

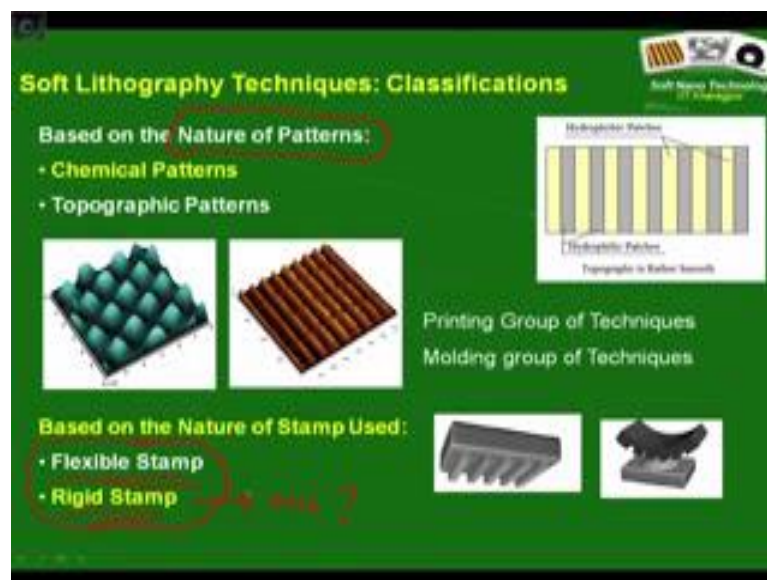
**Soft Nano Technology**  
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**Lecture -19**  
**Soft Lithography – 2**

Welcome back. We continue our discussion on Soft Lithography which we started in the previous class and we already realize that Soft Lithography is a genetic technique for patterning different types of polymers of soft materials and is not limited like photo lithography which can pattern on the photo resist layer.

We also realized one more thing that unlike photo lithography, which refers to a very specific technique. Soft Lithography talks about a suite of methods that are compatible for patterning polymers and soft surfaces. Therefore it is also important to classify and understand the different key techniques that constitute soft lithography.

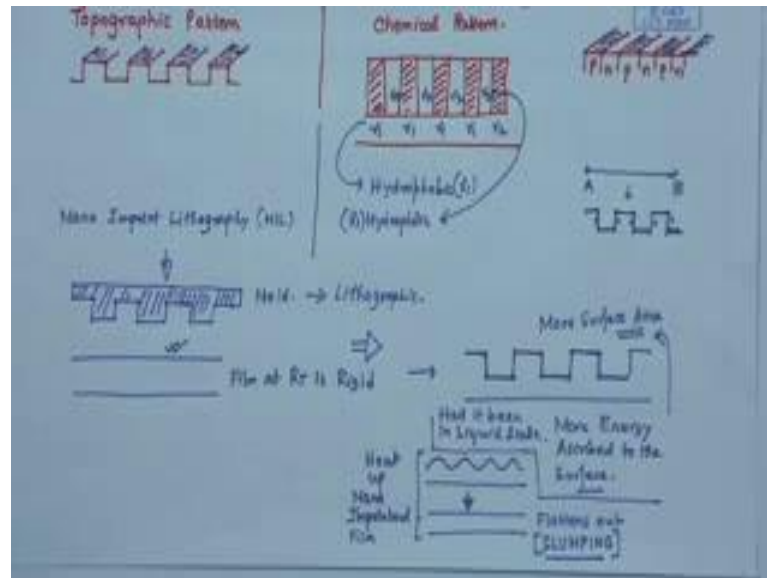
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Classification itself can be a philosophical. So, how would you like to classify? Based on what would you like to classify, these so called Soft Lithography techniques. One of the ways to classify is based on the nature of patterns you would like to create. What is the

nature of patterns? You have seen some regular structure and we are talking about nano and meso scale structures that is obvious, but even from photo lithography you can in fact, take the clue patterns can be primarily of 2 types and those are either a topographic pattern or a chemical pattern.

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In fact, if you recall your discussion, our discussion on photo lithography photo lithography at different stages makes both. Though finally, it makes a chemical pattern because the final product after the doping reaction and etcetera is a flat wafer which has domains of P and n type areas. So, this is in a way a chemical pattern. You must you should be able to appreciate it now it is flat. So, there is no topography, but in a run up to make this as you now understand the method of photolithography, you should be able to recall that at 2 stages photo lithography makes topographic patterns, one is a photo resist layer and then after you have performed the etching one is the pattern barrier layer of the outside layer, so that simply that is a topographic pattern where you have structures like this.

So, Soft Lithography is capable of making both. So, one of the classification and the other thing I must highlight in the context of Soft Lithography a chemical pattern, typically refers to structures on a flat surface with different wet ability areas. So, you

essentially talk about a flat surface, which can be wafer, which can be metal coated glass, metal coated wafer whatever. So, if you look at the line profile with an atomic force microscope surface profilometer it will be flat, but this shaded areas refers to let us say surface energy is  $\gamma_1$  and these areas let us refer to  $\gamma_2$  and it is very common to have let us say  $\gamma_1$  is hydrophobic and  $\gamma_2$  is hydrophilic.

So in the context of photolithography, in the context of Soft Lithography, you may refer to a chemical pattern is a surface which has specially varying domains of with different wet ability areas, particularly let say alternating patches of hydrophobic and hydrophilic domain. Much later when we talk about deviating, you will see that these type of chemically pattern surfaces with alternating patches of hydrophobic and hydrophilic domain are excellent candidates for ordering the instability structure.

So, this is one way of classifying methods that are capable of producing topographic patterns versus metals, which are capable of producing let us say chemical patterns. Another classification approach can be whether and this is a very pretty important one, whether you are using, what is the nature of the stamp? Whether it is a flexible stamp or it is a rigid stamp and I already mentioned that there are certain questions of an asked whether nano imprint lithography, belongs to a Soft Lithography technique or it you would like to categorize it as an embossing technique and say that if I will it is not exactly Soft Lithography and the reason that question is asked is nano imprint lithography in fact, uses a rigid stamp.

It is a rigid stamp we will see what it uses. Unlike most other Soft Lithography techniques which in fact, use as flexible stamp and immediate question to passes flexible stamp will be something like this, immediate question to ask is; what is the material of the flexible stamp? And it turns out that we have already discussed it.

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# Capability of Handling Soft Materials - Generally,  
# Non-Planar Surfaces - Flexible Surfaces,  
# Processing Condition is Gentle.  
# There is NO diffraction limitation.

Stone/  
Mold/  
Master.

PDMS → Poly dimethyl Siloxane  
Inorganic Polymer

(A) Oligomer  
(B) Cross linker,  
Thermally Heated

Sylgard 184  
Cross Linkable  
PDMS<sub>n</sub>

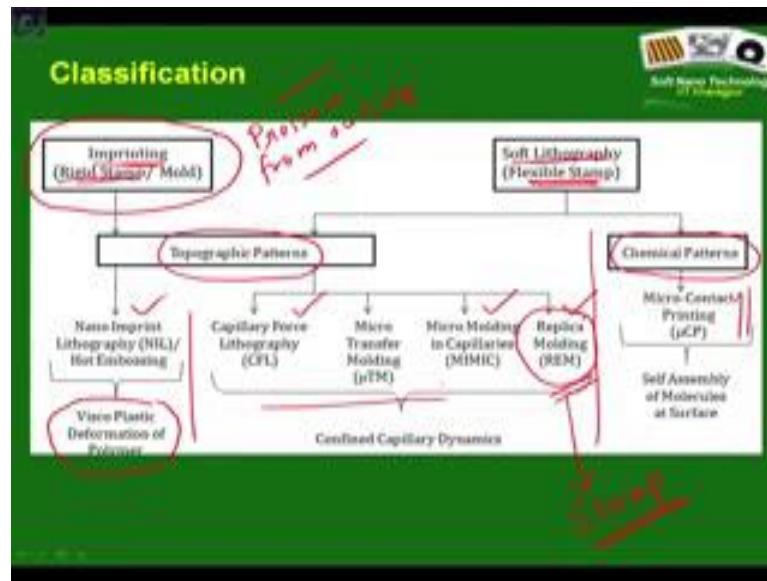
REPLICA MOLDING  
Anneal it  
Toluene  
130°C  
4-6 hrs  
Liquid → Elastic Solid

-C-C-C-C-C-  
-Si-O-Si-O-Si-O-

Yes, this is the most favored material for stamp making. In fact, the simplest technique we will soon talk about it replica molding. This very simple though the original paper was I think published in the journal of nature or science, I think it was published in nature above 20 years back. It actually makes this stamp for other techniques.

So as I said that this is again a philosophical difference or a difference as to what type of a stamp material you are using. Nano imprint lithography let me just spend a minute and when we discuss it with detail you will again see, the reason I consider and many others consider I will to be also a Soft Lithography technique is though it uses a rigid stamp; ultimately it is patterning a soft material. So, it is soft from that stand point if the stamp might be hard, but ultimately it is performing its function on a soft material. And therefore, this is sort of a classification, that I would prefer to use this is what I will be following for the whole of this course.

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So, I include an IL into this group, but I mention that it is actually an imprinting technique rather than classical Soft Lithography technique, which requires a flexible stamp. So, the moment you are imprinting you are bringing in the rigid stamp and then you are actually applying pressure from outside, excess pressure from outside. But none the less you are creating topographic structures which soft materials like polymers. So, therefore, I would consider it here though the exact pattern transfer replication mechanism in fact, is visco plastic deformation of the polymer because you are applying lot of pressure.

So, one of the advantages of Soft Lithography what we mention that it is, it is a very gentle processing condition is in fact not valid for nano imprint lithography. How we saying that it is also a fact that nano imprint lithography is a technique, which on its own merit has gone to the commercial level and instruments are available for performing and implementing nano imprint lithography, it is a very simple technique and very robust and useful technique.

So, anyway the way we will be looking at it is the imprinting best techniques and the classical Soft Lithography, which will which uses the flexible stamp and then again we classify them into 2 broad categories, whether they are capable of creating a topographic

pattern, or a chemical pattern and there is only one major technique that talks about fabrication of chemical patterns we will on that, that is micro contact printing. On the other side for topographic pattern there are various, as I mentioned each one of this methods it is not you can also create chemical patterns by this method, that method and things like that.

Each of the method has certain uniqueness's and that is why I have identified only these 5 methods including nano imprint lithography, because if you understand that their basic operational philosophy you will you sort of understand most of the methods. Of course if you are practicing researcher in this area, you will come across very many different names but you can immediately identify 2 things, how to which method it is closest to and how exactly it is different from the parent method.

So, we will be talking about these methods nano imprint lithography, capillary force lithography, micro molding in capillaries, replica molding this is the first one we will get started because this sort of supplies the stamp for most other Soft Lithography technique. It is so simple that if you have Sylgard 184 at your disposal, you will be trying to do replica molding and you actually do not need lithographically fabricated stamp or anything, you just you can do it on a coin and you can create a very beautiful replica of whatever in curve I mean, whatever is there on the surface of a coin or any hard material one flexible matrix. It is pretty similar to sort of a way one makes a rubber stamp with some advancement and these few methods we will discuss.

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**Soft Lithography Techniques: Classifications**

**Topographic Patterns:**

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

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

- REM (Replica Molding)
- MIMIC (Micro Molding in Capillaries)
- SAMIM (Solvent Assisted Micro Molding)
- CFL (Capillary Force Lithography)

**Chemical Patterns:**

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

Micro Transfer Molding (μTM): 3D structures

So, let us move on. And we have already talked about these classifications this resource will be with you.

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**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.

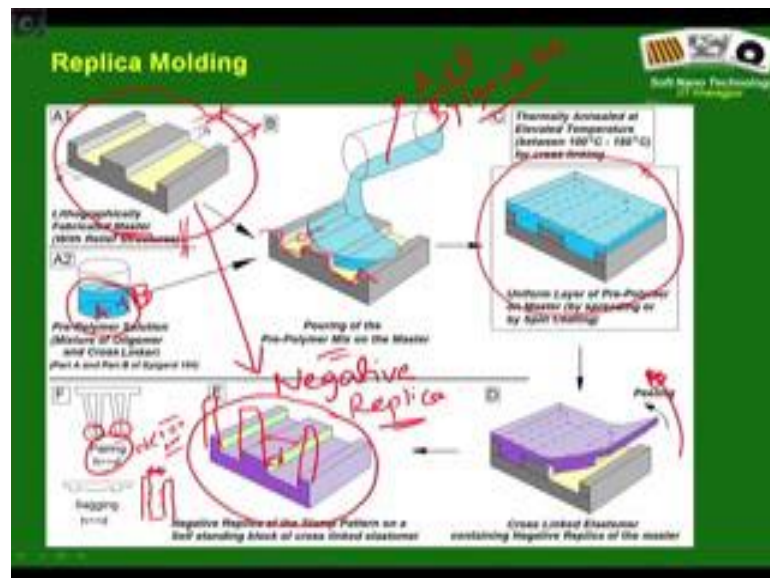
**Sylgard Group of Products from Dow - Corning USA**

So, material for replica molding, is something we have already discussed it is Sylgard 184 and in fact, those of you who have interest in Microfluidics, another very advanced

area where lot of research in worldwide and also in India is actually going on. Microfluidics also many and most of the cases experimental Microfluidic devices are fabricated using Sylgard 184.

So it is a very a popular material now and you already know what is there. So, it has this is a cross linkable material it comes in 2 part. So, this is the part A and this is the part B. All you need to do is you need to mix them, as you mix them it is an a it is an a purely viscous state then you thermally a nil it transform to visco it transform to an elastic state and that elastomer is what you actually want.

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So, this is replica molding in a Naxal. What you need is a lithographically fabricated master with relief structure. This is something you need and this is the master or the mold or whatever you want to say, this is analog us to the mask you need in photo lithography because this is where it contains the original pattern. How do we get this? While you can use either of this forecast and beam or electron beam lithography to creates these masters, but you can also use photolithography it itself to create this master may be a pattern photo resist layer or an h burial layer, you do not go all the way up to the doping and all that, but that it itself serves the purpose of your master.



What are the advantages of Soft Lithography? That is something you will see right now. So, what you do? What is this? This is in fact, at room temperature a freshly prepared mixer of A plus B of pure Sylgard 184. Many people referred this PDMS which correct Sylgard 184 is not pure PDMS, it is cross link PDMS. So, please take care because PDMS is not an elastomer at room temperature PDMS is a liquid. Sylgard 184 is first cross link PDMS that is fine or you can use the commercial name also that is also perfectly understandable, but this is not the only thermo curable elastomer, there are other competing products also available in the market. So, all you do you take a biker you mix requisite proportions of A and B.

In that as you try to mix is a very high viscosity; so this part A is a very high viscosity liquid. So, as you try to mix there will be lot of air bubbles interrupt in the mixer. So, one can do summit of degassing by putting it in a vacuum desiccators or one can just wait for some time for the bubbles too sort of float up and disappear, typically one does a beat of vacuum exposure. So, that the solution is bubble free, simply put it on the this is the original A plus B mixer, people a polymer mix as it is called you Pour, it on the relief structure of the lithographically fabricated master you have. So, this is what you have because of slow dynamics and a liquid forms. So, it will slowly fill up conformally the contours of the stamp it gets completely filled up you take this assemble at this whole.

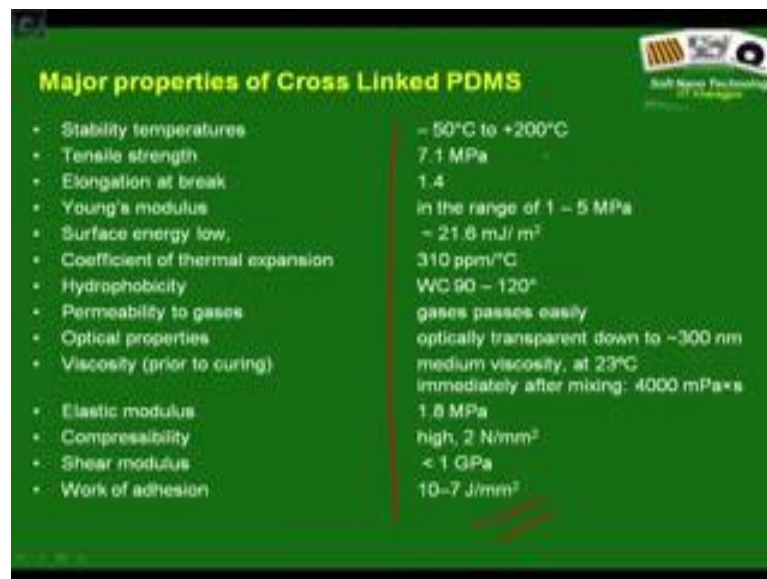
So, you keep the master in a petri dish or something or you take the whole thing and put it in an Owen for curing at let us say 100 to 120 degree centigrade for a requisite duration of time may be four to 6 hours, this cross link now and as it cross link just like a rubber. So, once you take it out you can simply peel it off from one side right and what you have is, you have created not a positive replica, but a negative replica of the original stamp in this Sylgard material or this flexible polymeric material. And this is block of that flexible material, which is used as stamp for most of the Soft Lithography techniques which says that it requires a flexible stamp.

So, other than replica molding almost all other Soft Lithography techniques used a stamp that has been made by replica molding. Interestingly in most cases a replica molding use as a rigid stamp you can do clever twisting of processing conditions by which you can. In fact, use a Sylgard stamp to replica molds Sylgard, but it require certain additional

modifications that is not the most common thing people would do. So that is it, I mean you have already learn one Soft Lithography technique is just sort of molding. What you have done in your childhood only the structure is very small here. What you need to understand is that once you have a stamp let us say which as very narrow dimensions right, there is in principle, no difference, and no restriction, why those small dimensions cannot be replicated on your replica. So, there is it is no longer limited by diffraction of light wave length etcetera nothing like that.

There are certain issues because this material is soft. So, if one tries to make very tall structures these tall structures and particularly if they are very narrow if the periodicity of the line with this very small, they might sort of fuse. They might join up and why do they join up? Well you have 2 tall structures, which are flexible, which are very close to each other remember that 100 nanometer gap we talked about 100 nanometer mark. So, if this separation distance is less than 100 nanometers. There can be some sort of an active Van Der Waals interaction between these 2 and these might lead to fusing. So, these are issues, but these are very critical issues and let us not worry too much about them replica molding works fine with most in most cases. So, let us take to that.

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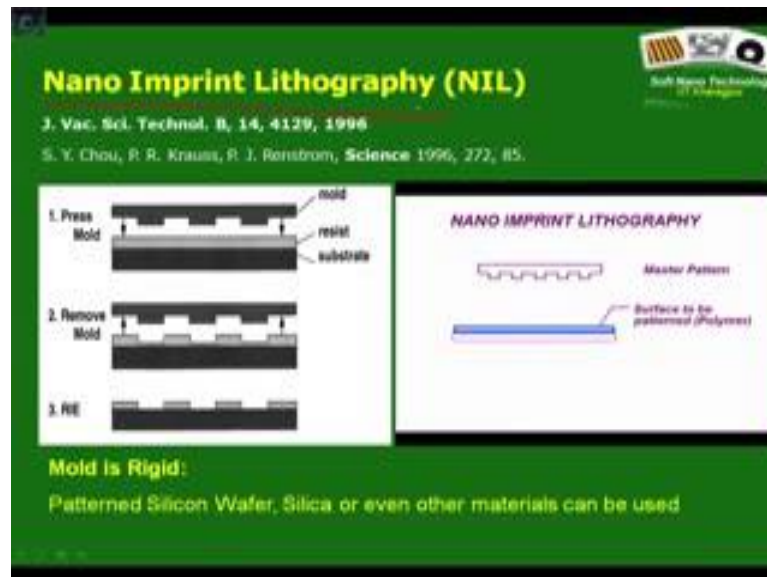


Major properties of Cross Linked PDMS	
• Stability temperatures	- 50°C to +200°C
• Tensile strength	7.1 MPa
• Elongation at break	1.4
• Young's modulus	in the range of 1 – 5 MPa
• Surface energy low,	~ 21.6 mJ/m <sup>2</sup>
• Coefficient of thermal expansion	310 ppm/°C
• Hydrophobicity	WC 90 – 120°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

So, here a certain properties of cross link PDMS and please do not worry about what is

there and what is. So, there is a very good material and that as very good thermal stability which bears compatible etcetera it is transparent. So, that is why it has been it is very popular amongst the people.

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Next what we do is we straight away move on to nano imprint lithography. We talk about NIL first, as I say it is one of the most popular techniques and then we will discuss the other methods. What are the basic requirements? What we require here, is a film which is going to be patterned which is the polymer film we have written and in most cases it is a glassy polymer film.

So, what does it mean? That film at room temperature is rigid. You need a mold as they call. Mold is more of a parabolic term use for NIL, in principle there is no difference this one and a mold if it is made on a rigid material. NIL in its classical form cannot work with a soft reflexible stamp. So, you have a mold, typically this is made by some lithographic technique which is fine. All you need to do is you are going to emboss this mold against the film, but at if you try to do that at room temperature as I already mentioned that the film is rigid.

So, it is not going to work out right, but now you have one unique advantage the

polymers have and that to take advantage of the fact that, if you heat up the polymer beyond its glass transition temperature it becomes soft it behaves like a liquid and any soft material you can deform right. So, that is exactly what is done this is a cartoon, it should ideally capture their basic essence of NIL. So, these are the hardware elements what we have is you have a rigid master you have a film and see what we do.

So, first step is you simply heat up the film beyond its glass transition temperature. So, that it is now soft. Then you simply bring in the stamp press it that is where the term imprinting comes in, nano imprint lithography. Apply adequate pressure that something that is not written over here and then what you do is you simply cool down the film while the stamp or the mold is in contact. So, what would happen? What would happen is the structures will sort of freeze because as you cool down the viscosity again goes up and then once it is cool down, you simply remove the original mold and you get a negative replica of the patterns that are there on your mold on the surface of the film. It is a very simple technique and it is a very robust technique.

The structures are predictable because of the simple fact that they are deformed. So, these deform surface in fact one thing should click in your mind is since the surface is deformed, as compared to a flat surface, there is now more surface area and this leads to more energy ascribed to the surface and yes you actually needed to apply the external pressure to create this additional surface area. So, this whole process is not something that is in the direction of a natural thermodynamic process. You are applying extra energy to create this negative replica and at this film been in a liquid form, there would have been some flow. From zones of what again you know from zones of higher Laplace pressure to zones of lower Laplace pressure right.

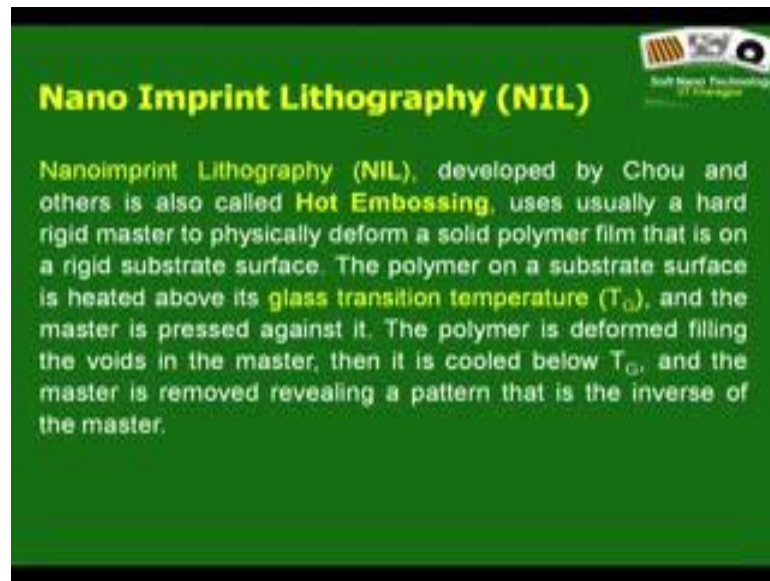
And eventually had it been a liquid please follow this carefully. Had it been in liquid state what would have happened is eventually these patterns would have flattened out. In fact, if you heat up a nano imprinted film once the patterning is achieved it flattens out. So, if you heat up if you are interested in creating a pattern surface person application you will not be doing it, but if you are interested in the fundamental science you sometimes do crazy things which might even lead today structure of the structures.

So if you heat up nano imprinted film it flattens out and this phenomenon is entirely driven by surface tension because for a film a flat surface profile corresponds to the minimum energy configuration. So, this is also important. We always know that minimum energy configuration corresponds to a hemispherical shape that is for a drop, but if you have a film if you have enough material that it actually form a film then in fact a flat surface corresponds to the minimum energy configuration is simply this consideration that between 2 points, the minimum distance is if you join them straight away. So, it is exactly like that.

So, what you have done is, it was flat initially like here you have patterned it and therefore, you have enhanced the surface area. So, all these areas in fact, you have enhanced. So, that is why you need the pressure which create this surface, but if you sort of reheat this film, it now realizes that it is not in its lowest surface energy configuration therefore, it simply tries to flatten out due to what is known as slumping. But the advantage is you are cooling down the film while it is in a liquid state it is adhering conformally to the stamp and therefore, it creates a negative replica. If you are using a polymer which has a reasonably high TG let us say 100 degree centigrade and you are down to room temperature of course, you will understand soon may be in the next class that these structures contain a lot of residual stresses, but the structures are permanent and they serve your purpose. So, this is what nano imprint lithography is; we discussed a bit of critical issues, I must admit.

So, let me just quickly repeat this particular video again. So, you take a polymer film, a glassy polymer film heat it up beyond its glass transition temperature. So, it becomes in the soft stage bringing the stamp rigid stamp press it hard, cool down while the stamp is in contact with the film, the pattern is formed. Then you withdraw the stamp. It is easier said than done there are several issues that we will soon realize which are very practical issues.

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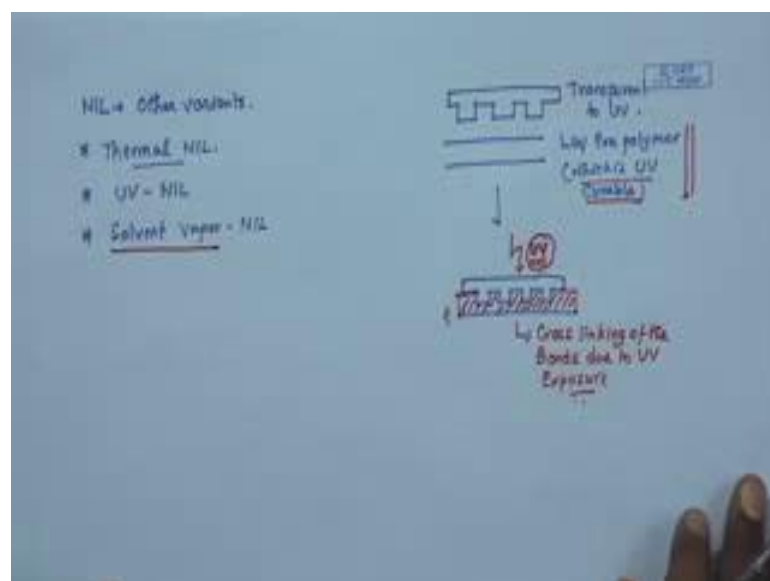


**Nano Imprint Lithography (NIL)**

Nanoimprint Lithography (NIL), developed by Chou and others is also called **Hot Embossing**, uses usually a hard rigid master to physically deform a solid polymer film that is on a rigid substrate surface. The polymer on a substrate surface is heated above its **glass transition temperature ( $T_g$ )**, and the master is pressed against it. The polymer is deformed filling the voids in the master, then it is cooled below  $T_g$ , and the master is removed revealing a pattern that is the inverse of the master.

So, this is nano imprint lithography, it is also called hot embossing at times. So, it take advantage of this, this is the nano imprint lithography in the most common form, the classical form the thermal NIL as it is called because you use temperature to heat up the film beyond it is  $t_g$  there are other variance of NIL.

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NIL = other variants:

- \* Thermal NIL
- \* UV-NIL
- \* Solvent Vapor-NIL

Diagram illustrating the UV-NIL process:

Top: Master with pattern + Polymer layer on substrate. Labels: "Transfer to UV", "Low flow polymer", "Curing UV", "Transfer".

Bottom: Patterned polymer on substrate. Label: "Cross linking of the Bonds due to UV Exposure".

So, what we discussed the most classical one is the thermal NIL. You can also have an UV NIL and each one as it is own advantages. I will not spent too much time on this because thermal NIL is the most popular one. Solvent vapor or SV NIL, UV NIL what we do is very simple you take a liquid free polymer, which is UV curable and take a rigid stamp again, but this has to be transparent to UV.

Next step is you emboss it again this free polymer, but since the free polymer is at liquid at room temperature no thermal cycling is required and how do you make the patterns permanent this is UV curable. So, once you have embossed then shine UV from the top, your mold is UV transparent. So, this pattern frees now. There is in fact, physical cross link of the bonds due to UV exposure and it becomes like a solid after UV exposure.

So, this is UV NIL there are advantages one of the advantages is there is no requirement of a thermal cycling, what is? There are issues that we will discuss in the next class because I am running out of time in this particular class, of course the movement you talk about thermal cycling there are issues like mismatch in the coefficient of thermal expansion. So, that problem is not there you do not need the heating set up, but then it becomes limited again to very specific class of polymers or materials that are UV curable rather similar to the photo resist not exactly photo resist, but something that response to UV in contrast glassy polymers are much more general much more generic. So, you can handle a host of glassy polymers by the thermal NIL. In fact, solvent vapor NIL is sort of a good compromise between both of them and I think I will discuss it in the next class.

So, I will stop now and next class also I will continue with some of the aspects critical aspects of nano imprint lithography.

Thank you.