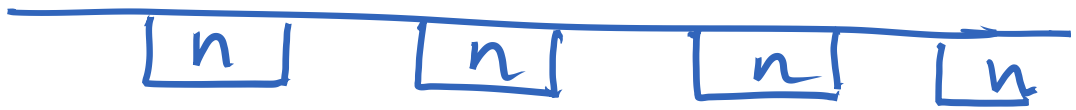
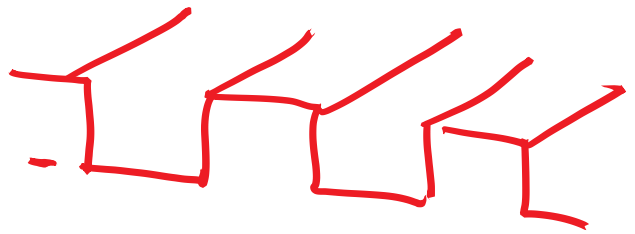
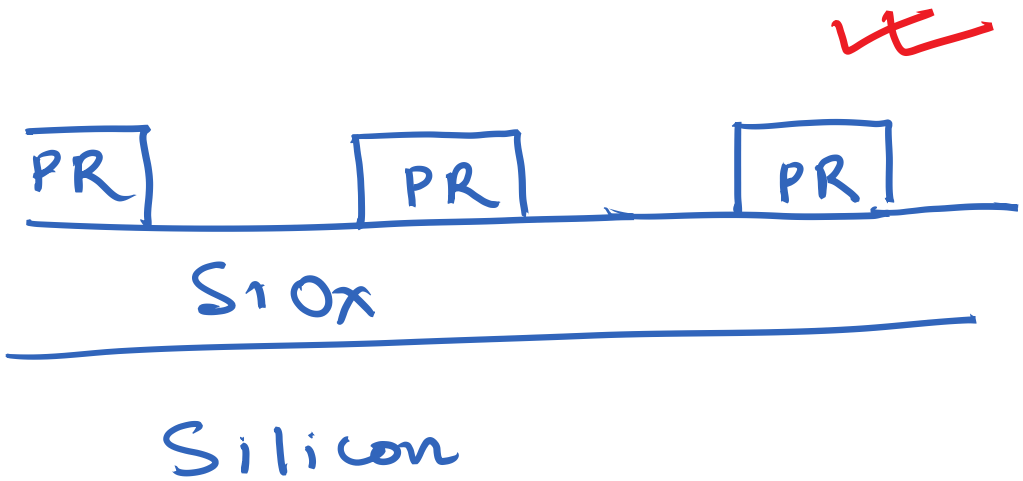
Photolithography →



P

↓ Intermediate Step





and

Physico - Chemical Patterns

(Topographic Features Also)

Introduction to Soft Lithography → New (1990s)

Photolithography → Very Specific Technique

Soft Lithography → A Collection of Techniques →

↳ Generic Techniques for Pattering Soft Materials

→ Polymers.

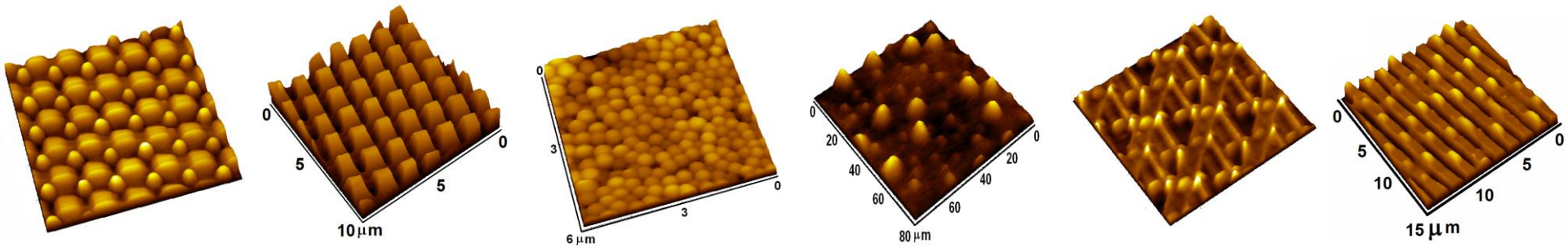
→ Gels.

→ Inorganic materials like Oxides through 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, Bilogical 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 (~ cm^2) patterns with good reproducibility
- The ability to create defect free structures should be reasonable.

Topographically Patterned Master / Mould / Stamp.

This can be made by Photo litho itself

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

Types of Polymer → Long Chain molecule

→ $-C-C-C-C-C-$ → organic materials

Entanglement → ↳ Straight Chain / Branched.

↳ Entanglement higher

Polymers are solid like at Room Temp.

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

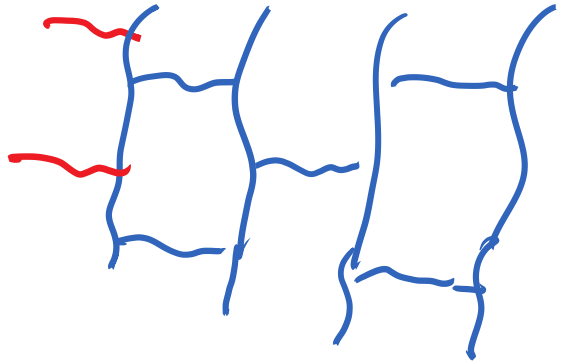
T_g → It becomes soft / Drop in Viscosity / Adequate translational KE so that the molecule can move.

No Physical Cross Link

Thermo Plastic / Glassy

Type 2: Chains are cross linked →

(Thermo Sett Polymer) →



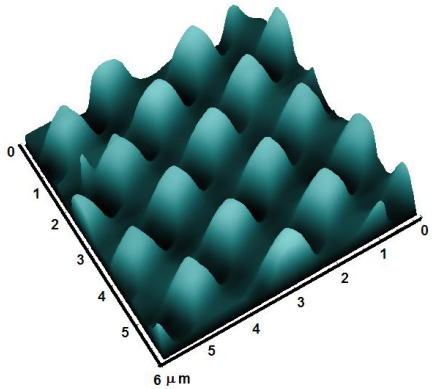
Flexible

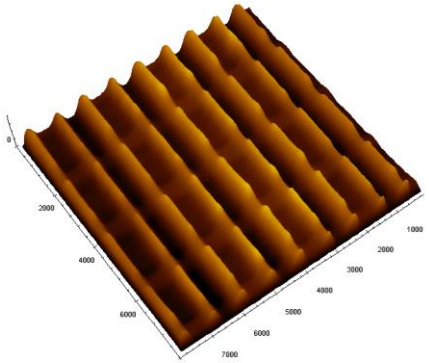
Visco-Elasticity

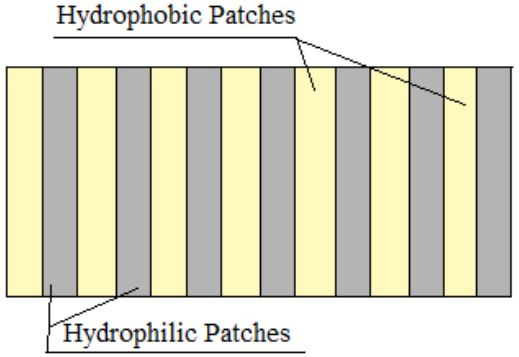
Soft Lithography Techniques: Classifications

Based on the Nature of Patterns:

- Chemical Patterns
- Topographic Patterns







Topography is Rather Smooth

Based on the Nature of Mold or Stamp Used:

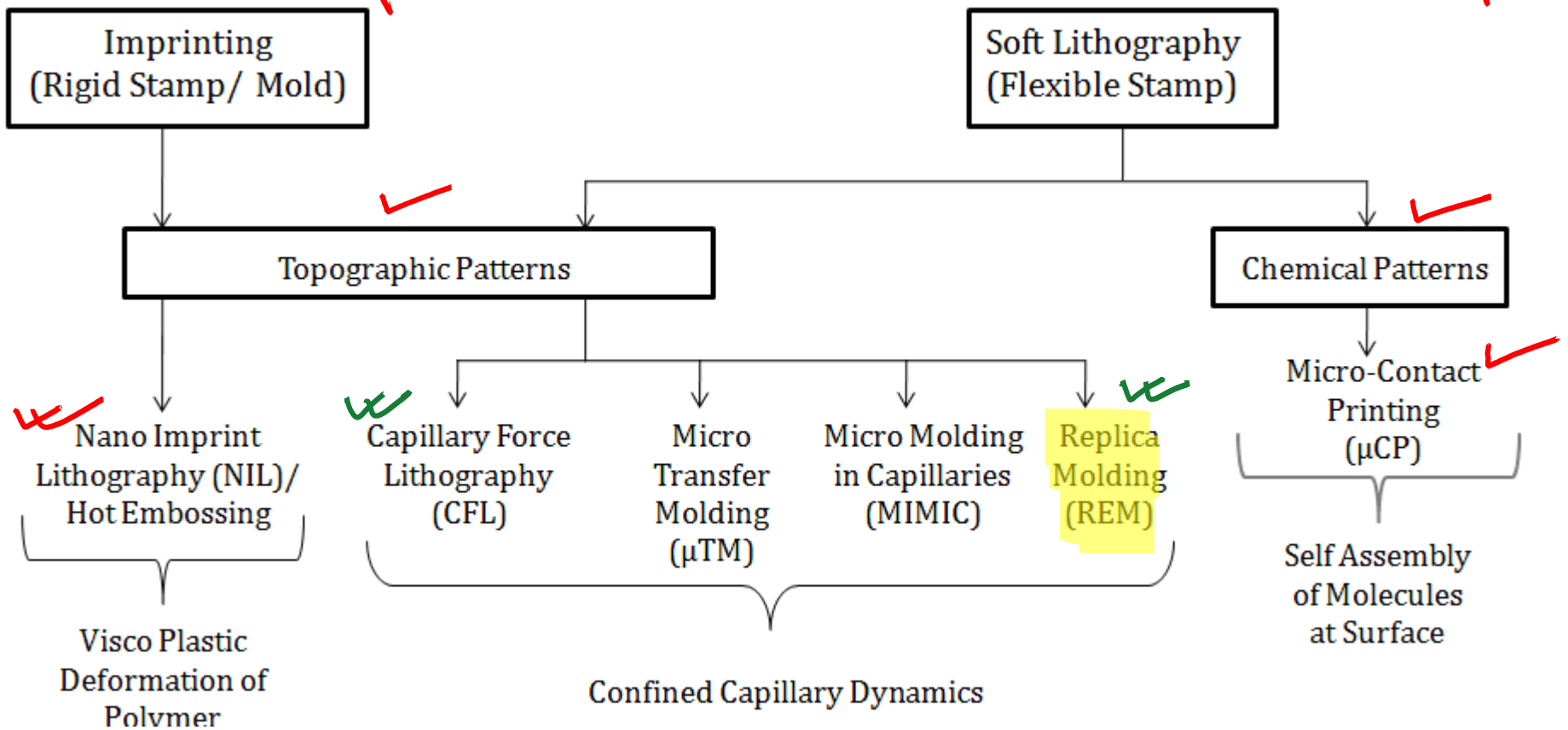
- Rigid Stamp
- Flexible Stamp
- Dissolvable Stamp

Soft Lithography Techniques: Classifications → 1990's

George Whitesides → Harvard.

Stephen Chou → Princeton.

Chou's Grop.



Soft Lithography Techniques: Classifications

Based on the Pattern Transfer Mechanism:

Chemical Patterns

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

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** (Capilary Force Lithography)
- **MIMIC** (Micro Molding in Capillaries)

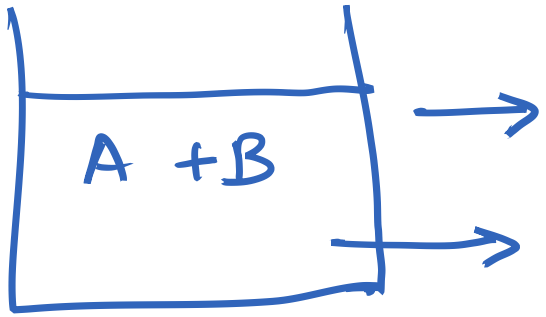
Polydimethyl Siloxene (PDMS) → Silicone Oil.

It's a high Viscosity Liquid at Room Temperature →

Thermo Curable PDMS → Sylgard 184.

A → Oligomer (Longer chain Monomer) → High Viscous Liquid

B → Cross linker - Catalyst

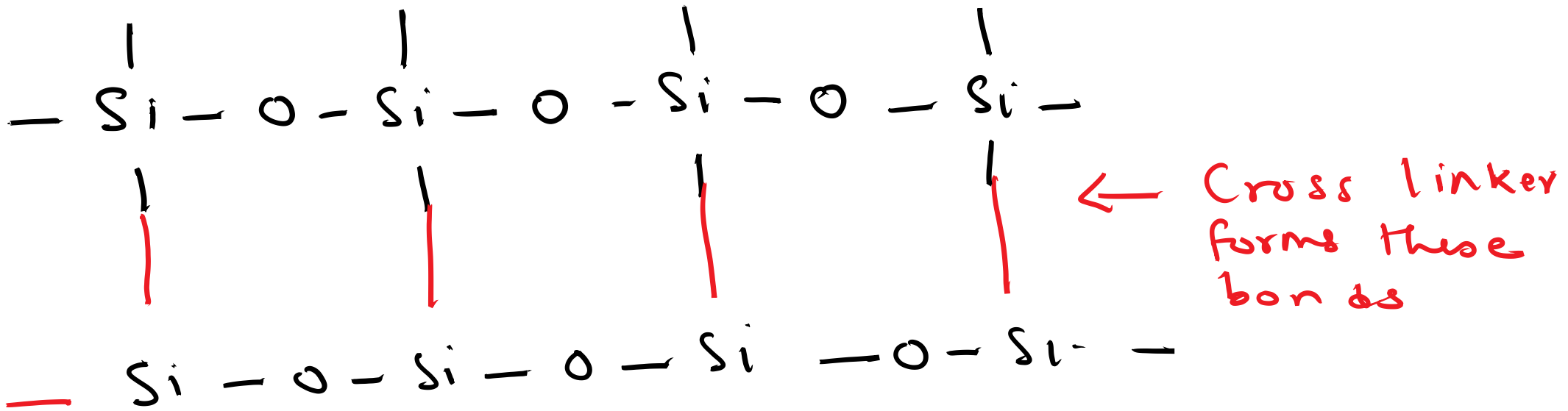


Heat it (120°C / 6 hrs)

Soft Deformable Solid.

→ Physical Cross linking of the chains.

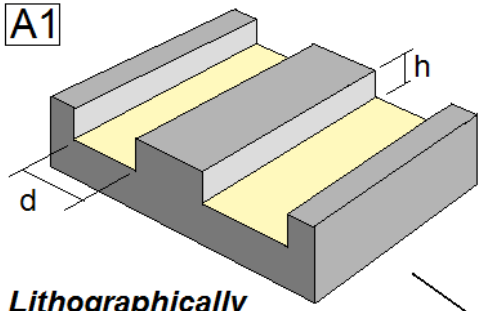
PDMS - Silicone based Polymer



→ Inorganic Polymer

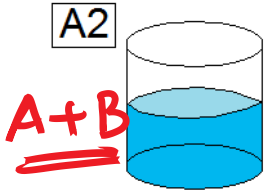
Replica Molding

A1



Lithographically Fabricated Master (With Relief Structures)

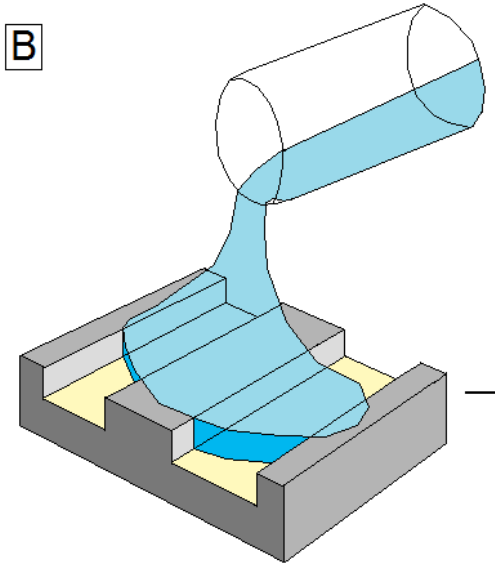
A2



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

(Part A and Part B of Sylgard 184)

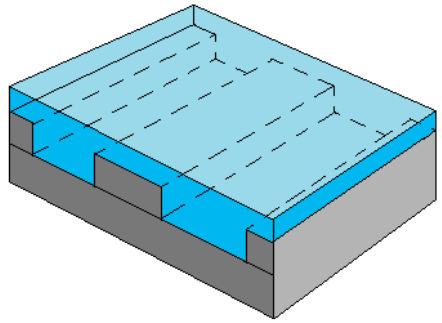
B



Pouring of the Pre-Polymer Mix on the Master

C

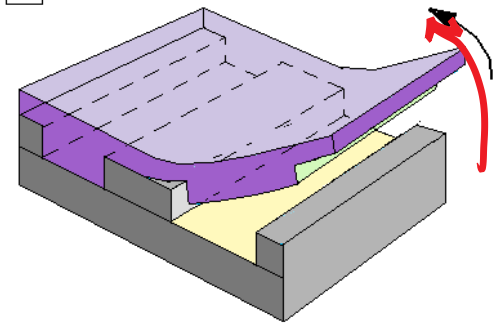
Thermally Annealed at Elevated Temperature (between 100°C - 150°C) for cross linking



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

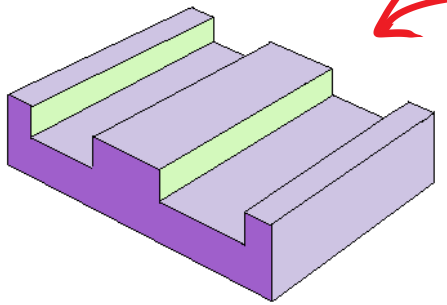
D

Peeling



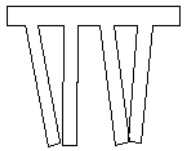
Cross Linked Elastomer containing Negative Replica of the master

E

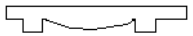


Negative Replica of the Stamp Pattern on a Self standing block of cross linked elastomer

F



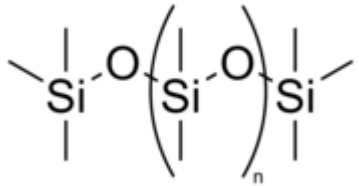
Pairing
h>>d



Sagging
h<<d

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, *Tg*.
- *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

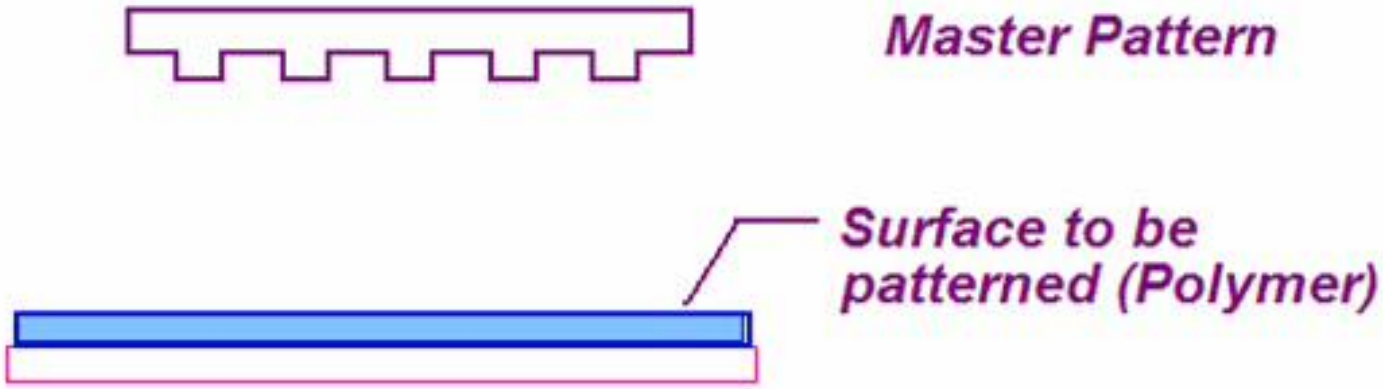
Cross Linked PDMS

- 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 23ºC
  immediately after mixing: 4000 mPa×s
- 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

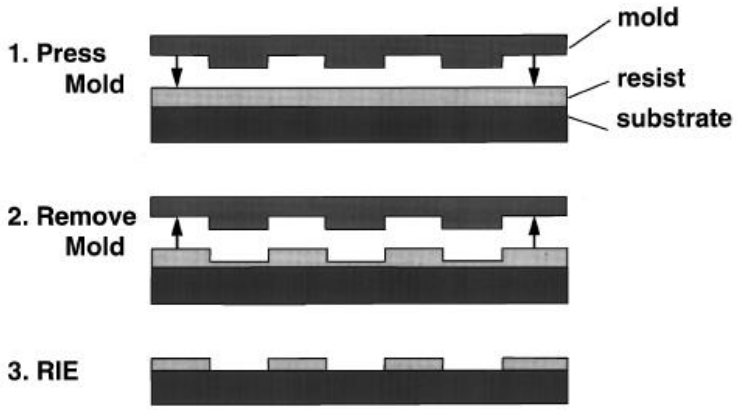


→ Thin Film of a Glassy Polymer

→ 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

~ 5 x10 $^{-5}$ per °C

Low Pressure Shrinkage Coefficient

~ 3.8 x10 $^{-7}$ per psi

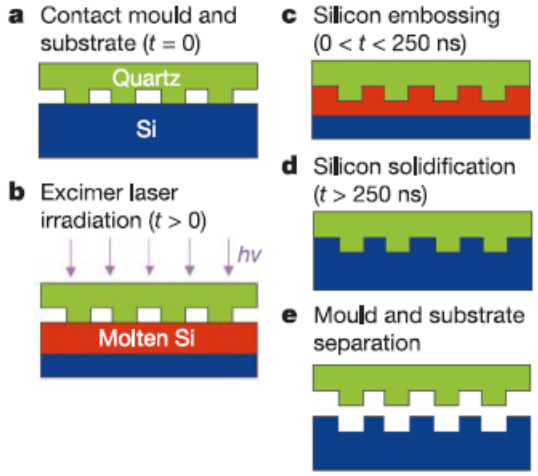
Typical Temperature: 120 – 150 ^{O}C

Typical Pressure: 30 – 50 MPa

Mold is Rigid:

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

Extended Beyond Polymers

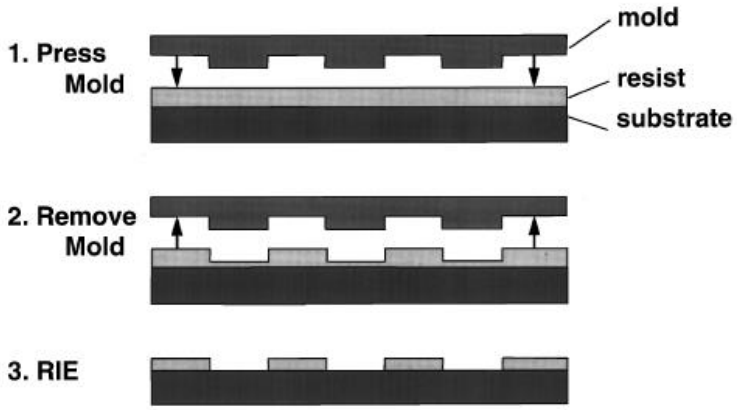


Chou, Nature, 417, 835, 2002

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

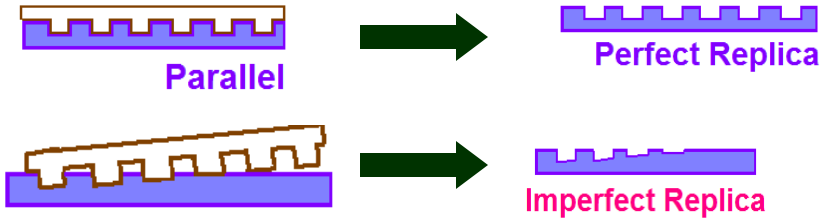
High Temperature

High Pressure

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

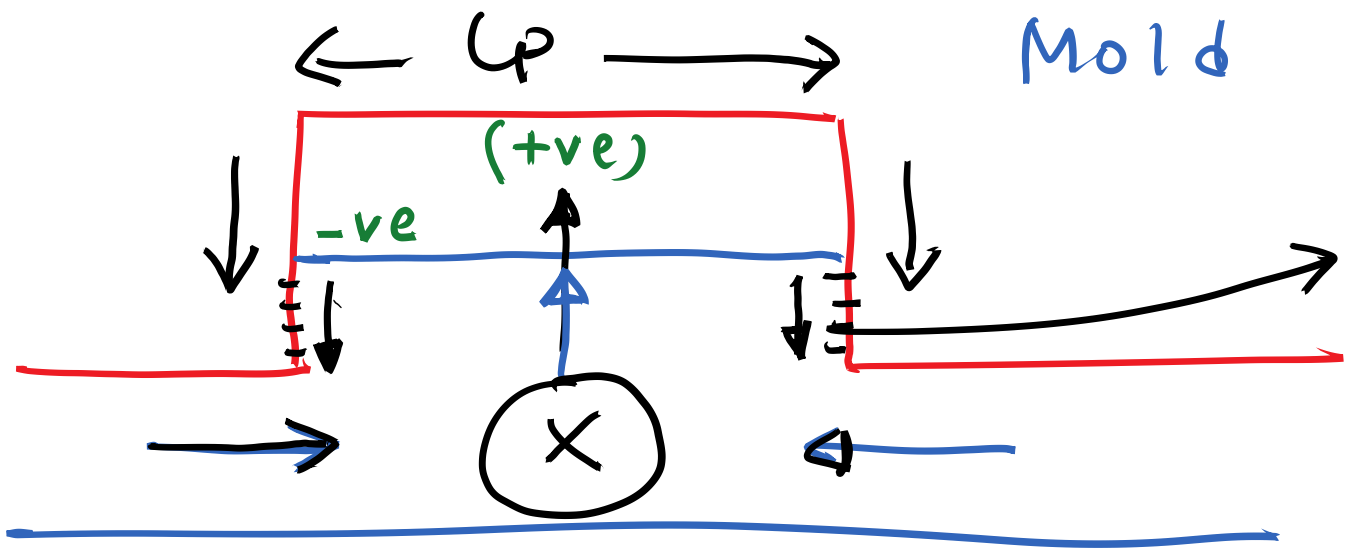
Critical Parallelism between mold and film has to be ensured!

Non Planar Surfaces cannot be patterned



Mold Release agents

l_p is Small



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

$\tau_{xy} = \mu \frac{\partial V}{\partial x}$

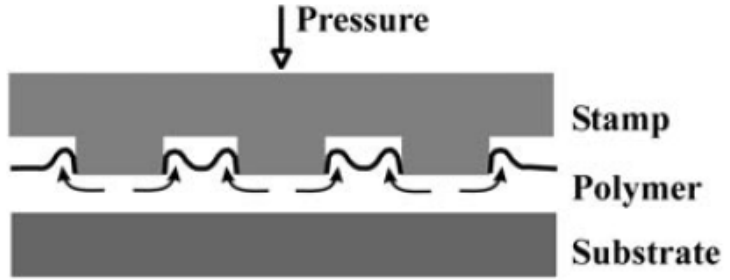
3. As you cool down μ ↑

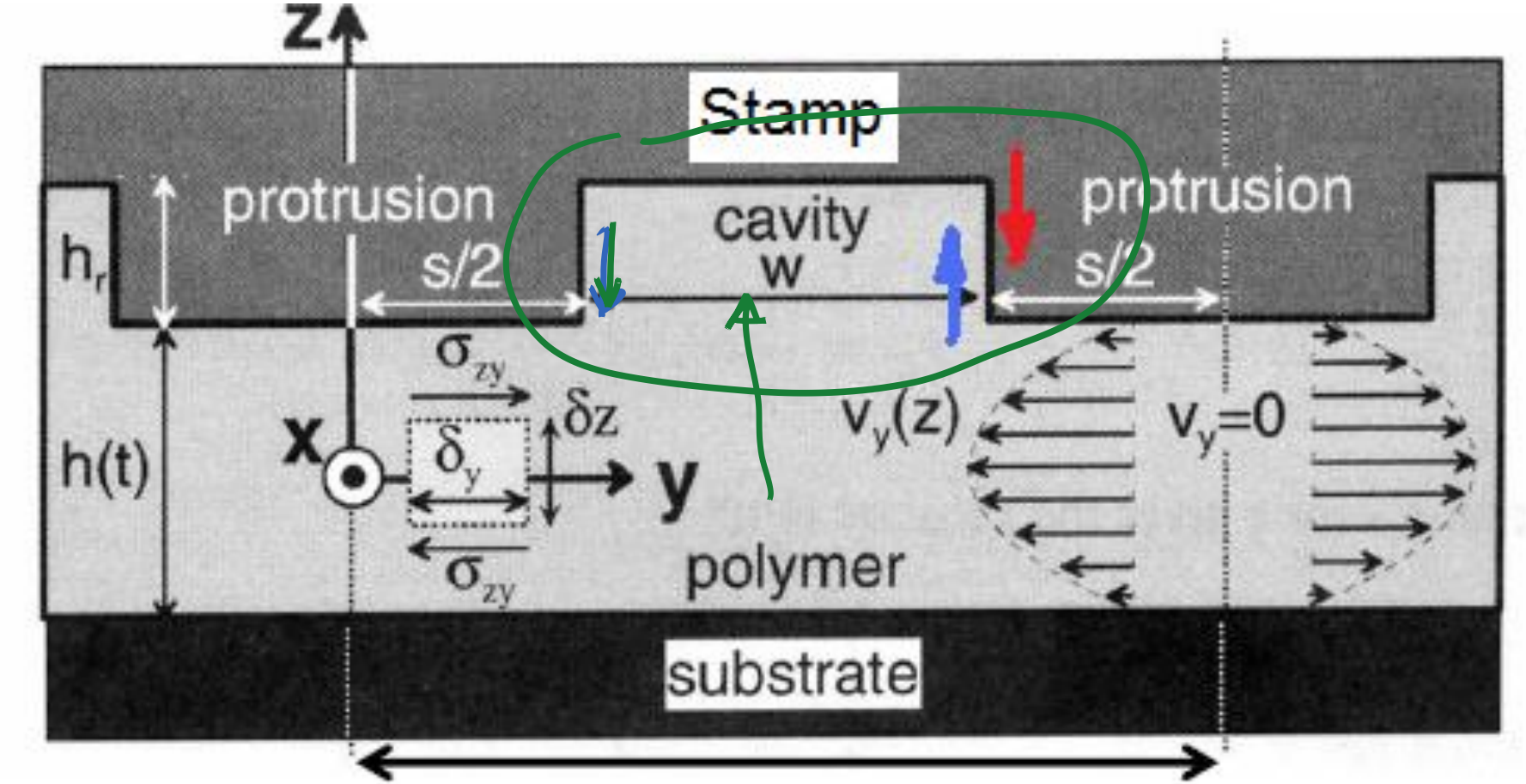
↳ Because of the material

Hot Embossing → Some Technique with Large features

Nano Imprint Lithography (NIL)

Hydrodynamics and Stresses



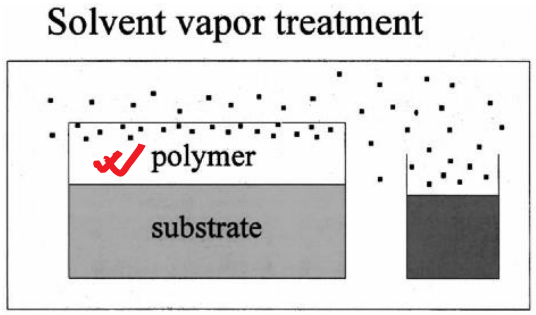


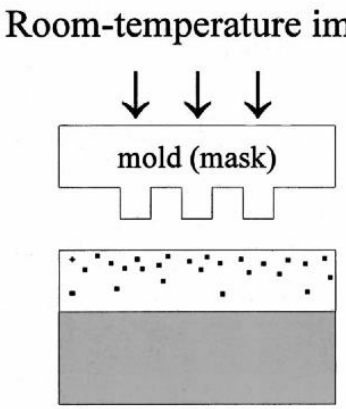
By NIL the structures we make have high residual stress.

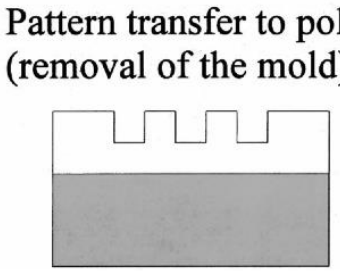
Nano Imprint Lithography (NIL) Group of Methods

- 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





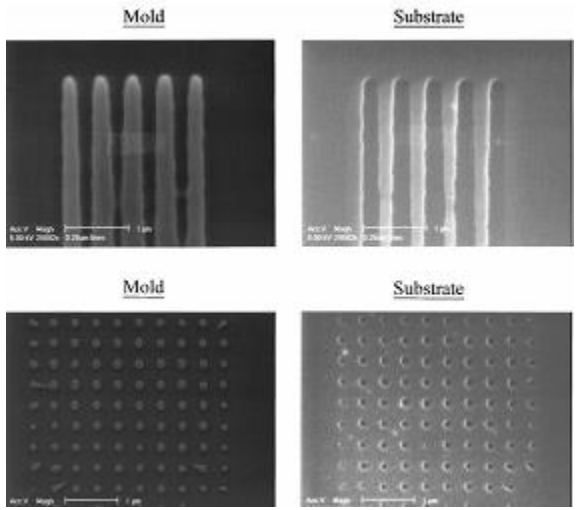


Penetration of solvent molecules into the polymer matrix

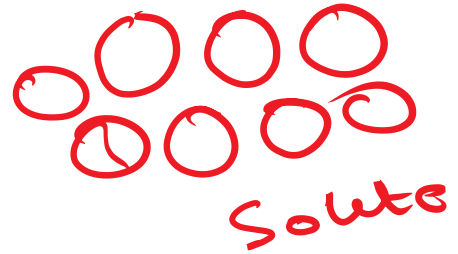
Swelling and reduced cohesion

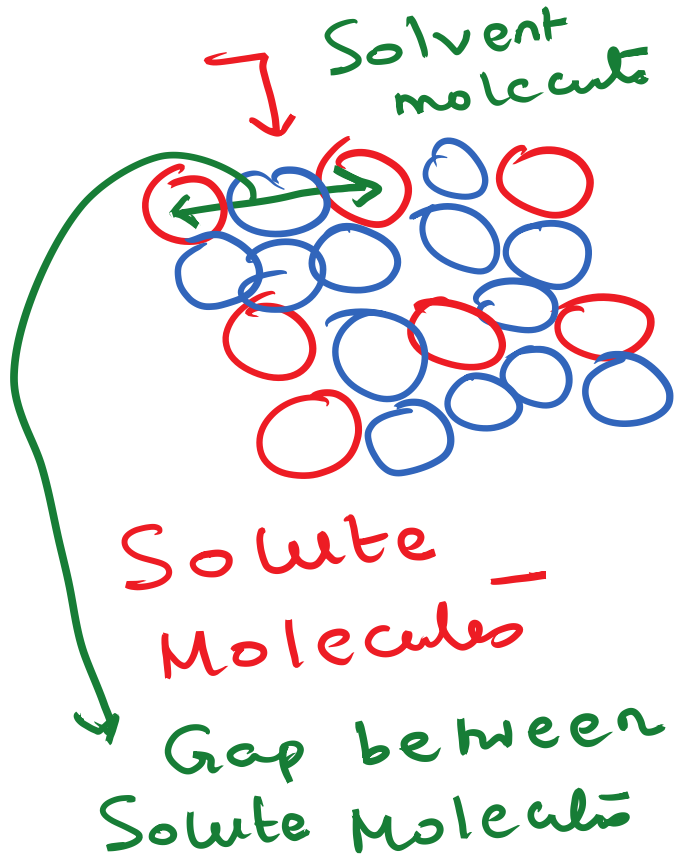
Reduction in Viscosity

Effective reduction in glass transition temperature below room temperature.



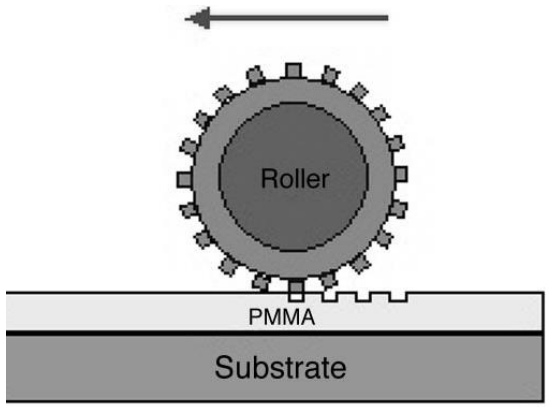
Hong Lee: Applied Physics Letters, 76, 870, 2000



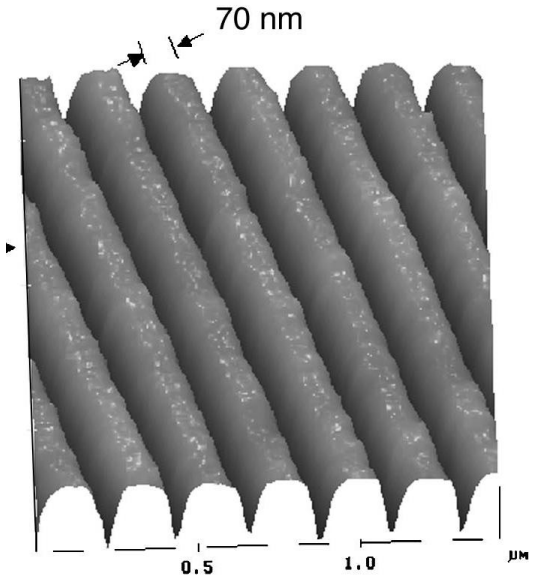


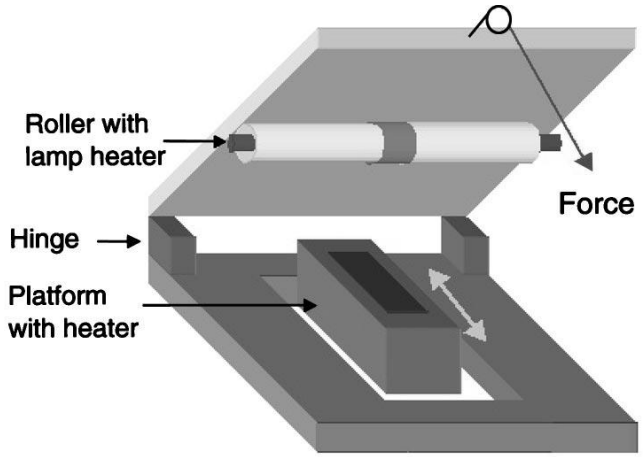
Roller Nano Imprint Lithography

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



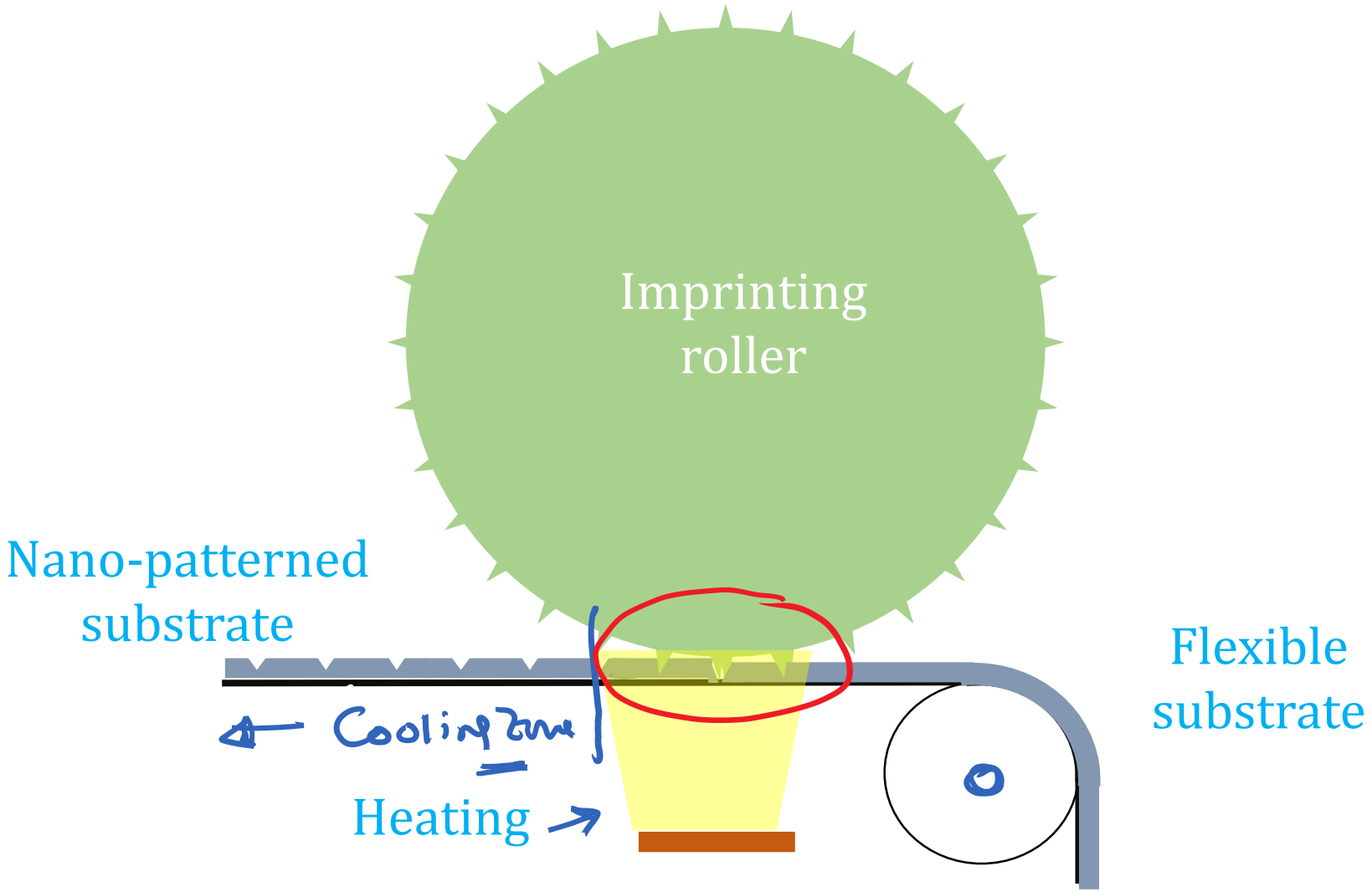
(a)





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

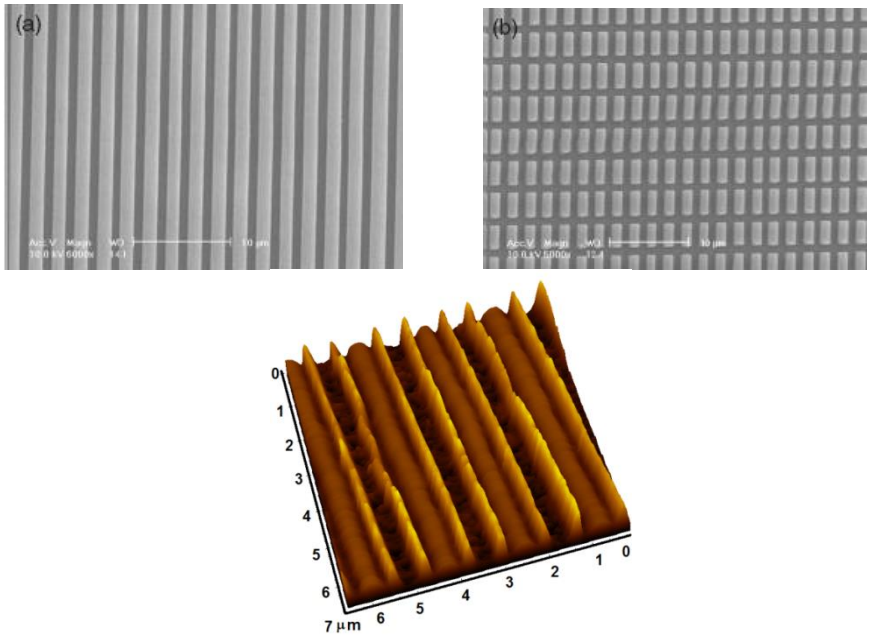
Roll-to-Roll Nanoimprint Lithography

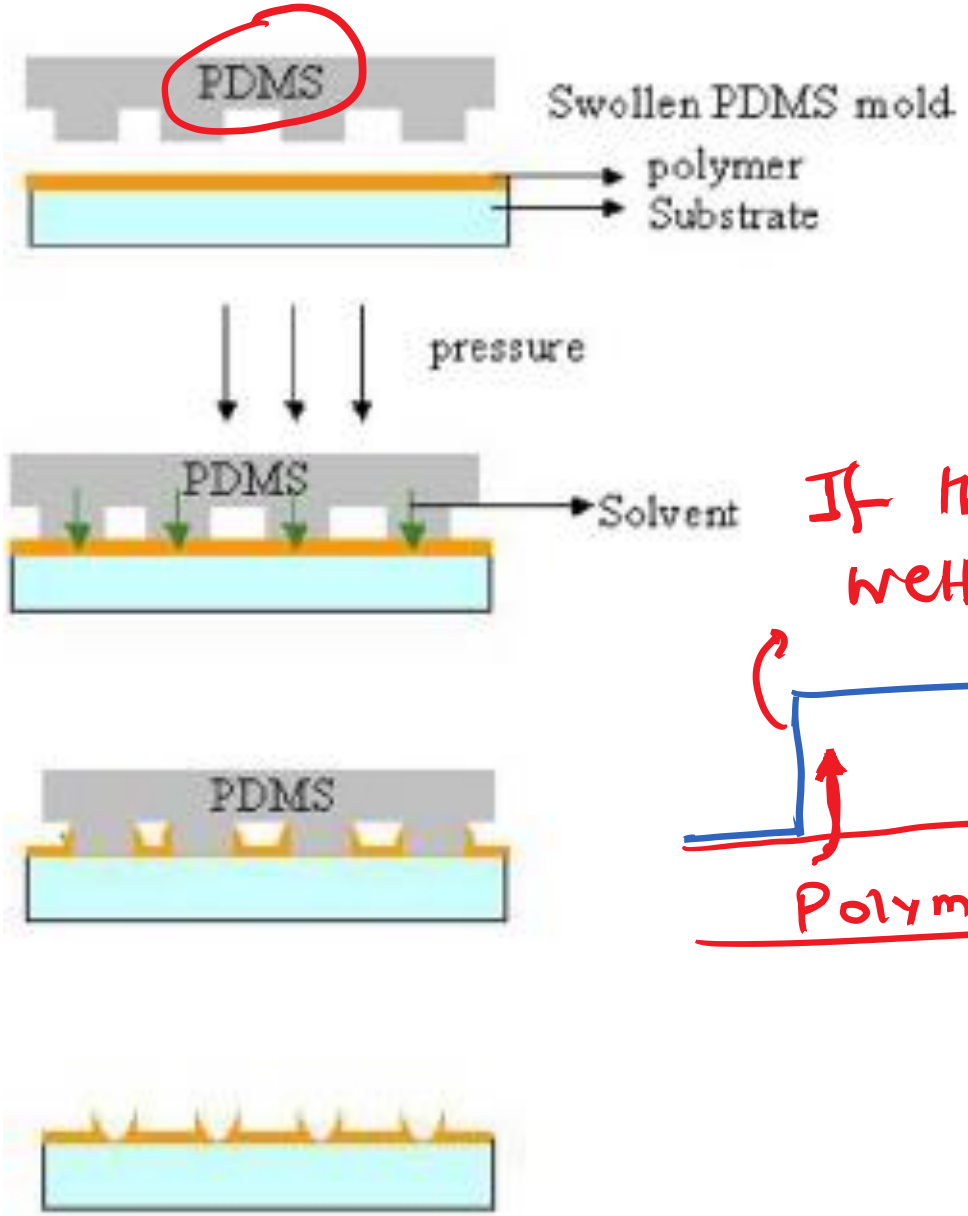


Instability and Soft Patterning Laboratory
भारतीय प्रौद्योगिकी संस्थान खड़गपुर
Indian Institute of Technology
Kharagpur

Capillary force Lithography

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

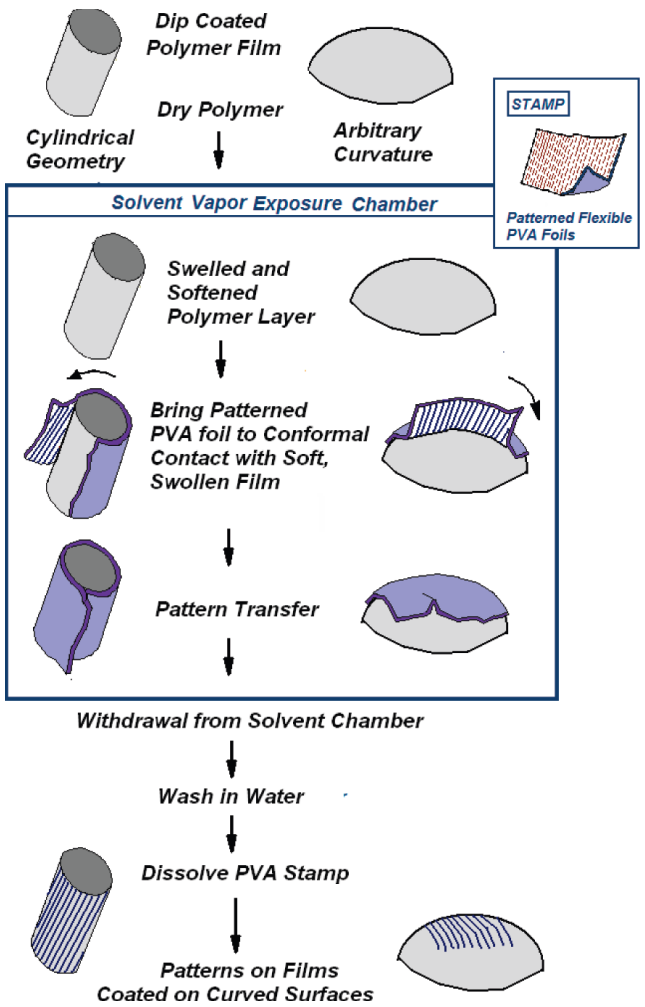


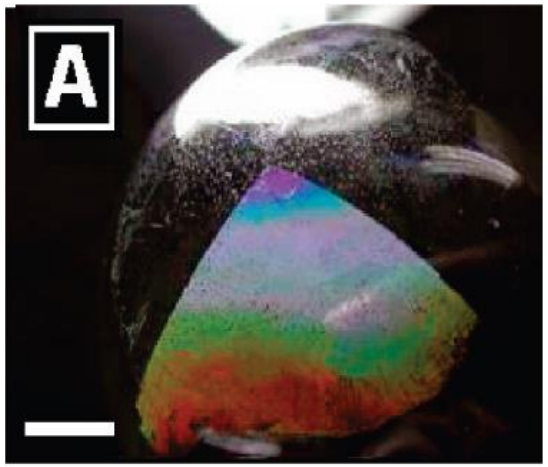


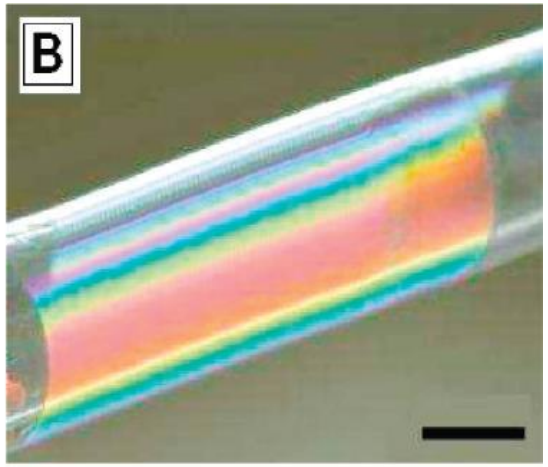
If the Stamp is wettable

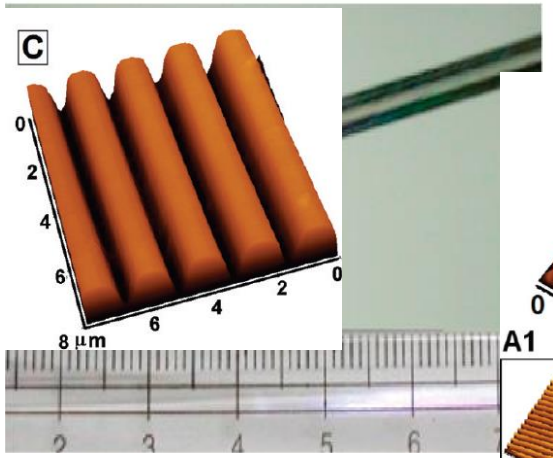
Lee, Adv. Mater, 2001, 13, 1386, Lee, Adv. Mater, 2004, 176, Han, Polymer, 2005, 11099

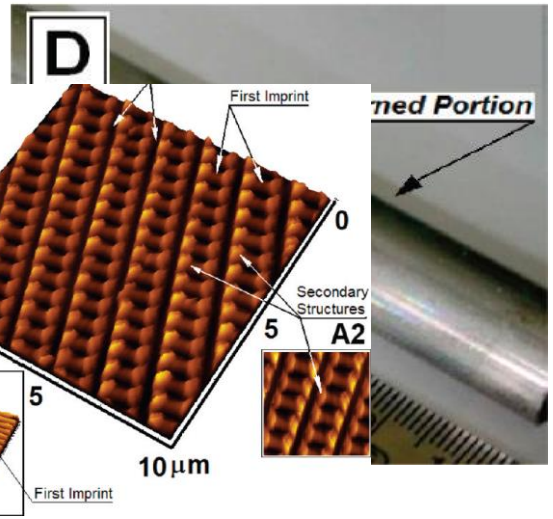
Solvent Vapor Assisted Imprint Lithography for Curved Surfaces









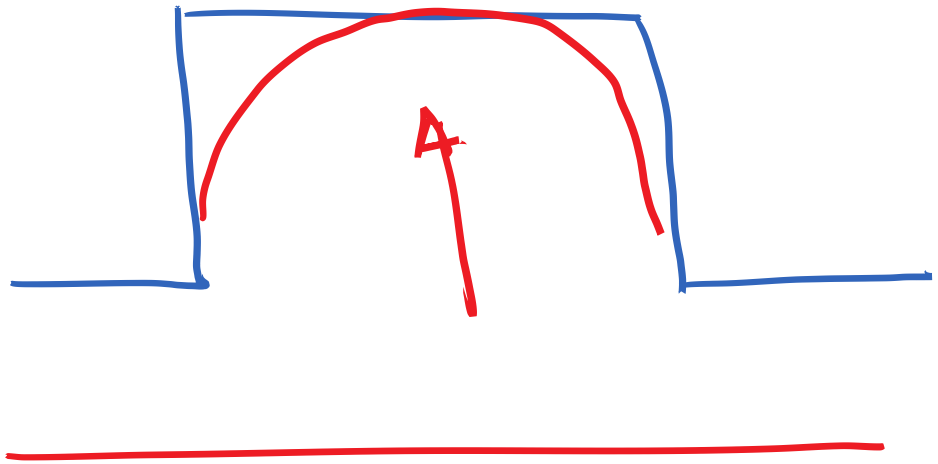


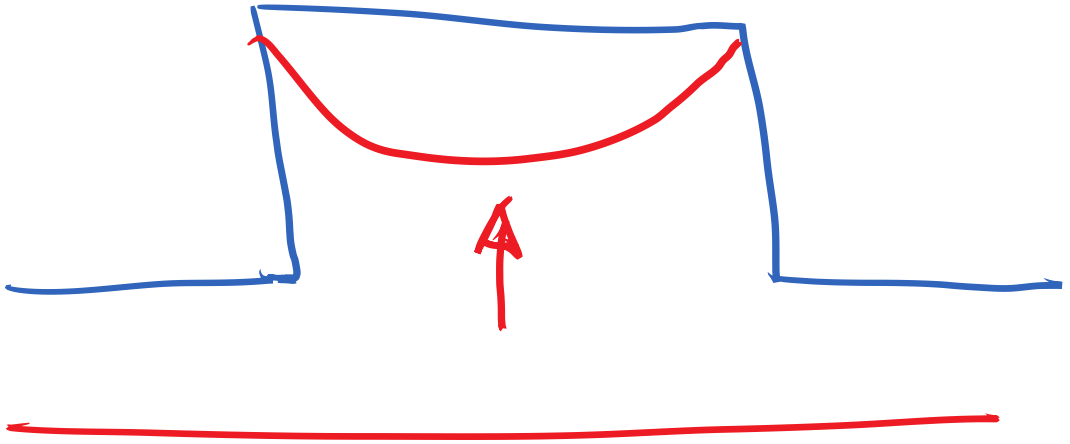
Mukherjee, *Ind. Eng. Chem. Res.* 2009, *48*, 8812–8818

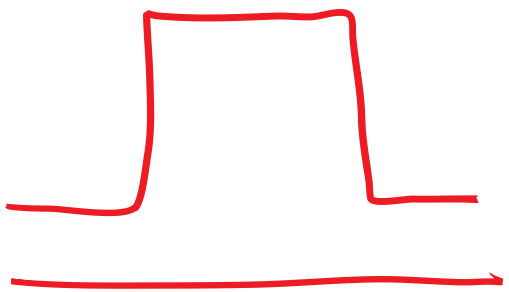
NIL

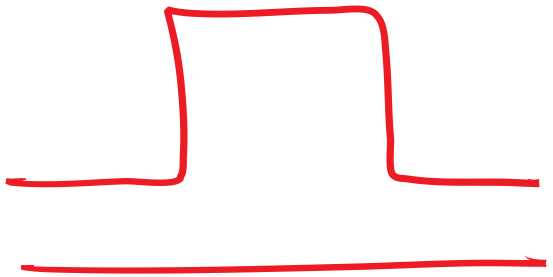
Mold Filling

CFL



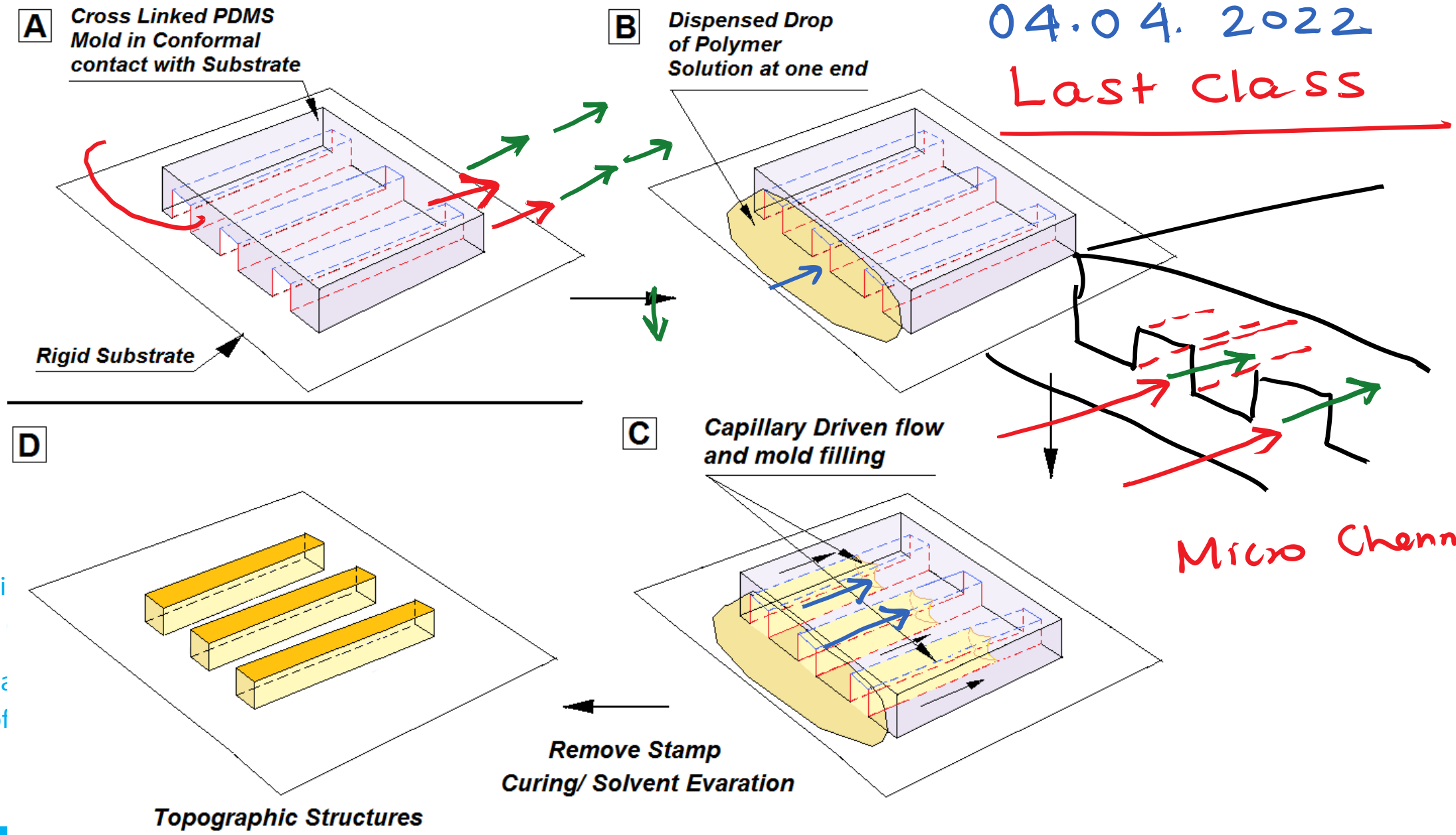






Micro molding in Capillaries (MIMIC)

Class # 36
04.04. 2022
Last Class

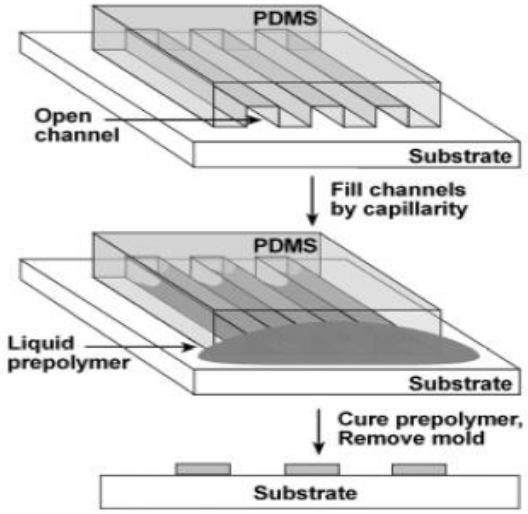


Micro Channel

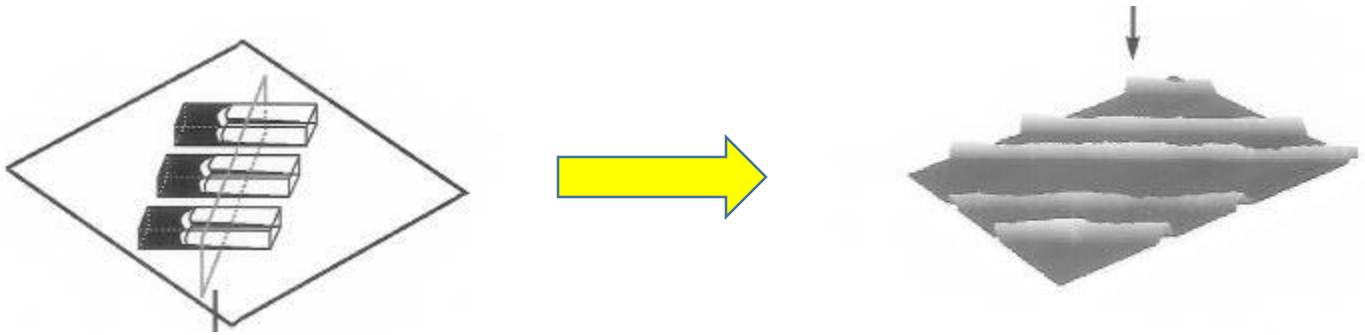
- The techni
  conformal
- **MIMIC** is a
  energies of

Micro molding in Capillaries (MIMIC)

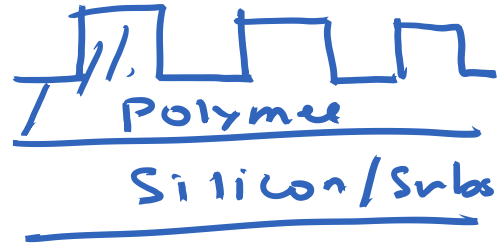
- The filling of capillaries and rate of liquid flow in capillary is determined by the surface tension and viscosity of the liquid.
- Viscosity of liquid is a determining factor that controls the filling rate.

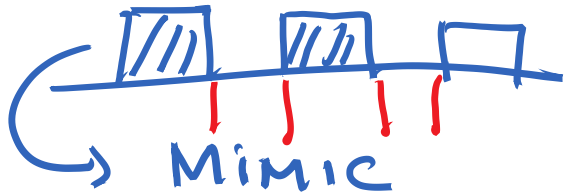


The time allowed for pattern replication is also important as Initially a fluid fills the capillaries only partially, particularly the corner regions.



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





allows formation of Isolated polymer strips

There is no remnat layer

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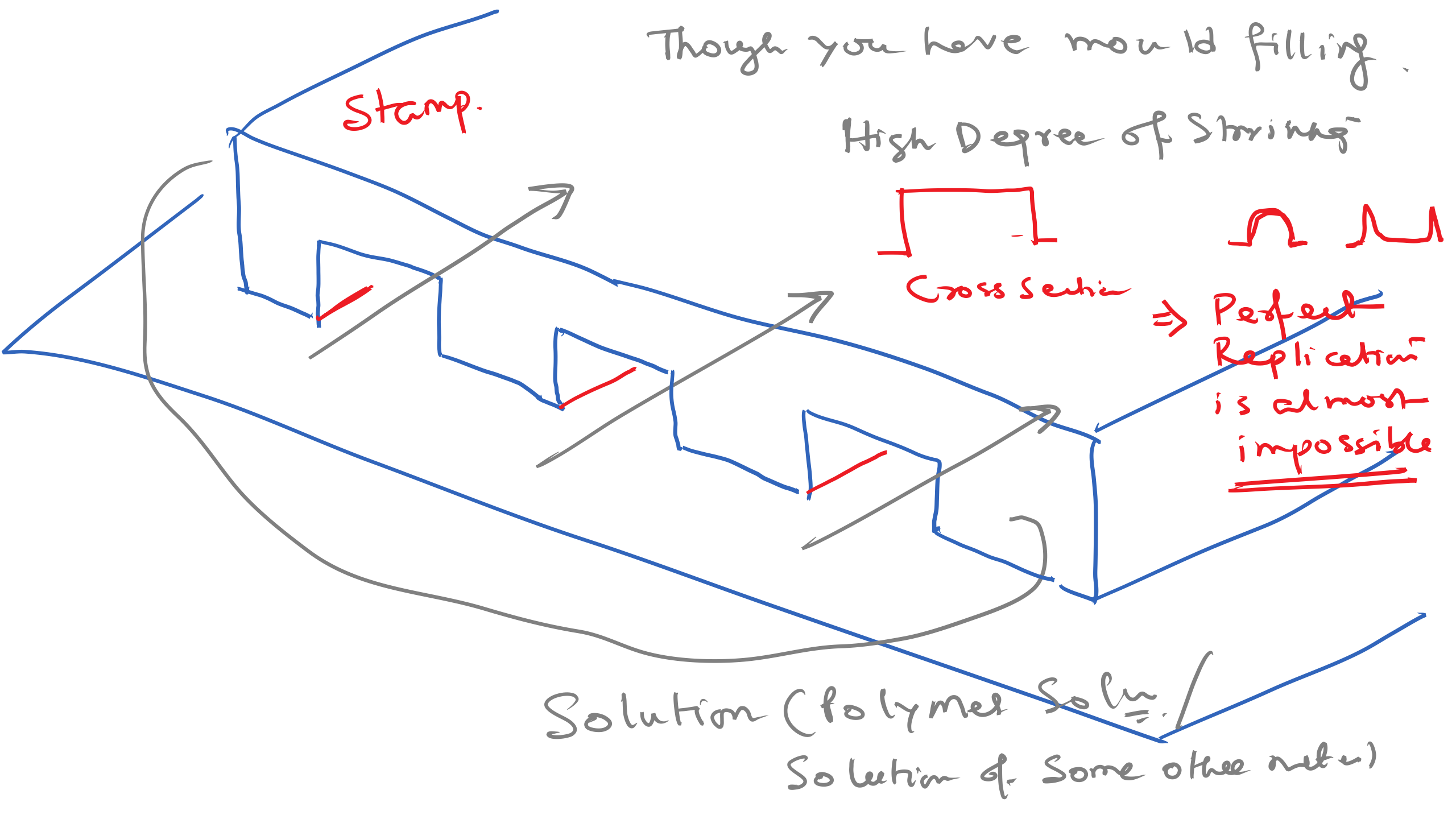
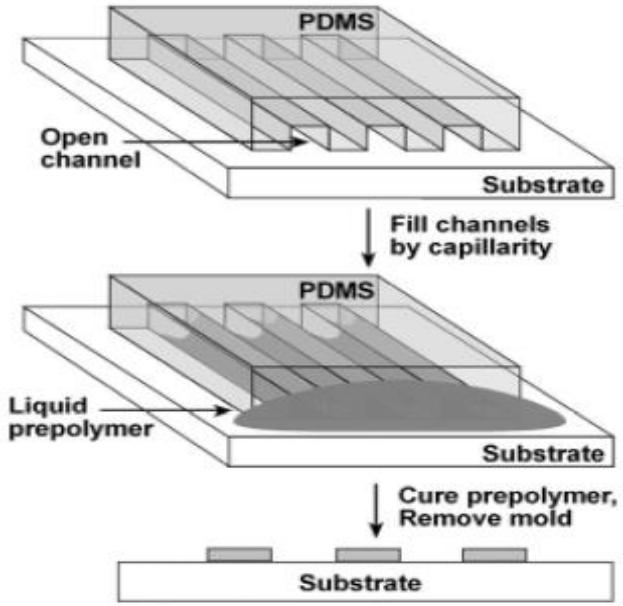

Though you have mould filling.
Stamp.
High Degree of Shrinkage
Cross Section
⇒ Perfect Replication is almost impossible
Solution (Polymer Soln.
Solution of some other material)

Micro molding in Capillaries (MIMIC)

The rate of capillary filling is given by

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

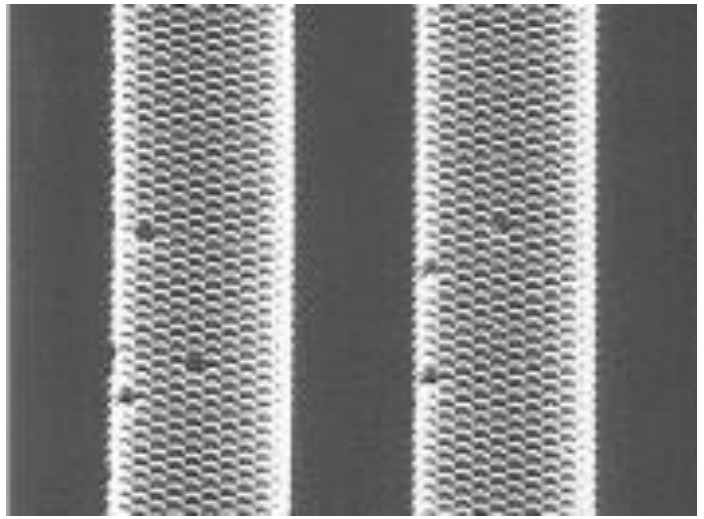
η is the kinematic viscosity (μ/ρ)
γ is surface (interfacial) tension of liquid,
R is the radius of the capillary,
z length of the filled section of the capillary

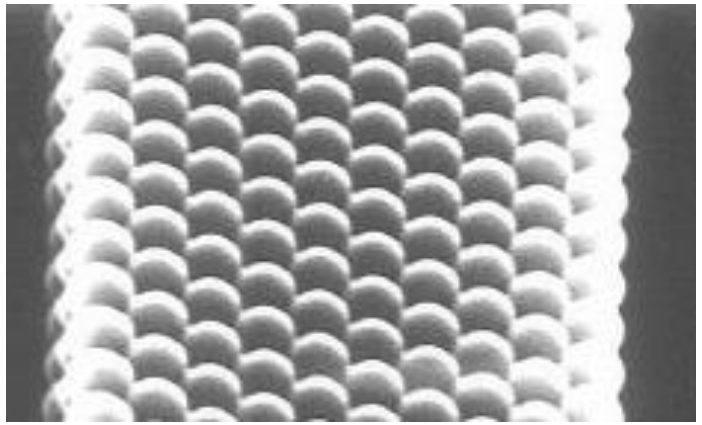


Capillary filling over a short distance (up to 1 cm) can be achieved quickly and efficiently; over a large distance, the rate of filling decreases significantly due to the viscous drag of the fluid in the capillary and the distance over which the fluid has to be transported.

Micro molding in Capillaries (MIMIC)

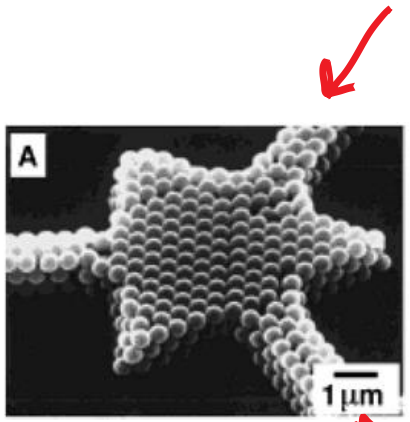
- The method therefore does not remain limited to a polymer solution only and several functional materials have been patterned by this method.
- In a recent study **Conductive Sub-micrometric Wires of Platinum-Carbonyl Clusters (**$[Pt_{15}(CO)_{18}]^{2-}$) have been patterned by MIMIC
- Ceramic Materials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



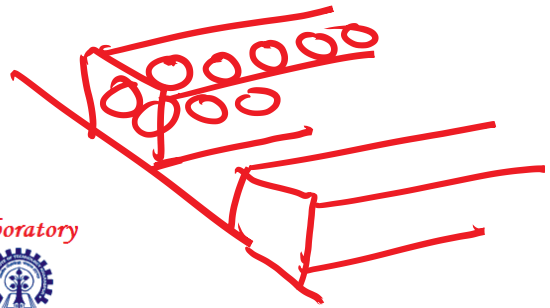


An assembly of Colloids is also possible by MIMIC.

Uniqueness of MIMIC!



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



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The presence of a ligand (Y(CH2)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.

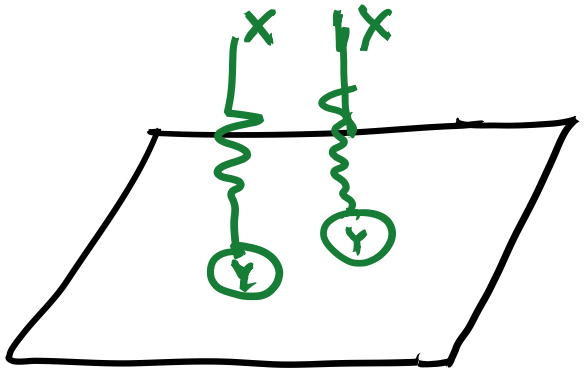
Double Headed.

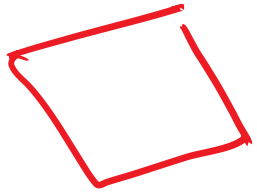
(Two functional groups at the Ends.

X → Hydrophobic / Hydrophilic →

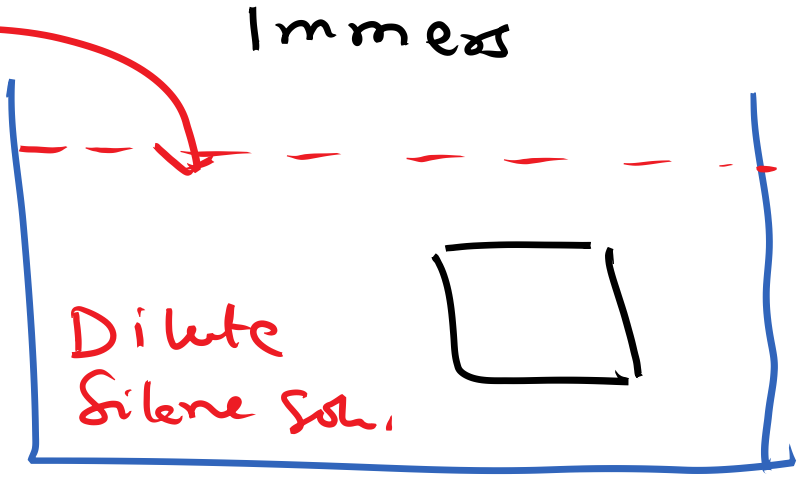
Depends on the Nature of the Silene.

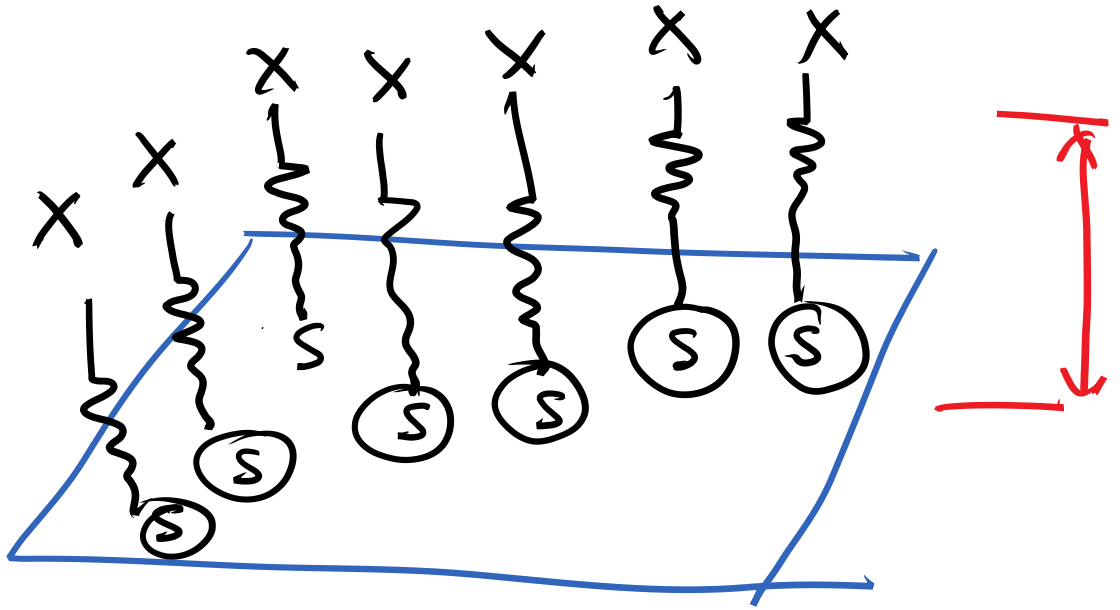
Y or S → Attaches to Certain Surfaces





Take a surface to which the Silene molecule can attach.



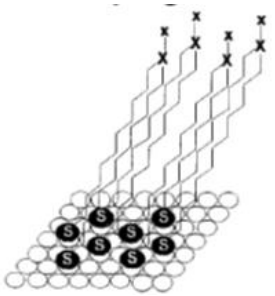


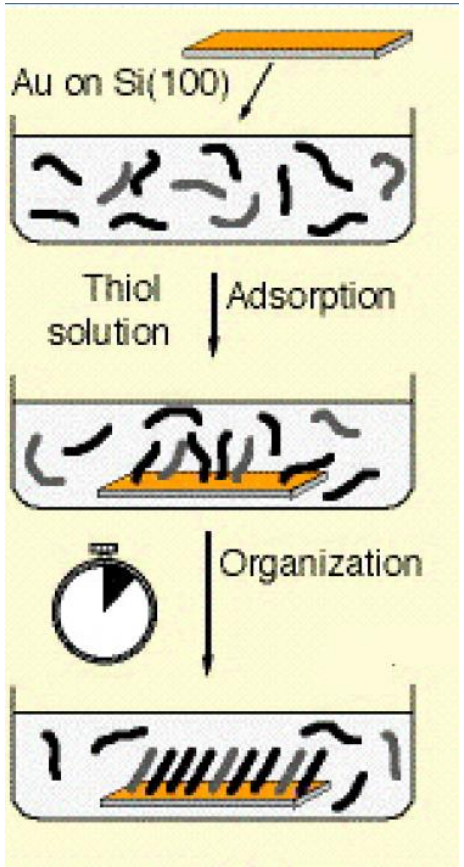
Coverage is by a single layer of the Silene molecule ONLY.

All over the surface the Silene molecules have attached.

SAM (Self Assembled Monolayer)

- The presence of a ligand ($Y(CH2)_nX$) 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/Al_2O_3, glass etc. also exhibit good attachment properties.





SAM
Self
Assembled
Monolayer

MICRO CONTACT PRINTING

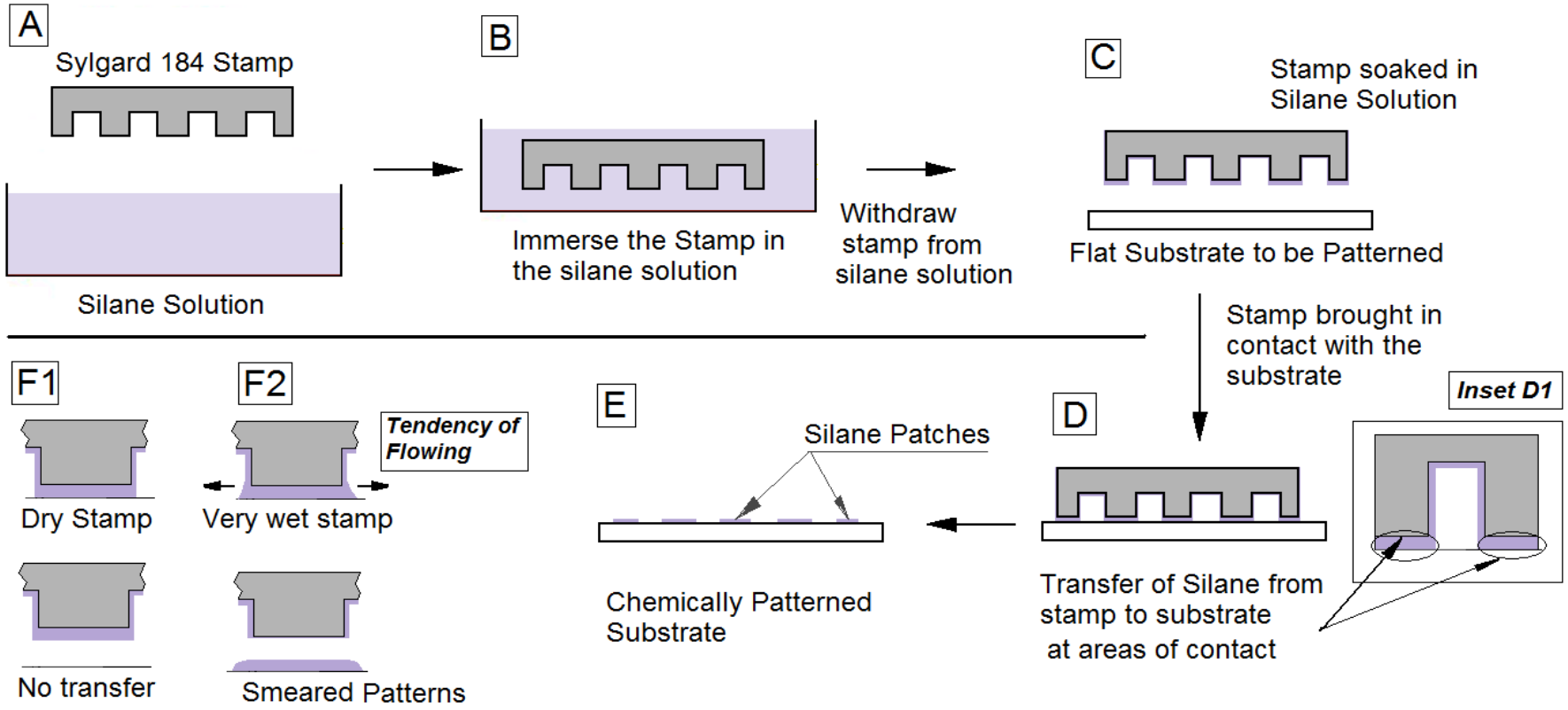
Master Pattern

Ink

Surface to be patterned

Polymeric or non polymeric

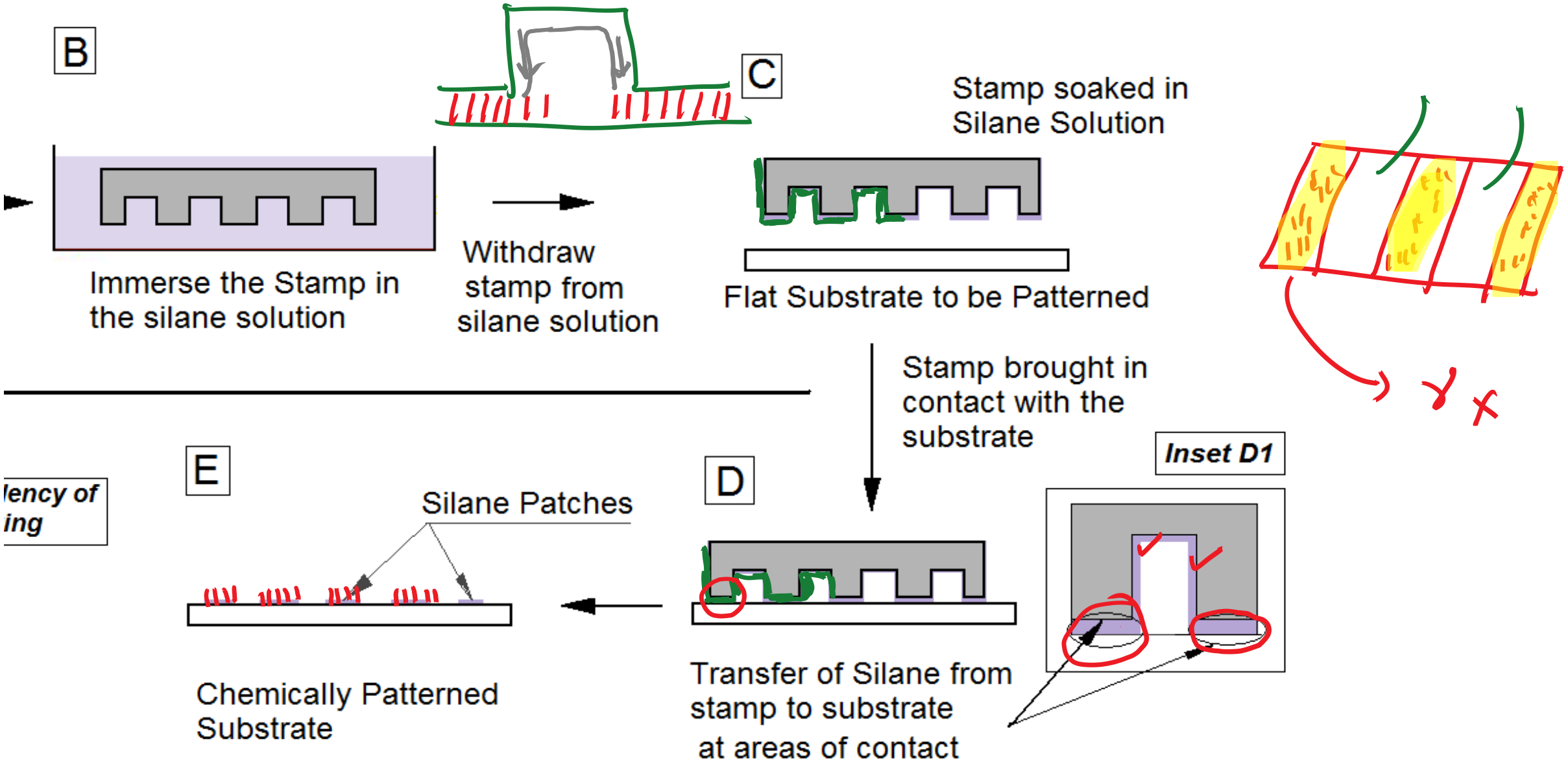
Micro-contact Printing



- **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 Whiteisdes and Amit Kumar, Appl. Phys. Letts., 1993, Science, 1994

Micro-contact Printing

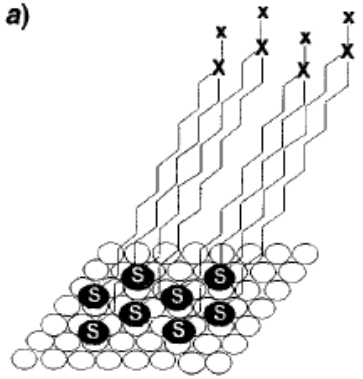


Methods of Applying Alkanethiols (Resist) on Stamp

- 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

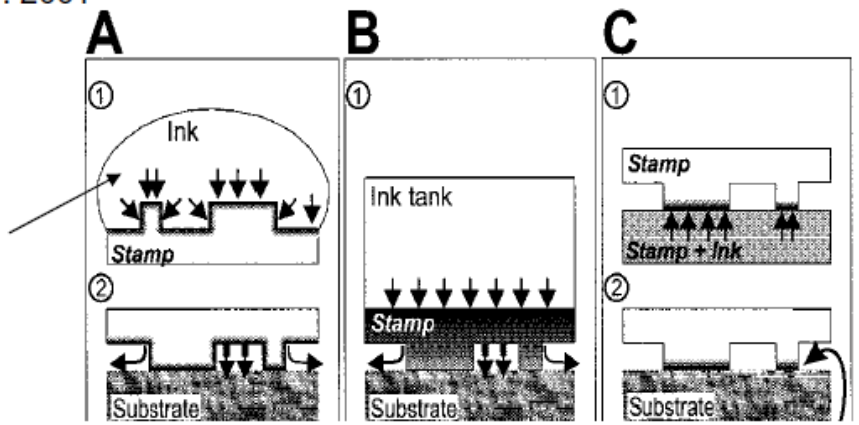
158 g mol^{-1} (dodecanethiol, DDT)
258 g mol^{-1} (hexadecanethiol, HDT)
314 g mol^{-1} (eicosanethiol, ECT)

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



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

Ethanolic solution of a thiol



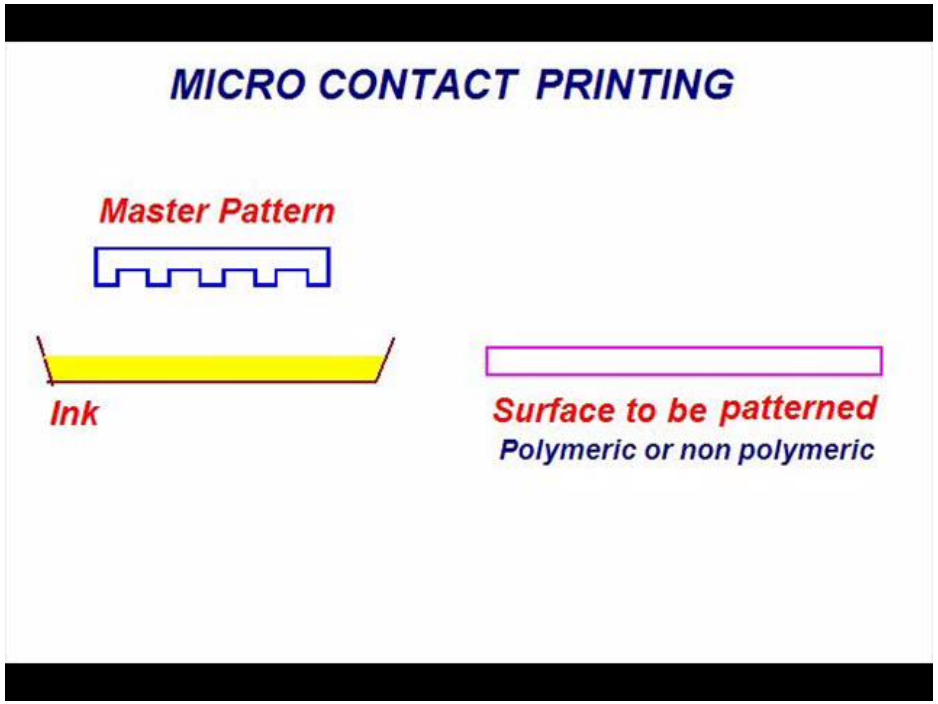
L. Libioulle et al, *Langmuir (ACS)* 1999

Mold is Soft:

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

Micro Contact Printing (μCP)

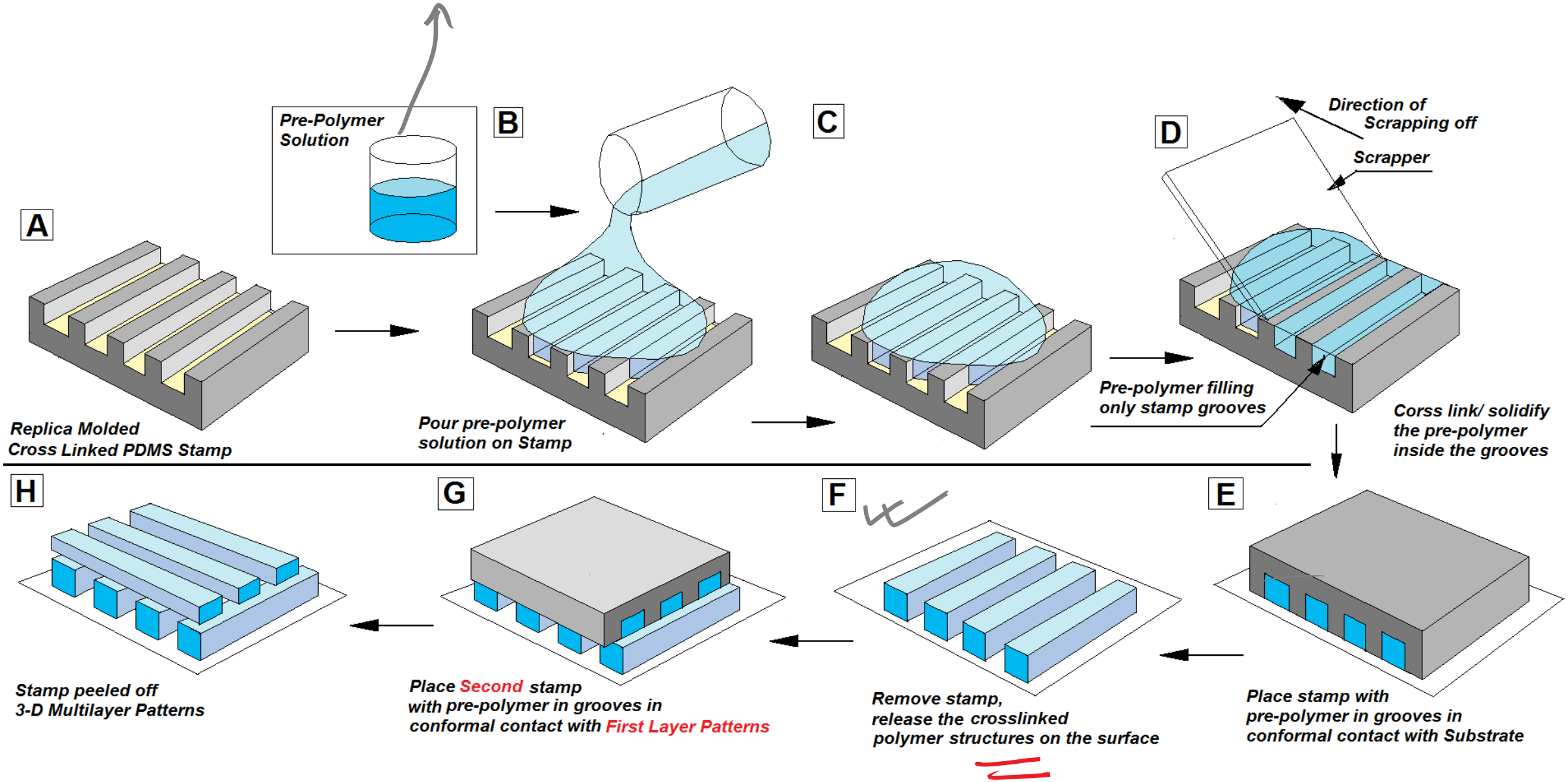
- SAM is used as ink (*n-Alkanethiols)*
- *Thiols, Silanes etc.*
- Chemically patterned surfaces obtained.



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

Micro Transfer Molding

UV Curable pre-polymer



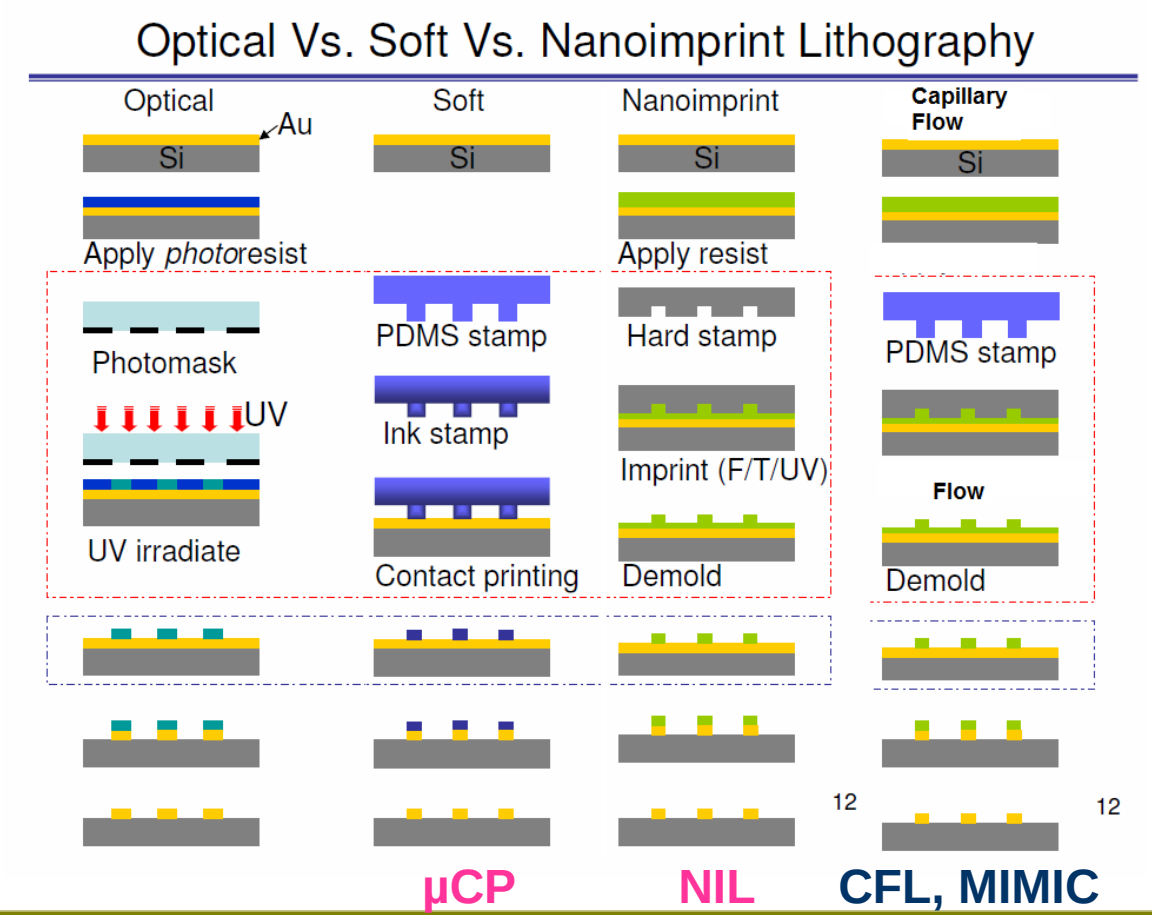
Soft Lithography Techniques:

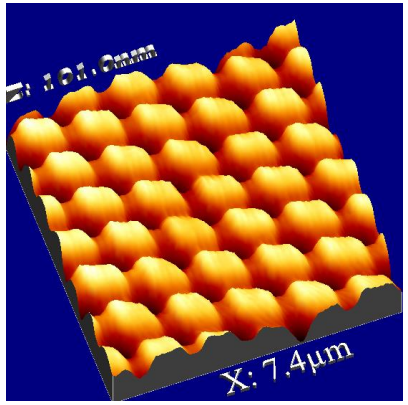
Broadly 3 Categories:

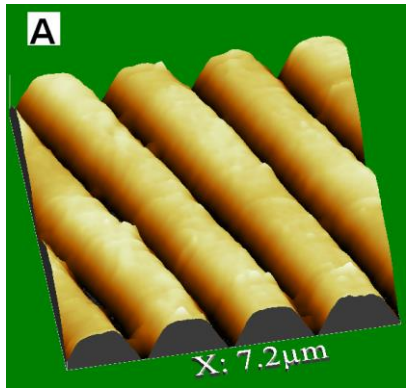
Micro Contact Printing: Inking, Chemical Patterns

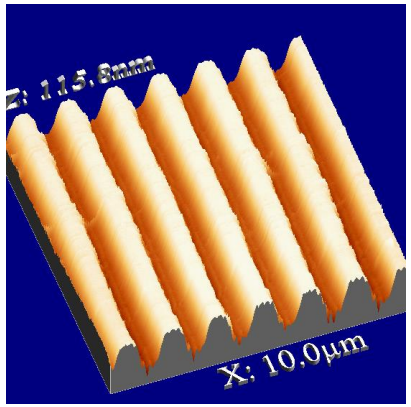
Nano Imprint Lithography: Molding

Capillary Flow Lithography: Flow Induced Patterning









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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