31.03.2022

Soft Lithography

1990's : Primarily to Circumvent the problems of Photo-Lithography.

Stephen Chou → Princeton → Nano Imprint Lithography

George Whitesides → Harvard → REM.

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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.

Photolithography is every well defined technique.

Soft Litho : A suit/ collection of different techniques

All SL techniques are capable of patterning soft material including polymer (PR is not reqd.)

Photo Lithography:

Aimed at the micro electronic industry. Defect tollerence is very very low. Defect is NOT allowed. → aimed for perfection.

Soft Lithography:

Aimed at bulk – nano applications that require meso and nano scale patterns over large areas ….. Like self cleaning surface. So even if there are some defects here and there, its accepted.

↳ can work for wide variety of soft materials – polymers, Gels, Sol-Gel derived inorganic materials etc.

Discussion on Classification of Polymers

Glassy Polymer (Thermo Plastic)

- Long chain entangled polymers. No physical cross links between the chains
- T_G (Glass Transition Temperature) is an important property. Above T_G there is a sudden drop in viscosity. The polymer starts behaving like a liquid.
- Such polymers can be softened in presence of a Solvent as well. The solvent molecules penetrate into the polymer matrix and results in reduction of effective T_G of the polymer.

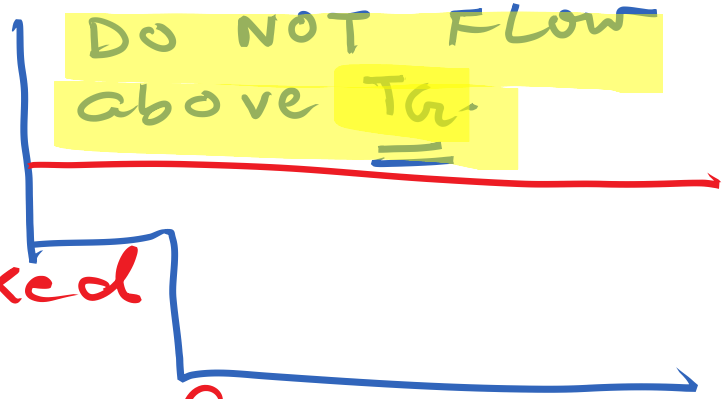
Long chain
Non cross linked
melts / Softens above Tg
η drops

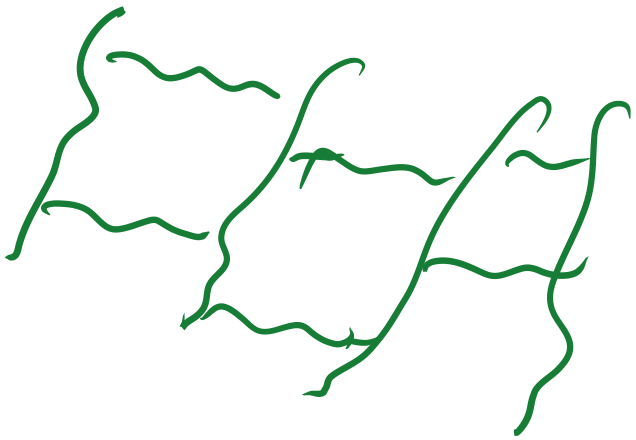
Cross Linked Polymer (Thermo Set)

- The chains are physically crosslinked.
- Depending on the chain configuration these polymers can be flexible. (Rubbery)
- Heating will degrade the polymer (wont make it fluid like).
- In presence of solvent molecules can swell, but wont lose structural integrity.
- Many rubbery, cross linked polymers have sub zero T_G.

→ Cross linked polymers
→ Elastic like

Cross Linked Polymers (or Thermo Set)



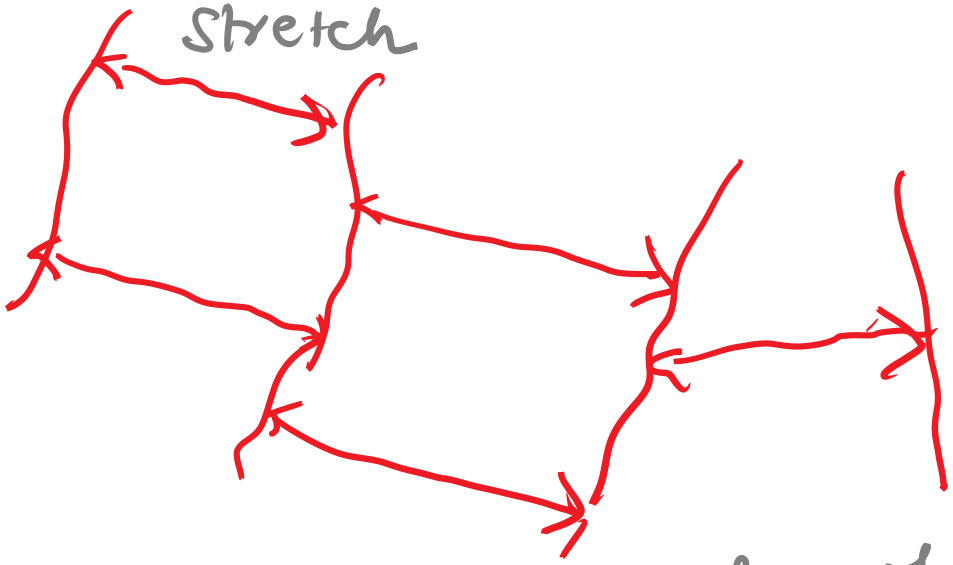


→ Chains are cross linked

→ Stretch (apply force from outside)

→ The energy supplied for Stretching → remains stored as elastic deformation energy within the chains

→ They do not dissipate.



→ When the external force is withdrawn, this energy is released & object takes back its original shape.

Glassy Polymers →

1st April 2022

There is no cross link.

But there are long chain molecules →

there is entanglement → So at Room Temp. the individual molecule cannot move / change position w.r.t each other → behave as Solids.

→ As you heat up → The translational K.E of the molecule (K_BT) increases → So the chains can overcome cohesive interaction and entanglement → starts to move / can change position w.r.t each other / Liquid Like.

Above a critical Temp → The material starts behaving like a liquid →

→ Chains / molecules change position w.r.t to each other

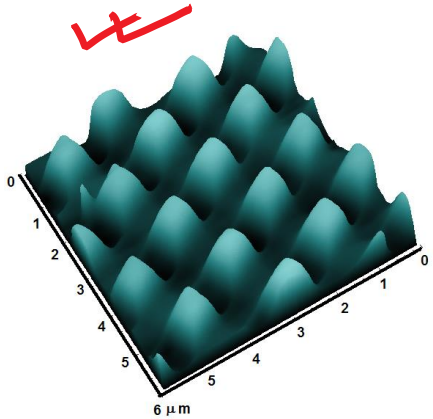
→ Viscosity drops. (η)

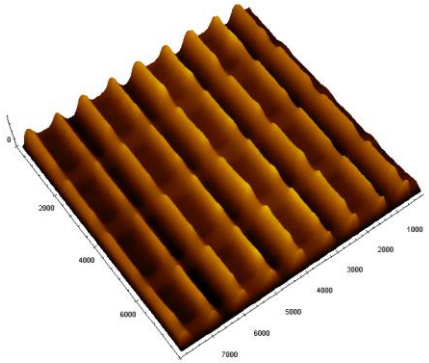
Temp at which $\eta \downarrow$, Glass Transition Temp.

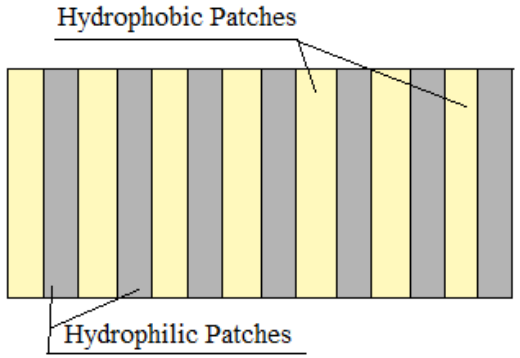
Soft Lithography Techniques: Classifications

Based on the Nature of Patterns:

- Chemical Patterns
- Topographic Patterns







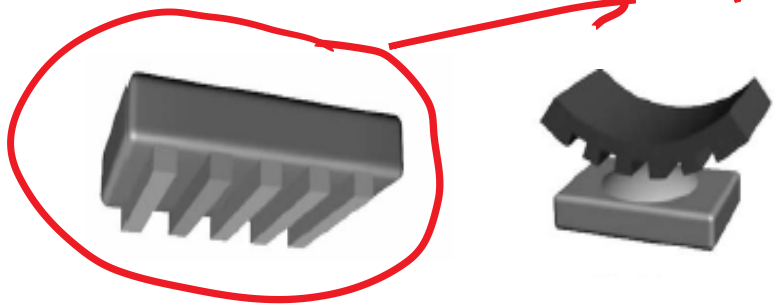
Topography is Rather Smooth

Printing Group of Techniques

Molding group of Techniques

Based on the Nature of Stamp Used:

- Flexible Stamp
- Rigid Stamp



Topographically patterned stamp.

Eqv. to the mask in photolithography

Master // Stamp / Mold

Soft Lithography Techniques: Classifications

Topographic Patterns:

Nano Imprint Lithography (NIL): Visco Plastic Deformation of a Softened Polymer Layer under External Pressure

Chemical Patterns:

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

Micro Transfer Printing (μTP): 3D structures

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Classification

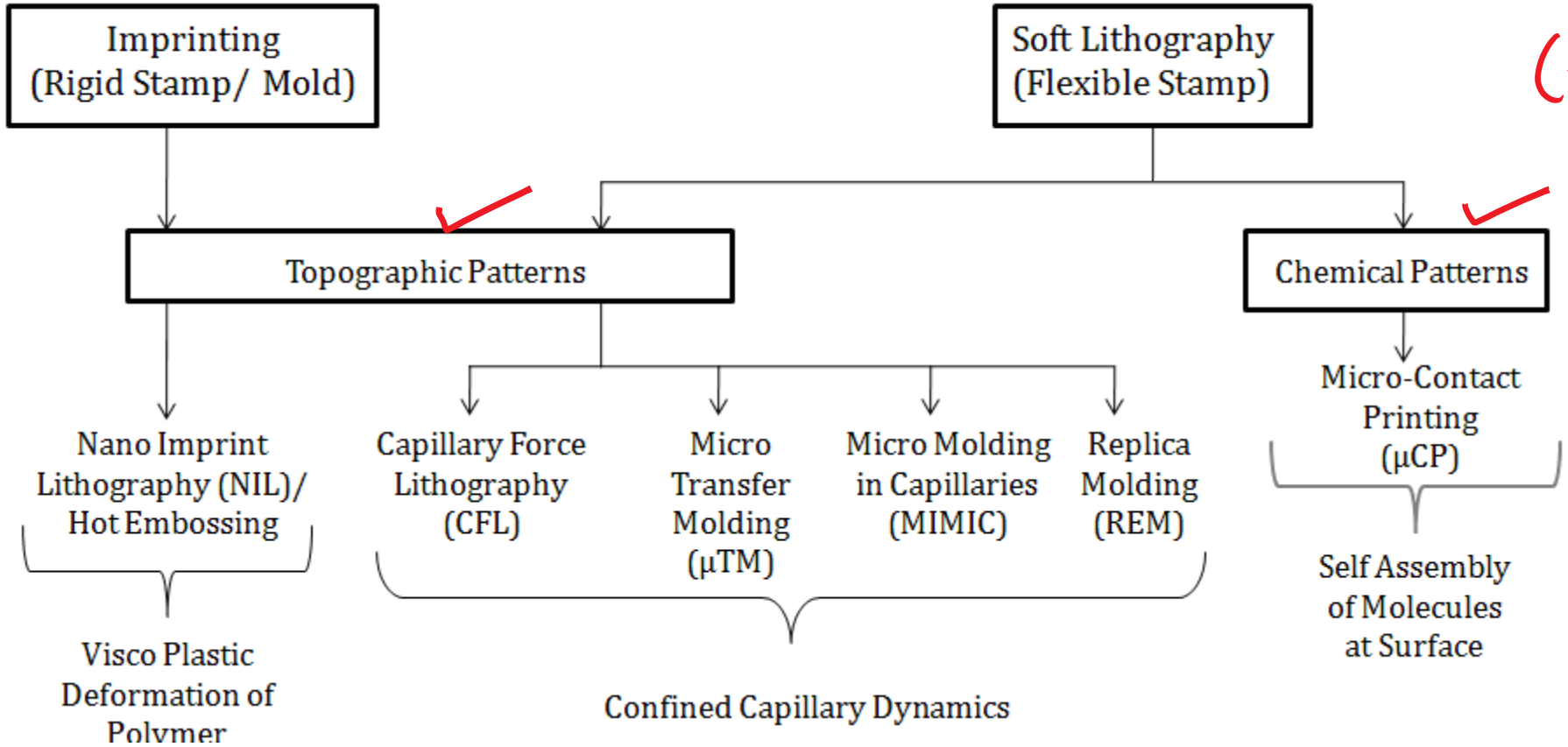
Soft Lithography

(1) Based on Type of Pattern

(2) Based on the type of the stamp.

→ Rigid

→ Flexible stamp



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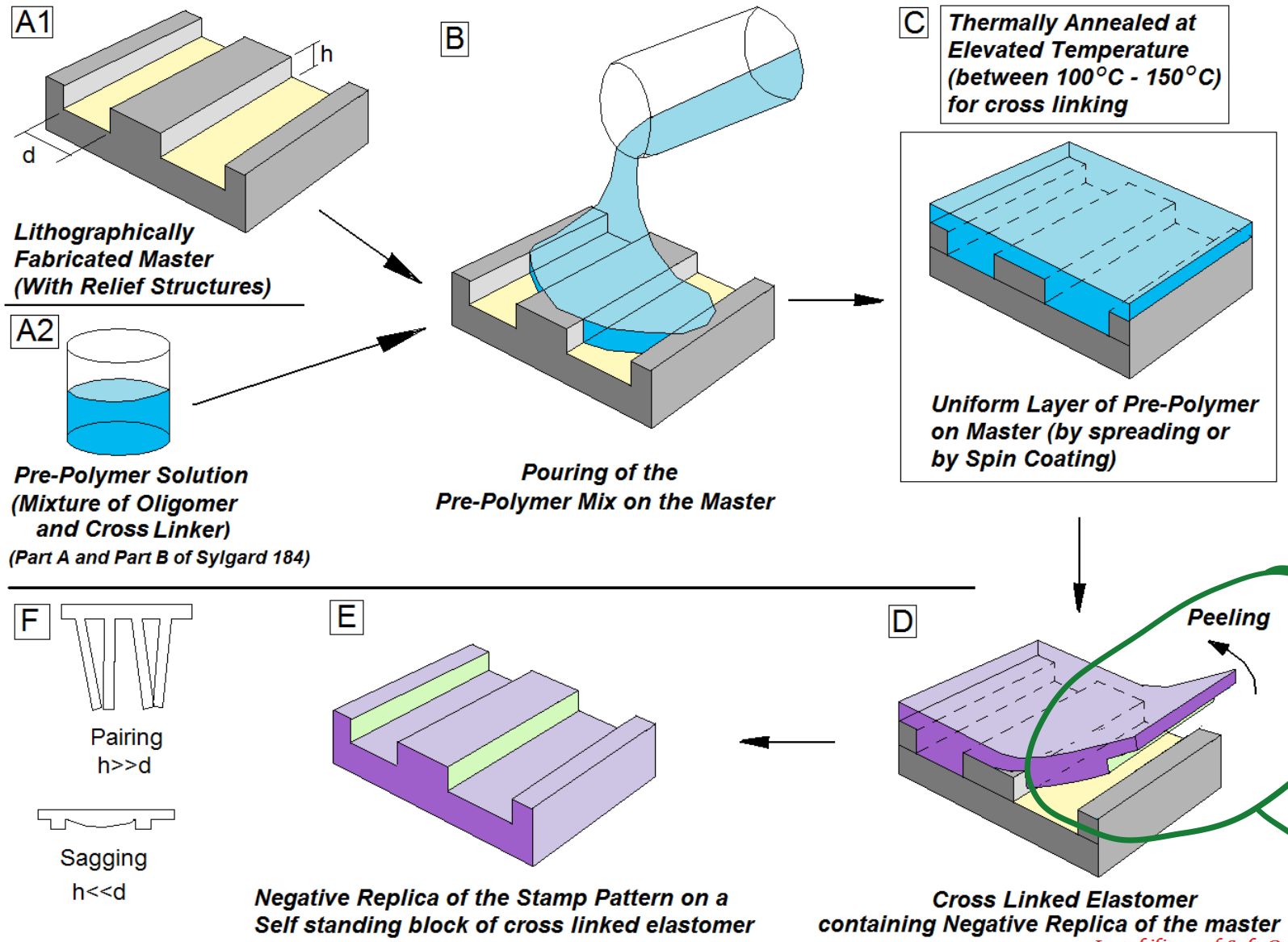
Replica Molding



Special Type of Material →

Thermo "curable" Elastomer

Cross linked Poly Di Methyl Siloxane (PDMS)

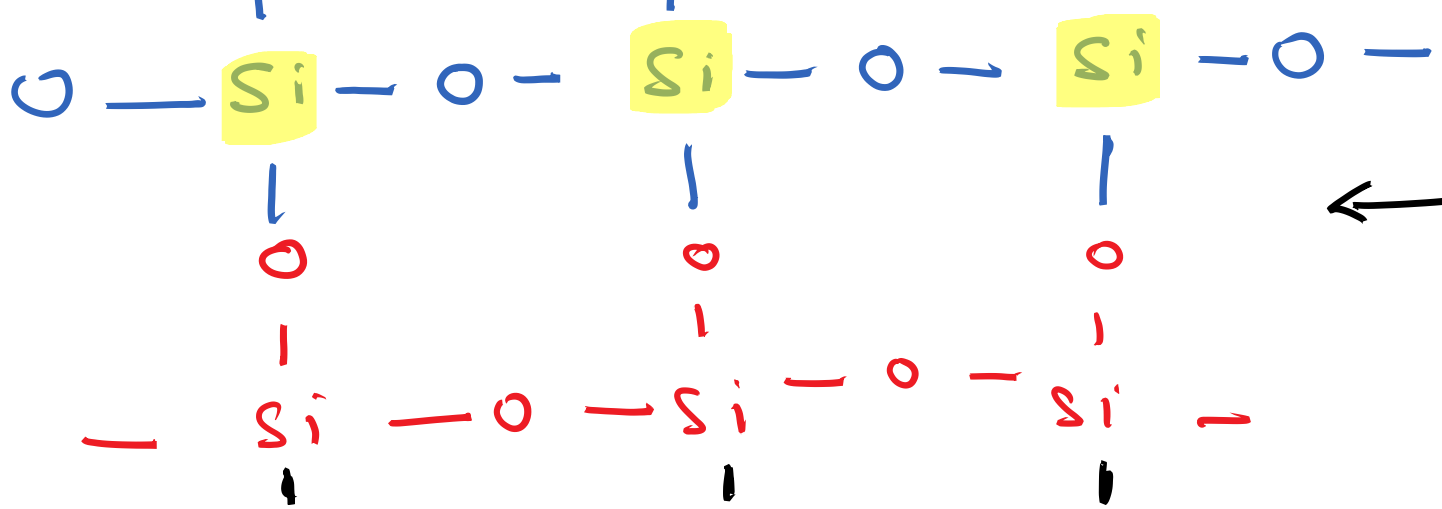
PDMS at Room Temp is Liquid

It's Tg is below Room Temp. Glassy Polymer is NOT flexible !! So can't Peel.

PDMS → Poly di methyl Siloxene (Silicone) → Inorganic Polymer

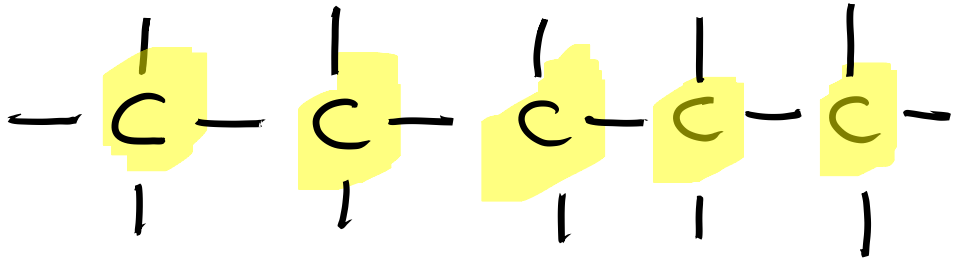
Thermo Curable

Since Si is present at alternate location → Get more flexibility.



As you heat up the adjacent polymer chains join up. (Cross linking reaction happens at elevated Temp)

Polymer (C-C back bone, organic molecule)



→ Soft/ Flexible Solid

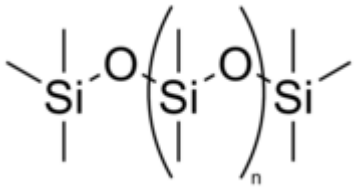
Material for Replica Molding

- 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.

A - Oligomer

10:1

B → Cross linker, Catalyst



Commercial Product:

Sylgard 184

Shape: Shape of the container.

As you thermally anneal

A high viscous Liquid

↓ (Δ) 120°C, 6 hrs

Soft Elastic Solid

Sylgard Group of Products from Dow – Croning USA

A → Oligomer

B → Cross Linker (Catalyst)

$\xrightarrow{\Delta}$ There is cross linking only when you heat up.

X

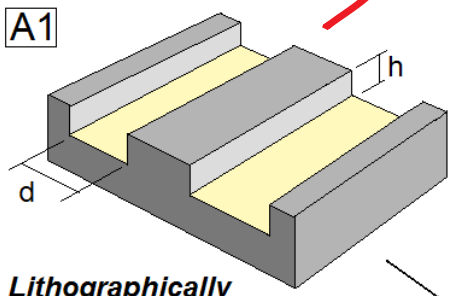
If you mix A and B → Just Keep it at room temperature → Then also there is cross linking → rate of cross linking is low (process is slow)

Thermal Annealing only expedites the cross-linking process.

Replica Molding

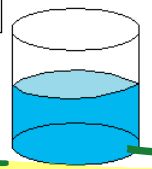
Topographically patterned stamp → Patterned Pho to resist Film.

A1



Lithographically Fabricated Master (With Relief Structures)

A2



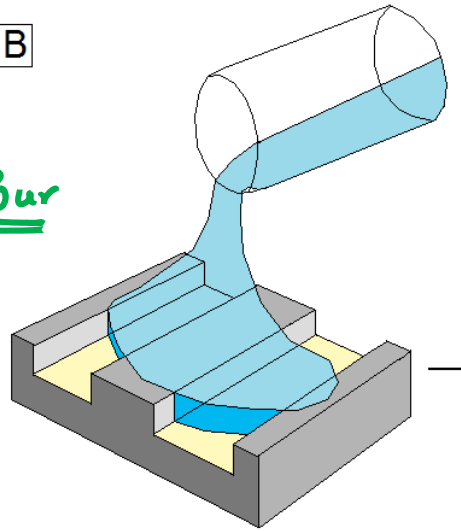
Pre-Polymer Solution (Mixture of Oligomer and Cross Linker) (Part A and Part B of Sylgard 184)

A+B

High Viscosity Liquid

B

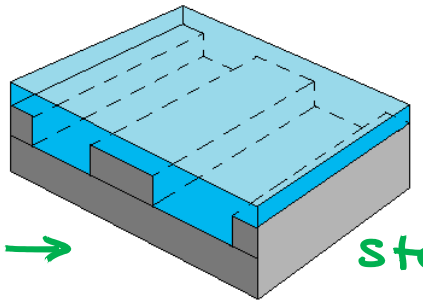
Pour



Pouring of the Pre-Polymer Mix on the Master

C

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

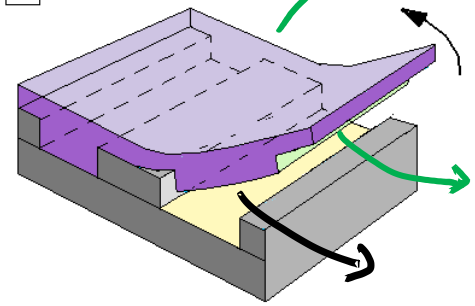


Uniform Layer of Pre-Polymer on Master (by spreading or by Spin Coating)

Stamp Submerged under the liquid.

Height → X Not an important Parameter

D



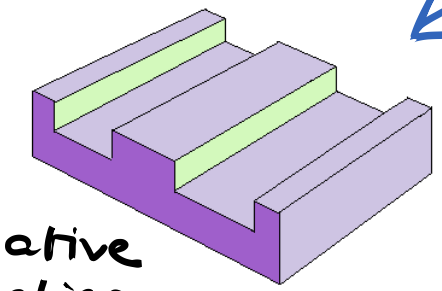
Peeling

Cross Linked PDMS block (Soft Solid)

Cross Linked Elastomer containing Negative Replica of the master

The face of the block that was in contact with the stamp → Negative Replica of the stamp pattern.

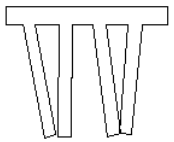
E



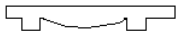
Negative Replica

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

F



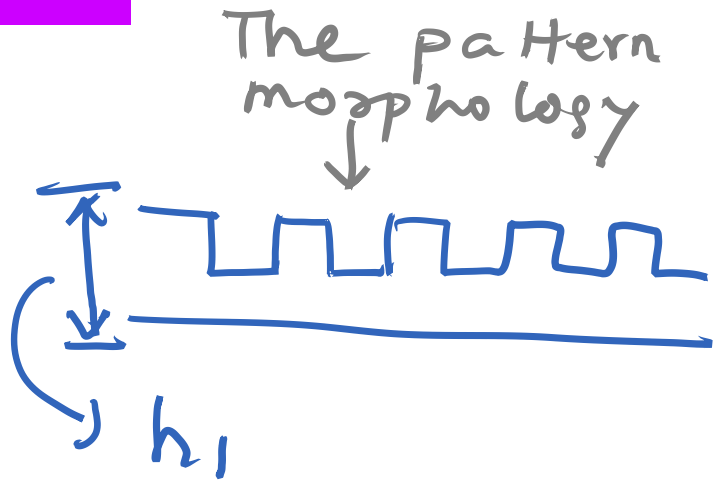
Pairing
h>>d

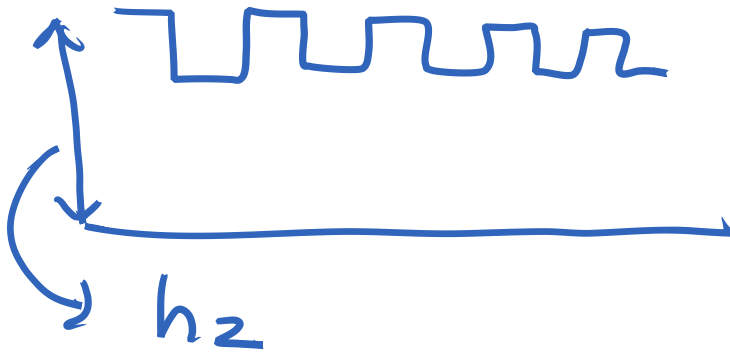


Sagging
h<<d

Cross Linked PDMS

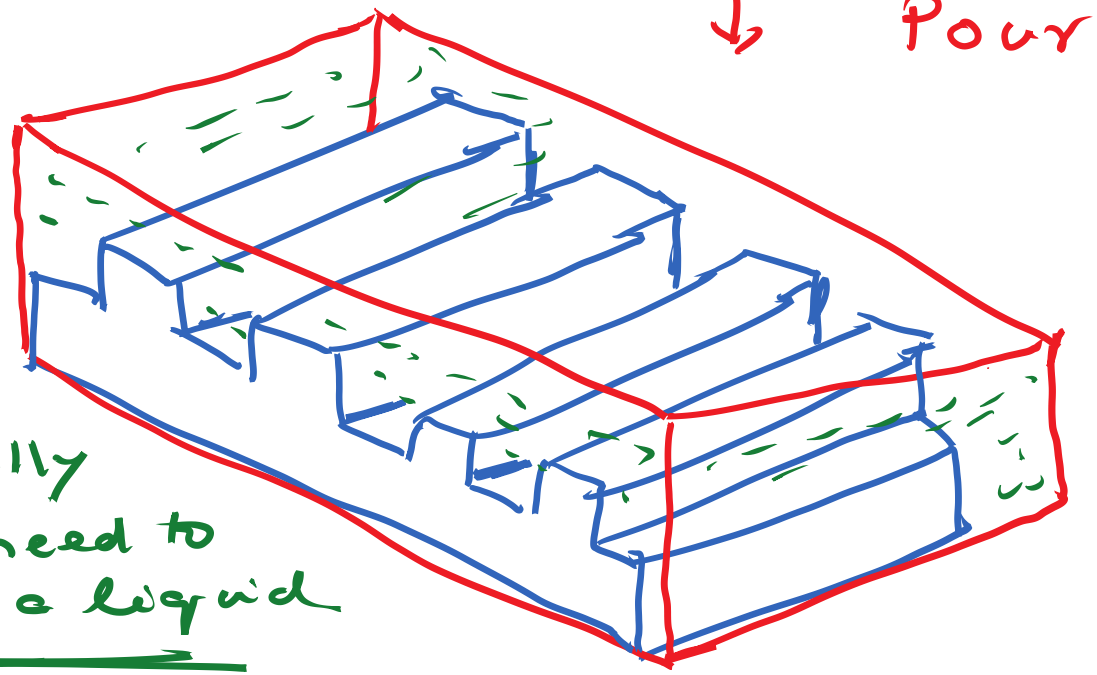
- PDMS consists of an inorganic siloxane backbone and organic methyl groups attached to it.
- It is a flexible elastomer that can be used in a wide temperature range, it is optically transparent, biocompatible, inert and non-toxic and resistant to many chemicals.
- It is non- flammable and gas-permeable.
- 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





So is block Thk important

The pattern morphology is independent of the Thickness of the block.



↓ Pour Liquid → liquid will drain out

Initially you need to have a liquid

How small you can get

→ Simply depends on the feature dimension on the Stamp.

Replica Molding (REM)

→ Soft Lithography Technique

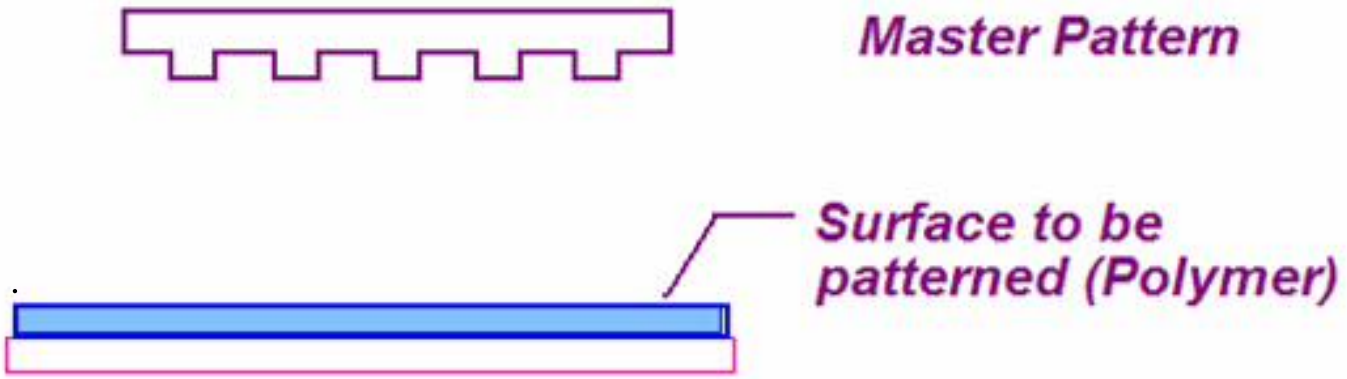
→ Secondary Patterning Technique

Does it work for a Glassy Polymer?

Thermo Plastic??

By replica Molding → we get a self standing block of cross linked PDMS.

NANO IMPRINT LITHOGRAPHY



T_G

(1) Thin Film of a glossy Polymer (Spin Coating)

(2) RIGID Stamp.

1. Heat up the film above T_G
2. Press the Stamp against softened film with Excess External pressure

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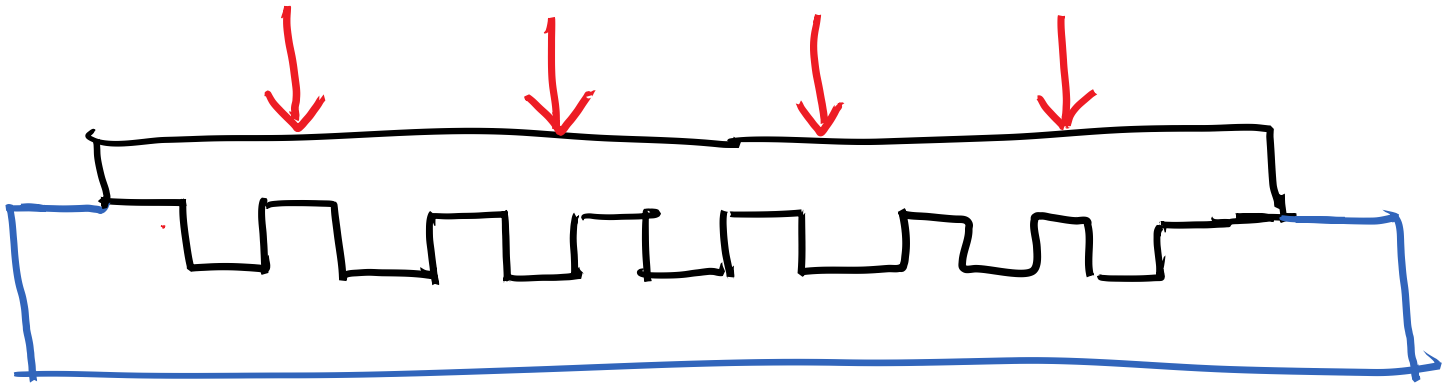
Major operational Problem (NIL)



(1) NIL → Can't be implemented without heating.

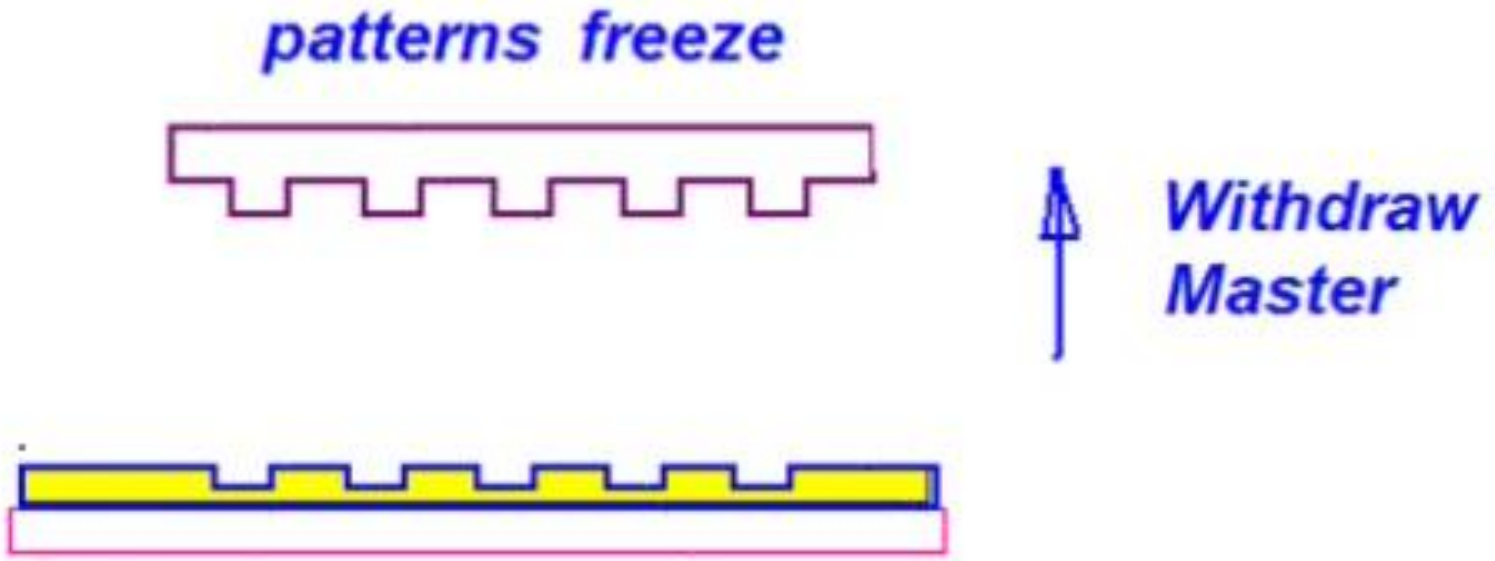
(2) NIL as well as REM → Both produce a Negative Replica.

(3) Applying Pressure from outside

→ Mould breakage due to high External pressure

→ Repeated usage + mechanical Wear & Tear

NANO IMPRINT LITHOGRAPHY



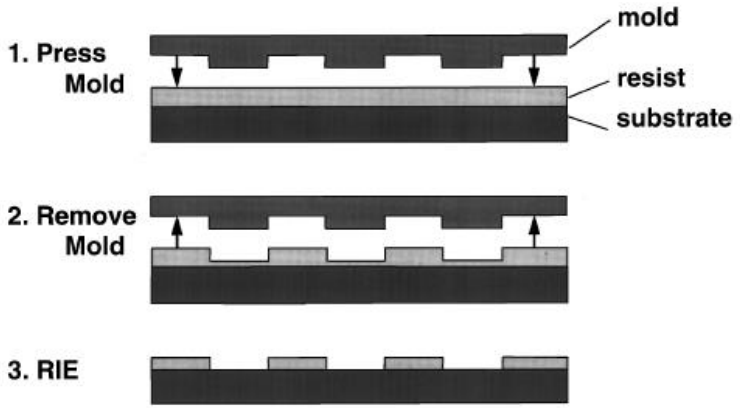
Major Problem :→ Mould Release

Rigid Stamp → Peeling Does not Work.

→ Coat the Surface of the mould with Some low Surface Energy Coating → Stamp Release Agent.

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

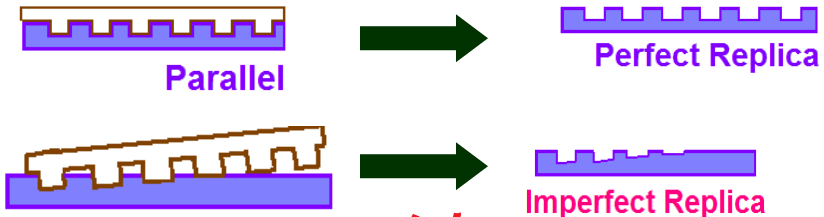
High Pressure

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

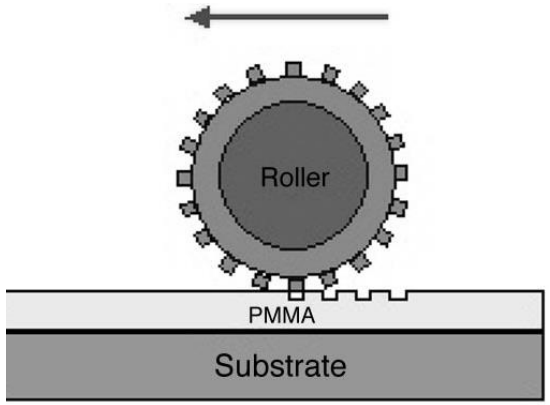
One Limitation of all Lithography Techniques that we discussed so far → All are Batch Process.



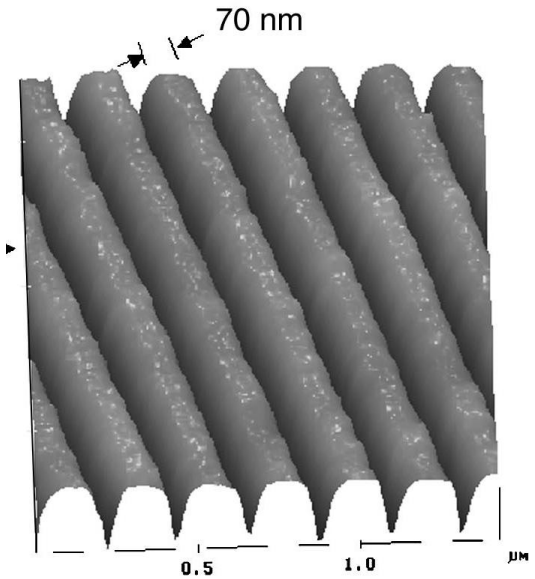
Mold Release agents

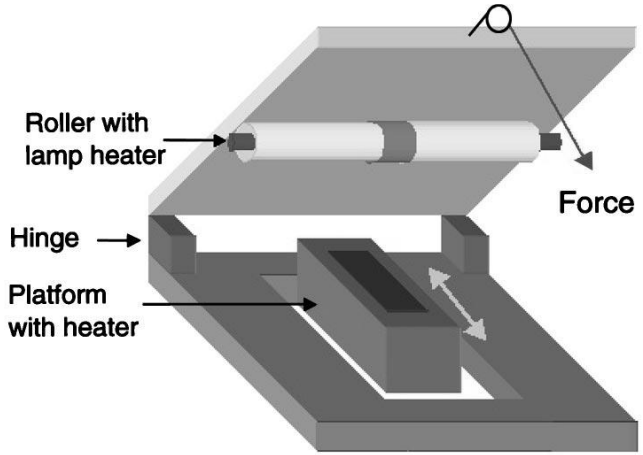
Roller Nano Imprint Lithography

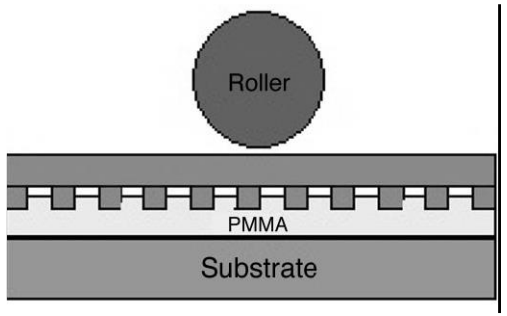
All the configurations discussed so far, make the imprinting group of techniques batch type operation.



(a)







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

Roll-to-Roll Nanoimprint Lithography

Continuous patterning possible.

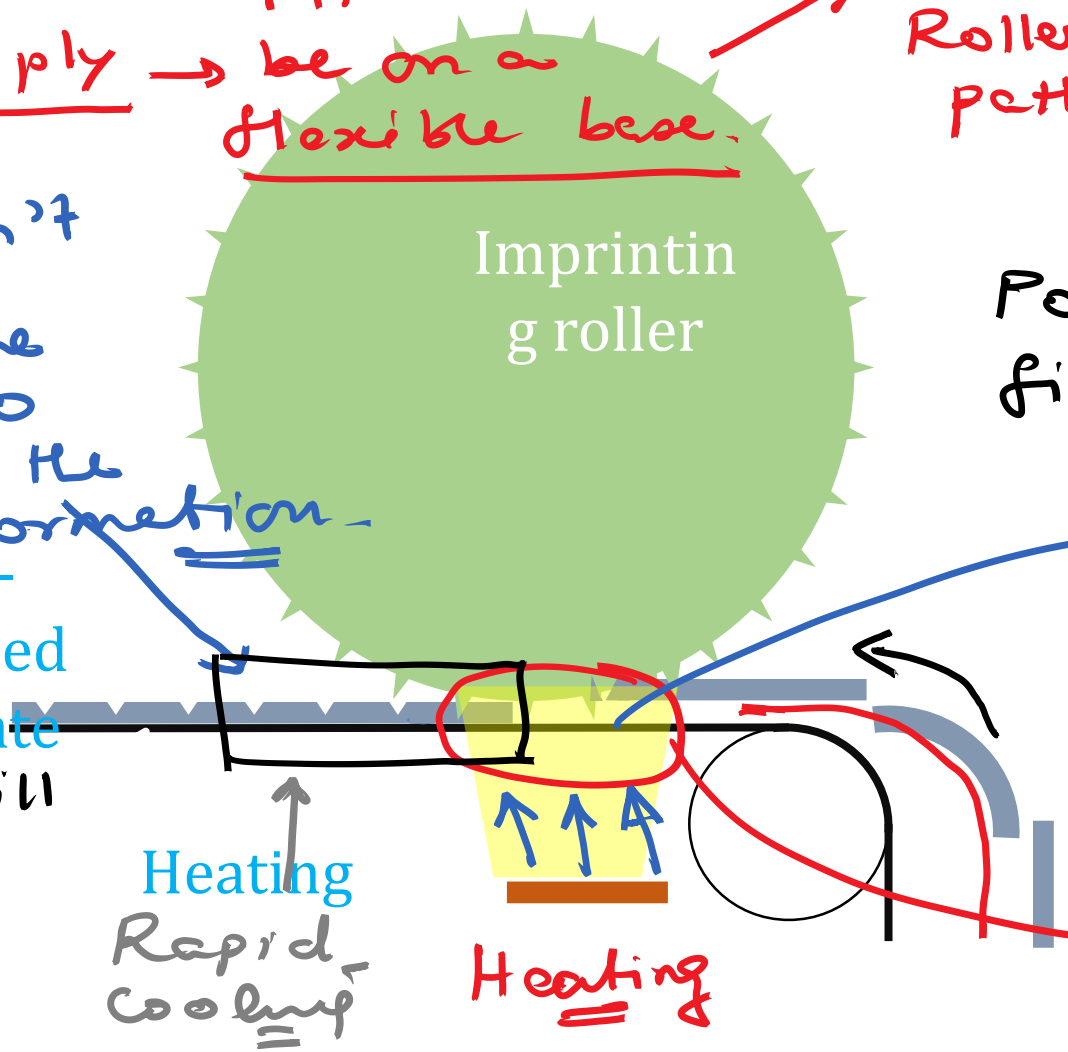
*T&C apply → Film must be on a flexible base.

Surface of the Roller drum to patterned.

*Rate of heating
*Roller speed
*Film Drawup speed
*Rate of Cooling
→ Synchronized.

Possible to have polymer films on a Flexible Base

You don't have the stamp to ensure the deformation.



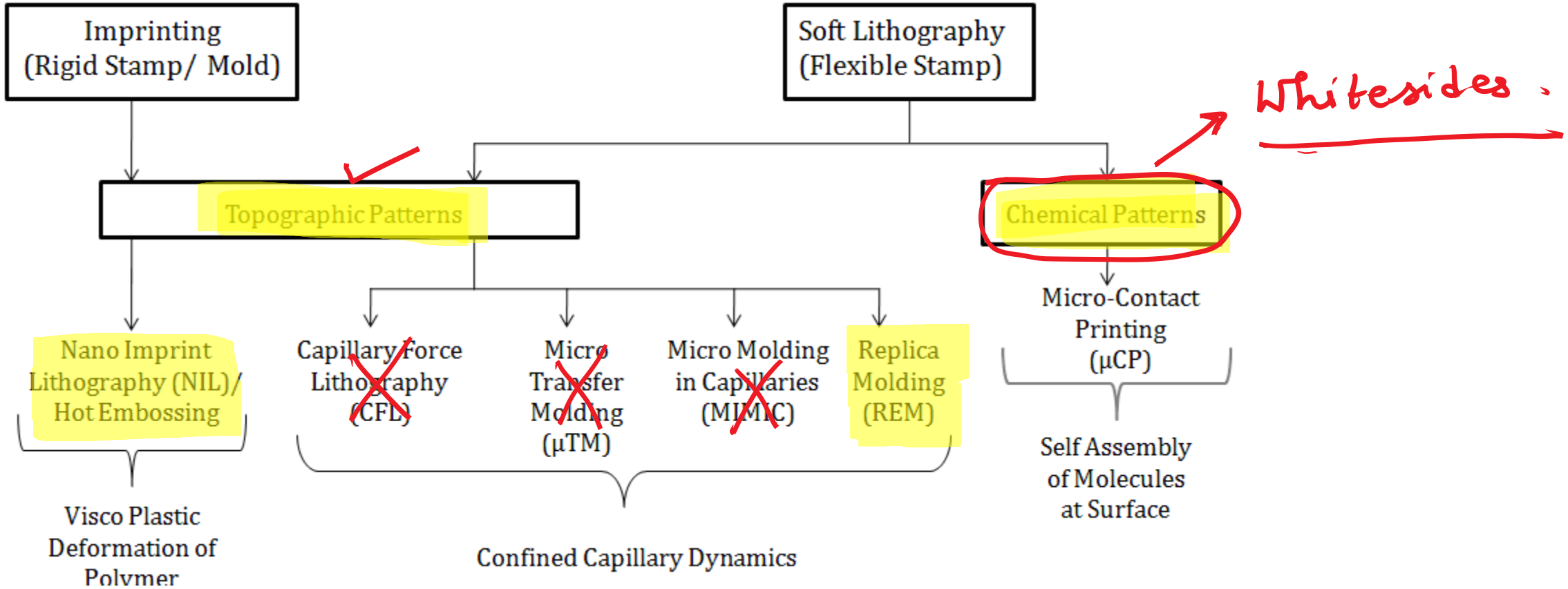
Locally Temp is high. Viscosity is low...

Film will try to flatten

At this location the film becomes soft → So that it can deform

Classification

Soft Lithography



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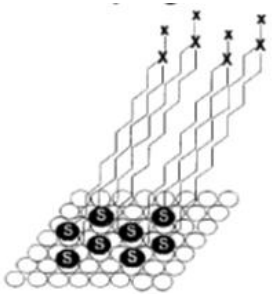
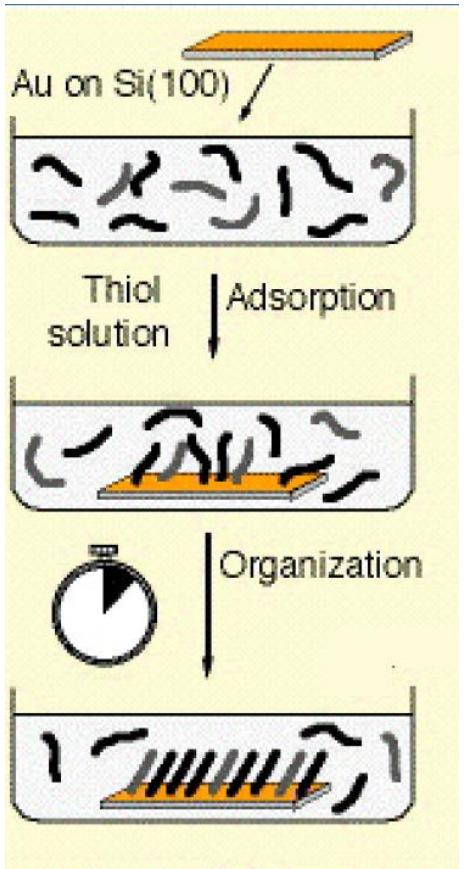
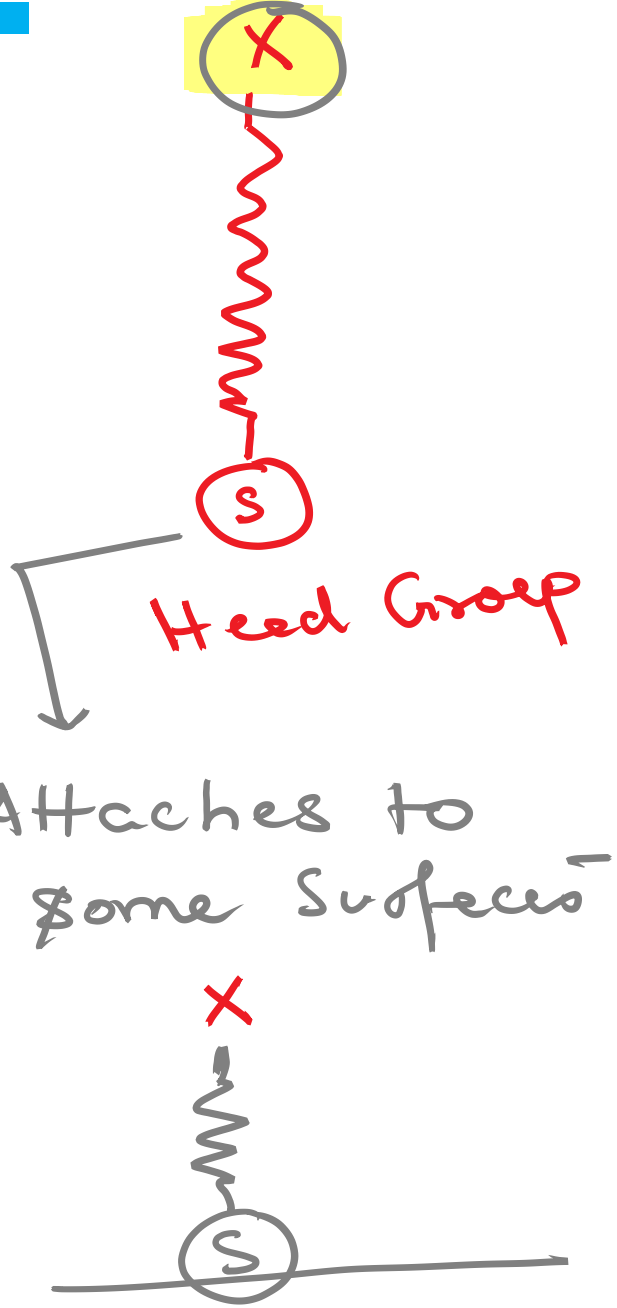
SAM (Self Assembled Monolayer)

- 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.

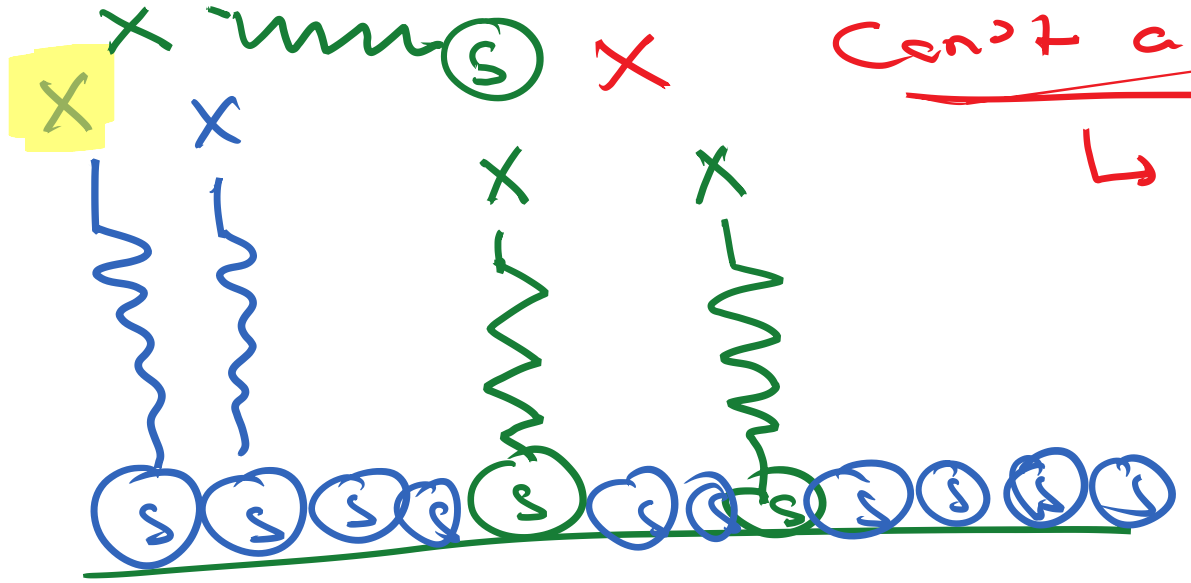


Silane





X → Can be hydrophilic / hydrophobic



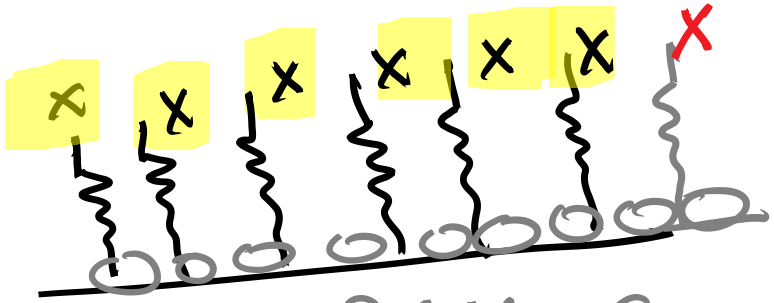
Can't attach here

↳ Can attach only to the surface.

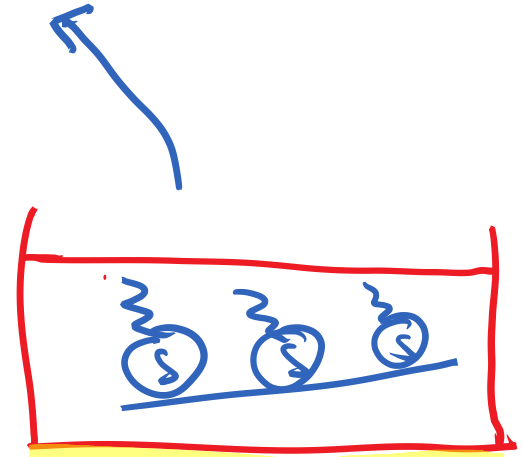
Surface is Covered with a "monolayer" of these molecules.

Self assembled monolayer (SAM)

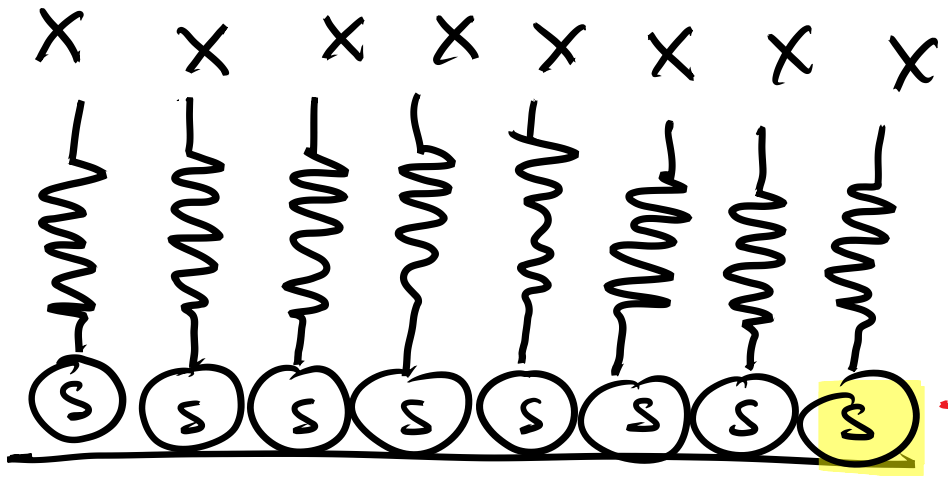
Effective wettability is governed by 'X'



SAM Covered Surface



Dilute Soln. Containing Silene molecule



SAM formation →
Method for modulating wettability.
→ What about Chemical patterns?

Once a Silene molecule gets Stuck (adsorbed) on the Surface → it does not move.

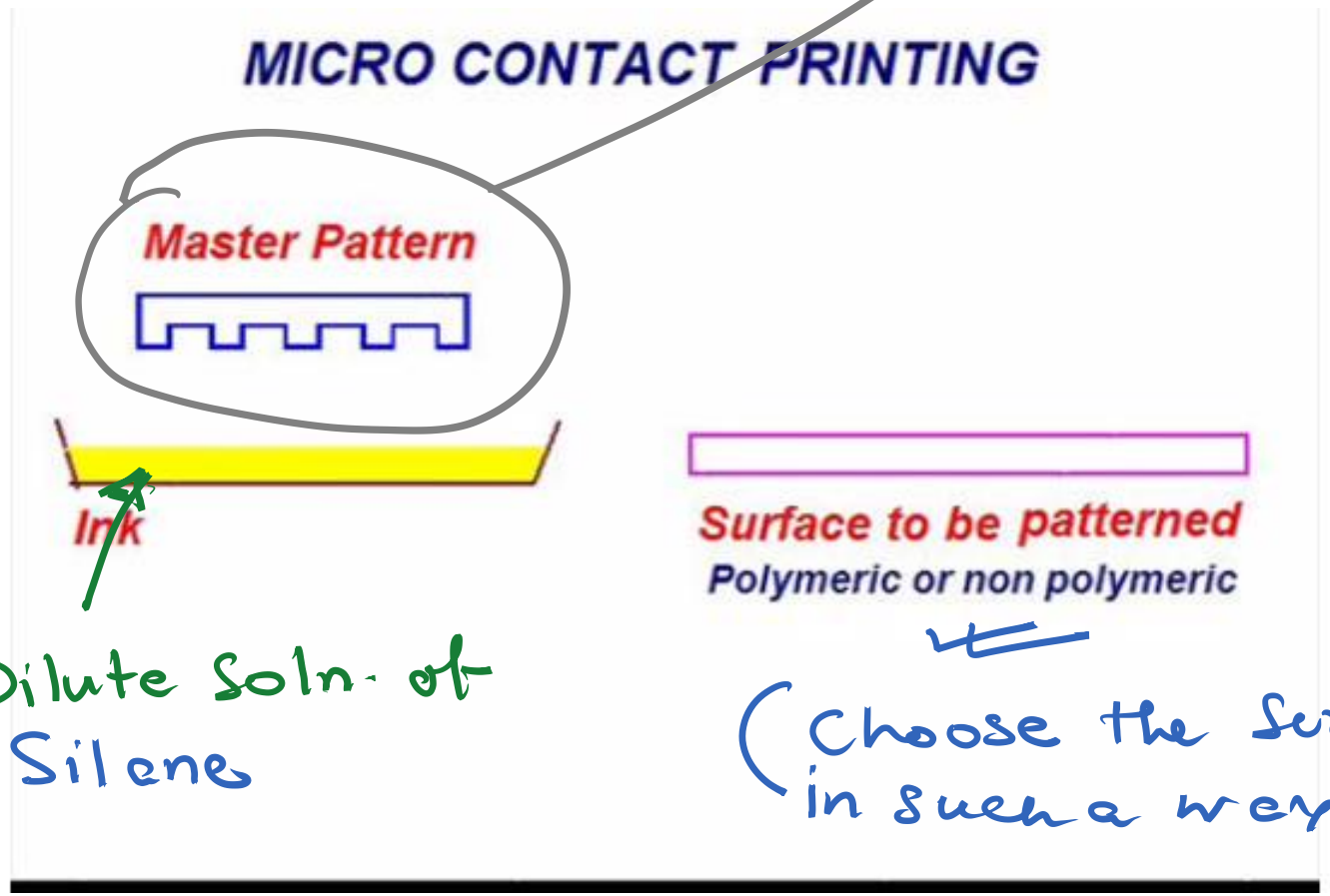
(2) Maximum Coverage
→ Complete monolayer.

(3) Strategy for Controlling the effective Wettability of the Surface.

Can't be used for all Surfaces → Can only be used for Surfaces to which Some Silene attaches.

Micro Contact Printing (μCP)

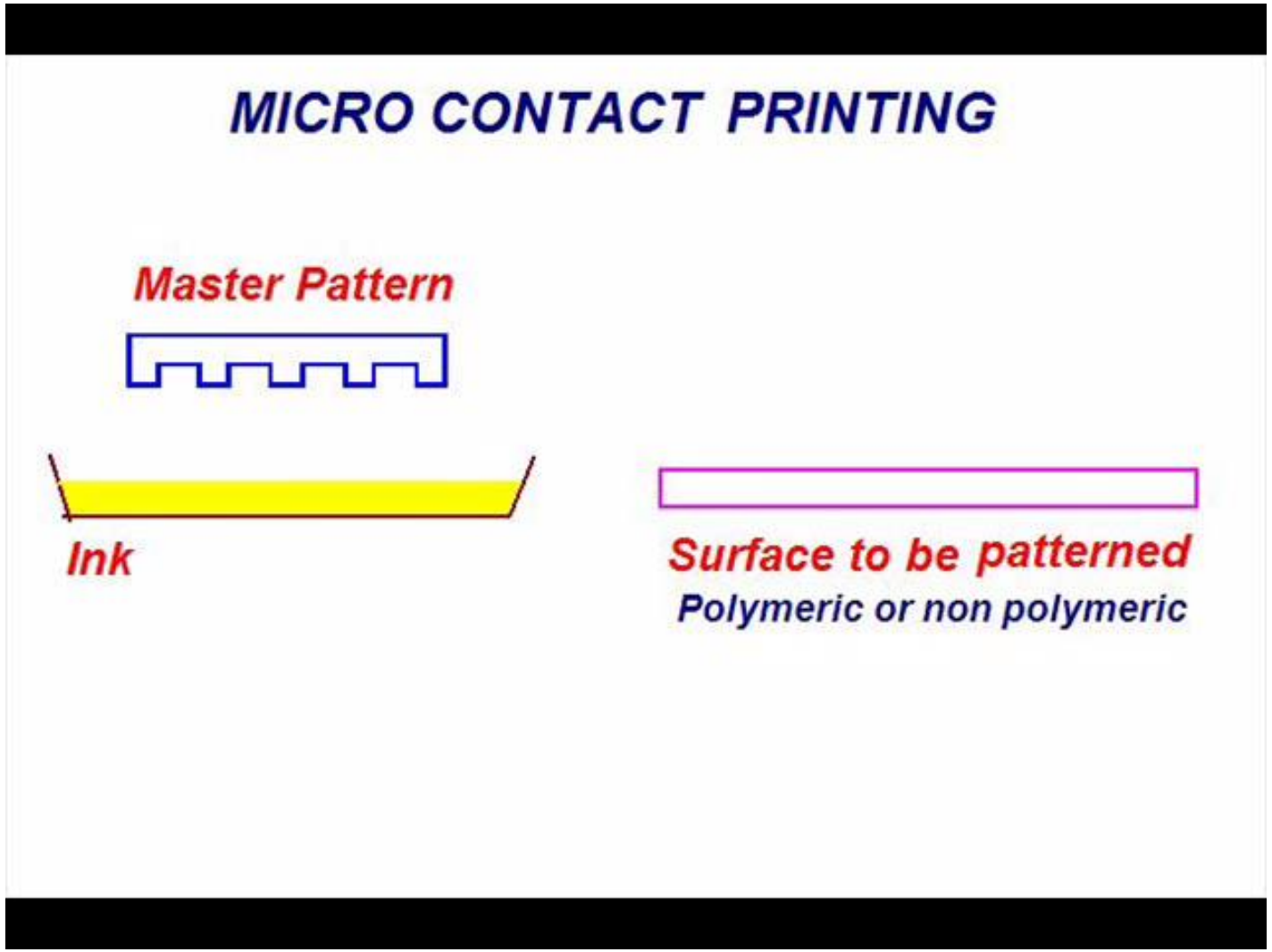
Sylgard Block created by replica molding.



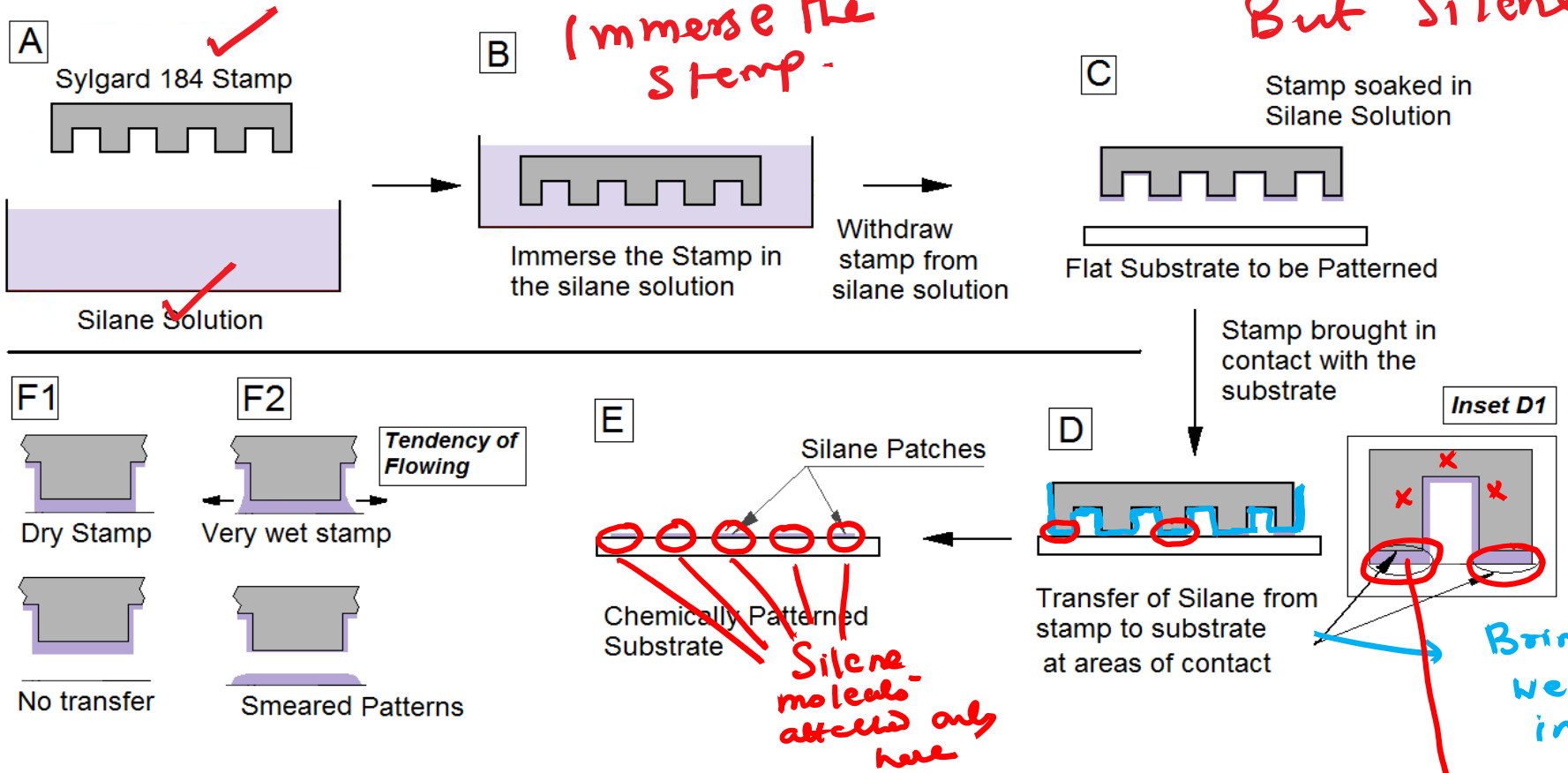
Dilute Soln. of Silene

(Choose the surface in such a way that it has affinity to the Silene molecules.

Micro Contact Printing (μCP)



Micro-contact Printing



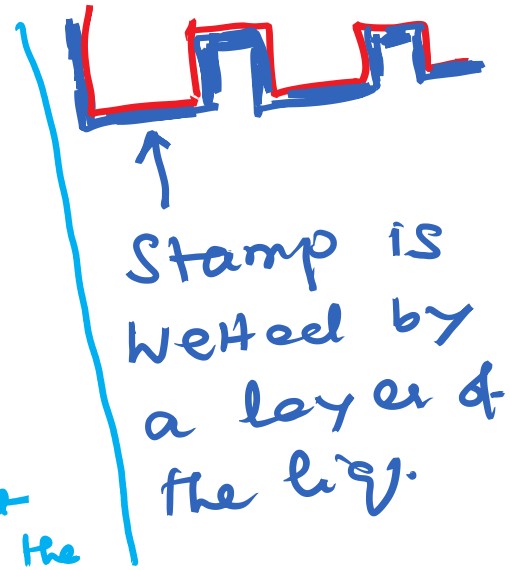
Immerse the stamp.

Stamp is Now wet. But Silane molecule do not have preferential affinity to Sylgard.

Silane molecule attach only here

Bring the wet stamp in contact with the surface to be patterned.

Silane molecule of these areas find a surface to attach to

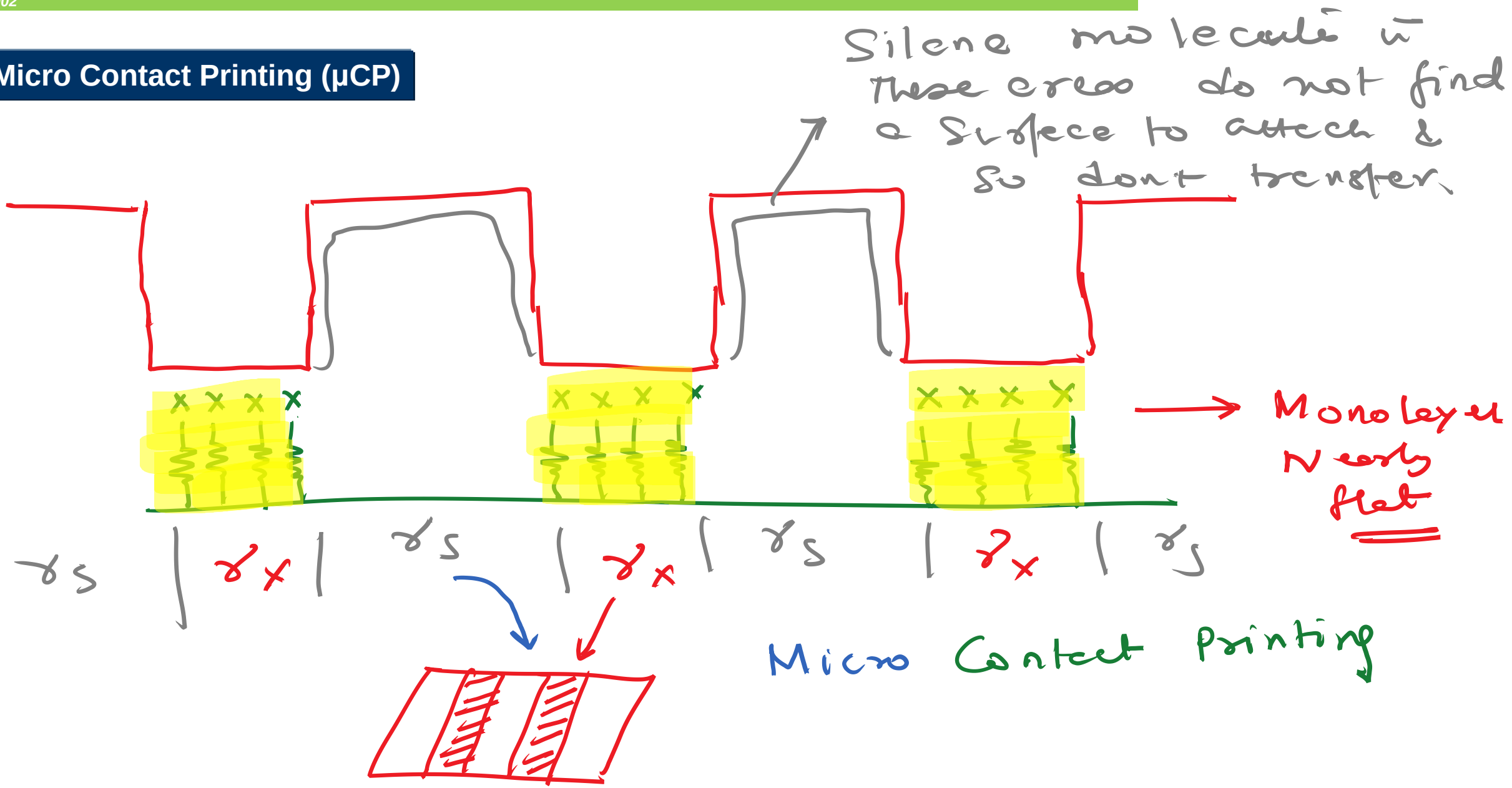


Stamp is wetted by a layer of the liq.

- 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.

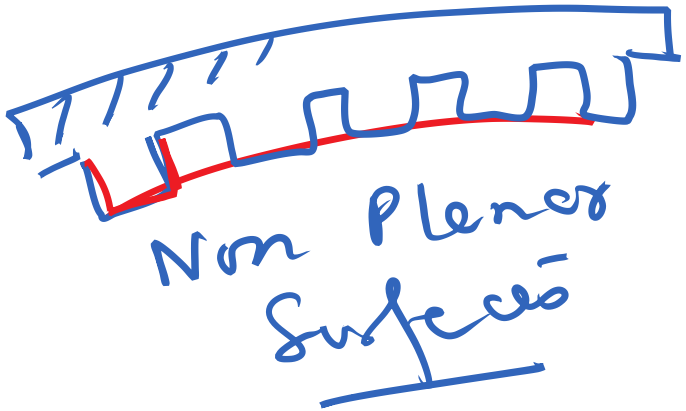
G M Whiteisdes and Amit Kumar, Appl. Phys. Letts., 1993, Science, 1994

Micro Contact Printing (μCP)



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



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Indian Institute of Technology
Kharagpur

Advantages of Soft Lithography

- Generation and replication of three-dimensional topographies 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

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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.

Soft Lithography is a Secondary Patterning Technique, as it can **ONLY** produce a **NEGATIVE** replica of a given stamp or a master.

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