나노 기술의 이해
(Understanding Nanotechnology)

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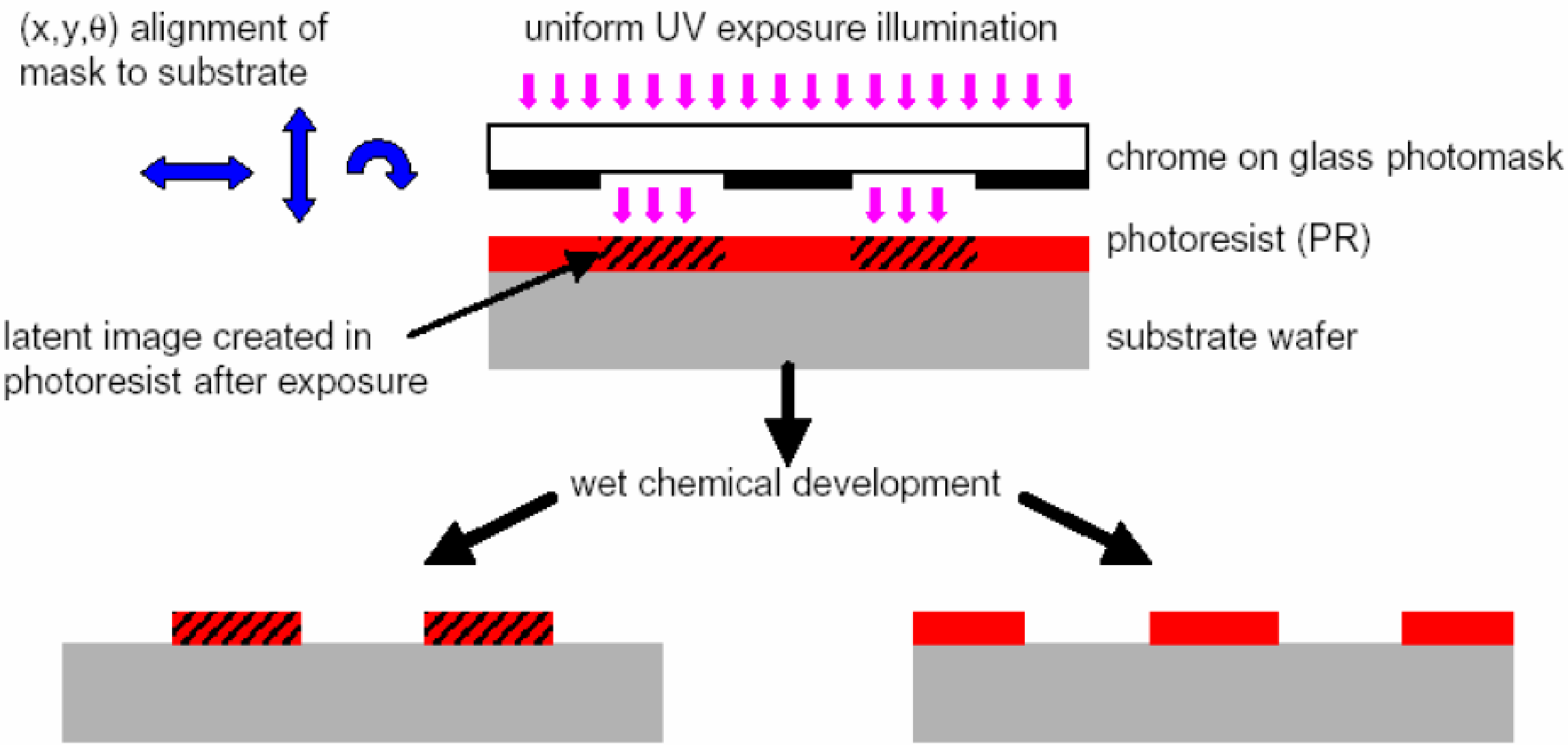
Lecture 9.
Unconventional lithography

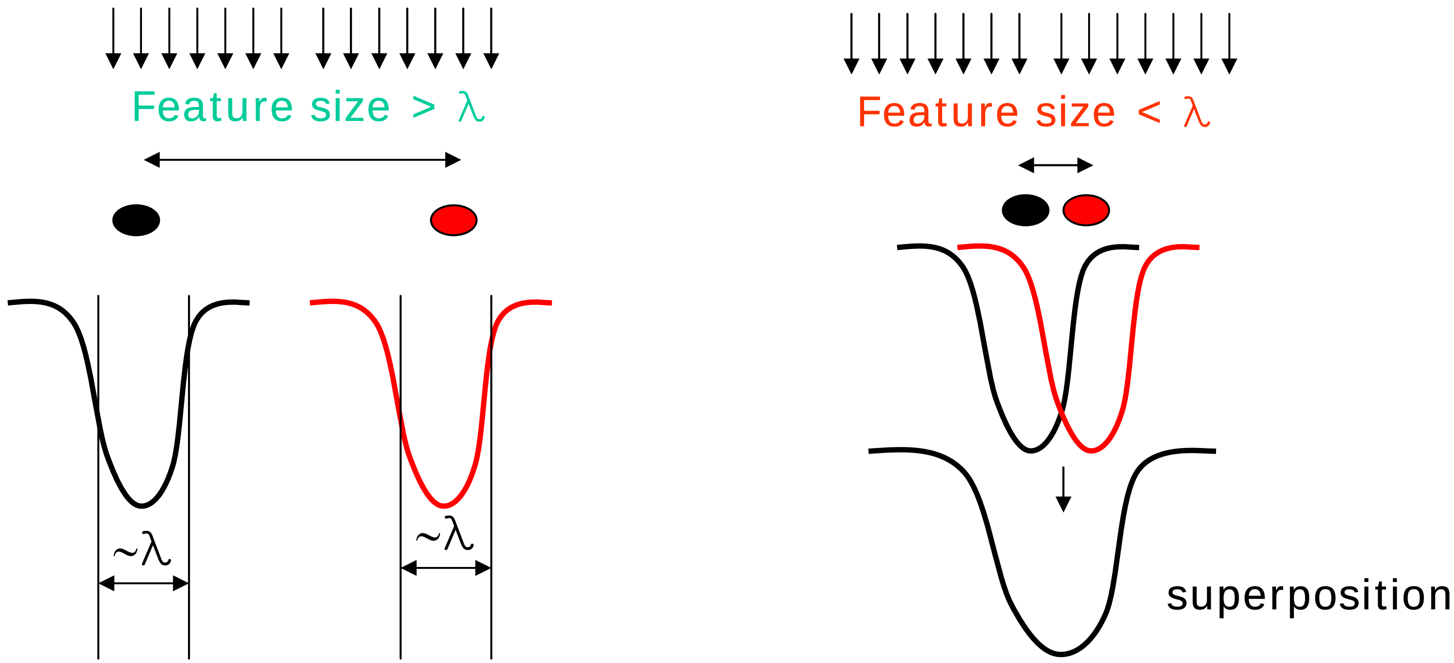
Photolithography



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.

Resolution limit



Can resolve the spacing

Can not resolve the spacing

- Diffraction dominates when feature size shrinks
  E-beam, X-ray → **expensive**
- **Not compatible** with biofunctional materials

Unconventional nanofabrication

- **Top-down approach (Lithography)**

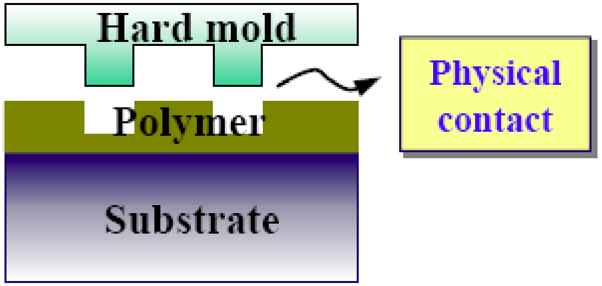
  - Nano imprint lithography : mechanical pressing, plastic deformation ...
  - Soft lithography : molding, replication, contact printing ...
  - Capillary lithography : capillary force, viscosity, surface tension ...
  - Dip-pen lithography : nano contact printing, surface diffusion ...

- **Bottom-up approach (Self assembly)**

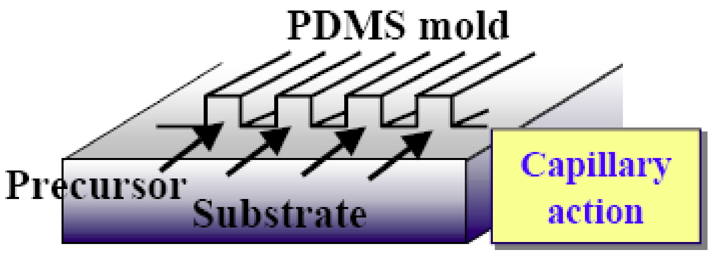
  - Self assembled monolayers : covalent bonding, crystallization ...
  - Colloidal self assembly : capillary force, evaporation/condensation ...
  - Dewetting/buckling : intermolecular forces, elastic stress, surface tension ...

Unconventional lithography

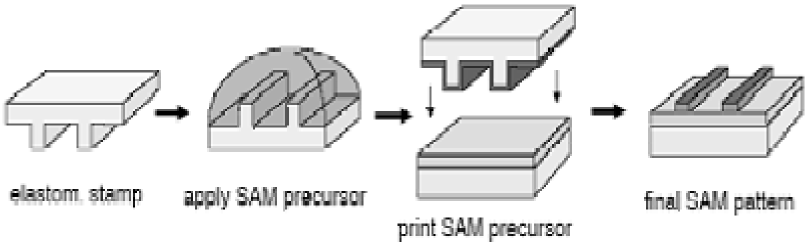
Imprint lithography
(Chou et al., Science, 1996)



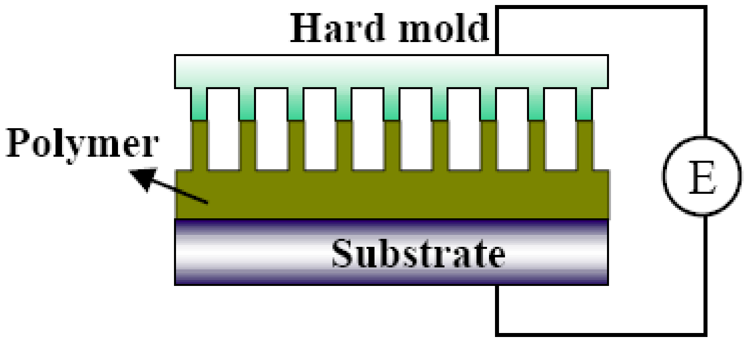
Micromolding in capillaries
(Whitesides et al., Nature, 1995)



Microcontact printing
(Whitesides et al., JACS, 1992)

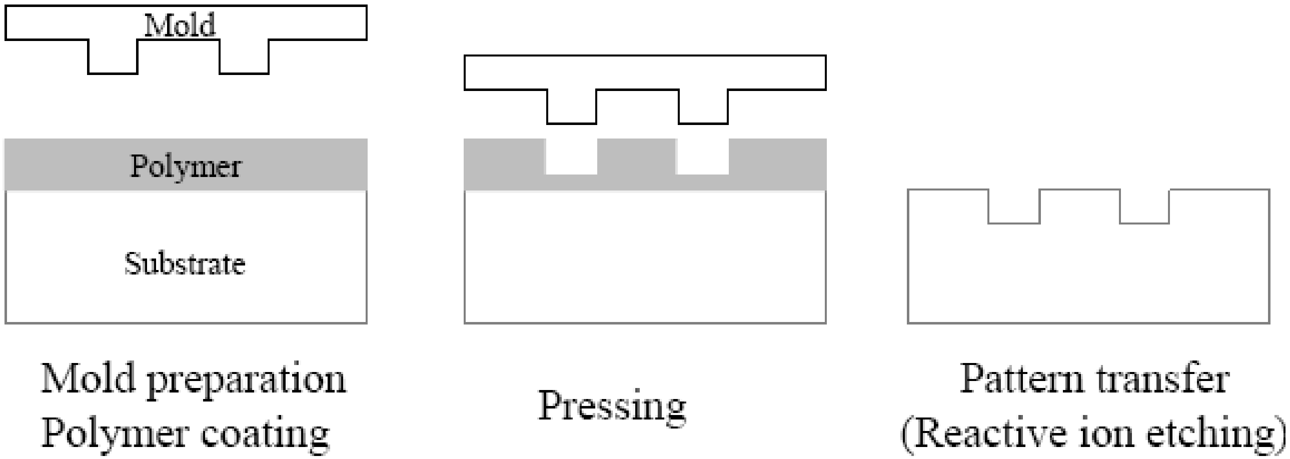


Electrically induced structure formation
(Schäffer et al., Nature, 2000)



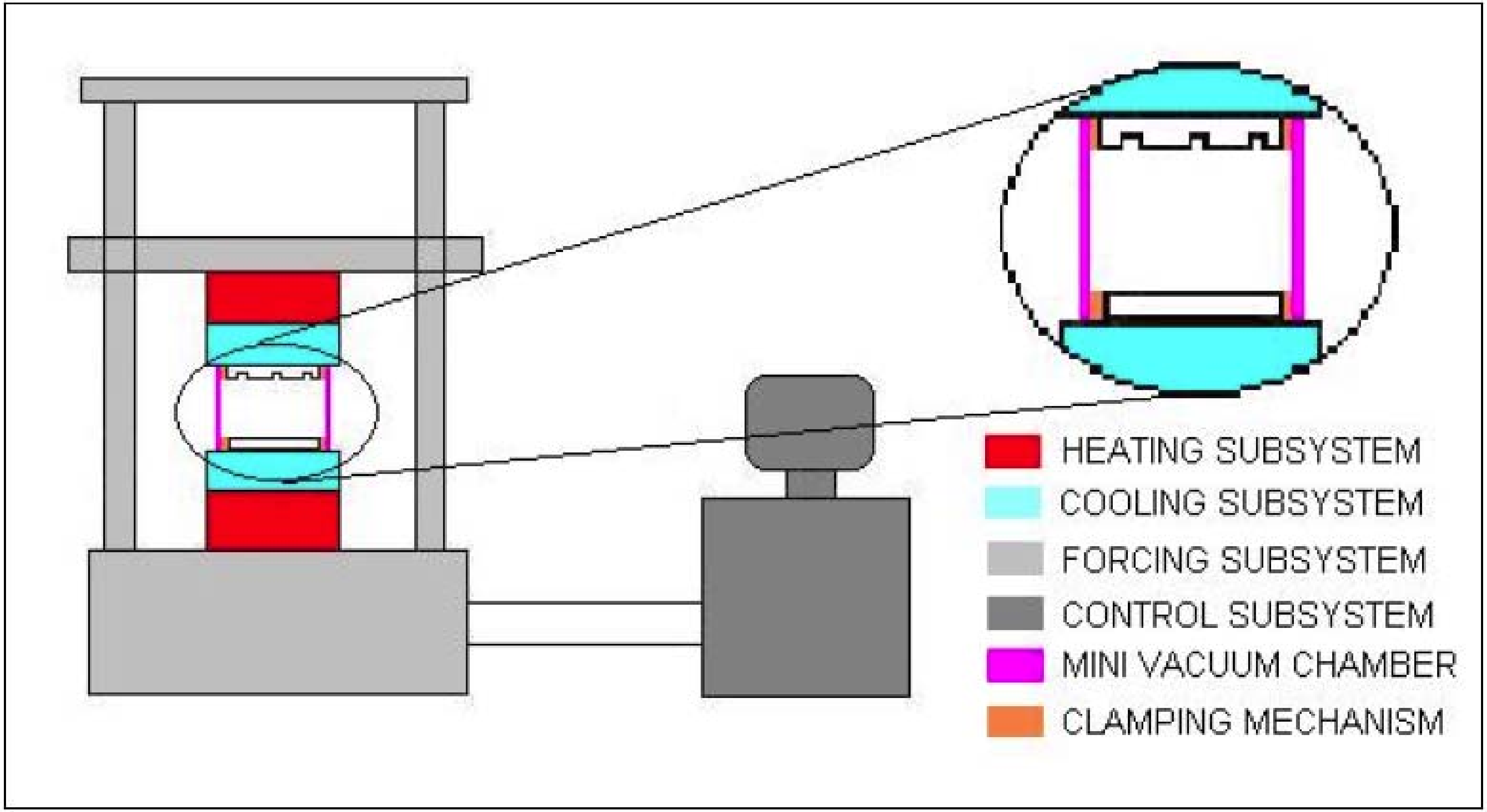
What is NIL?

Hot embossing is a technique of imprinting nanostructures on a substrate (polymer) using a master mold (silicon tool)



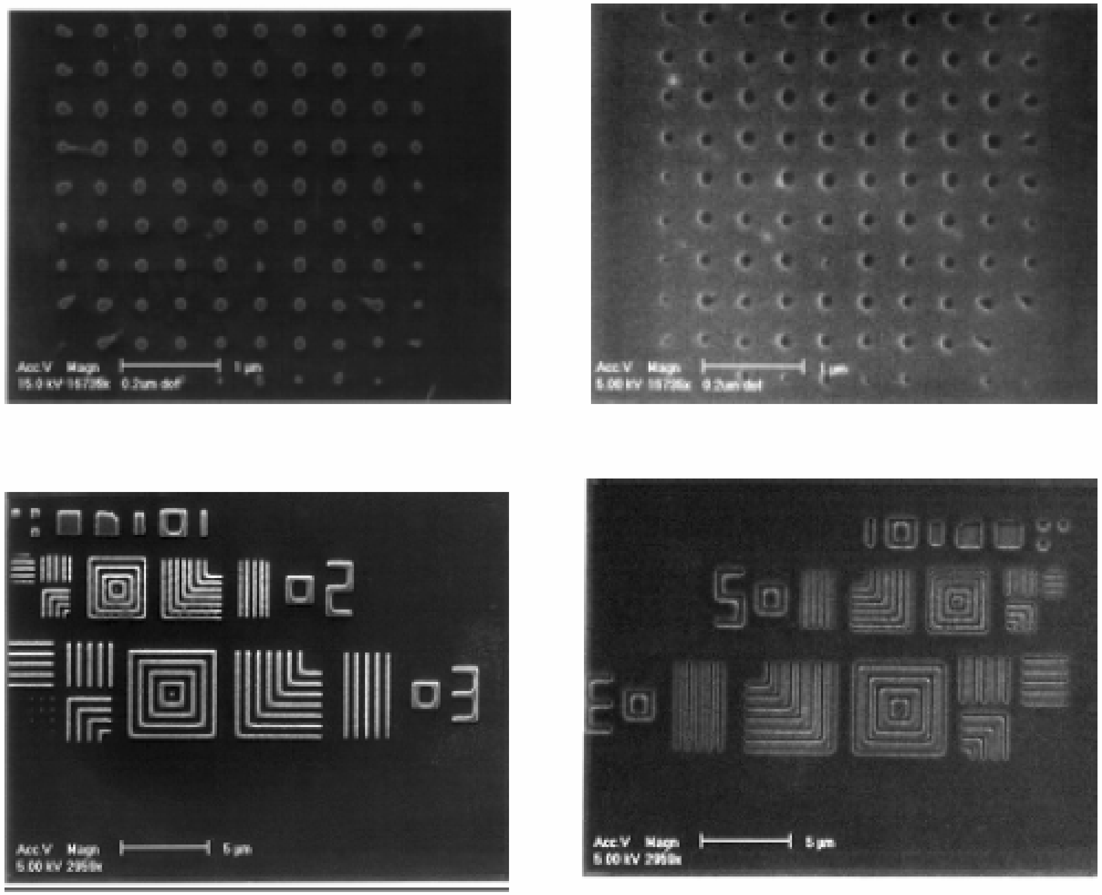
Master/mold from photo-lithography → Heat the substrate and mold to just above T_g of the substrate → Apply embossing force on the substrate via the mold under vacuum → Cool the substrate and mold to just below T_g → De-embossing of the mold and substrate

Schematic of NIL setup



Examples of generated patterns

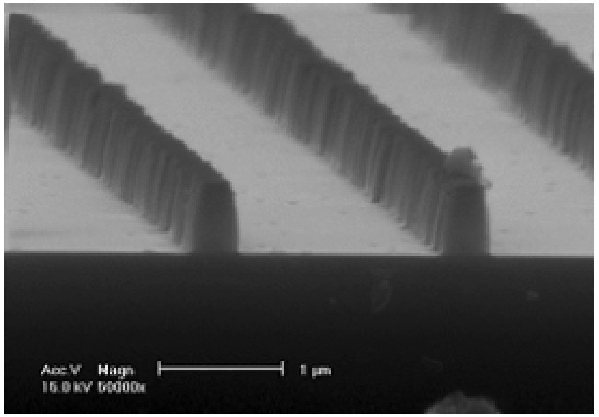
200nm dots



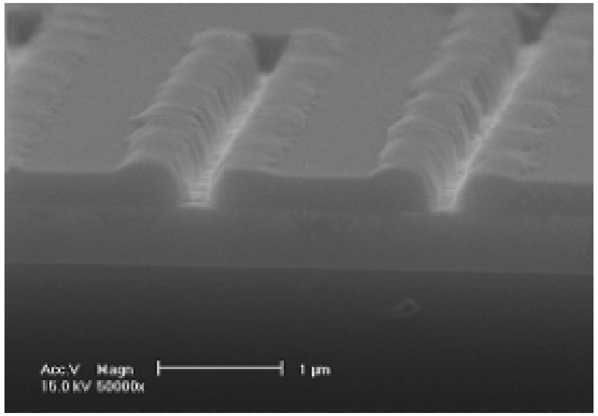
Mold

Substrate

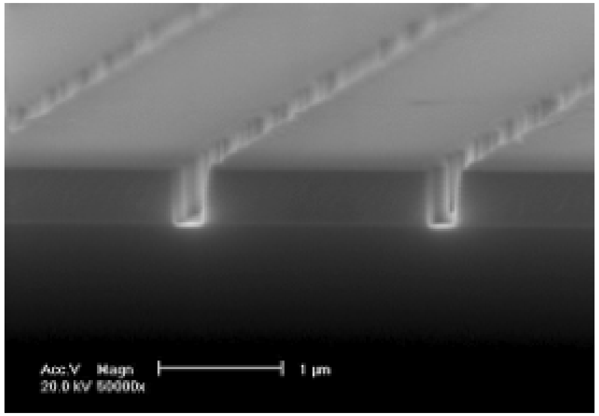
Imprinting + Etching



Mold



Imprinted



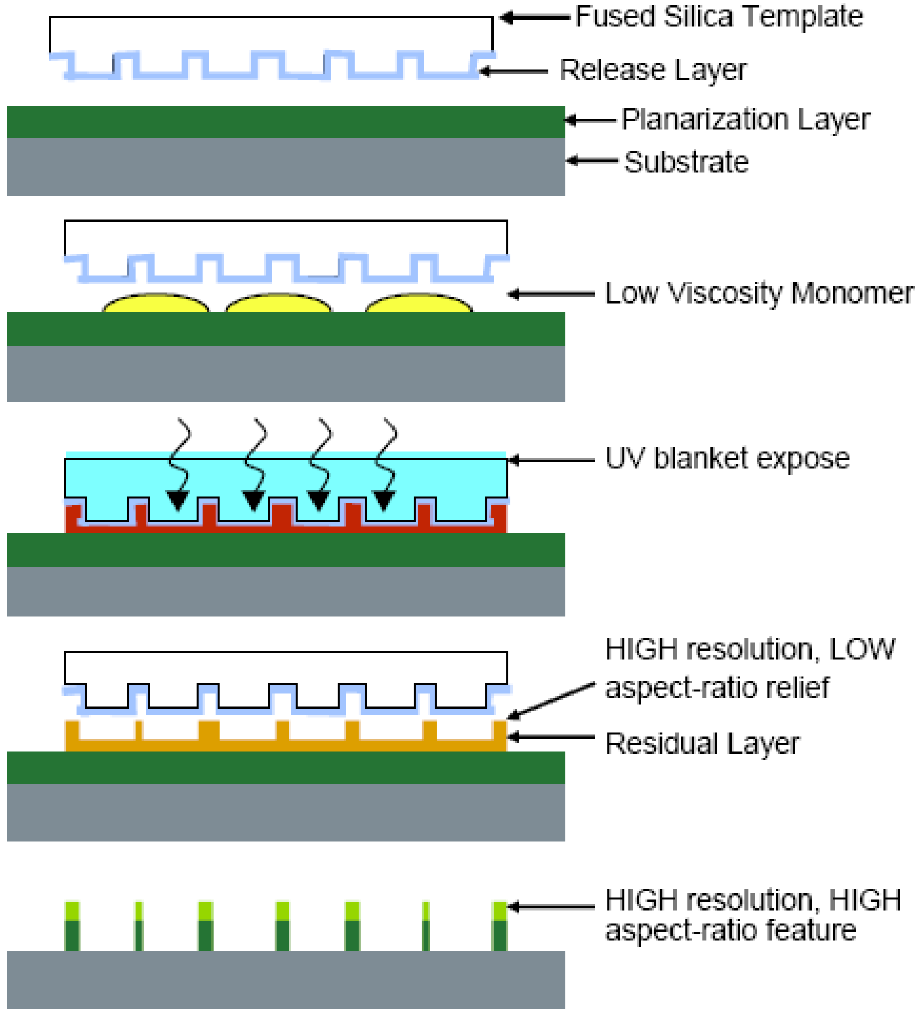
Reactive-ion-etched

Advantages of Hot Embossing System

- ***Cost effective*** – Easy manufacturability
- ***Time efficient*** – Fast process
- Fabrication of ***high aspect ratio*** features
- ***Biocompatible surfaces*** – Polymer substrates used
- ***Disposable*** – Low cost for volume production

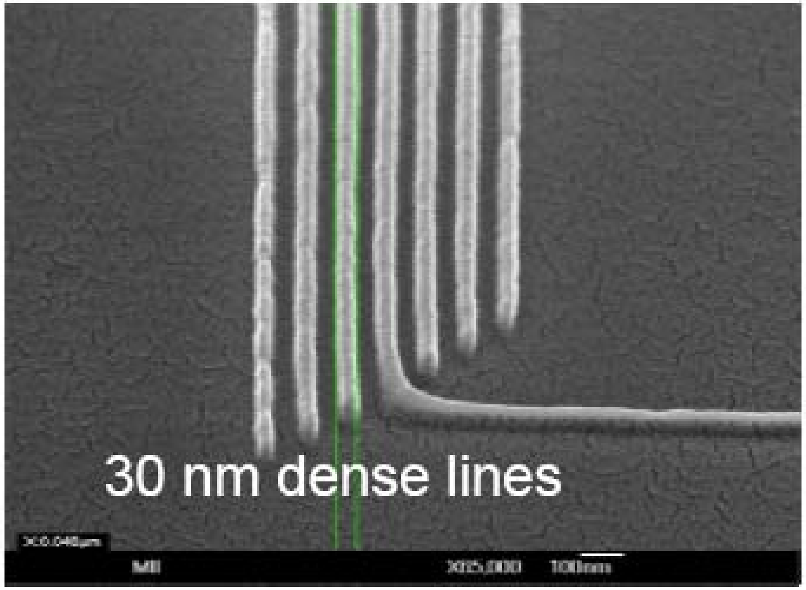
UV-assisted NIL

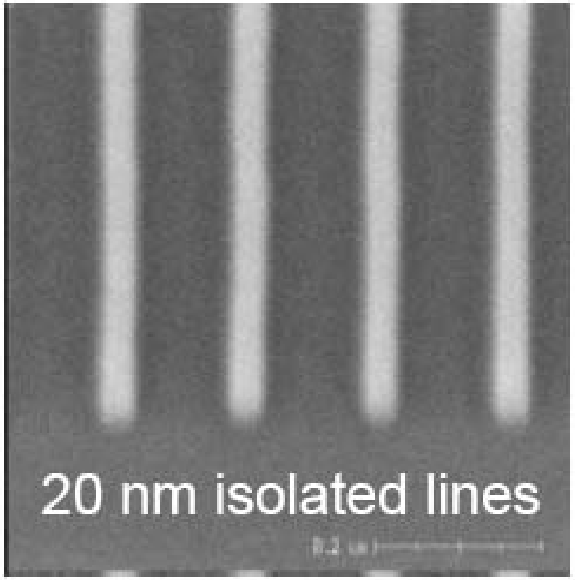
1. Orient substrate and treated template
2. Dispense drops of low viscosity UV curable low viscosity organosilicon monomer
3. Close gap and illuminate with UV (Room Temperature, Low Pressure)
4. Separate the template from the substrate
5. Halogen break-thru etch followed by oxygen etch



Step and Flash Imprinting Lithography (S-FIL™):
Profs. C. G. Wilson S. V. Sreenivasan. (UT Austin)

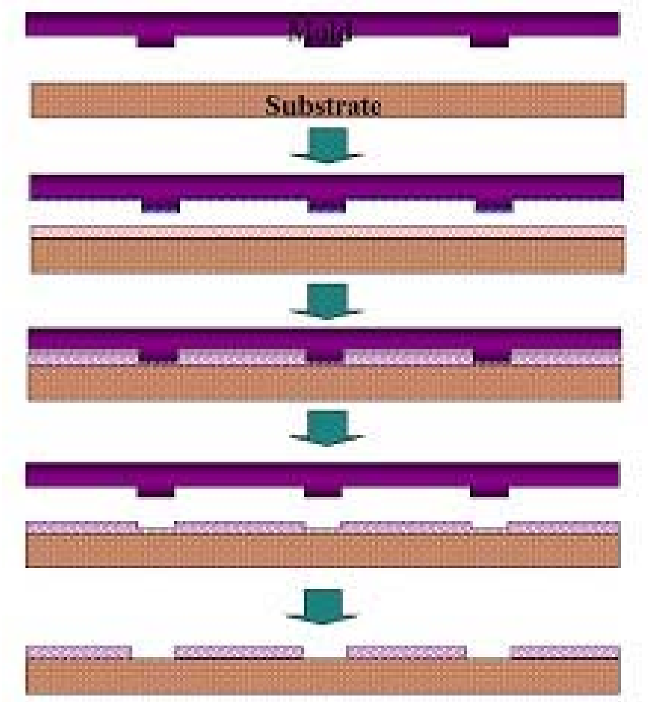
UV-assisted NIL

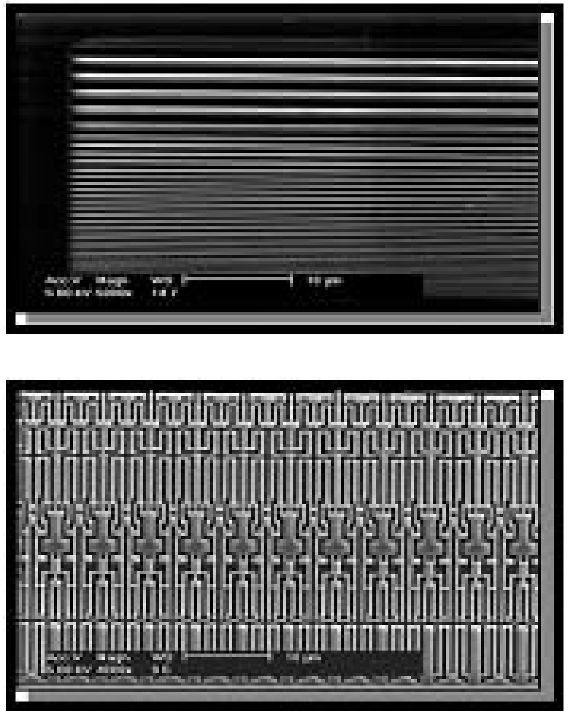




Room Temperature Imprint Lithography

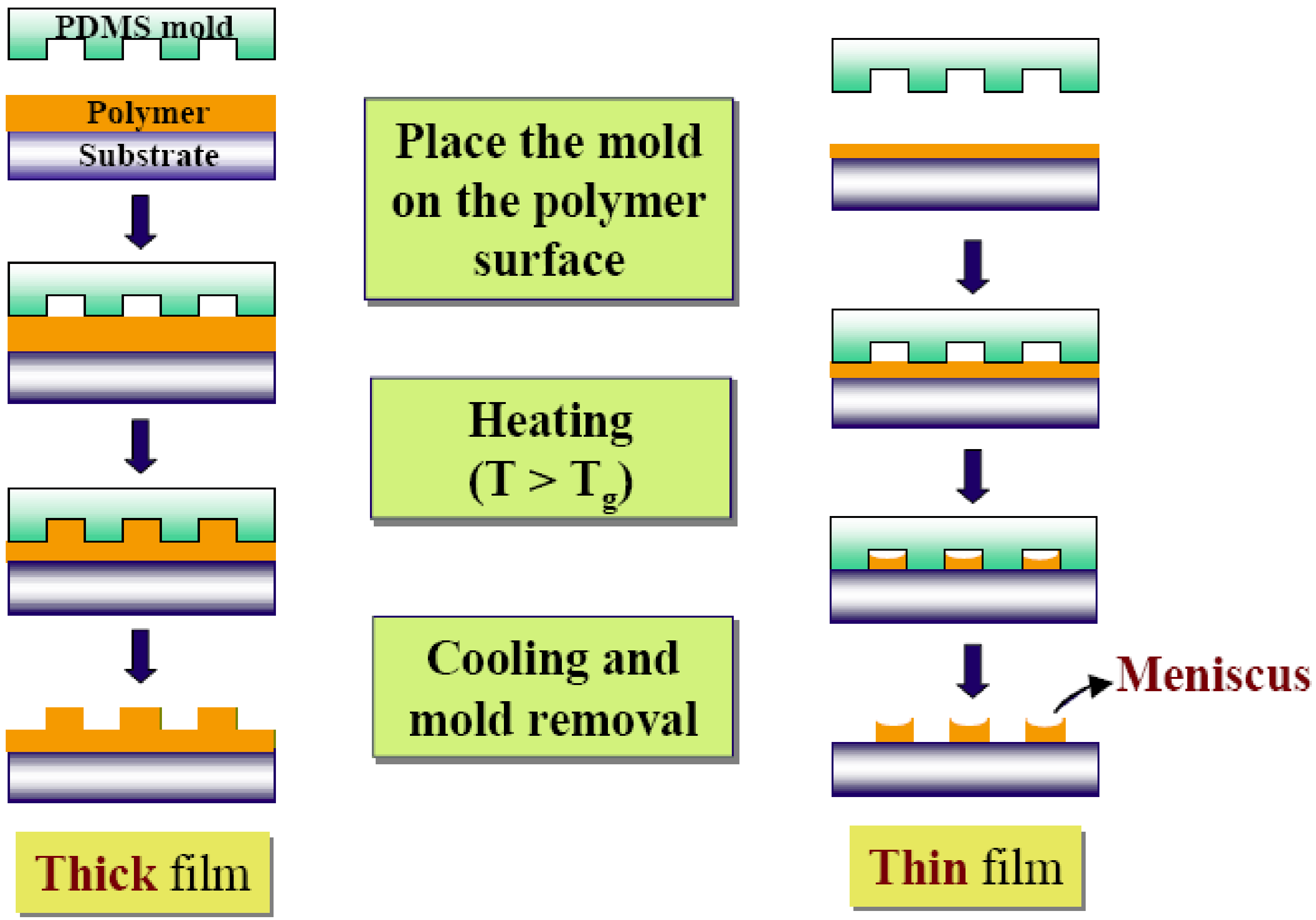
RT-NIL process has the unique features of enabling step-and-repeat and multiple imprinting , which is impossible in the conventional high-temperature imprint processes.





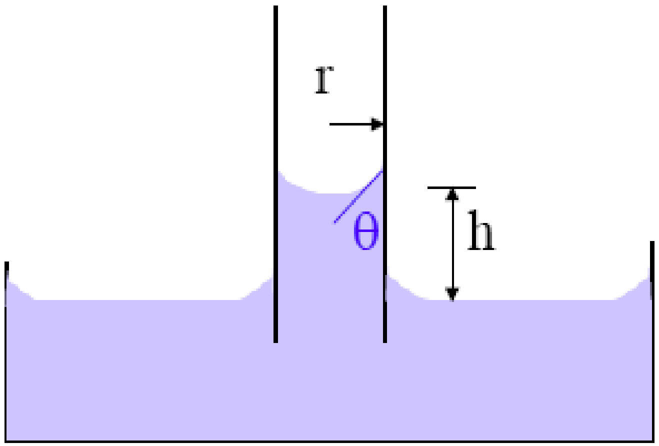
D. Y. Khang, H. Yoon and H. H. Lee, “Room-Temperature Imprint Lithography”, *Adv. Mater.*, **13**, 749 (2001)

What is Capillary Force Lithography (CFL)?



Patterning by temperature-directed capillarity

Basic concept in CFL



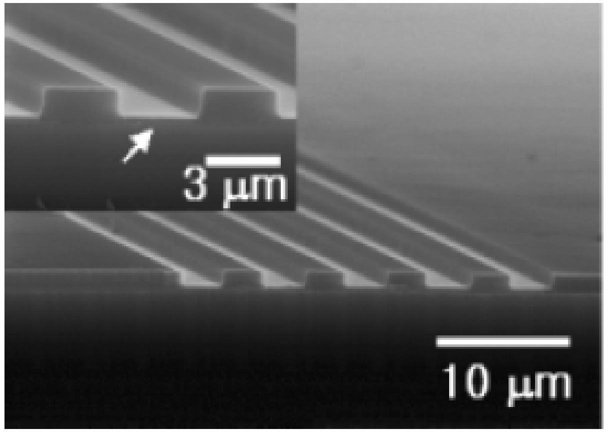
➢ Young-Laplace equation

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

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

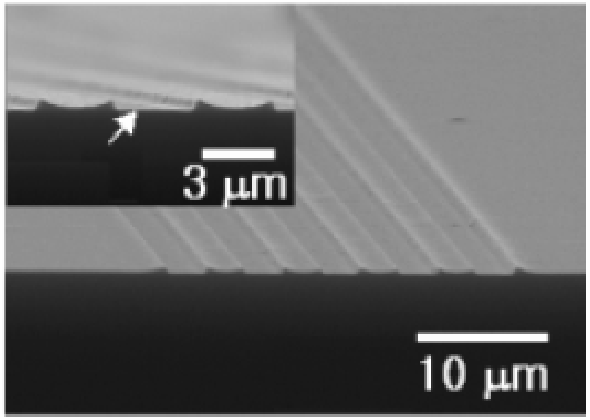
CFL examples

Thick and Thin polymer films



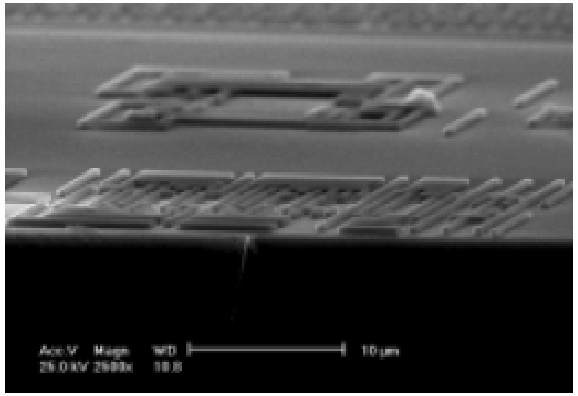
Film thickness: 1.5 µm

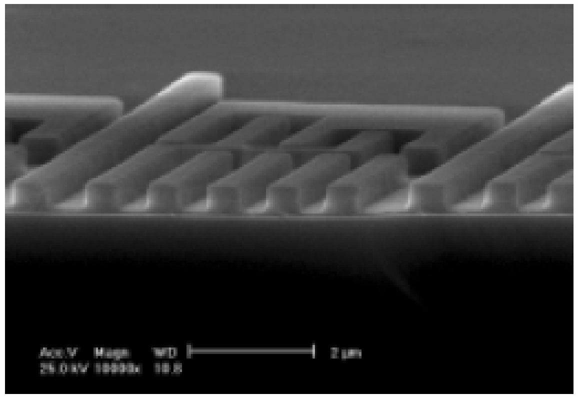
Polystyrene, 130°C, 24 hrs



Film thickness: 180 nm

Complex and Large-area patterning

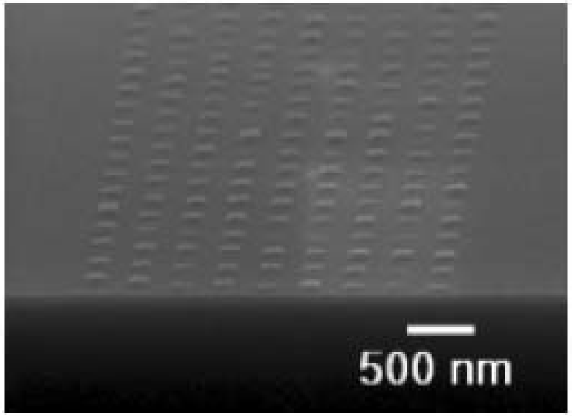




Styrene-Butadiene-Styrene copolymer
120°C, 24hrs

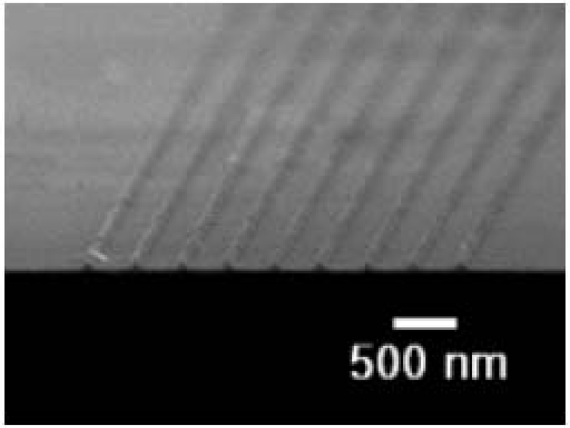
Patterning + Etching

Fine structures



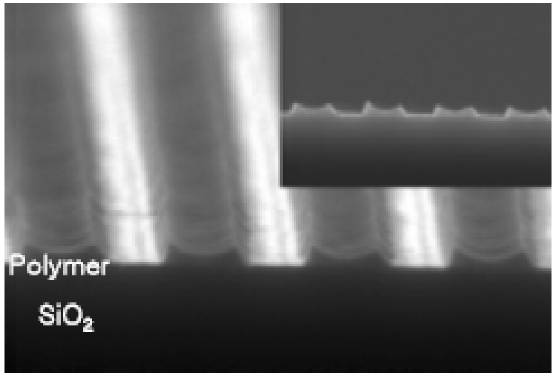
150nm dot patttern

Polystyrene, 130°C, 24 hrs

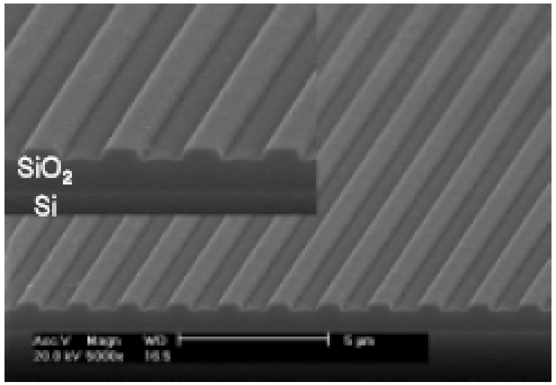


100nm line pattern

Pattern transfer to a substrate



Dry etching



Etching condition
- CH_3 (40 sccm)
- CF_4 (10 sccm)
- 50 mTorr
- SiO_2 substrate

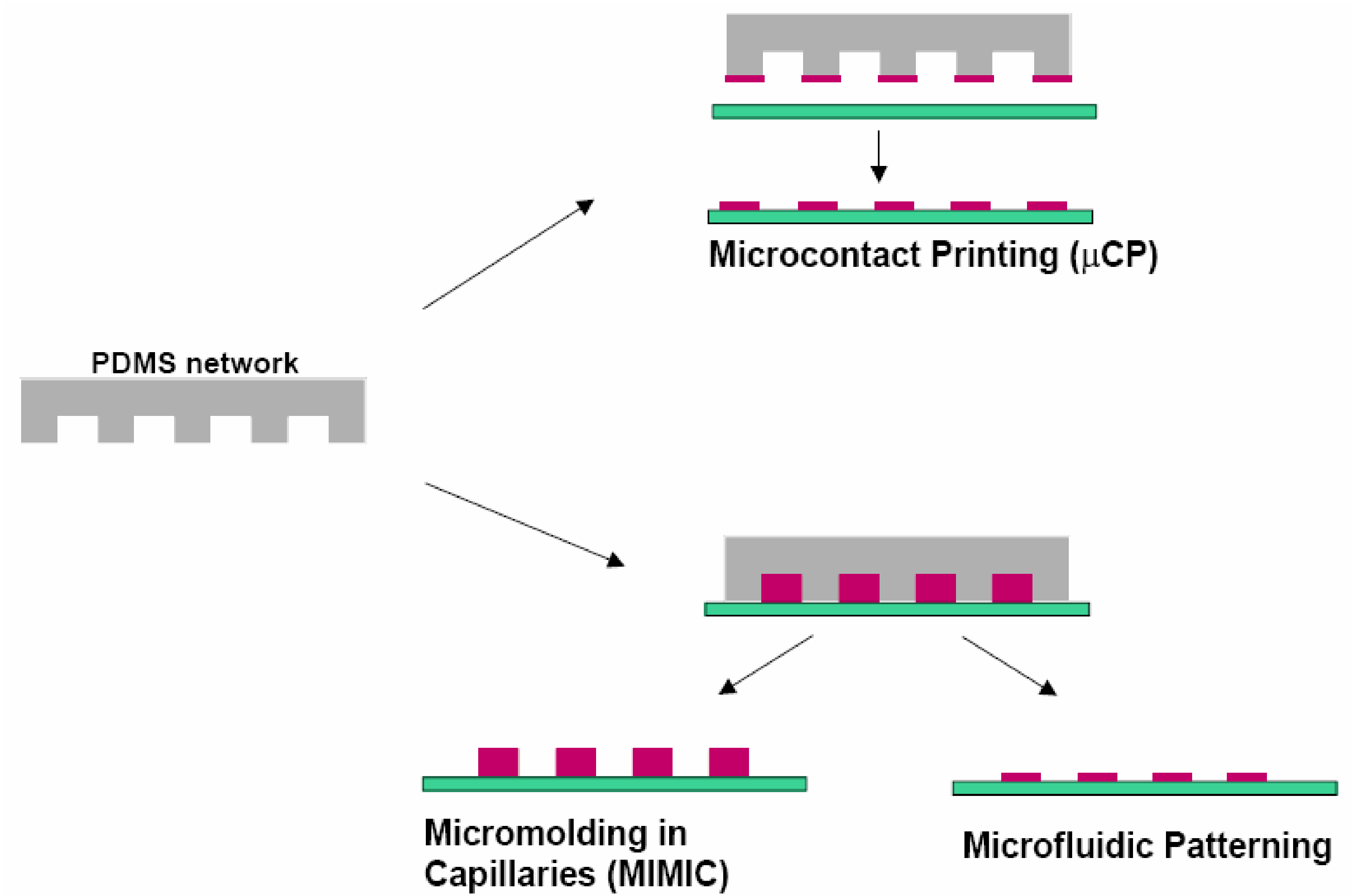
What is Soft Lithography?

A class of techniques involving a soft elastomeric mold such as poly(dimethylsiloxane) (PDMS)

Forms of Soft Lithography

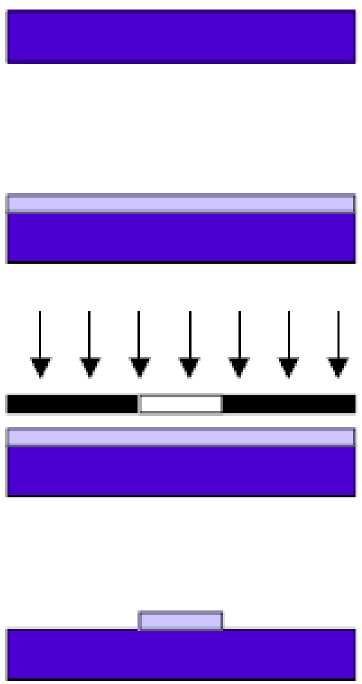
- Microcontact Printing (μCP)
- Replica Molding
- Hot Embossing
- Microtransfer Molding (μTM)
- Micromolding in Capillaries (MIMIC)
- Near-Field Phase Shift Lithography
- Related techniques, e.g. film mask lithography

Representative Soft Lithography Techniques



Fabrication Methods: Master and Replication

In clean room:



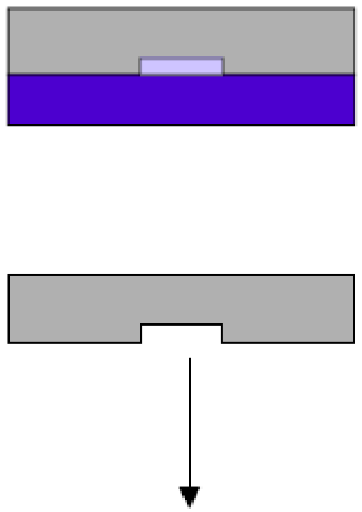
Clean Si wafer

Spin coat photoresist

Exposure to UV light through mask

Develop

On lab bench:



Mix and pour PDMS over master

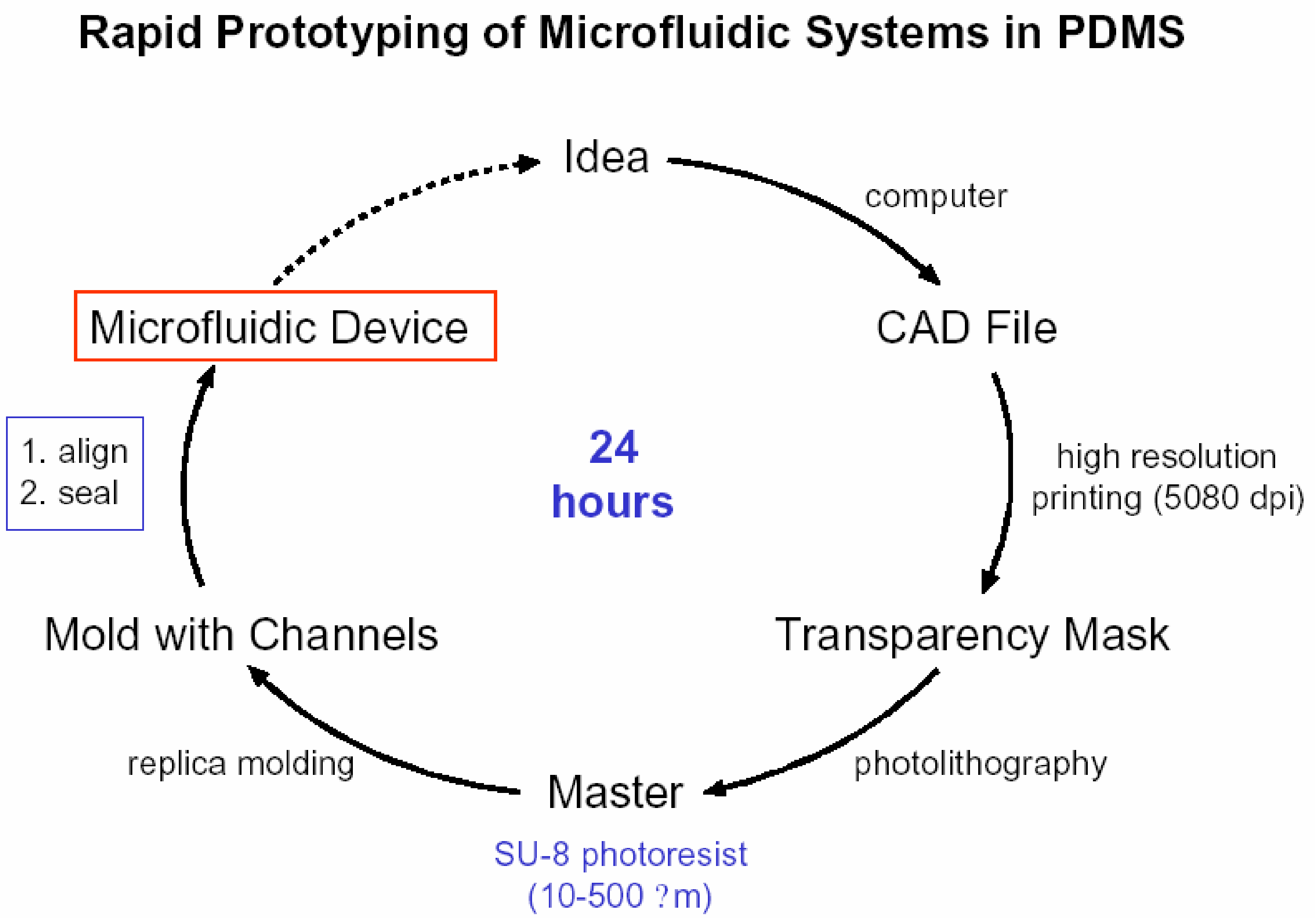
Allow to set; peel from master

Microfluidics
Contact Printing
Micromolding
Imprinting/Embossing

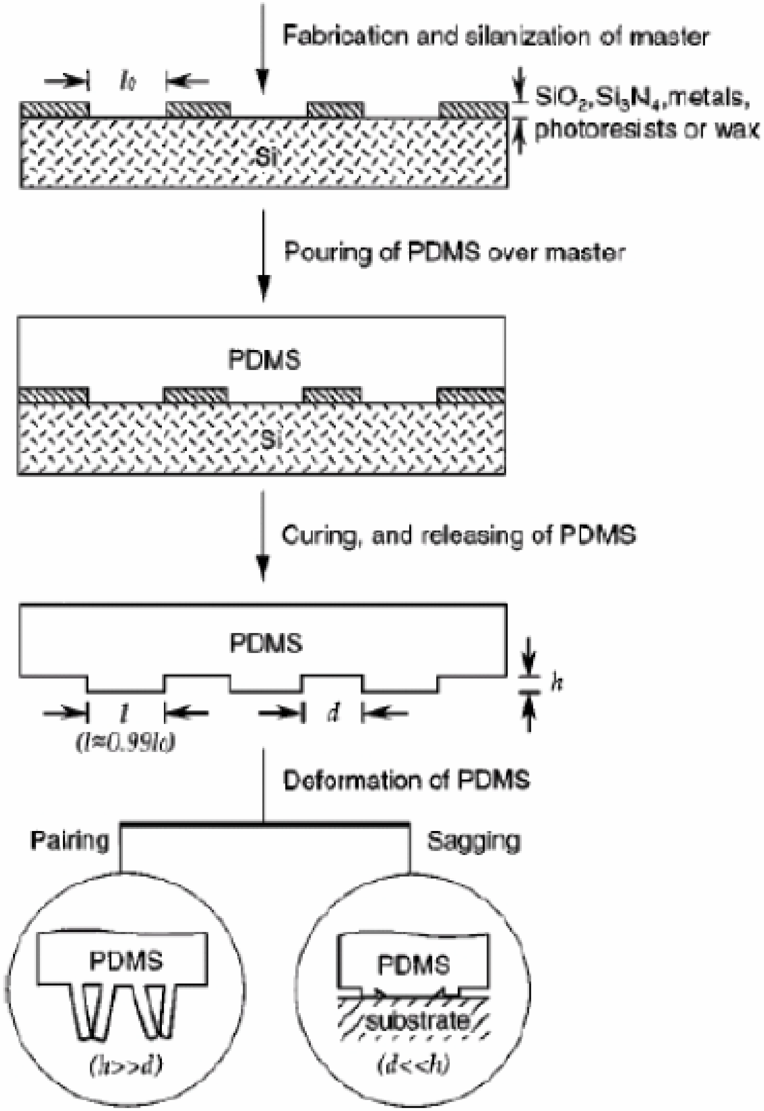
Replica molding using PDMS

- Low interfacial free energy (21.6dyn/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℃ in air)
- Prepolymers being molded can be cured thermally
- Optically transparent down to 300nm; 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
- Durable when used 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

Rapid Prototyping



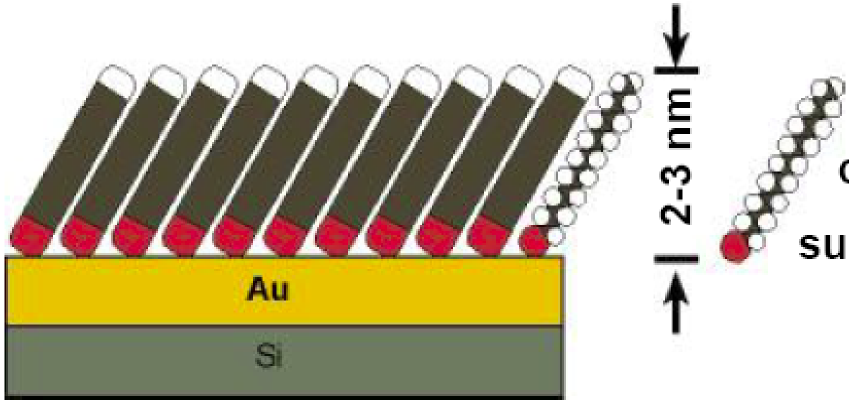
Resolution limit in PDMS



Microcontact Printing (μCP)

- An "ink" of alkanethiols is spread on a patterned PDMS stamp (an alkane is hydrocarbon which is entirely single bonded: C_nH_{2n+2}. A thiol is a sulfhydryl group: SH)
- The stamp is then brought into contact with the substrate, which can range from metals to oxide layers
- The thiol ink is transferred to the substrate where it forms a self-assembled monolayer that can act as a resist against etching
- Features as small as 300 nm have been made in this way.

Self-assembled monolayers



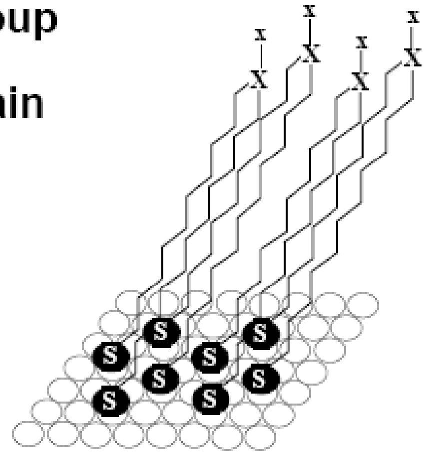
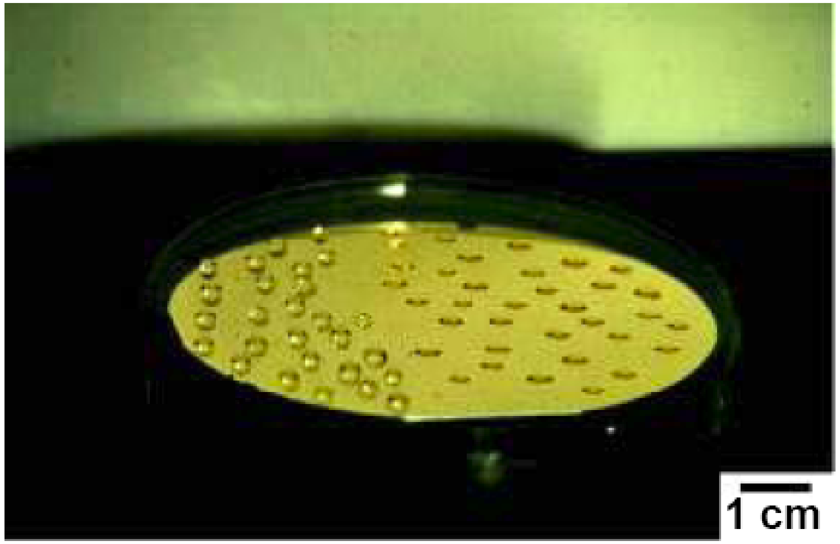
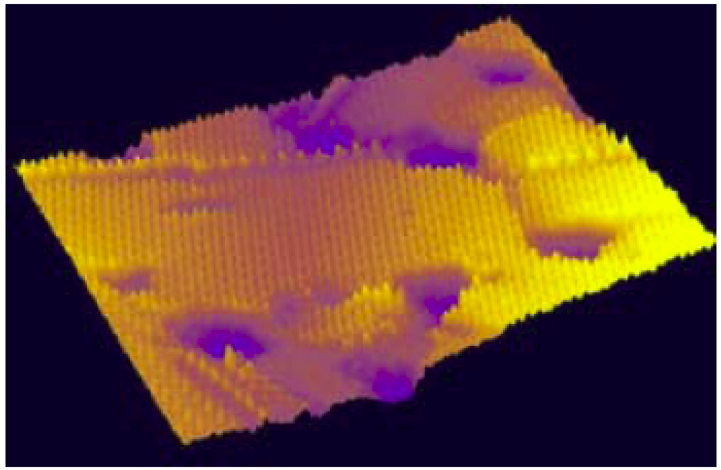


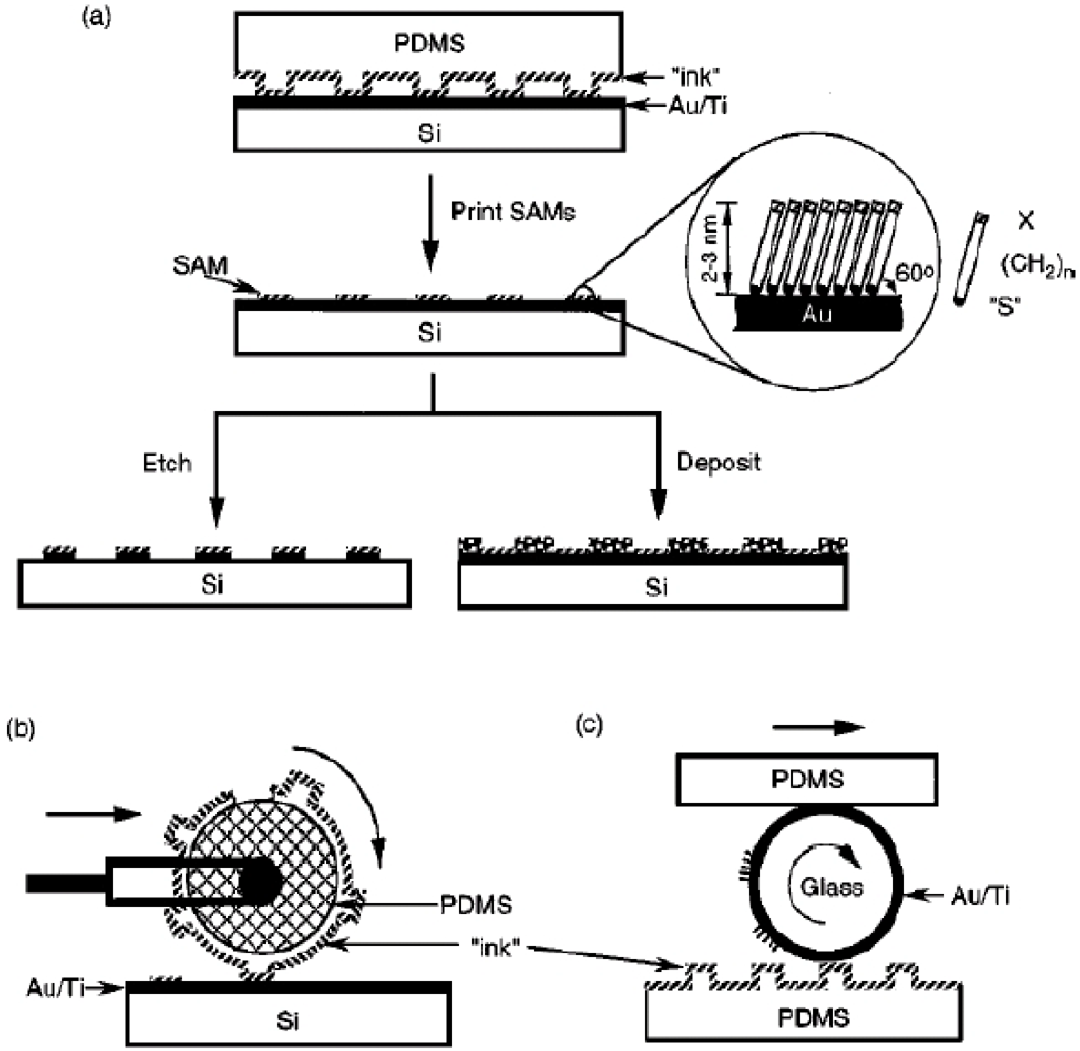
Image of Gold Surface Patterned with Hydrophobic and Hydrophilic SAMs





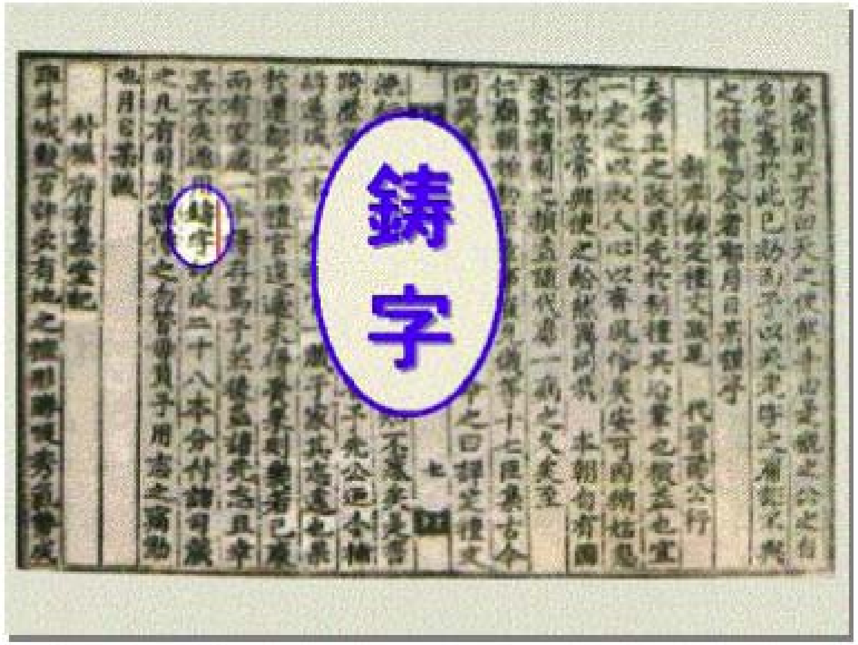
STM Image of a SAM 26

Microcontact Printing (μCP)

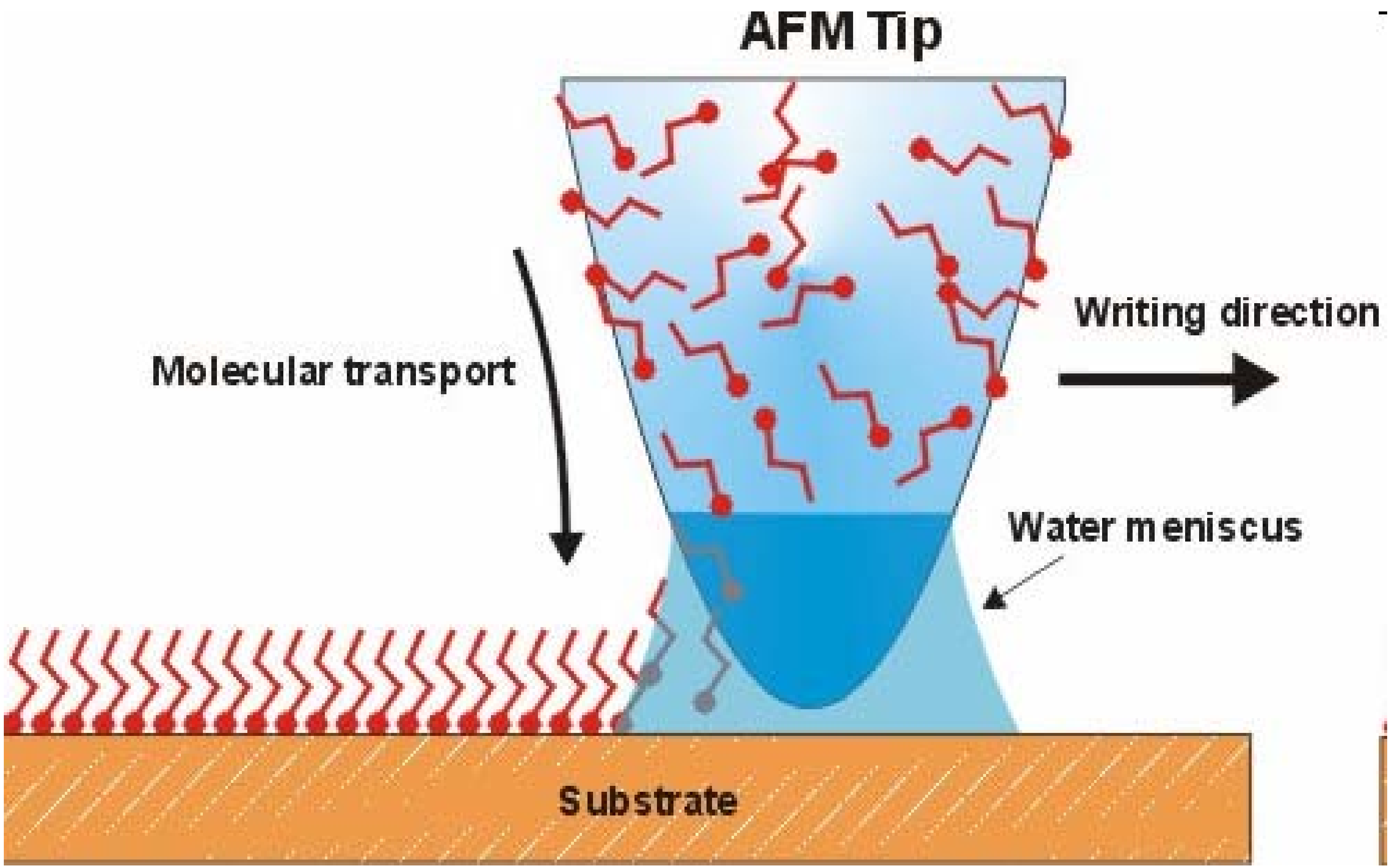


Origin of imprint and soft lithography

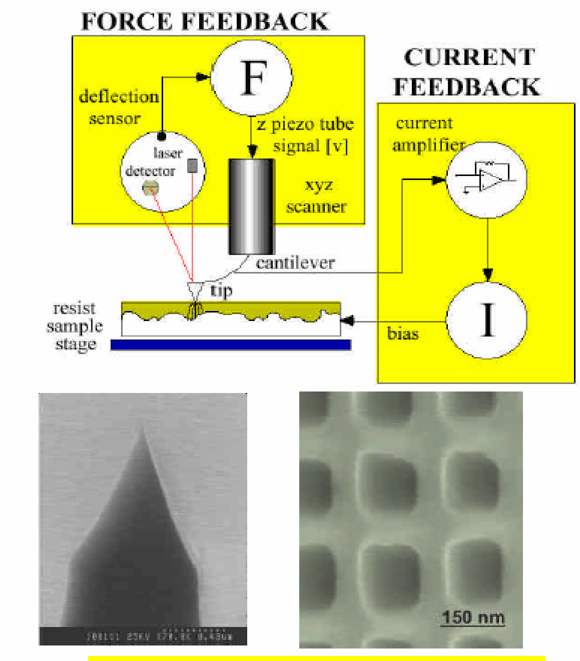
The world's first printed masterpiece called "직지심경" was invented in Korea in the early 11th century, which precedes that of Germany by more than 200 years!

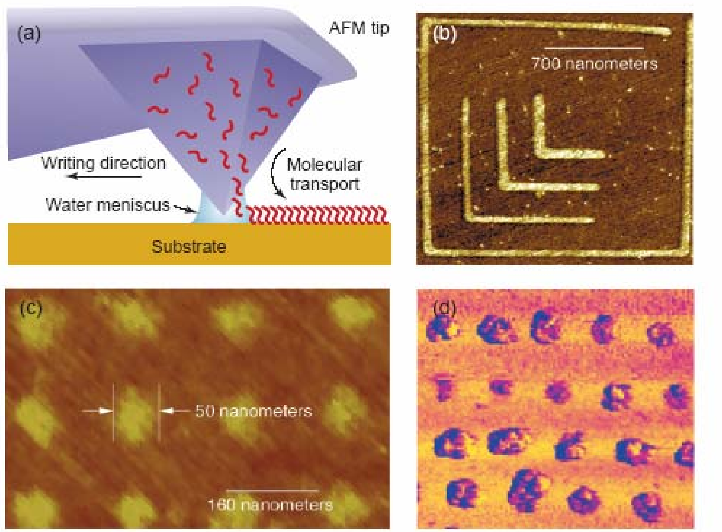


Dip-pen Nanolithography

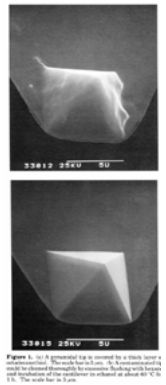


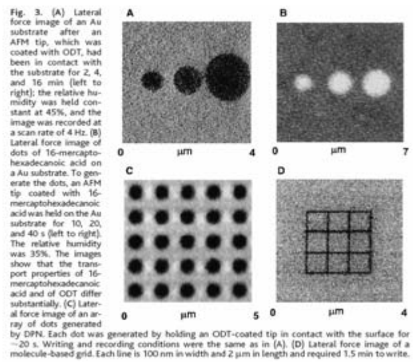
Dip-pen Nanolithography





(a) Schematic of dip-pen nanolithography technique. Friction force images of (b) logos, (c) dots drawn on gold, and (d) colloid particles adsorbed preferentially on the dots. Features are composed of 16-mercaptohexadecanoic acid. The lines are 40 to 50 nanometers wide.



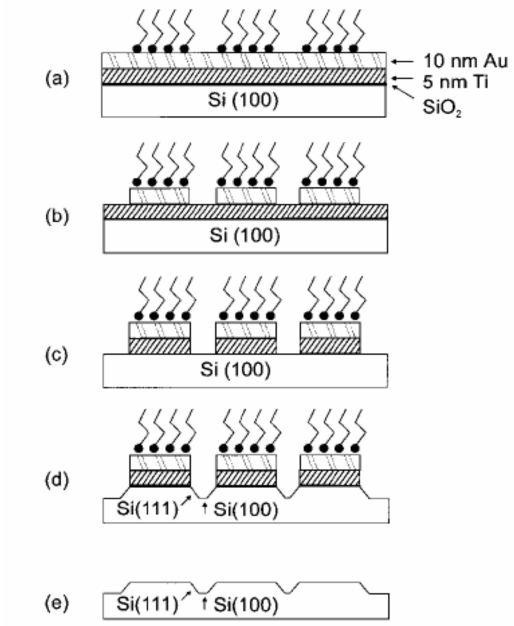


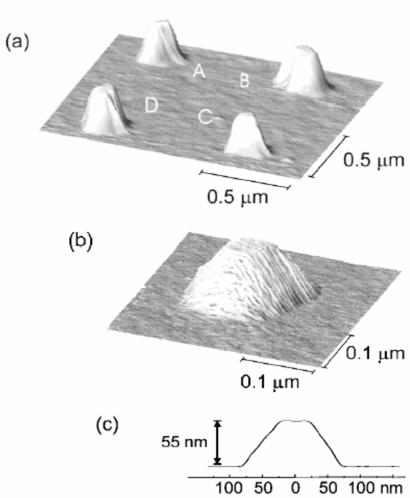
- Butt (1995)
  the creation of aggregates of octadecanethiol on mica
- Mirkin (1997)
  transport of water to and from polymer and mica substrates as effected and observed by LFM
- Mirkin (1999)
  organic patterns of dot arrays or lines with thiol-based molecular inks on polycrystalline gold and Au(111)

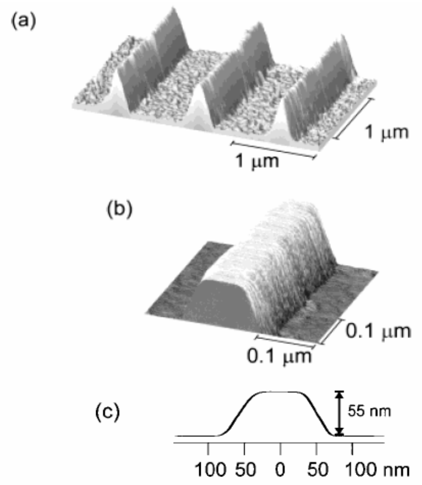
Dip-pen Nanolithography

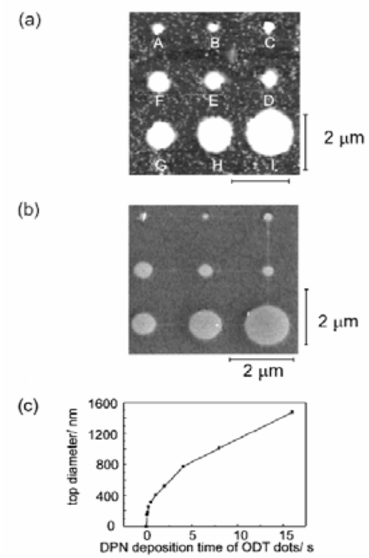
Nanopatterning via DPN and wet etching

- Deposition of ODT onto an Au surface of a multilayer substrate using DPN
- selective Au/Ti etching with ferri/ferrocyanide-based etchant
- selectiveTi/SiO2 etching and Si passivation with HF
- selective Si etching with basic etchant and passivation of Si surface with HF
- removal of residual Au and metal oxides with aqua region and passivation of Si surface with HF



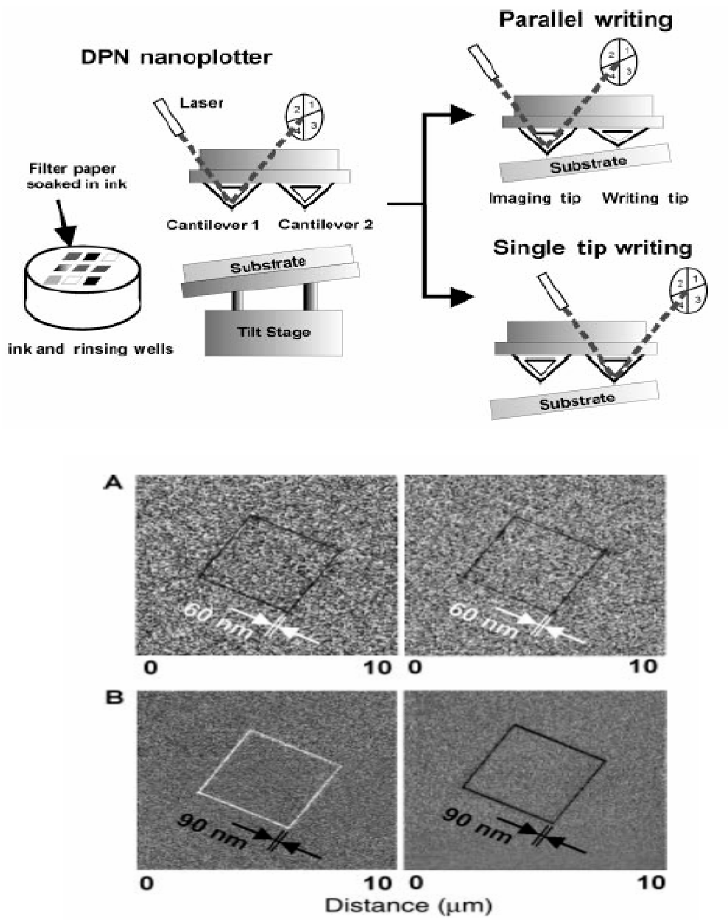






Dip-pen Nanolithography

Parallel and serial writing DPN



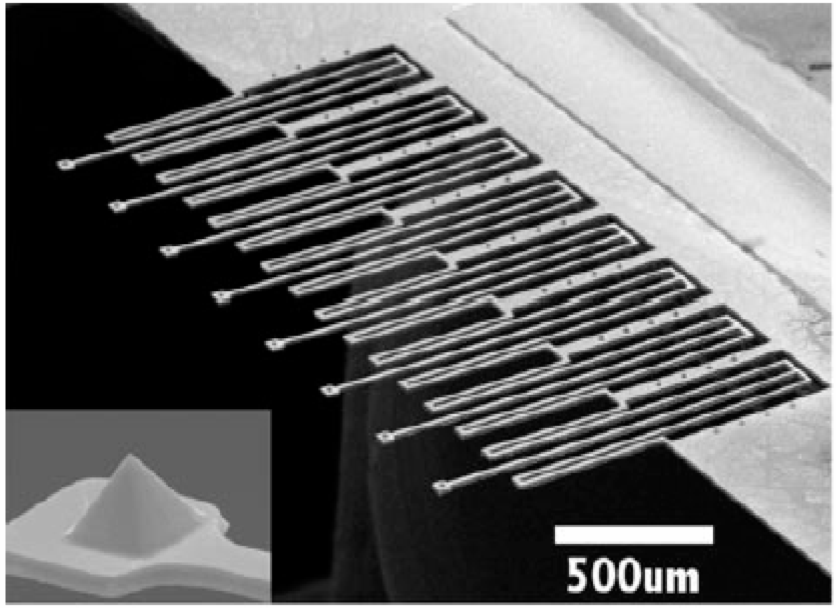


Figure 7. SEM micrograph of a type-2 eight DPN probe array. The insert shows a magnified view of a single tip at the end of a beam. The radius of curvature of this tip is estimated to be 100 nm.

Dip-pen Nanolithography

Nanoparticle/Protein arrays generated by DPN

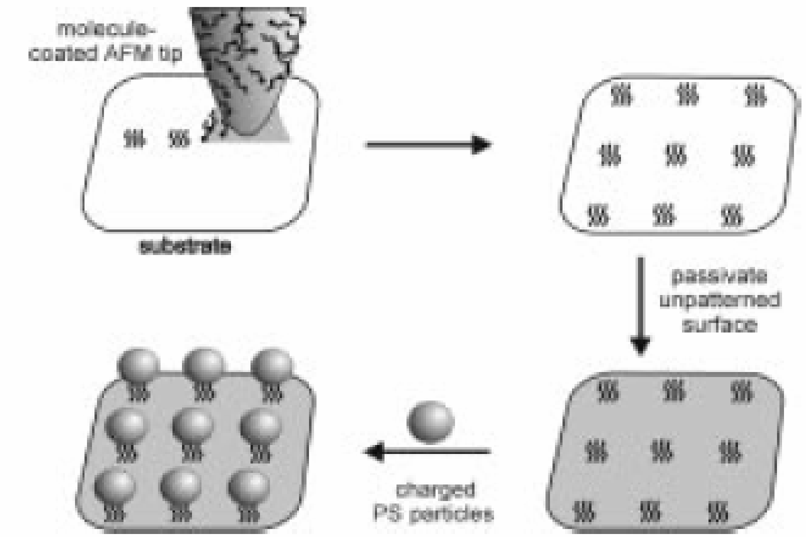


Figure 1. A schematic representation of the DPN-based particle organization strategy.

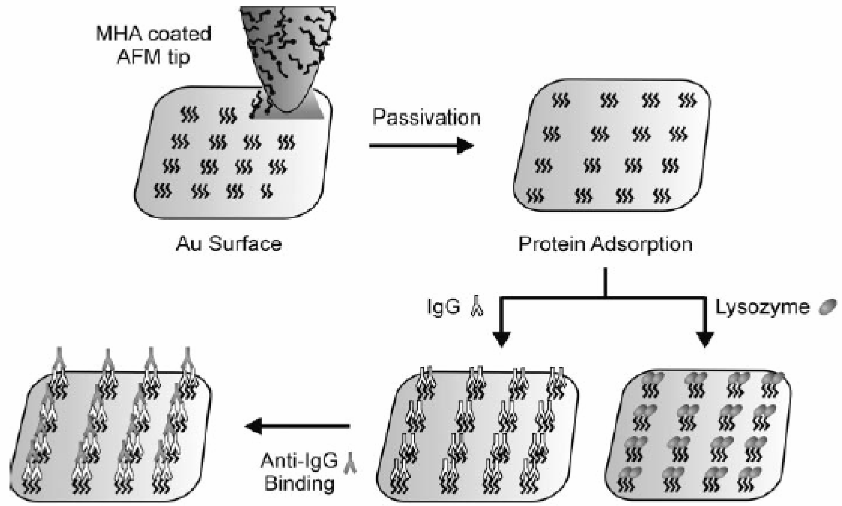


Fig. 2. Diagram of proof-of-concept experiments, in which proteins were absorbed on preformed MHA patterns. The resulting protein arrays were then characterized by AFM.

Dip-pen Nanolithography

Electrochemical DPN

- E-DPN technique can be used to directly fabricate metal and semiconductor features with nanometer dimensions.
- tiny water meniscus as a nanometer-sized electrochemical cell in which metal salts can be dissolved, reduced into metals electrochemically, and deposited on the surface

$$PtCl_6^{2-} + 4e \rightarrow Pt + 6Cl^-$$

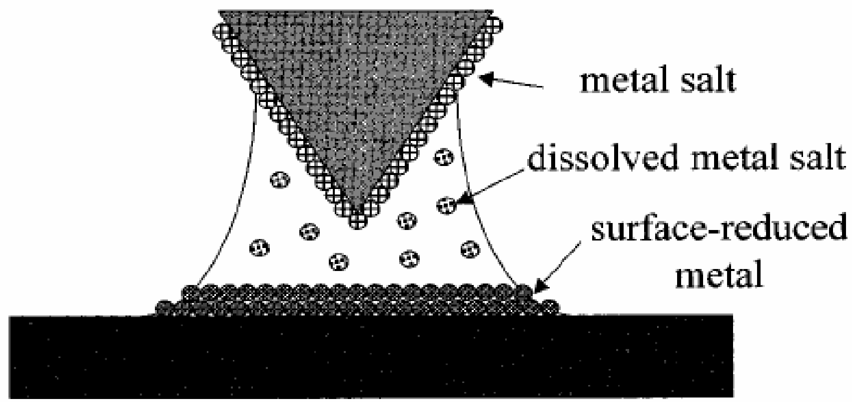


Figure 1. Schematic diagram of the experimental setup.

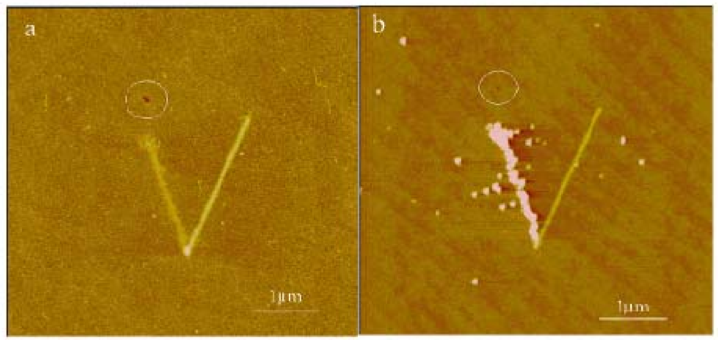


Figure 3. (a) The character "V" composed of platinum (left) and silicon oxide (right). The Pt line is drawn with a voltage of +4 V between the tip and the wafer and a scan speed of 10 nm/s. The SiO_2 line is created with a −10 V voltage to oxidize the surface and the scan speed is 50 nm/s. The relative humidity is 58%. (b) The same area of the wafer after heated at 500 °C under the atmosphere of ethylene in argon for an hour. The white circles highlight a surface defect as the landmark.

Dip-pen Nanolithography

Direct-Write DPN of Proteins