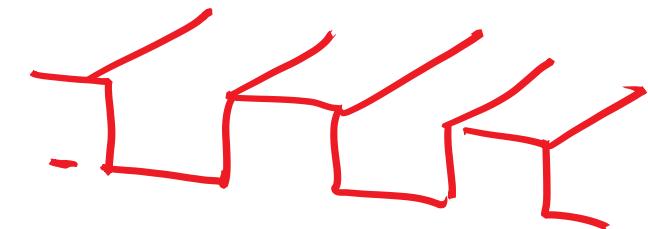
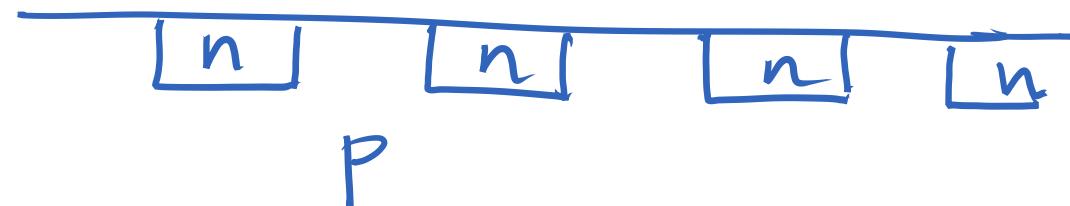
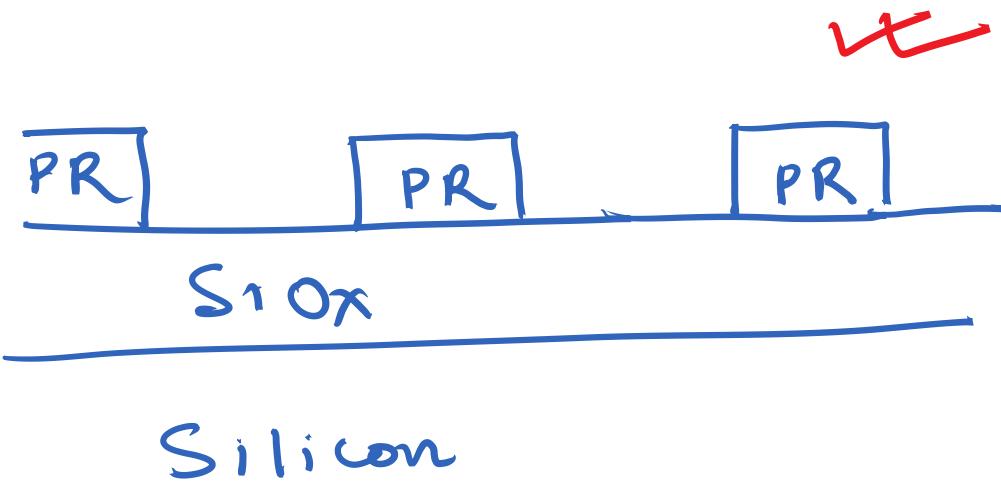


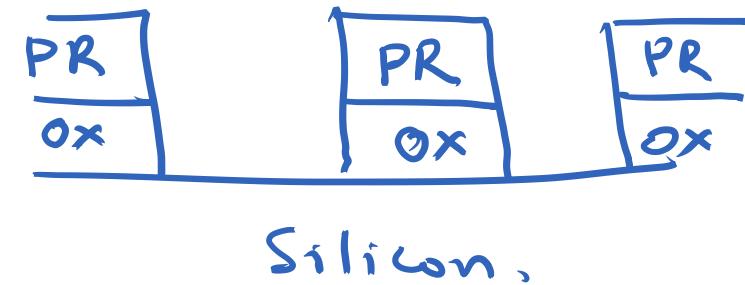
Photo Lithography →



Intermediate Step



and



Physico-Chemical Patterns
(Topographic Features Also)

Introduction to Soft Lithography → New (1990 s)

PhotoLithography → Very Specific Technique

Soft Lithography → A Collection of Techniques →

↳ Generic Techniques for Patterning Soft Materials

- Polymers -
- Gels -
- Inorganic materials

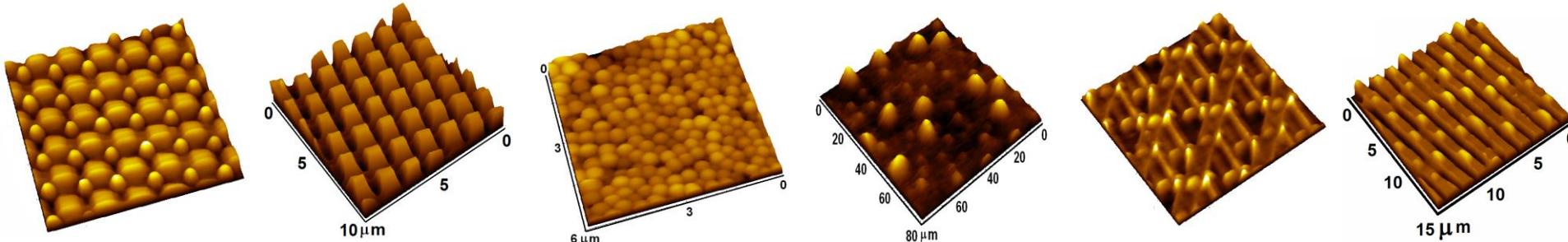
like
Oxides thru
Sol-Gel
Route.



Rabibrata Mukherjee

Department of Chemical Engineering, IIT, Kharagpur

CH 62052: Instability

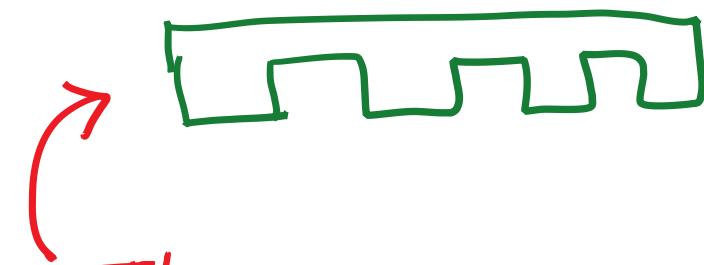


Soft Lithography Methods

- These are rather specific towards soft surfaces (polymers and gels) as well as for applications which do not require extremely stringent quality control or defect free patterns like micro electronics.
- There are several application areas, where large area meso and nano scale structures are necessary, but even if there are some defects here and there, it is fine.
- Sensors, Biological applications, structural color, textured hydrophobicity: progress in all these areas depend on availability of robust, simple, easy to execute and CHEAP patterning techniques that can create large area ($\sim \text{cm}^2$) patterns with good reproducibility
- The ability to create defect free structures should be reasonable.

Most cases, the concept works on getting a Perfect Negative Replica of the Original Stamp!

Topographically
Patterned
Master / Mould/
Stamp



This can be made
by Photo litho
itself

Types of Polymer → Long chain molecules
 → - C - C - C - C - C - → organic materials

Entanglement → ↳ Straight Chain / Branched.
 ↳ Entanglement higher

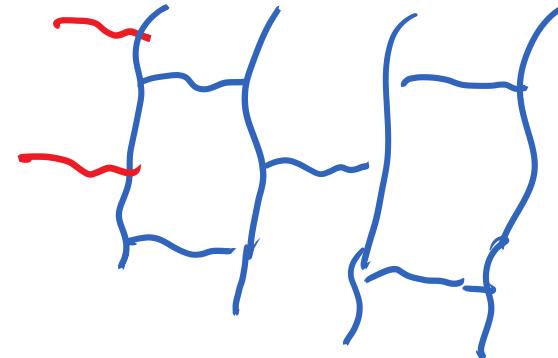
Polymers are solid like at room Temp.

Entanglement → Molecules can not move with respect to each other.

T_g → If becomes soft / Drop in viscosity /
 Adequate translational KE so that the molecules
 can move. No physical cross link
 Thermo Plastic / Glossy

Type 2: Chains are cross linked →

(Thermo Sett Polymer) →



Flexible

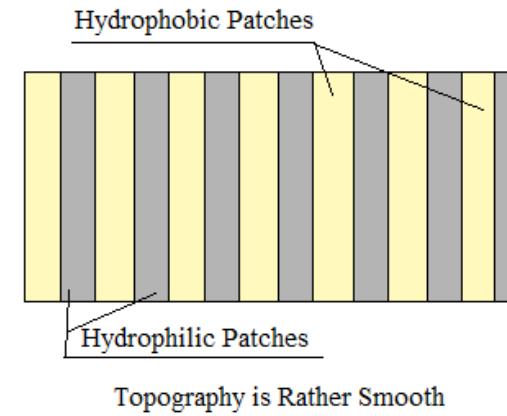
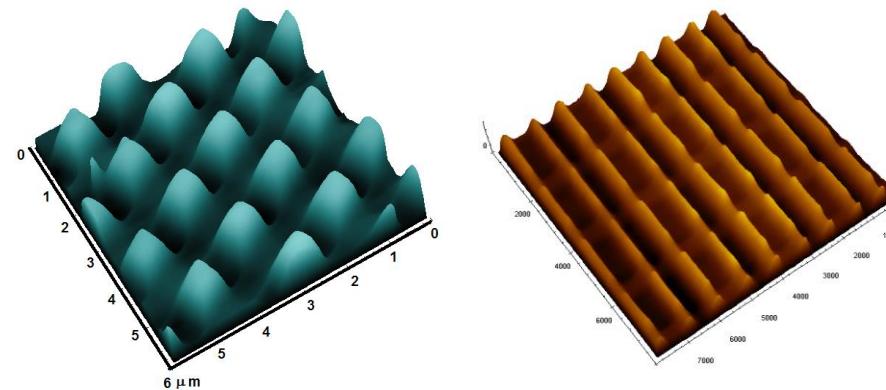
Visco-Elasticity



Soft Lithography Techniques: Classifications

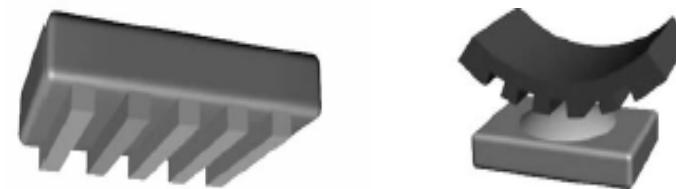
Based on the Nature of Patterns:

- Chemical Patterns
- Topographic Patterns



Based on the Nature of Mold or Stamp Used:

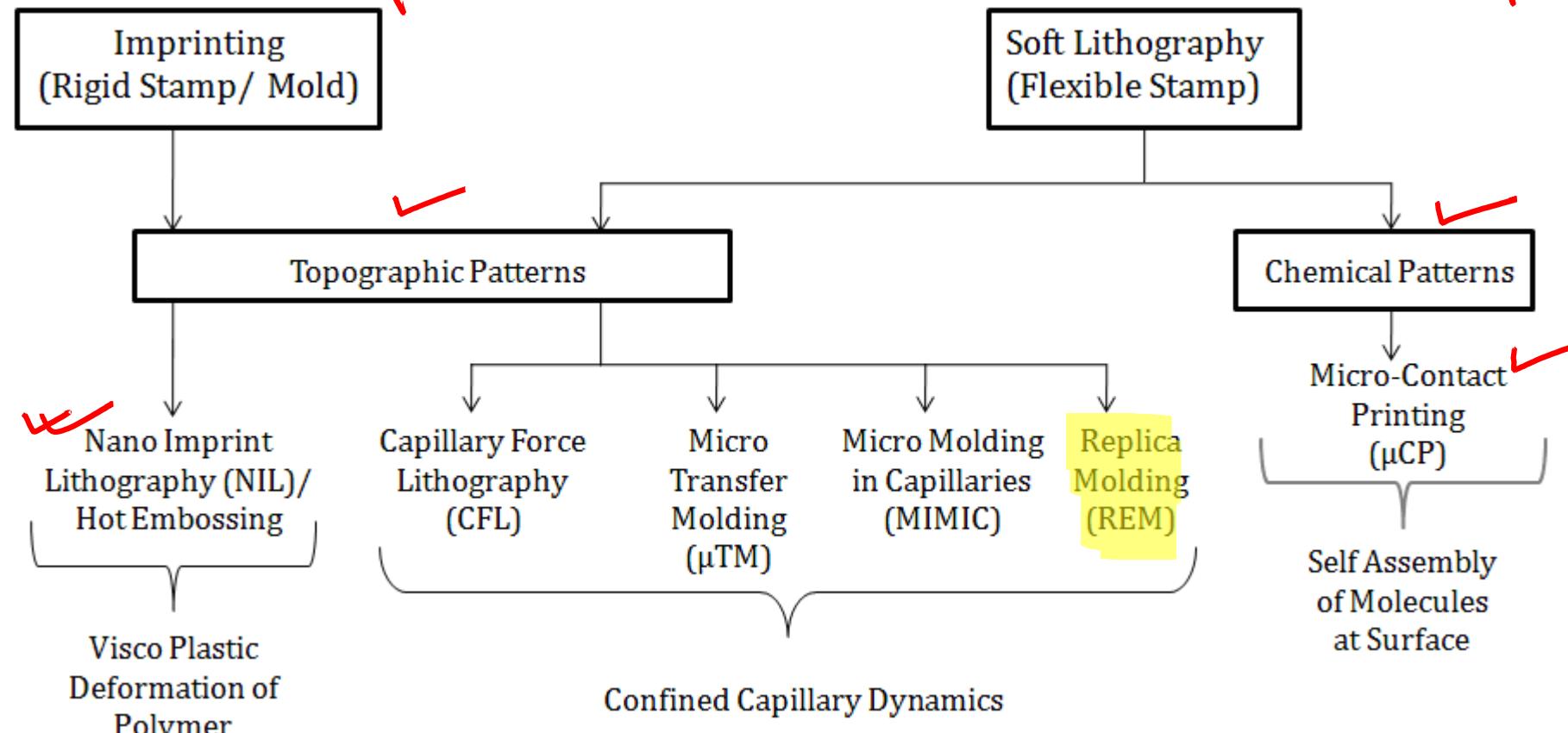
- Rigid Stamp
- Flexible Stamp
- Dissolvable Stamp



Soft Lithography Techniques: Classifications → 1990's

George Whitesides → Harvard.

Chou's Group.



Stephen Chou → Princeton.

Soft Lithography Techniques: Classifications

Based on the Pattern Transfer Mechanism:

Chemical Patterns

Are always based on some surface active molecules (Micro Contact Printing) (μ CP)

George Whitesides @ Harvard

Topographic Patterns:

Due to Visco plastic Deformation of a softened polymer Layer

(Nano Imprint Lithography Group of Techniques) (NIL)

Stephen Chou @ Princeton

Or

Due to Capillary Driven Flow of a Polymer solution of film in liquid state

(Whitesides, Hong Lee (Korea))

- CFL (Capillary Force Lithography)
- MIMIC (Micro Molding in Capillaries)

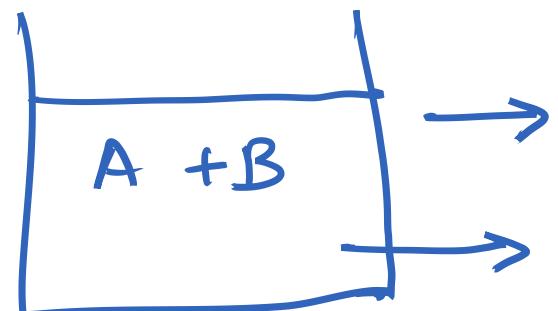
Polydimethyl Siloxane (PDMS) → Silicone Oil.

It's a high viscous liquid at Room Temperature →

Thermo Curable PDMS → Sylgard 184.

High Viscous
Liquid

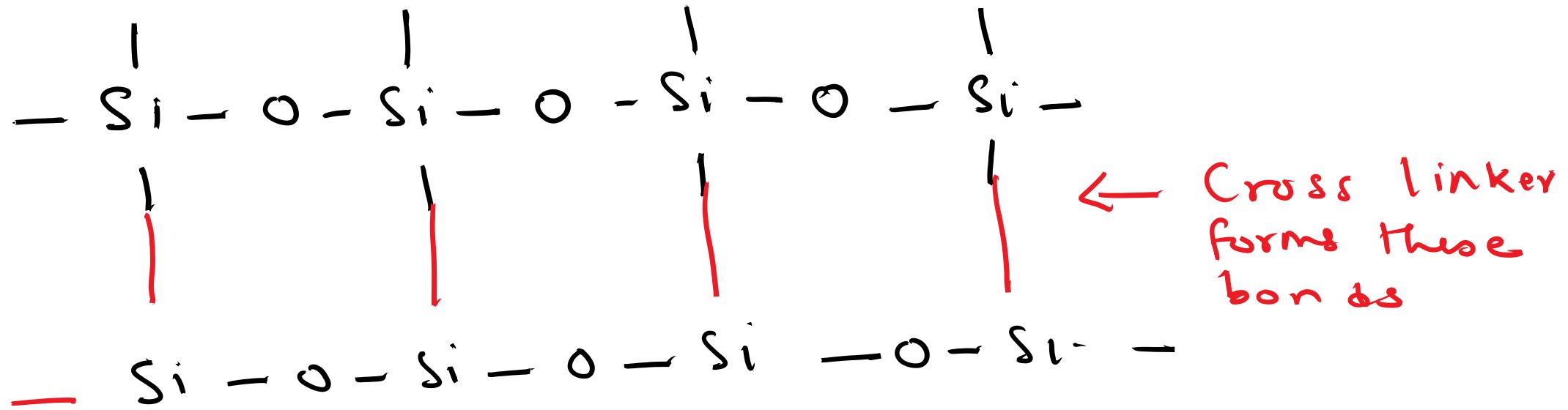
A → Oligomer (Longer chain Monomer)
B → Cross linker - Catalyst



Heat it (120°C / 6 hrs)

Soft Deformable Solid.
→ Physical cross linking of the chains.

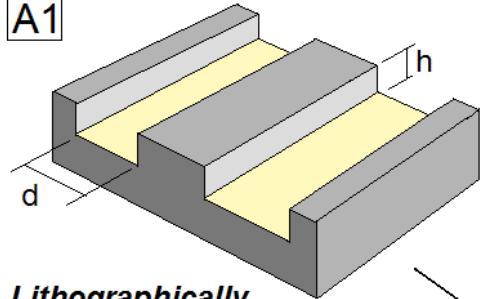
PDMS - Silicone based Polymer



→ Inorganic Polymer

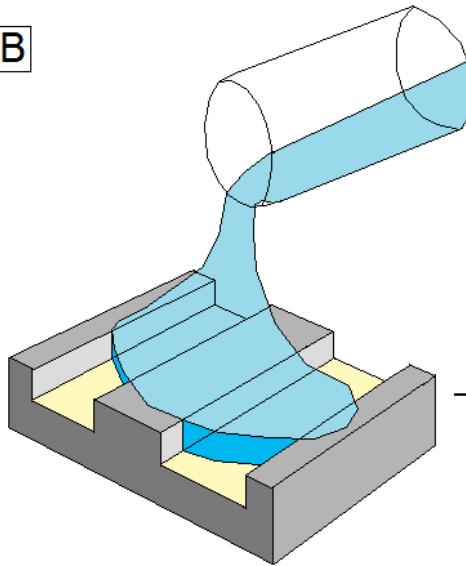
Replica Molding

A1



Lithographically
Fabricated Master
(With Relief Structures)

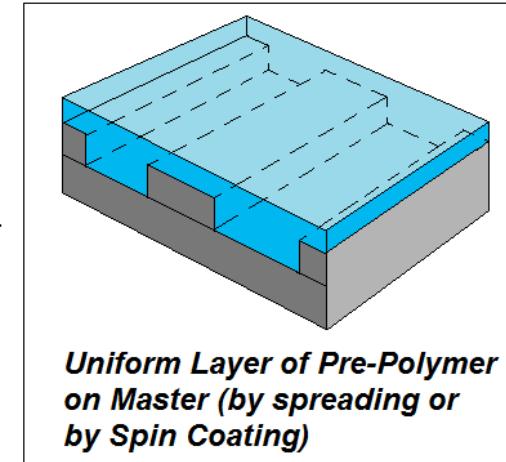
B



Pouring of the
Pre-Polymer Mix on the Master

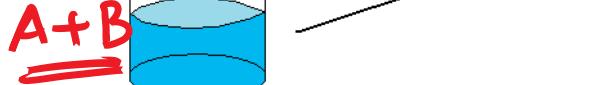
C

Thermally Annealed at
Elevated Temperature
(between 100°C - 150°C)
for cross linking



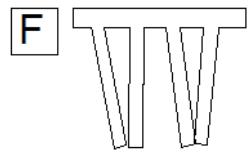
Uniform Layer of Pre-Polymer
on Master (by spreading or
by Spin Coating)

A2



Pre-Polymer Solution
(Mixture of Oligomer
and Cross Linker)

(Part A and Part B of Sylgard 184)

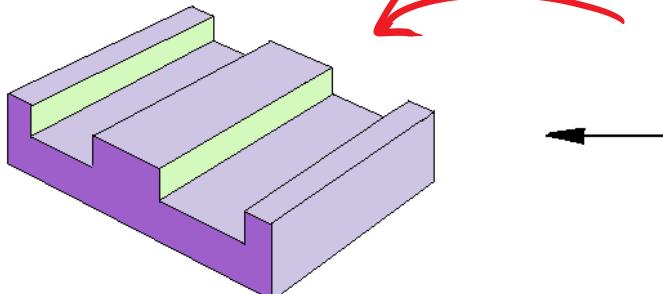


Pairing
 $h \gg d$



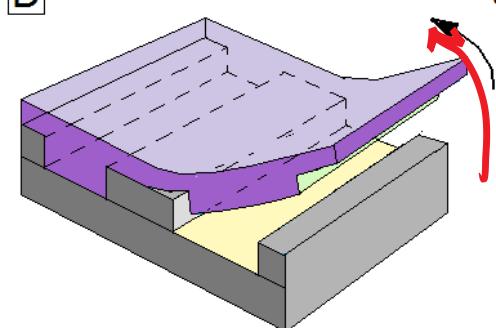
Sagging
 $h \ll d$

E



Negative Replica of the Stamp Pattern on a
Self standing block of cross linked elastomer

D

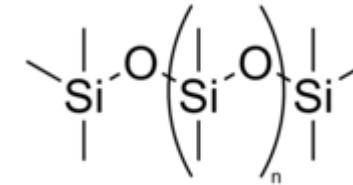


Cross Linked Elastomer
containing Negative Replica of the master

Peeling

Material for Replica Molding

- The material used for REM is Cross linkable Poly-dimethyl siloxane (PDMS), which falls into a general category of materials called elastomers.
- Elastomers are crosslinked amorphous polymers that are used at temperatures above their glass transition temperature, T_g .
- Above the glass transition temperature, molecules gain thermal energy that enables them to move in a coordinated manner, making the elastomers rubbery, soft and flexible.*



Sylgard Group of Products from Dow – Croning USA

Rabibrata Mukherjee



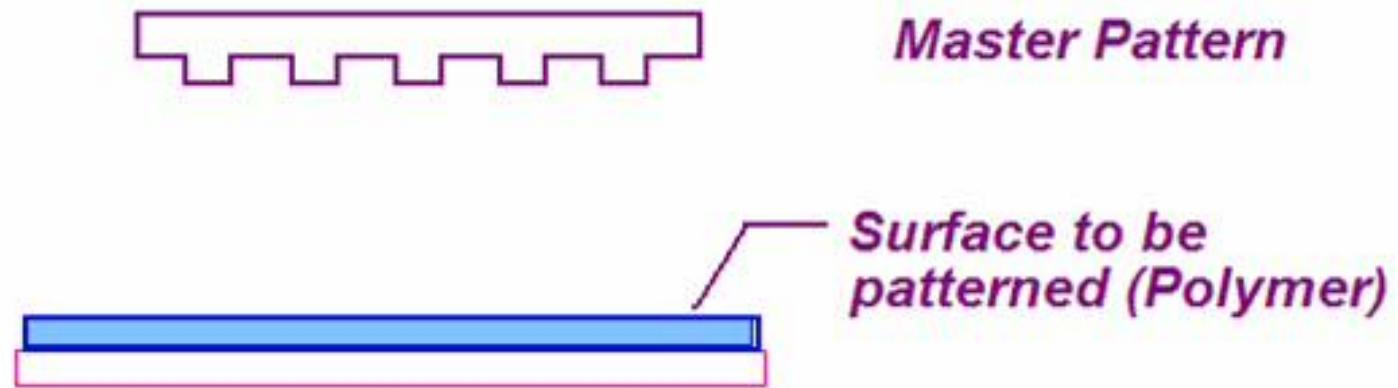
Cross Linked PDMS

- PDMS consists of an inorganic siloxane backbone and organic methyl groups attached to it.
- It is a flexible elastomer that can be used in a wide temperature range, it is optically transparent, biocompatible, inert and non-toxic and resistant to many chemicals.
- It is non-flammable and gas-permeable.
- Thermally and electrically it is insulating.
- The low surface energy of PDMS allows its release easily from templates and structures.
- Curing of PDMS can be done in room temperature, or rapid heat curing in temperatures of 60 – 120°C

Major properties of Cross Linked PDMS

• Stability temperatures	– 50°C to +200°C
• Tensile strength	7.1 MPa
• Elongation at break	1.4
• Young's modulus	in the range of 1 – 5 MPa
• Surface energy low,	~ 21.6 mJ/ m ²
• Coefficient of thermal expansion	310 ppm/°C
• Hydrophobicity	WC 90 – 120°
• Permeability to gases	gases passes easily
• Optical properties	optically transparent down to ~300 nm
• Viscosity (prior to curing)	medium viscosity, at 23°C immediately after mixing: 4000 mPaxs
• Elastic modulus	1.8 MPa
• Compressibility	high, 2 N/mm ²
• Shear modulus	< 1 GPa
• Work of adhesion	10–7 J/mm ²

NANO IMPRINT LITHOGRAPHY



→ Thin Film of a
Glossy Polymer

→ RIGID → Mould

Nano Imprint Lithography (NIL)

J. Vac. Sci. Technol. B, 14, 4129, 1996

For the original Work, PMMA was used as the resist (polymer) layer:

Low coefficient of Thermal Expansion

$\sim 5 \times 10^{-5}$ per $^{\circ}\text{C}$

Low Pressure Shrinkage Coefficient

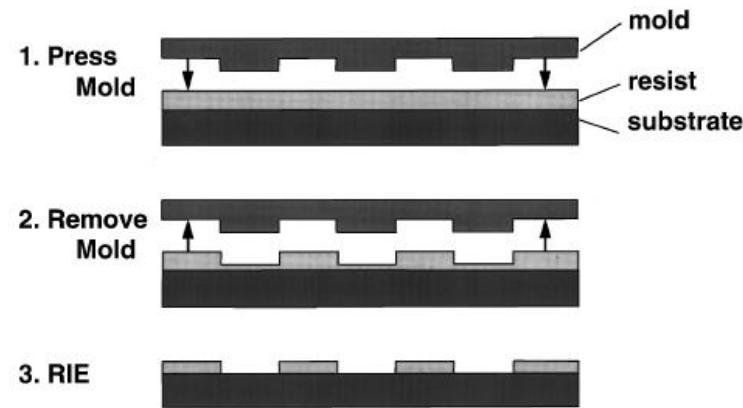
$\sim 3.8 \times 10^{-7}$ per psi

Typical Temperature: 120 – 150 $^{\circ}\text{C}$

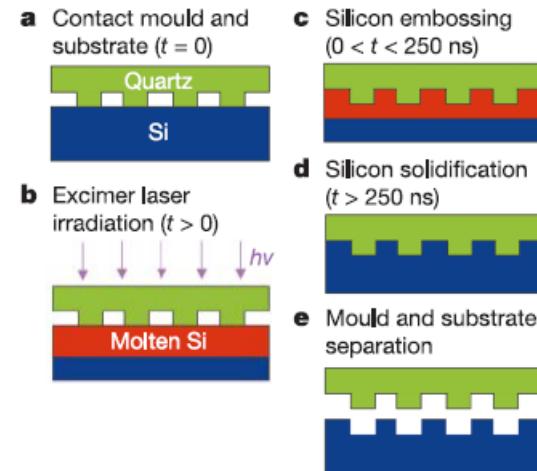
Typical Pressure: 30 – 50 MPa

Mold is Rigid:

Patterned Silicon Wafer, Silica or even other materials can be used



Extended Beyond Polymers



Chou, Nature, 417, 835, 2002

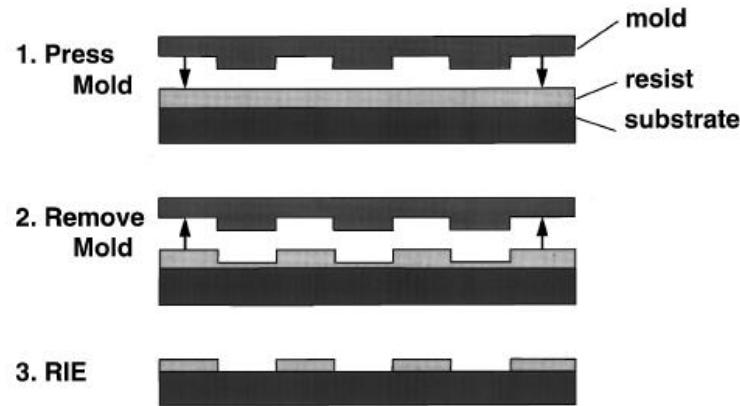
LADI: Laser Assisted Direct Imprinting

Nano Imprint Lithography (NIL)

J. Vac. Sci. Technol. B, 14, 4129, 1996

Advantage:

- Large area patterning capability
- Applicable for many different polymers.
- Resolution achieved ~ 10 nm.
- Possible to achieve patterns over fairly large area.



Some Critical Issues and Limitations

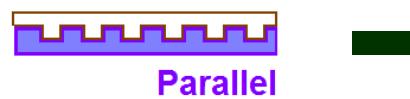
High Temperature

High Pressure

Adhesion of Mold with Resist (Polymer): Severe Chances of Mold Damage

Critical Parallelism between mold and film has to be ensured!

Non Planar Surfaces cannot be patterned

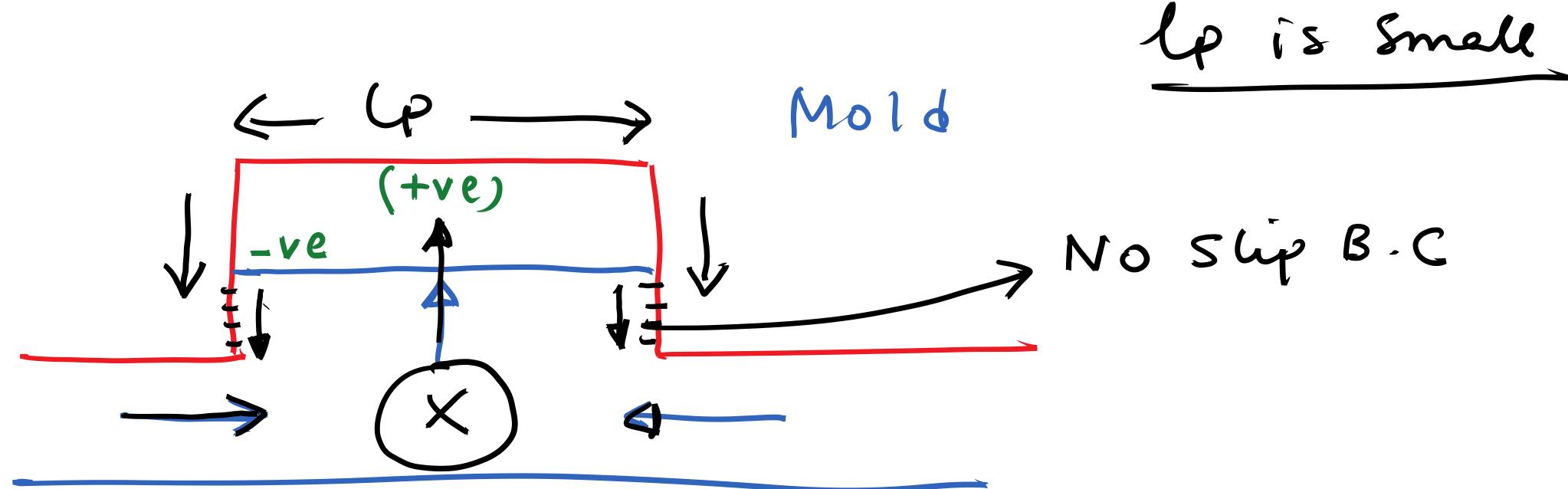


Perfect Replica



Imperfect Replica

Mold Release agents



$\frac{\partial v}{\partial x}$ = Large \rightarrow Velocity Gradient is high. \rightarrow Because of Geometry.

3. As you cool down $\mu \uparrow$

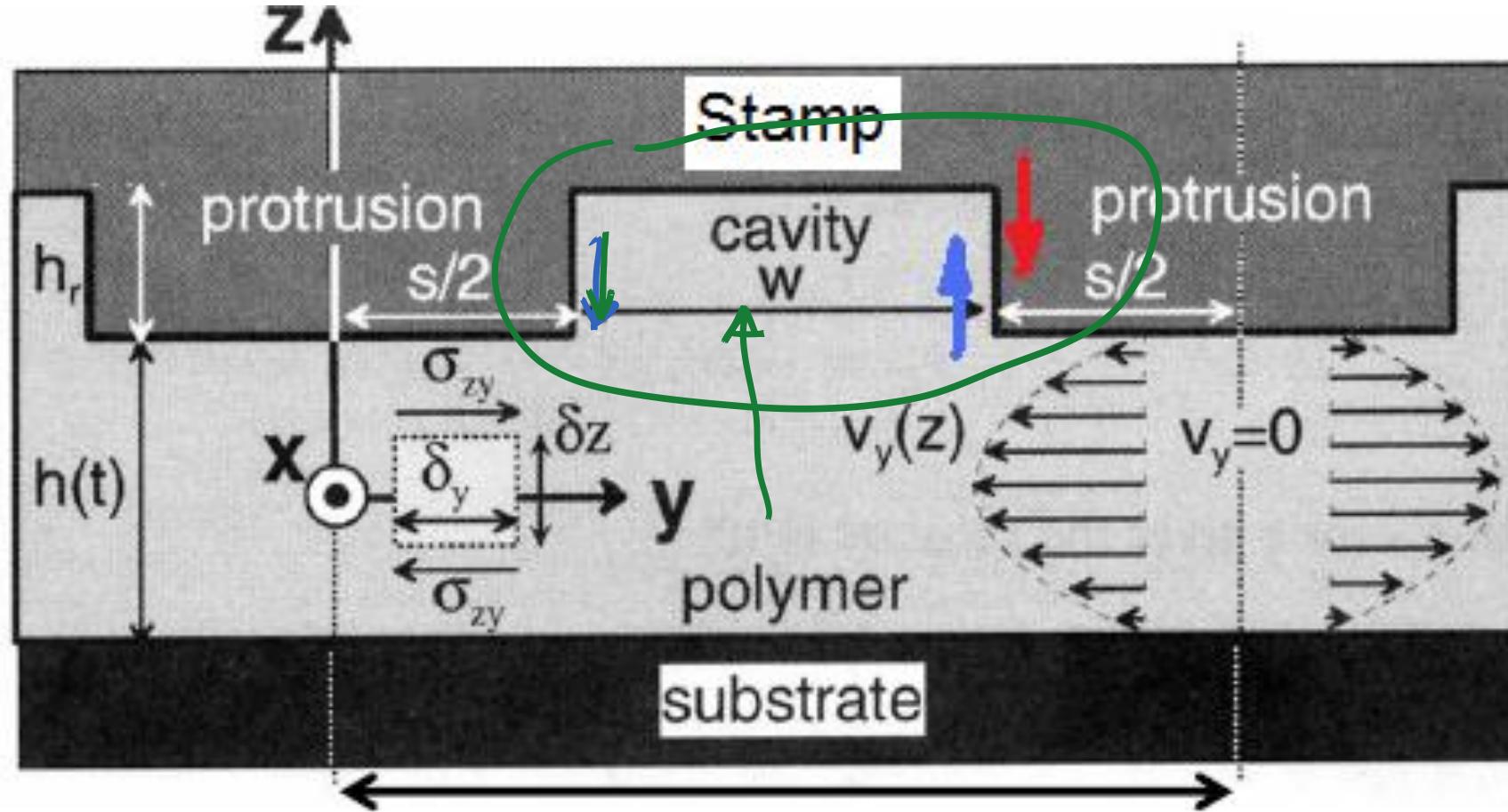
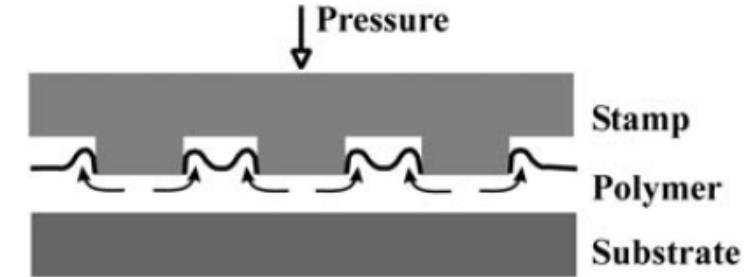
$$T_{xy} = \mu \frac{\partial v}{\partial x}$$

Because of the material

Hot Embossing \rightarrow Some Technique with Large feeters

Nano Imprint Lithography (NIL)

Hydrodynamics and Stresses



By NIL
the structures
we make have
high residual
stress.

Nano Imprint Lithography (NIL) Group of Methods

✓ Room Temperature Imprint Lithography (2001, Hong Lee)

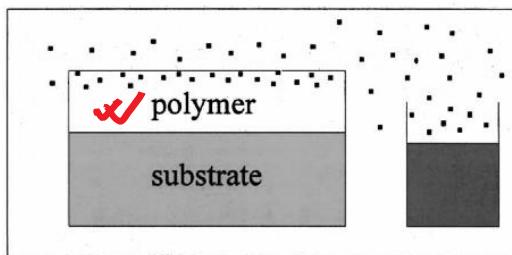
- Low Pressure Nano Imprint Lithography

✓ Solvent Vapor Assisted Nano Imprint Lithography

- Step and Flash Imprint Lithography
- Rapid flash patterning. (Hong Lee, 2004)
- Roller Nano Imprint Lithography

Solvent Vapor Assisted Nano Imprint Lithography

Solvent vapor treatment



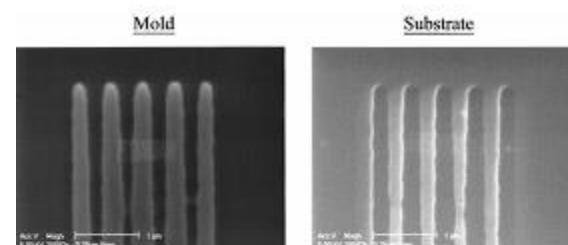
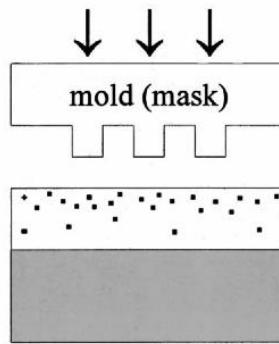
Penetration of solvent molecules into the polymer matrix

Swelling and reduced cohesion

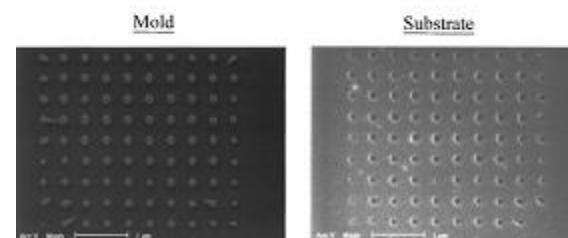
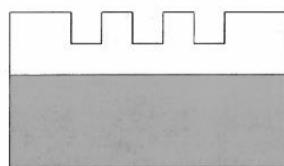
Reduction in Viscosity

Effective reduction in glass transition temperature below room temperature.

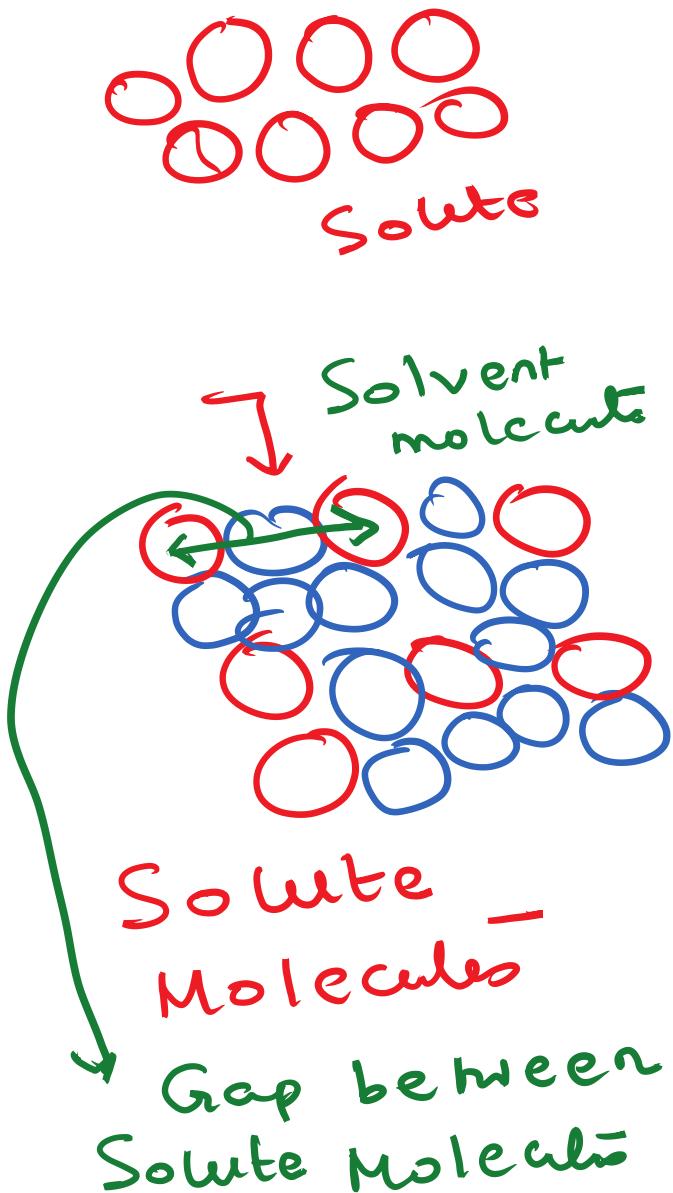
Room-temperature imprinting



Pattern transfer to polymer (removal of the mold)

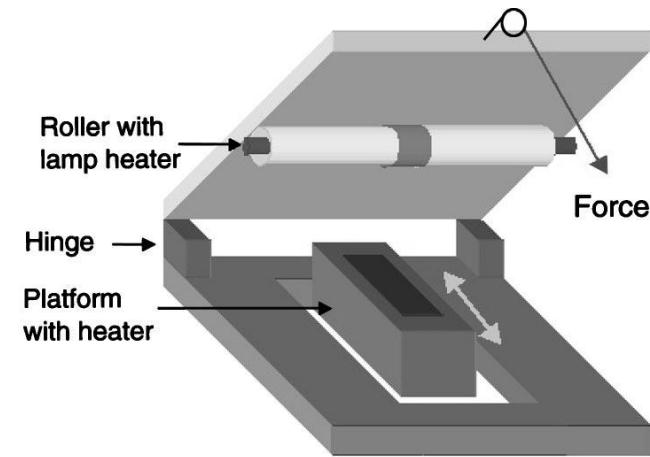
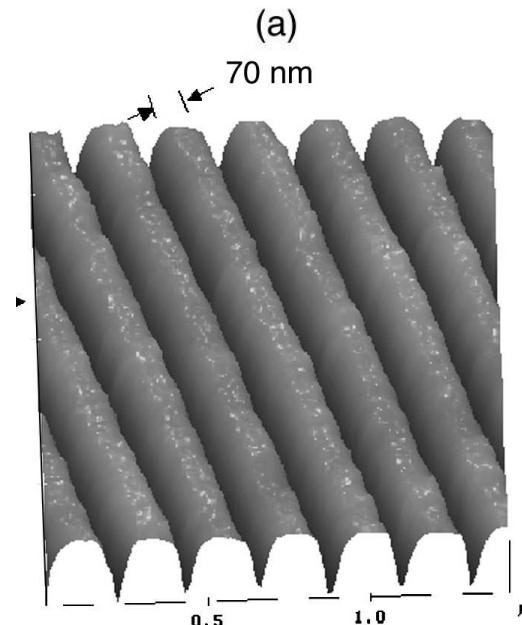
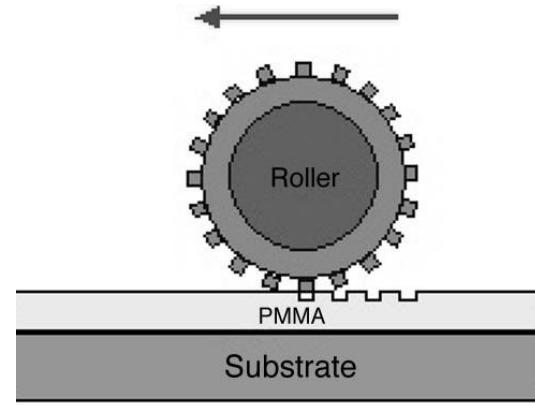


Hong Lee: Applied Physics Letters, 76, 870, 2000



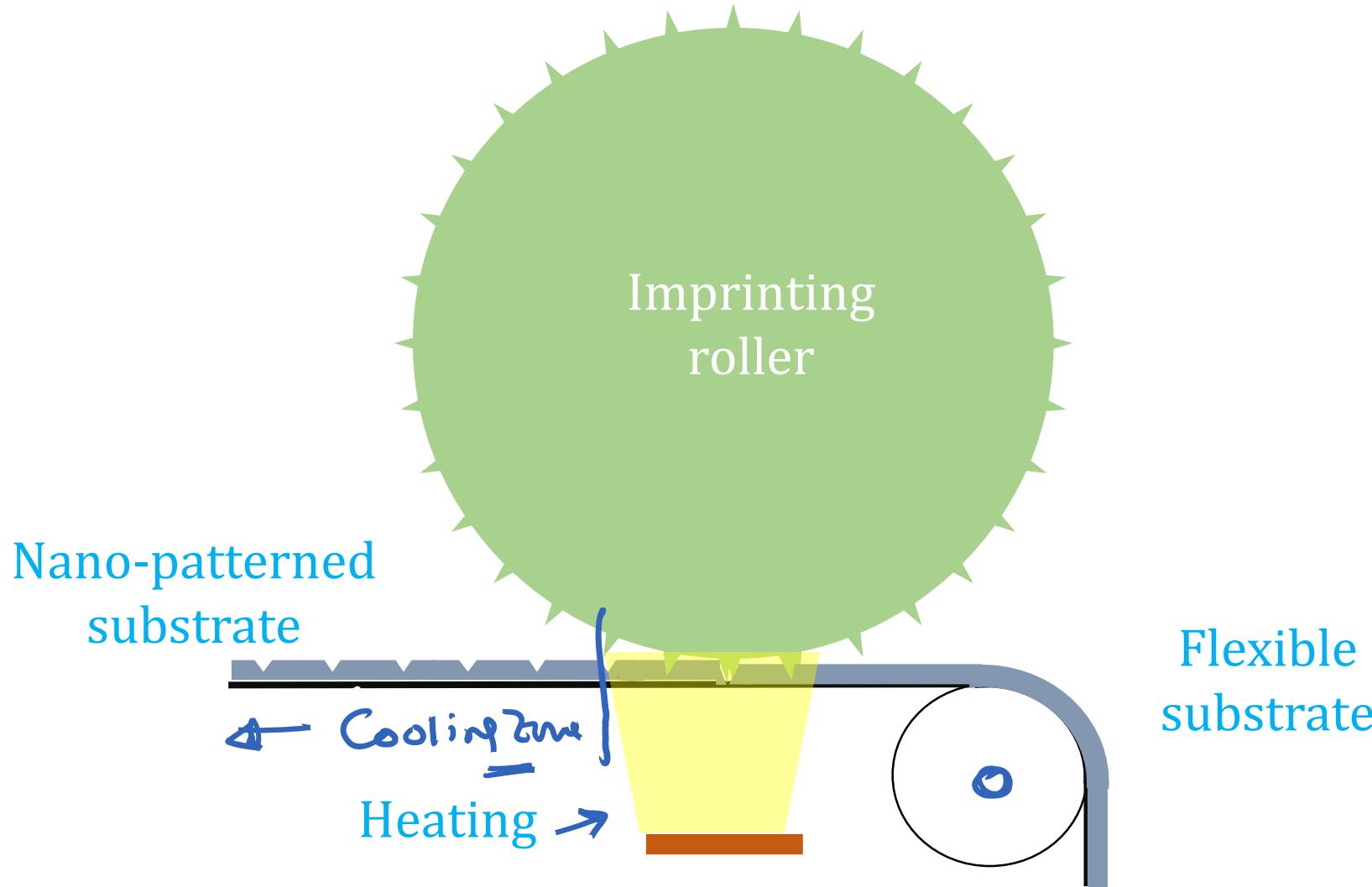
Roller Nano Imprint Lithography

All the configurations discussed so far, make the imprinting group of techniques batch type operation.



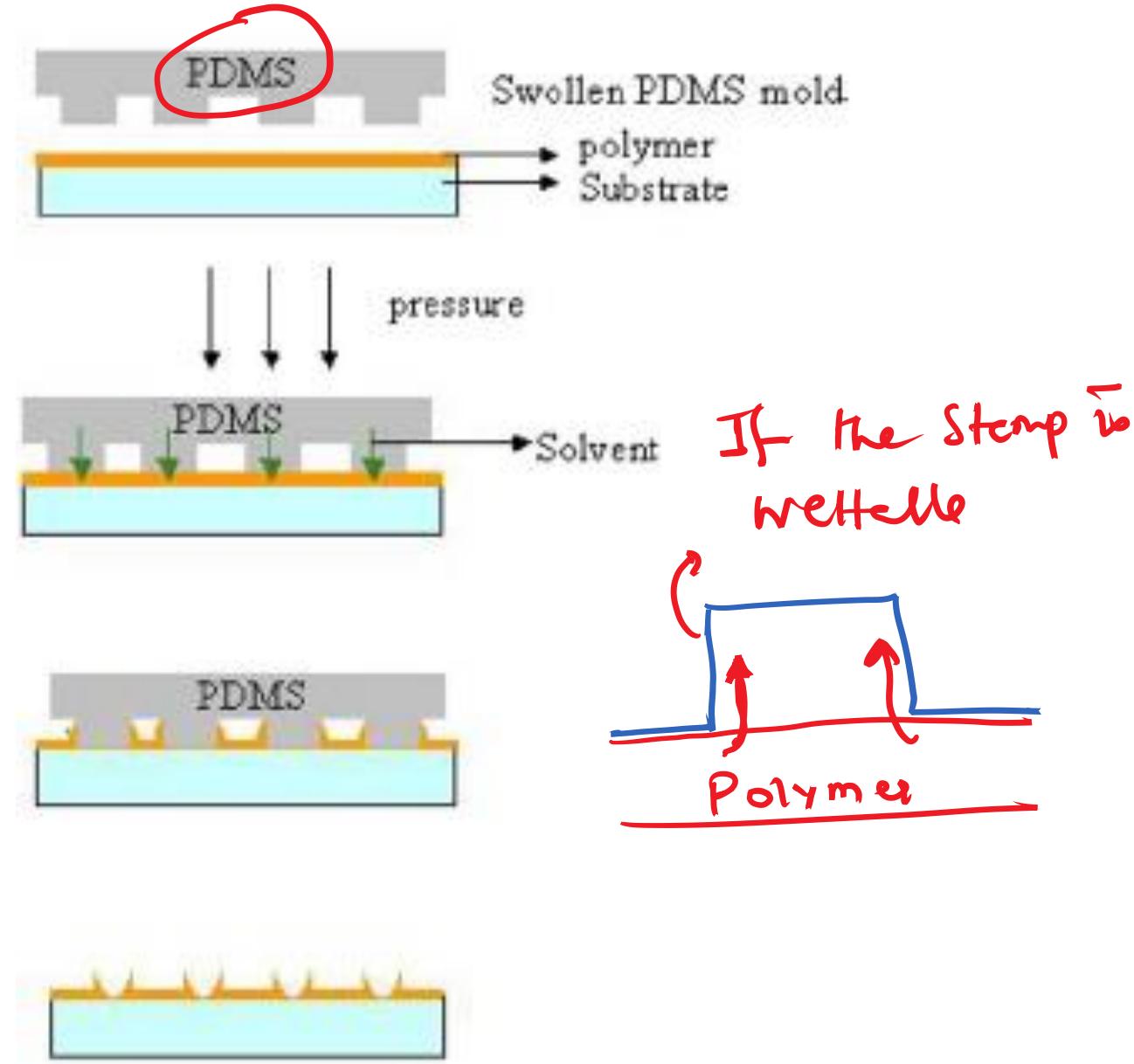
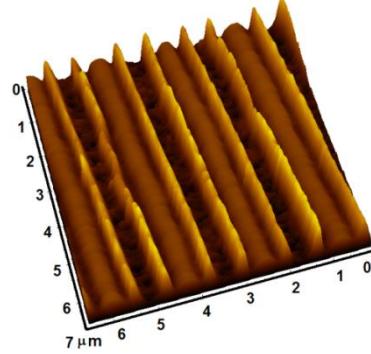
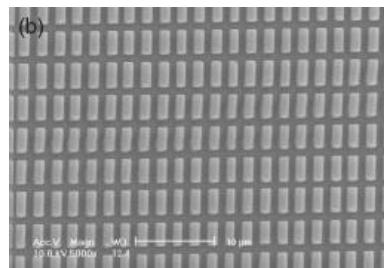
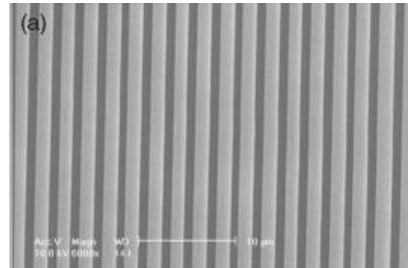
J. Vac. Sci. Technol. B, 16, 3926, 1998

Roll-to-Roll Nanoimprint Lithography

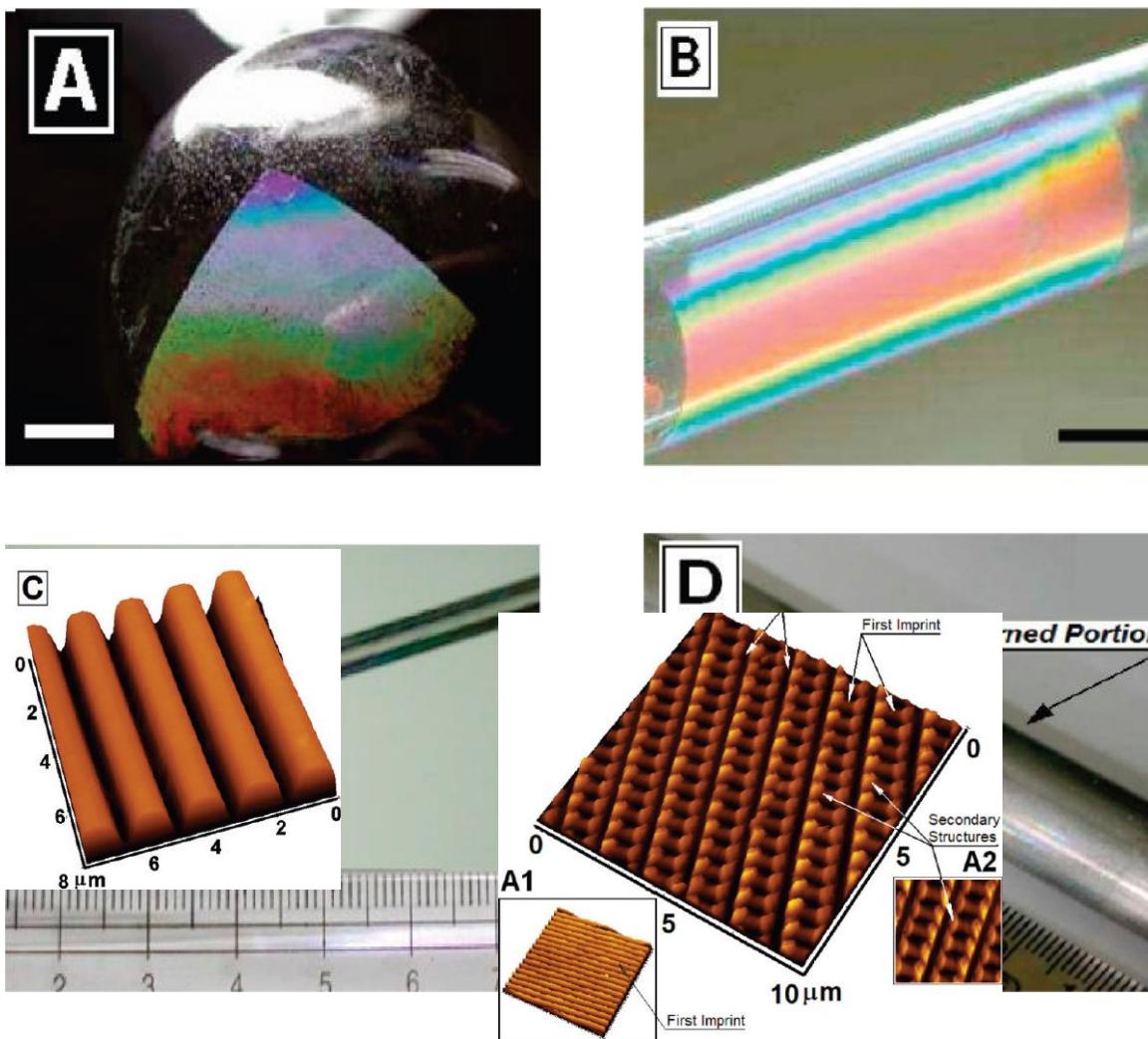
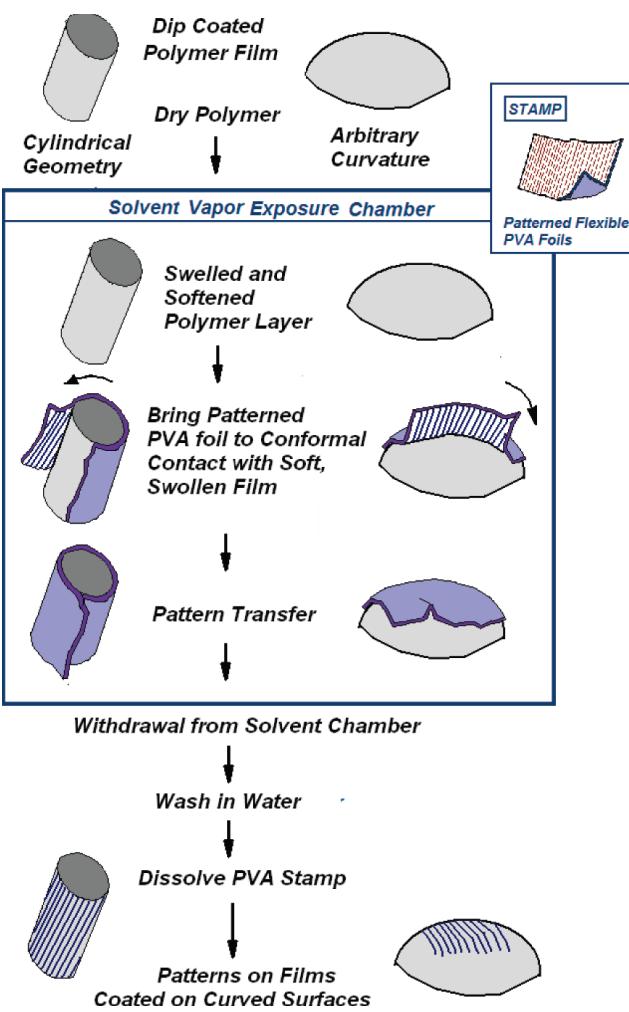


Capillary force Lithography

- Heat up the polymer film
- Place mold on top of the mold
- Liquid rises along the walls of the mold.



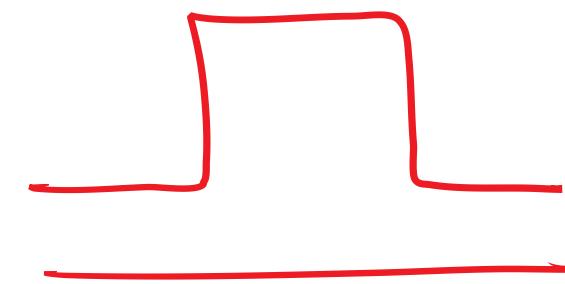
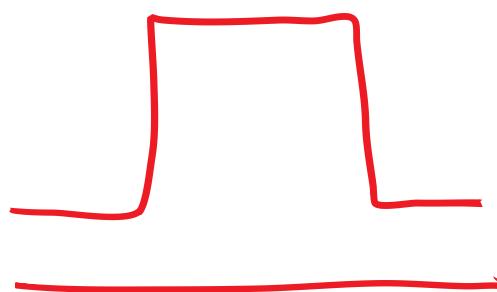
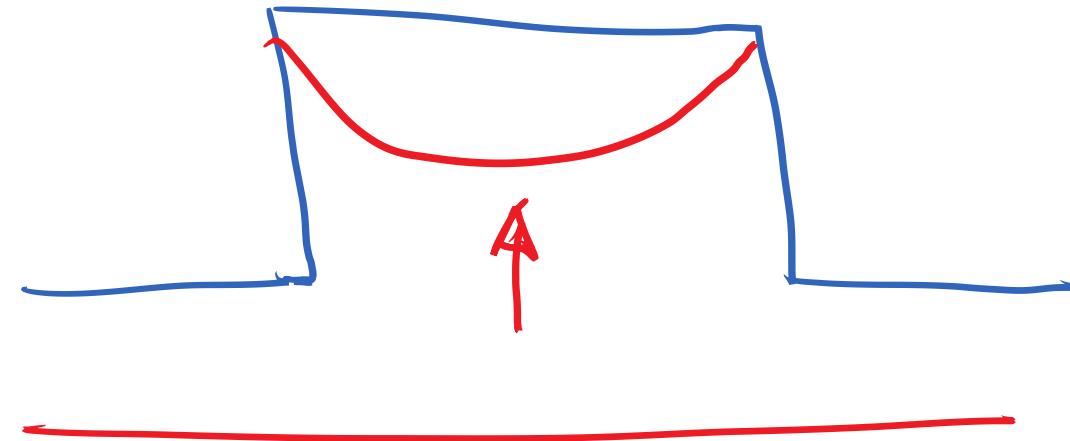
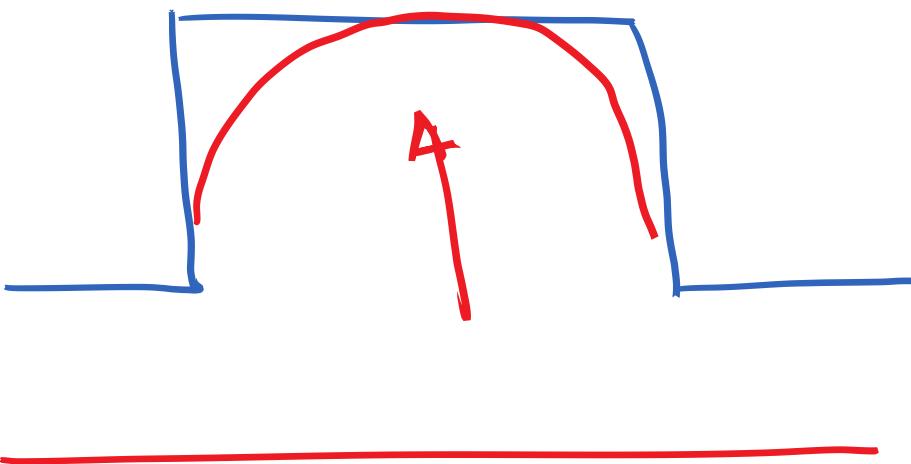
Solvent Vapor Assisted Imprint Lithography for Curved Surfaces



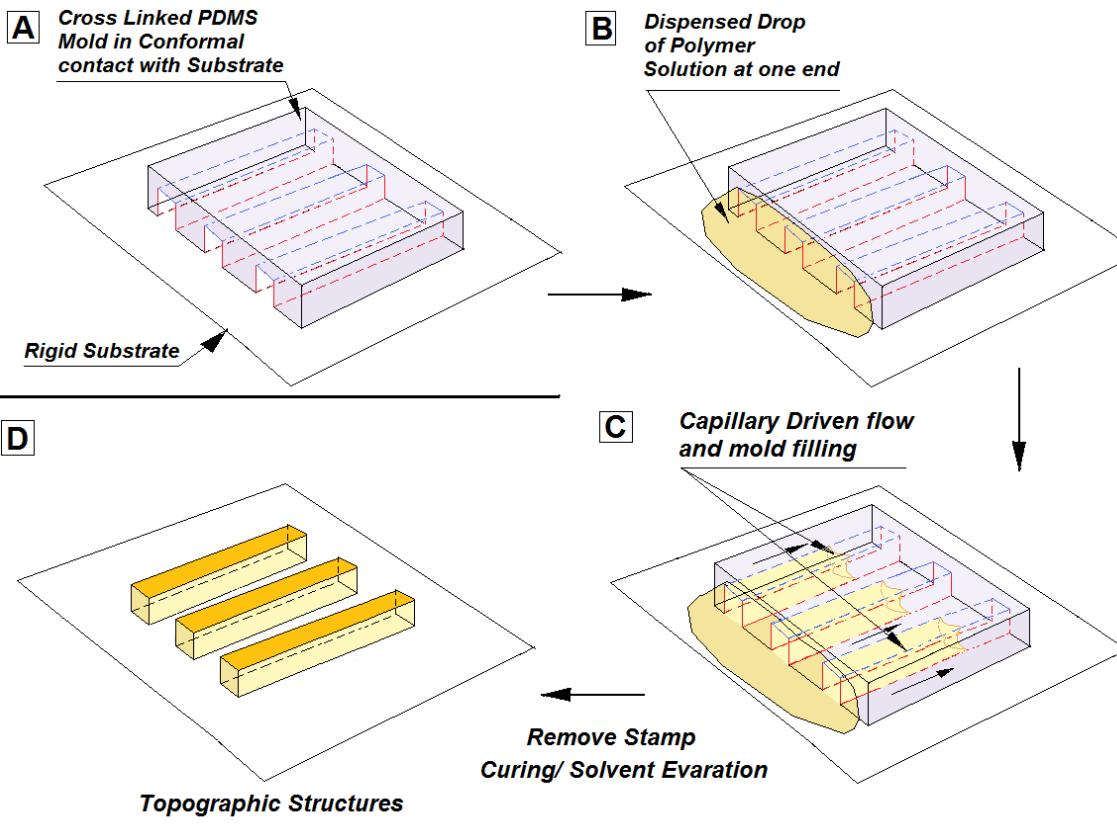
NIL

Mold Filling

CFL



Micro molding in Capillaries (MIMIC)



- The technique is based on the spontaneous filling of capillaries formed between two surfaces in conformal contact, at least one of which has a recesses relief structure.
- MIMIC** is a thermodynamically driven process: the liquid fill the capillaries to minimize the free energies of the solid-vapor and the solid-liquid interface.

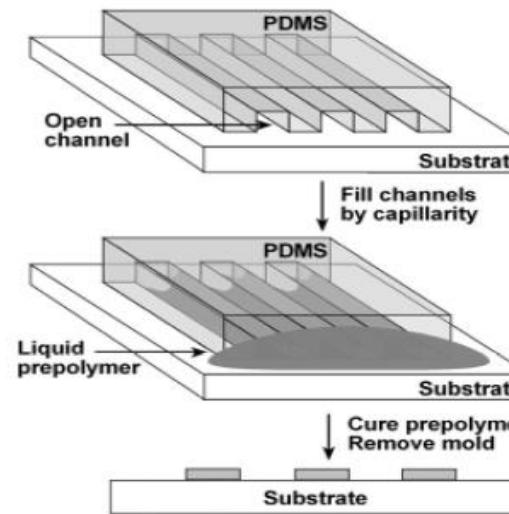
Whitesides, Nature, 376, 1995, 581

Instability and Soft Patterning Laboratory
भारतीय प्रौद्योगिकी संस्थान खड़गपुर
Indian Institute of Technology
Kharagpur

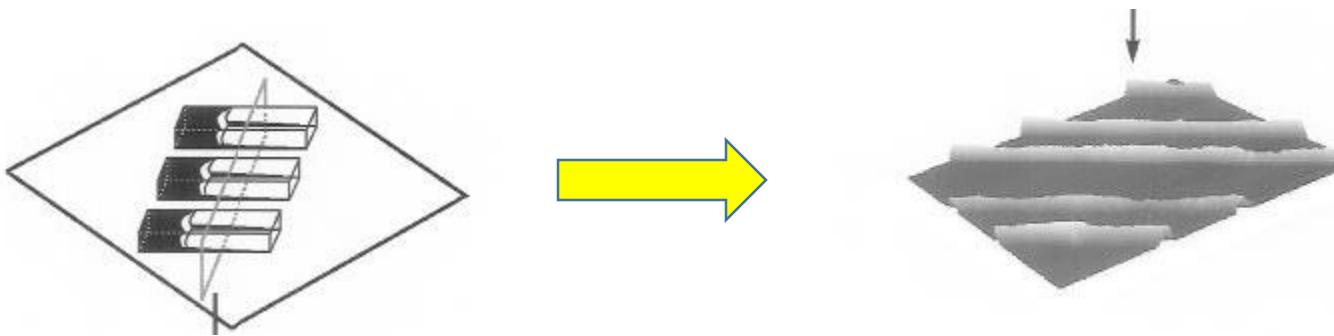


Micro molding in Capillaries (MIMIC)

- The filling of capillaries and rate of liquid flow in capillary is determined by the surface tension and viscosity of the liquid.
- Viscosity of liquid is a determining factor that controls the filling rate.



The time allowed for pattern replication is also important as Initially a fluid fills the capillaries only partially, particularly the corner regions.



J. AM. CHEM. SOC. 2008, 130, 1177-11

Micro molding in Capillaries (MIMIC)

The rate of capillary filling is given by

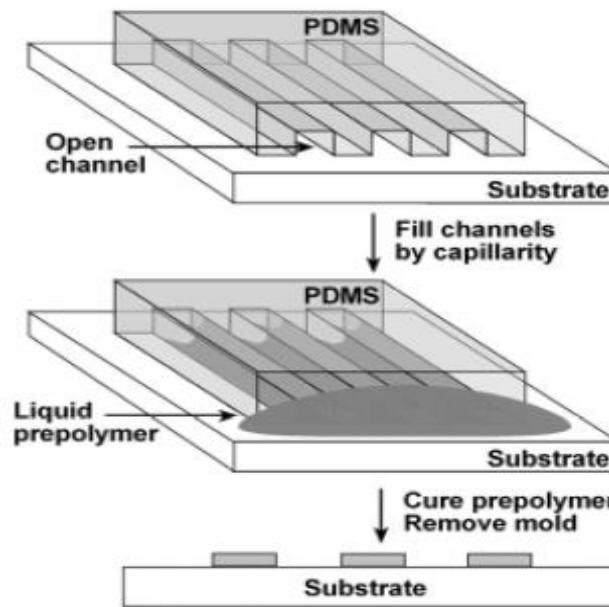
$$\frac{dz}{dt} = \frac{R\gamma_{LV}\cos\theta}{4\eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4\eta z}$$

η is the kinematic viscosity (μ/ρ)

γ is surface (interfacial) tension of liquid,

R is the radius of the capillary,

z length of the filled section of the capillary



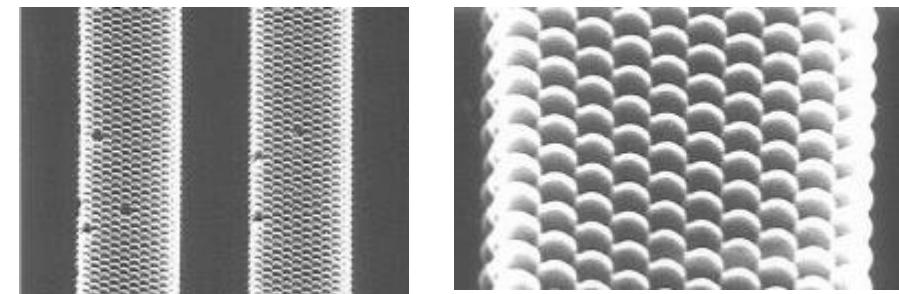
Capillary filling over a short distance (up to 1 cm) can be achieved quickly and efficiently; over a large distance, the rate of filling decreases significantly due to the viscous drag of the fluid in the capillary and the distance over which the fluid has to be transported.



Micro molding in Capillaries (MIMIC)

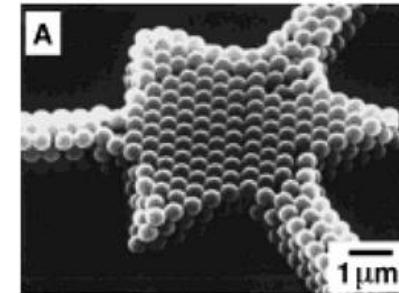
- The method therefore does not remain limited to a polymer solution only and several functional materials have been patterned by this method.
- In a recent study **Conductive Sub-micrometric Wires of Platinum-Carbonyl Clusters ($[Pt_{15}(CO)_{18}]^{2-}$)** have been patterned by MIMIC
- Ceramic Materials (sol – gel thin films) are also patterned by MIMIC.

An assembly of Colloids is also possible by MIMIC.



Uniqueness of MIMIC!

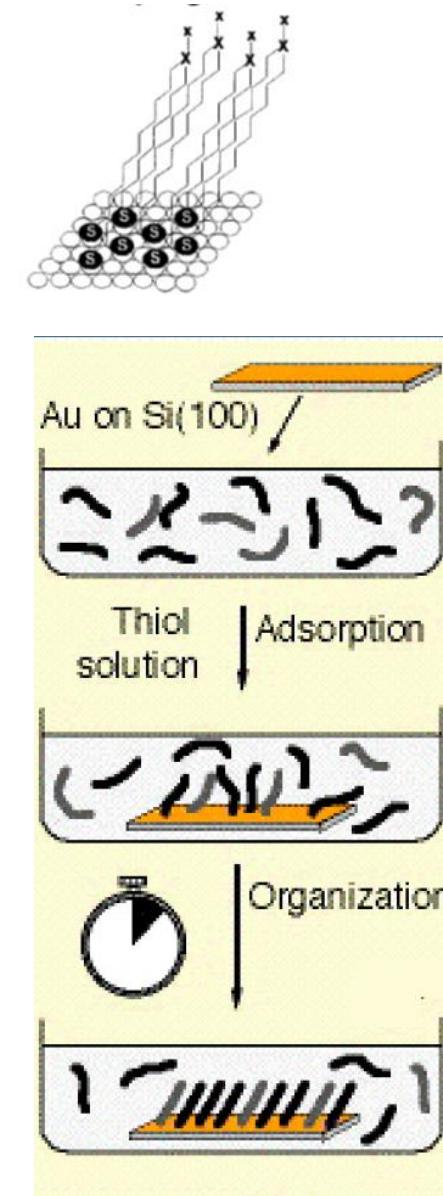
J. Am. Chem. Soc., 1996, 118 (24), 5722-5731



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Indian Institute of Technology
Kharagpur 

SAM (Self Assembled Monolayer)

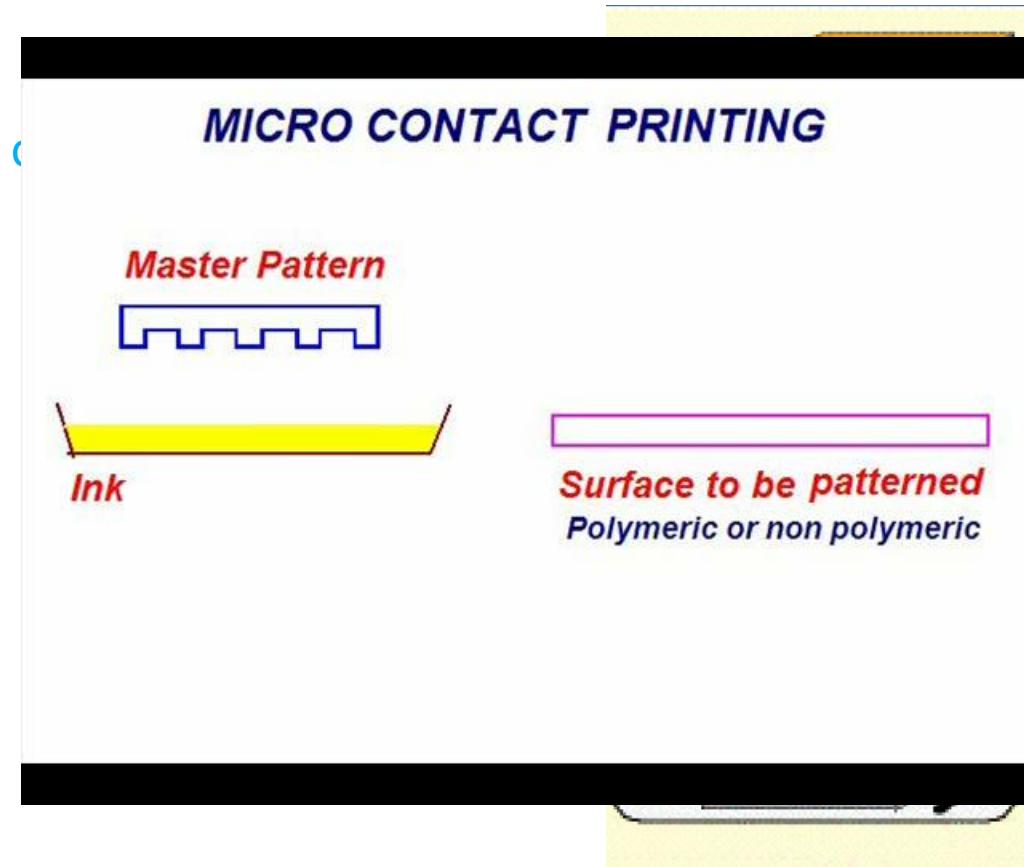
- The presence of a ligand ($Y(CH_2)_nX$) which is reactive toward the surface ensures the attachment of the silane molecules with the substrate. The surface properties of the SAM surface (primarily if the SAM coated surface is hydrophobic or hydrophilic) depends on the nature of the head group, X. On the other hand, the binding of the SAM molecules to the surface is determined by the group Y.
- Some surfaces like gold or silver show excellent binding ability towards the silane molecules such as alkanethiolates.
- Alkylsiloxanes on hydroxyl-terminated surfaces such as Si/SiO₂, Al/Al₂O₃, glass etc. also exhibit good attachment properties.



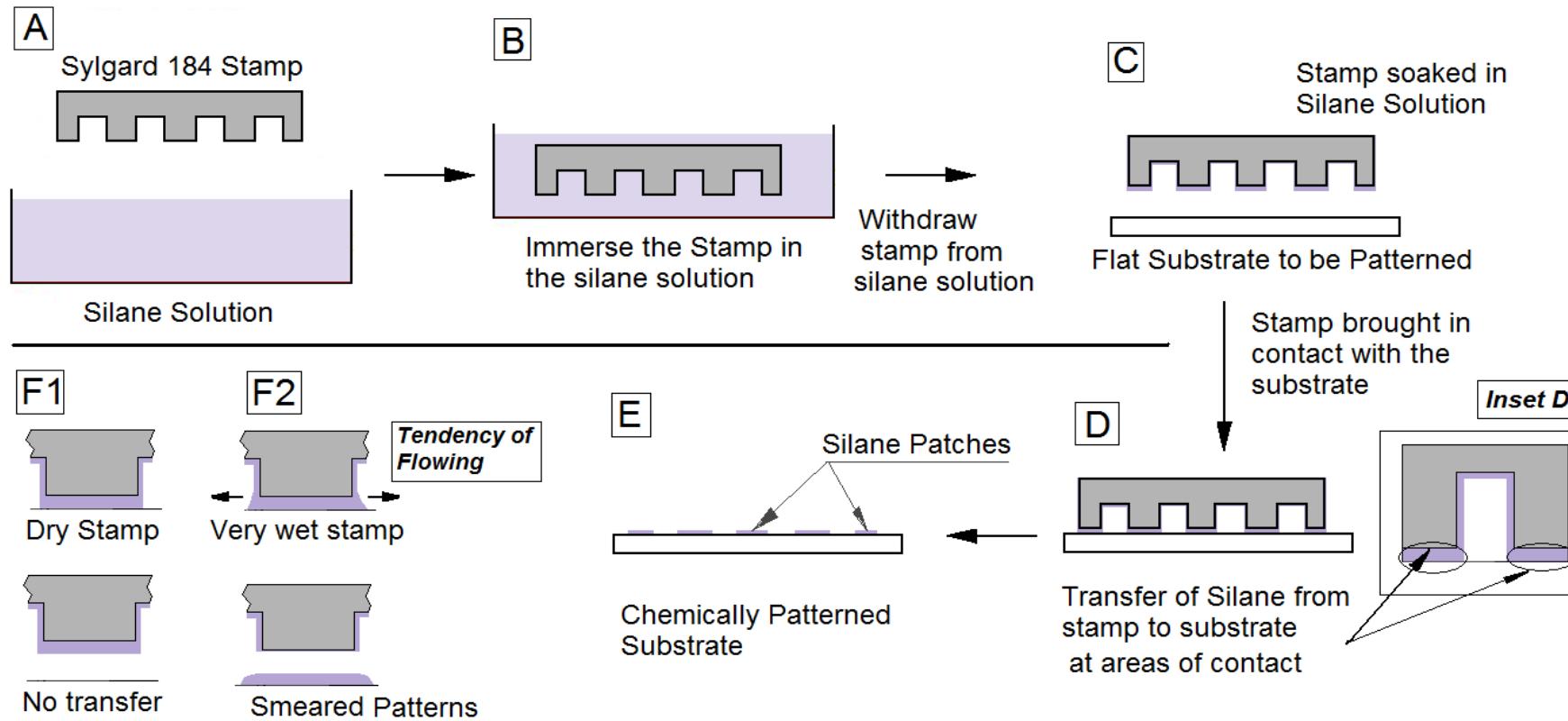
The presence of a ligand ($Y(CH_2)_nX$) which is reactive toward the surface ensures the attachment of the silane molecules with the substrate. The surface properties of the SAM surface (primarily if the SAM coated surface is hydrophobic or hydrophilic) depends on the nature of the head group, X. On the other hand, the binding of the SAM molecules to the surface is determined by the group Y. Some surfaces like gold or silver show excellent binding ability towards the silane molecules such as alkanethiolates. Alkylsiloxanes on hydroxyl-terminated surfaces such as Si/SiO₂, Al/Al₂O₃, glass etc. also exhibit good attachment properties.

Micro Contact Printing (μ CP)

- SAM is used as ink (*n-Alkanethiols*)
- *Thiols, Silanes etc.*
- Chemically patterned surfaces



Micro-contact Printing



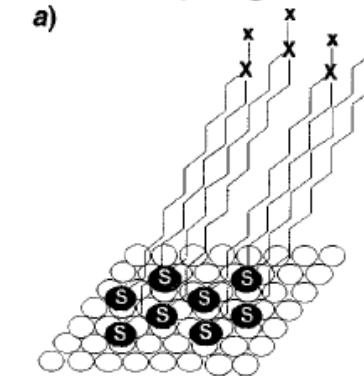
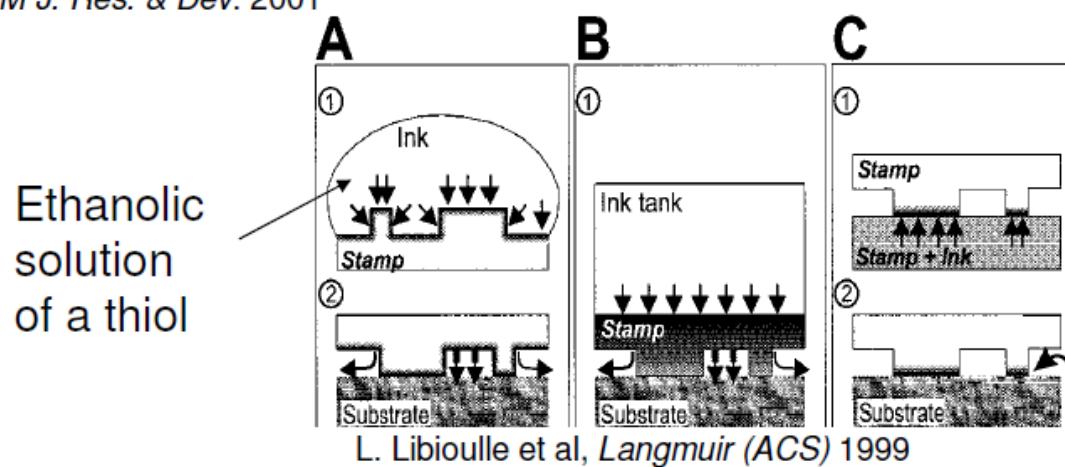
- Possible due to the ability of an elastomeric stamp to conform to a non-planar substrate with minimum distortion of the pattern on its surface.
- In this technique a patterned elastomeric stamp (typically PDMS) is inked with an alkanethiol and brought into contact with a gold surface.
- A self-assembled mono-layer of alkanethiolates forms at the stamp surface substrate interface.

G M Whitesides and Amit Kumar, Appl. Phys. Letts., 1993, Science, 1994

Methods of Applying Alkanethiols (Resist) on Stamp

- Alkanethiol molecules form self-assembled monolayer (SAM) on surface of noble metals (Au, Ag)
- These monolayers allow control over wettability, adhesion, chemical reactivity, electrical conduction, and mass transport to underlying metal
- Linear alkanethiols with various molecular weights
 158 g mol^{-1} (dodecanethiol, DDT)
 258 g mol^{-1} (hexadecanethiol, HDT)
 314 g mol^{-1} (eicosanethiol, ECT)

B. Michel *et al.*,
IBM J. Res. & Dev. 2001



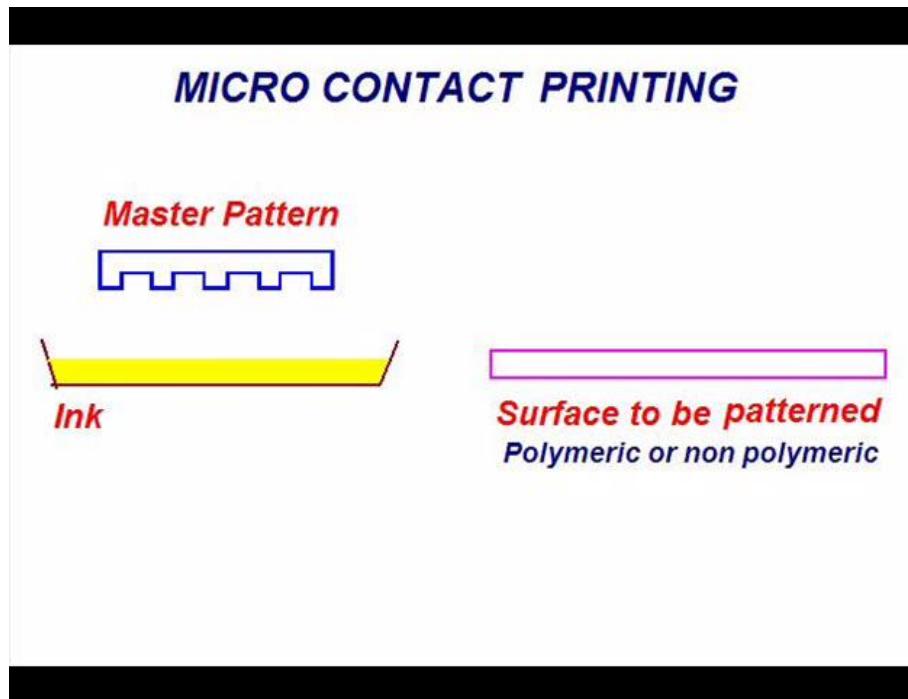
G. Whitesides *et al.*, *Ann. Rev. Biomed. Eng.*, 2001

Mold is Soft:

Most Cases it is a patterned Sylgard 184 block (Cross Linked PDMS) 19

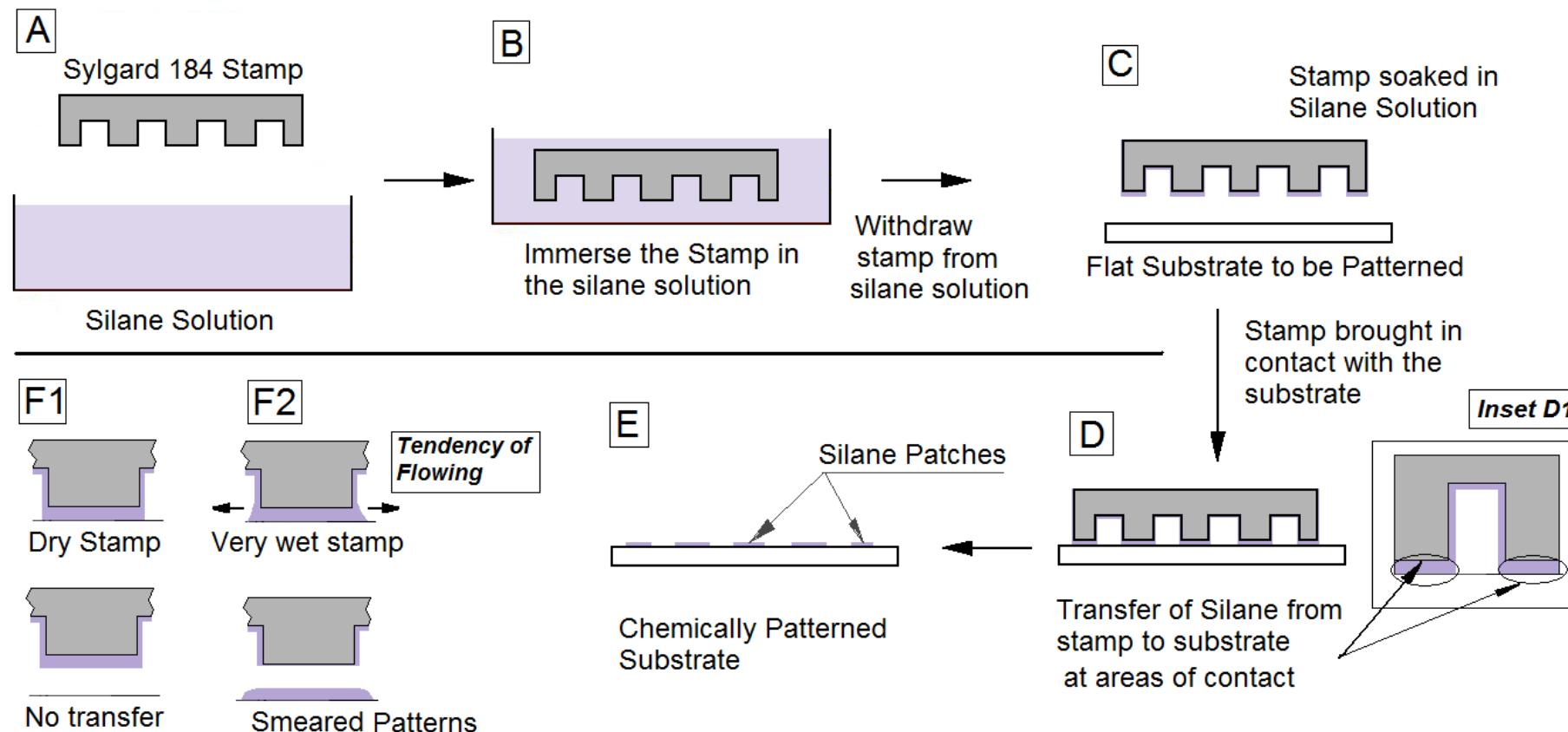
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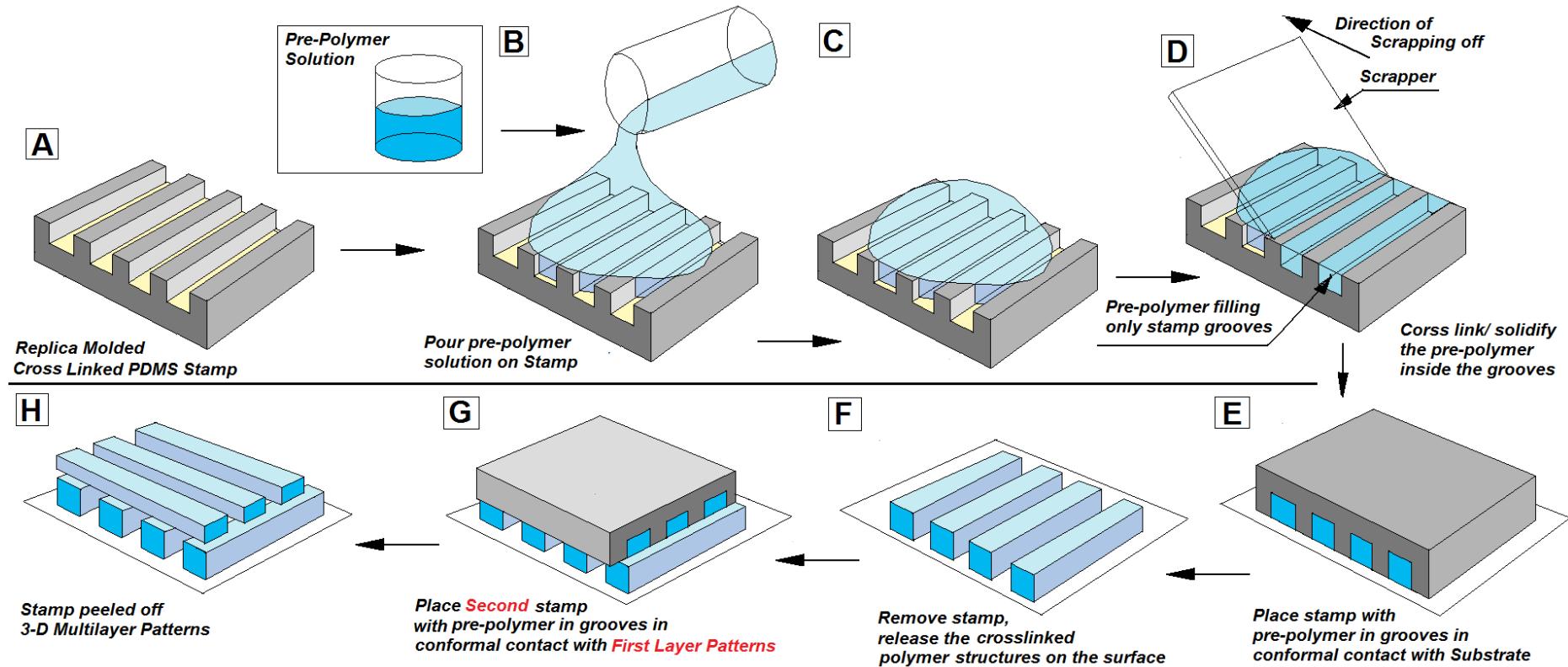
G M Whiteisdes and Amit Kumar, Appl. Phys. Letts., 1993, Science, 1994

Micro-contact Printing



G M Whitesides and Amit Kumar, Appl. Phys. Letts., 1993, Science, 1994

Micro Transfer Molding



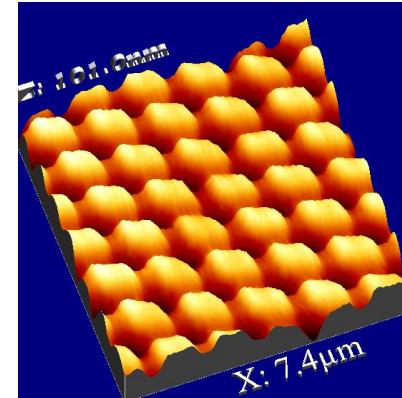
Soft Lithography Techniques:

Broadly 3 Categories:

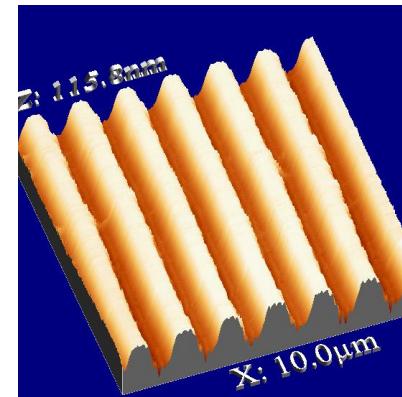
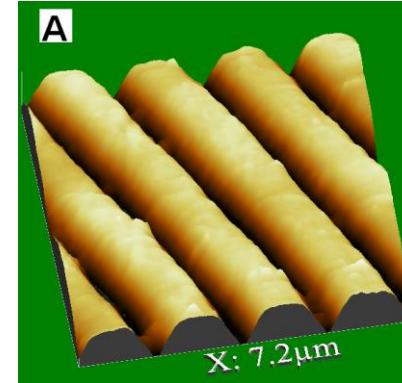
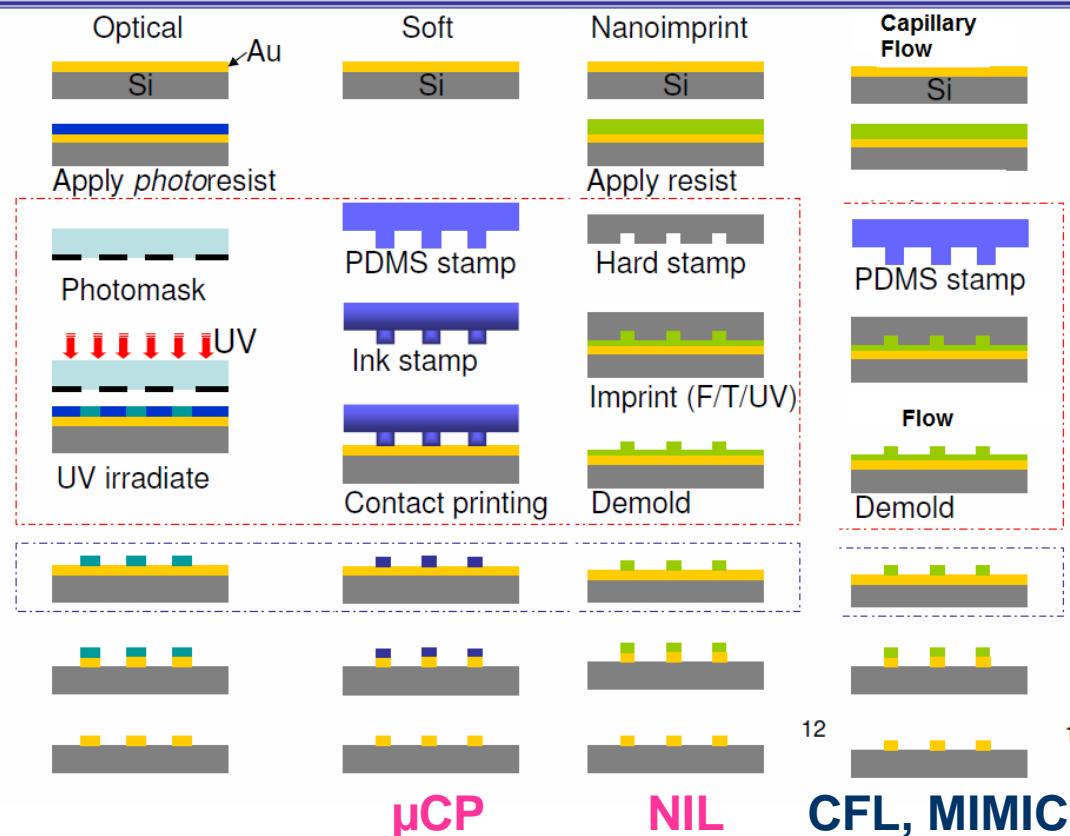
Micro Contact Printing: Inking, Chemical Patterns

Nano Imprint Lithography: Molding

Capillary Flow Lithography: Flow Induced Patterning



Optical Vs. Soft Vs. Nanoimprint Lithography



Advantages of Soft Lithography

- Convenient, inexpensive, accessible to chemists, biologists, and material scientists
- Basis in self-assembly tends to minimize defects
- Many soft lithographic processes are additive and minimize waste of materials
- Readily adapted to rapid prototyping
- Isotropic mechanical deformation of PDMS mold or stamp provides routes to complex patterns
- No diffraction limit; features as small as 30 nm have been fabricated
- Nonplanar surfaces (lenses, optical fibers, and capillaries) can be used as substrates

Advantages of Soft Lithography

- Generation and replication of three-dimensional topography or structures are possible
- Optical transparency of the mask allows through-mask registration and processing
- Good control over surface chemistry, very useful for interfacial engineering
- A broad range of materials can be used: functional polymers, sol-gel materials, colloidal materials, suspensions, solutions of salts, and precursors to carbon materials, glasses, and ceramics
- Applicable to manufacturing: production of indistinguishable copies at low cost
- Applicable in patterning large area

Soft Lithography: Limitations

- Patterns in the stamp or mold may distort due to the deformation (pairing, sagging, swelling, and shrinking) of the elastomer used
- Compatibility with current integrate-circuit processes and materials is not yet fully demonstrated
- Defect levels higher than for photolithography
 - * μCP works well with only a limited range of surfaces; MIMIC is slow; REM, μTM, and SAMIM leave a thin film of polymer over the surface