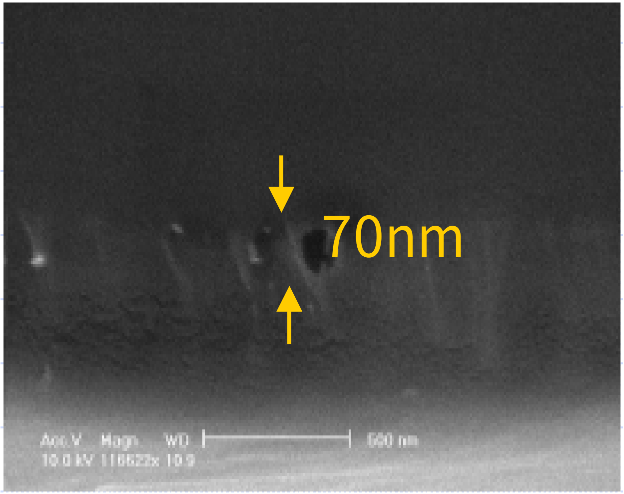
Applications of high AR nanostructures– (3) Nanochannel Fab.

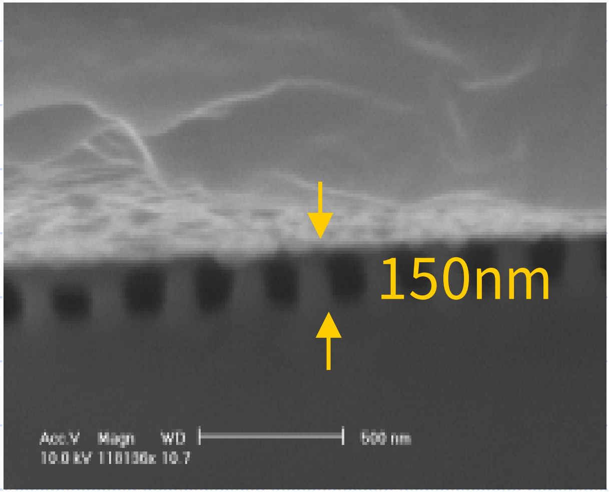


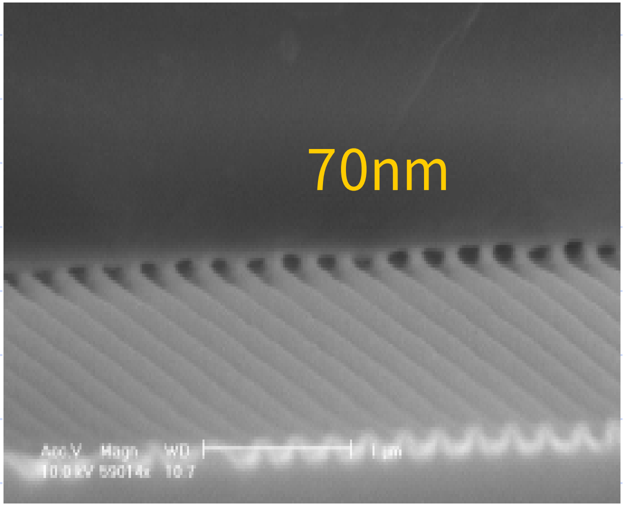


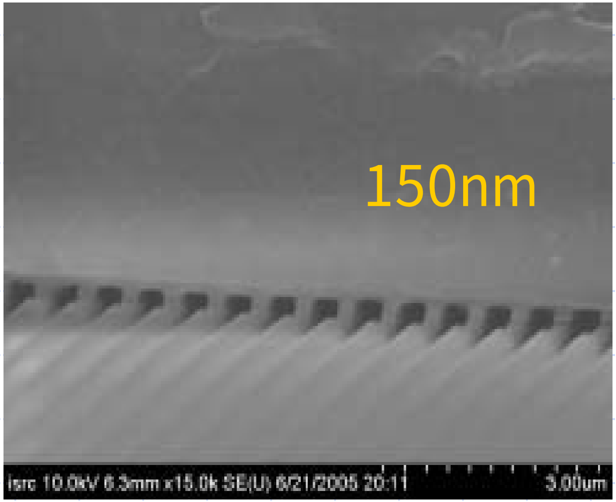


Various nanochannels fabricated by capillary lithography









Summary

1. Capillary lithography is a useful technique for fabricating robust, well-defined micro/nano structures on a large area.

2. At present, nanostructures down to 50 nm can be fabricated with reasonable pattern fidelity and reproducibility.

3. High aspect ratio nanostructures are useful for various applications such as biomimetics, nanotribology, and fabrication of nanochannel.

경청해 주셔서 감사합니다.