Instability & Pattering of Thin Polymer Films

Prof. R. Mukherjee

Department of Chemical Engineering

Indian Institute of Technology, Kharagpur

Lecture No. # 16

Soft Lithography – 1

Having completed discussion on photolithography as well as on Nano imprint lithography to a significant extent, we now move on to the most specific polymer specific pattering techniques or which is very, very popular and gaining property with every passing year or passing month may be, that is the generic group of soft lithography techniques.

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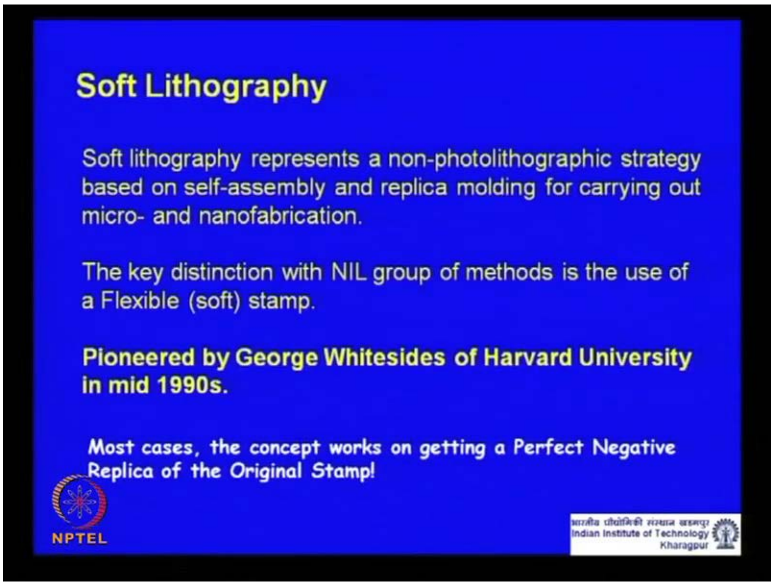

Soft Lithography

Soft lithography represents a non-photolithographic strategy based on self-assembly and replica molding for carrying out micro- and nanofabrication.

The key distinction with NIL group of methods is the use of a Flexible (soft) stamp.

Pioneered by George Whitesides of Harvard University in mid 1990s.

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

So, soft lithography represents a non photolithographic strategy based on self assembly and replica molding for carrying out micro and nanofabrication. As I told in the previous class that quite sides himself who is the sort of inventor of most of the soft lithography techniques along with his illustrious gradual student Y Zia himself regards that Nano imprint lithography can also be included as a soft lithography method, but in the classical form still if you look at the relevant literature, many times you will find that (( )) people prefer to sort of keep as separate entity.

So, you will typically find that people are talking about photolithography as a generic platform, Nano imprint lithography or embossing as a generic platform and soft lithography as on other generic platform. Though, we will see very shortly that in soft lithography itself, you can actually have two specific types of structures which can be created that itself will be partially interesting to you because,, most of the pattering structures, pattering of structures we are talking so far is we are talking of methods for creating topographic structures.

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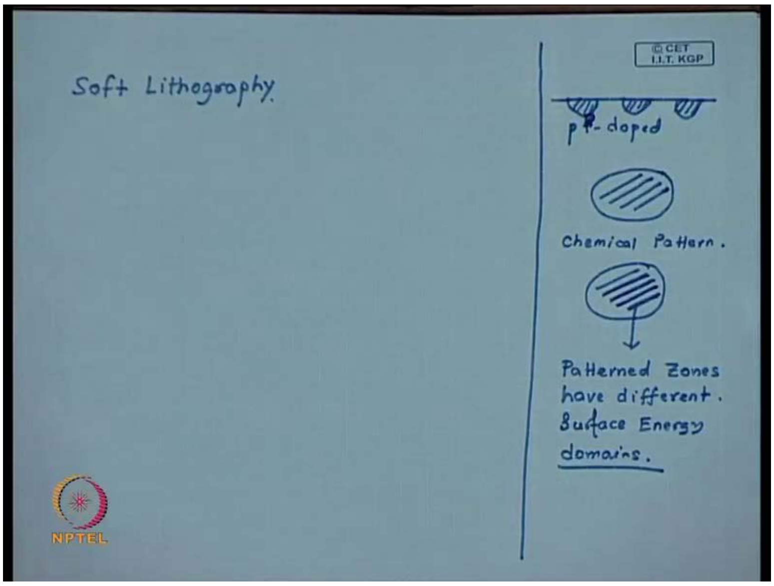

Soft Lithography

But, by soft lithography, it becomes possible to sort of create chemical patterns so chemically patterned reasons. So, you might wonder what that is, but in a way you should be should have an idea about what sort of chemical what a chemical patterned, chemically patterned substrate may mean or may look like because finally, if you remember by your photolithography, by the method of photolithography, you had actually created structures within silicon vapor let us say which was p type doped you have created n type domains.

So, this is also… So, if you look at it even microscopically it is perfectly flat, but electronically you have distant domains or due distant chemical domains or you have different domains each with where the domains have different doping properties in case of a silicon. But typically, a chemical pattern would mean similar topographic feature less domains, but in most cases it implies that these imprinted or patterned zones have different surface energy domains.

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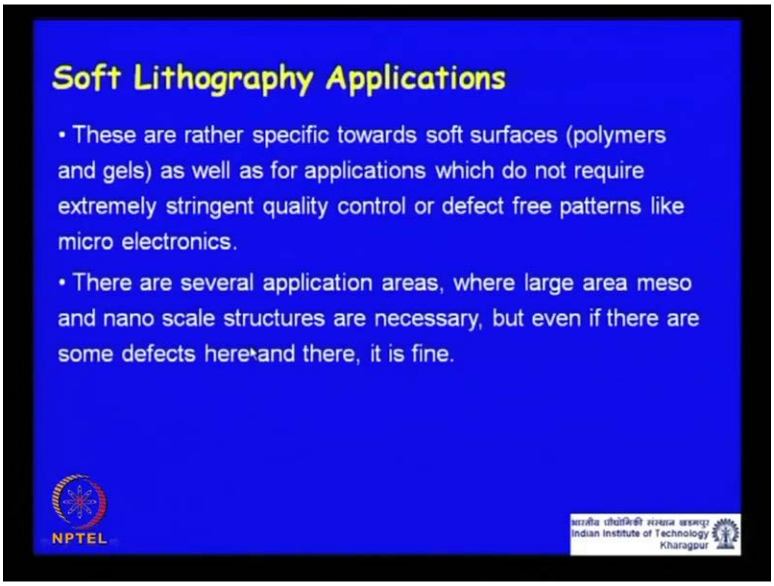

Soft Lithography Applications

- 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.

And, it becomes possible to create such domains by soft lithography. So, soft lithography essentially was pioneered by George Whitesides group in Harvard in mid 90s and these are rather specific towards soft surfaces, polymers and gels as well as, for application which do not require extremely stringent quality control or the requirement of defect free patterns is not as high as that is in micro electronics. We had talked about this as when we completed photolithography and started talking about Nano imprint lithography. But essentially, we are now talking of application areas which requires pattern surfaces, but the fidelity requirement, the critical dimensional tolerance, the sort of number of defects per millions of structures etcetera. The requirement is not as high as you would require in fabricating in IC cheap or micro electronics manufacturing, where one defect is going to spoil the functionality of may be your entire cheap or device.

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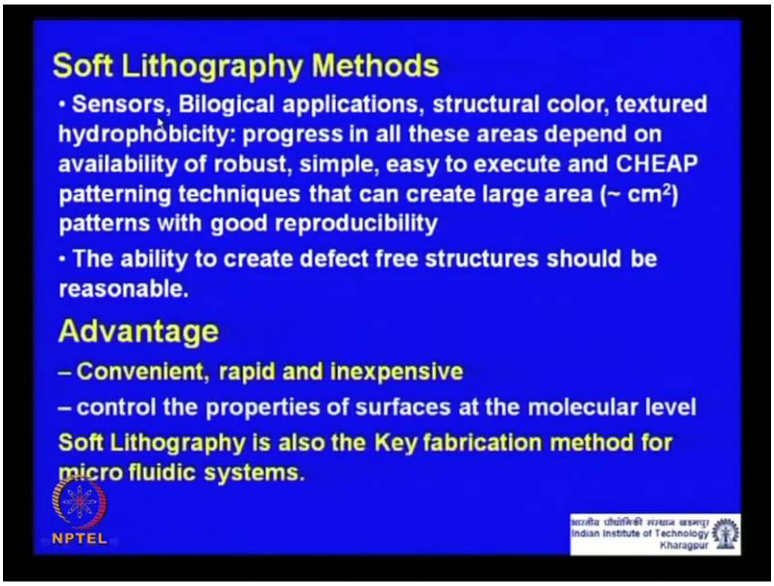

Soft Lithography Methods

- 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.

Advantage

– Convenient, rapid and inexpensive

– control the properties of surfaces at the molecular level

Soft Lithography is also the Key fabrication method for micro fluidic systems.

There are several application areas where you require large area meso and nano scale structures; for example, sensors, biological applications, structural color, textured hydrophobicity of textured hydrophobicity the progress in all these areas depend on availability of robust, simple, easy to execute and most importantly, cheap patterning techniques that can create large area spanning over a few centimeters square may be in some application with good reproducibility. And if you now remember, the first couple of lectures of this course, we did spend on giving some examples like structural color, structural hydrophobicity we talked about casi and vengels states.

So here, where the relevant of the course is initial slides or initial couple of classes, I introduced where patterned surface sort of finds application and then, what was not known to you was how this structures have to be made or can be made and in turns out that in many cases, the fabrication technique itself is non trivial which sort of makes this subject pretty exciting and pretty relevant. So, in these are the techniques; Nano imprint lithography of course is one such technique by which you can make such structures.

So, these structure let us say you want to make a self feeling surfaces or a structural color for some application and if you really want to sort of use photolithography, it is going to be prohibitably expansive. So, these are the methods particularly the soft lithography group of techniques which sort of find extensive application in those fabricating pattern surfaces necessary for these settings.

So, the bottom line is the ability to create defect free structures should be reasonable. Advantage is convenient; it is advantage of soft lithography and you can also include that, it can be regarded as the advantage of alternate lithography techniques or nano photo lithographic pattering techniques. That advantage can be convenient, rapid and inexpensive. Control the properties of surfaces at the molecular level which is also very, very important, very exciting also and we will see that, that you can sort of control properties at molecular level, and another very advance branch of engineering and which is sort of now as a significant presents is in bio also and bio technology and other biological areas that is micro fluidics. And micro soft lithography is one of the key fabrication method for micro fluidic devices and systems because of its convenience and also because of some historic origin because, one of the pioneers of micro fluidics Harvard stone Princeton did his post doctoral studies with George Whitesides sort of who is the pioneer of soft lithography.

So in many ways, the emergence of experimental micro fluidics is largely sort of attributed or dependent in sort of ability to fabricate micro and meso scale patterns in soft material like polymers and therefore, soft lithography a just the way sort of photolithography sort of mandatory. Even today for fabricating IC components or microelectronic devices, it is almost imperative that most of the micro fluidic devices and systems are fabricated by soft lithography techniques, which again is a huge application area and huge application of soft lithography itself.

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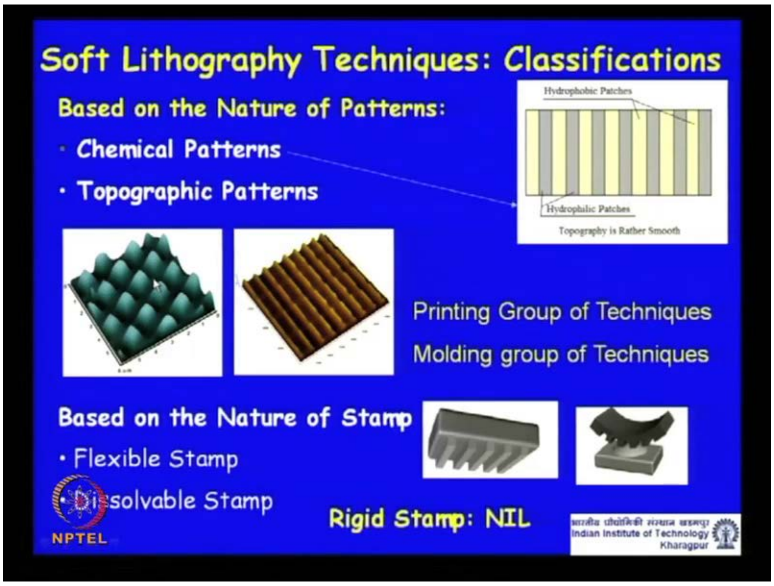

Soft Lithography Techniques: Classifications

Based on the Nature of Patterns:

- Chemical Patterns
- Topographic Patterns

Printing Group of Techniques

Molding group of Techniques

Based on the Nature of Stamp

- Flexible Stamp
- Dissolvable Stamp

Rigid Stamp: NIL

So, we just briefly talked about this already classification of the soft lithography techniques. So, this is for the first time you know introduce unlike in nano imprint lithography where essentially patterning always implied that, we are going to create topographically patterns structures. In soft lithography, you can depending on the method you are adopting, you can either have a chemically patterned structure or at topographically pattern structures.

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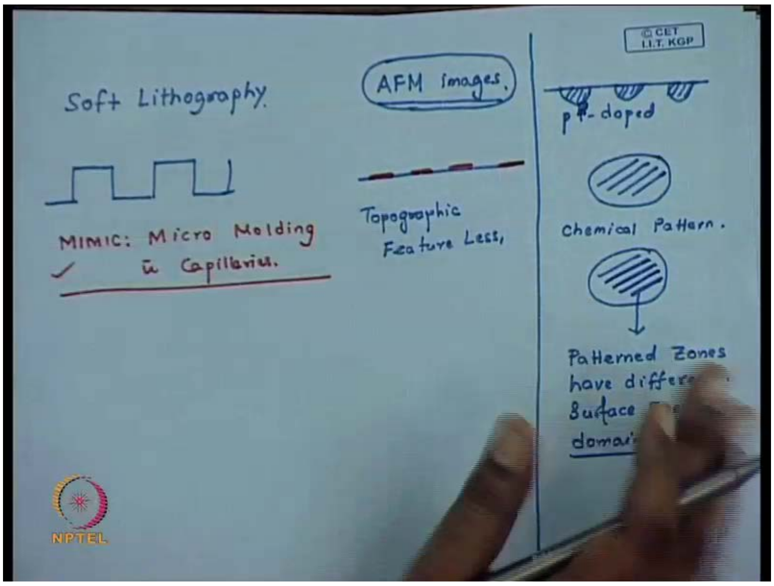

So, you all understand what is a topographically pattern structure by now. So, it can be relief getting like this or a some structure like in one of these two. By the way, I mean these images you might be seen pretty routinely now. These are I think I mentioned in one of the previous classes that, these are atomic force micro scope images or a m f images, which is again very, very advanced instrument for visualizing and analyzing micro nano and meso scale structures, and once may be planning of our next three or four classes, we complete our discussion on soft lithography and flow related aspects or related to nano imprint lithography and soft lithography. We will sort of have a detailed discussion on, how an atomic force micro scope works and you can create structures.

That also is very very interesting science is involve there, and I am sure you will learn lot of new thinks also. But coming back soft lithography; so here, based on the you can classify the soft lithography techniques based on the type of structures you are making. So, you can hither make chemical patterns which this gives an idea. So, it is ideally even after pattering, it is a topographic featureless this is important, but it has domains let us say alternate hydrophilic and hydrophobic domains.

In contrast topographic structure off course you know what it is. So, the techniques that lead to topographic structures by the soft lithography techniques that lead to topographic structures they are typically result; typically termed as the molding group of techniques. Today’s class, we are going to focus more on the molding group of techniques with specific discussion on one such of the most important such method that is mimic which is acronym of micro molding in capillaries. But if you are talking of implementing soft lithography based methods for creating chemically pattern surface, they are mostly classified or they are generically referred as the printing group of techniques.

Based on the nature of stamp well you do not really distinguished the technique based on the nature of stamp, but in principal remember, this is the key difference you have between a soft lithography technique and nano imprint lithography. In classical nano imprint lithography, you typically use a rigid stamp. A soft lithography most soft lithography methods including mimic and other methods we are going to discuss or talk about in where lively rely or in the classical form, they rely on flexible stamps.

Of course, there are some methods in which flexible as well as dissolvable stamps have also been implemented. This is a very new concept where, if you can sort of make stamps in a in a dissolvable polymer; let us say at a at a very low cost then, after you sort of achieve your imprinting, you do not want to sort of getting to the hassle of the stamp detachment which we talked in the contrast of nano imprint lithograph. And, we sort of talk about you have to use anti adhesion agents and think like that to sort of ensure a clean detachment. The concept is that once your pattering is over, you just wash it in a flowing steam of water or in solvent which does not affect your structure, but can sort of dissolve the stamp away.

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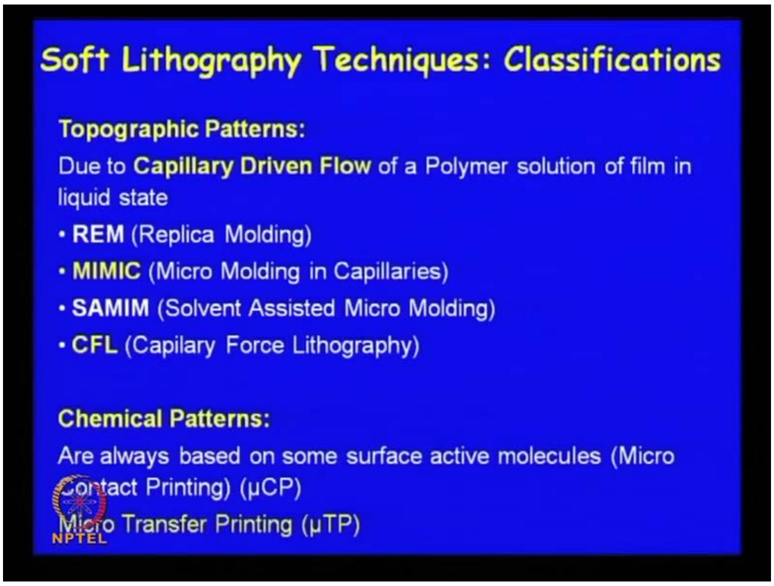

Soft Lithography Techniques: Classifications

Topographic Patterns:

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** (Capilary Force Lithography)

Chemical Patterns:

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

Micro Transfer Printing (μTP)

This is another new concept and I think I will give you some examples towards the end of the discussion. So, topographic patterns typically these are as we have mentioned these are the molding group of techniques. Typically, the pattern transfer or pattern replication is achieved by capillary driven flow of a polymer solution in liquid state. So, you might be noting down the differences of soft lithography or the molding group of techniques in comparison to nano imprint lithography. So the first difference is that, the stamp used in n I l was a rigid stamp in case in contrast to that here, we use a flexible stamp. I am… I will just come to what sort of a material you use for creating this flexible stamp.

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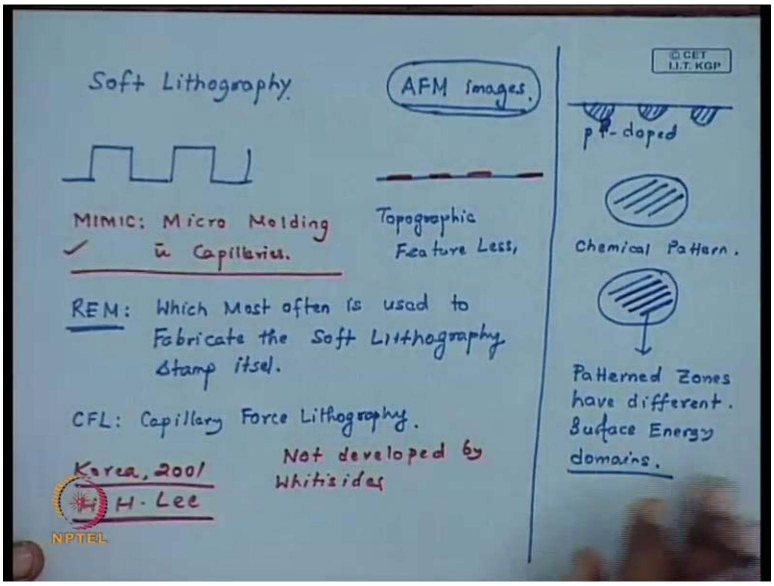

Soft Lithography

AFM images.

MIMIC: Micro Molding in Capillaries.

Topographic Feature Less,

REM: Which Most often is used to Fabricate the Soft Lithography Stamp itself.

CFL: Capillary Force Lithography.

Korea, 2001 H. Lee

Not developed by Whitesides

Chemical Pattern.

Patterned Zones have different. Surface Energy domains.

The second and the most important thing in terms of the pattern replication mechanism is that in you are in n I l you sort of relayed on viscose plastic deformation of a molten resist layer or a molten polymer film with the application of an external pressure. In contrast in soft lithography, you are talking about pattern replication by capillary driven flow of a polymer solution. So, the major molding group of techniques which result in topographically pattern surfaces they include REM or the replica molding which is the simplest one and though, this itself is a patterning technique, it is worth remembering that replica molding is actually the technique which most often is used to fabricate the soft lithography stamp itself.

But, replica molding for all practical purpose is also though, it is a very, very simple concept the moment we discuss it we will see that, but you will find that replica molding itself is it is a very simple method, but still it is a it is a integral member of the soft lithography families in terms of patterning or creation of meso scale structure. Then of course, we will be talking about mimic which I have just this briefly mentioned already which is micro molding in capillaries.

An extension of MIMIC to some extent is the method of SAMIM which is solvent assisted micro molding and finally, another very important class of technique which I much say that this is now a significant; now a strong member of the soft lithography group of families. But it is worth remembering the CFL or capillary force lithography is the only measure soft lithography technique that was not developed by the pioneer not developed by Whitesides group, and this was developed in Korea around 2001 by H H Lee group and other person who was very significant contribution in soft lithography; I mean, many of the methods though where they were initially sort of discovered by Whitesides and his group Hong lee as sort of exploited them or sort of extended them for various super functional applications.

But in addition to that, CFL I would say is very strong contribution from Hong lee group in the entire area of the of soft lithographical pattering. Chemical pattern or the printing modes the most important method in this regard is what is known as the micro contact printing. By which you actually create chemically pattern domains on a on a flat surface, and you might be happy to note that this was you might be happy. Of course, this is something you need to know this is nothing to be happy about it. But this is the first soft lithography technique that was actually discovered. In 1993, the first method that first soft lithography method that came in was micro contact printing.

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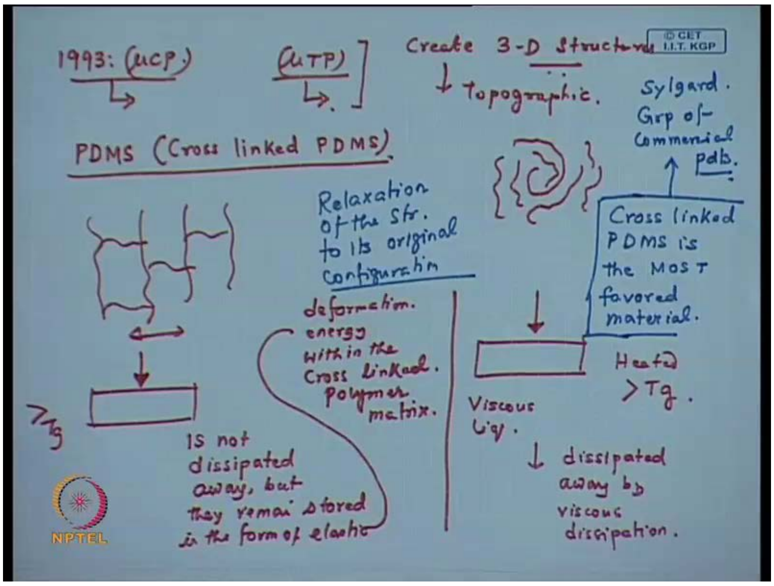

Now, coming back to what will make you happy well of course, I did not forget that this actually has a Indian origin because, the student who was associated with Whitsides who actually developed this technique was an Indian, Amith Kumar. So, this was 1993 the first printing technique. Subsequently, there has been another technique which has been developed which also essentially creates topographically not topographically, but chemically structured or patterned features and that is known as micro transfer printingor often refer to as mu TP.

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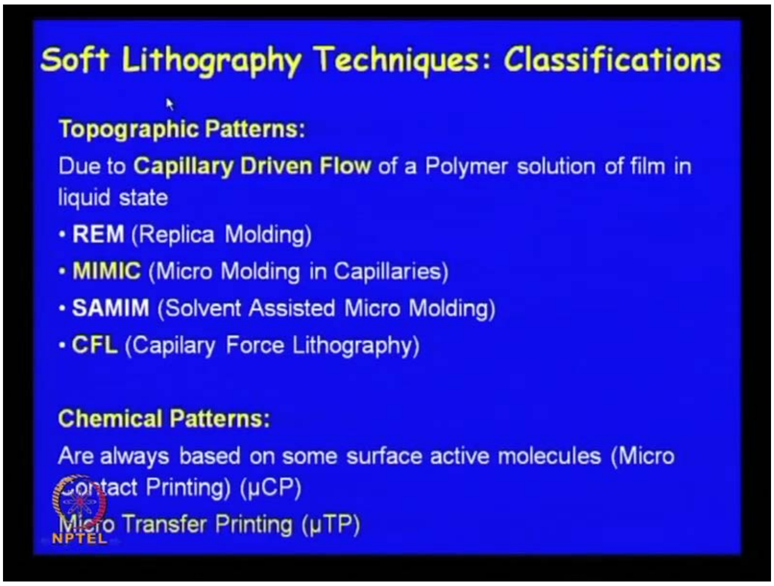

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Chemical Patterns:

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

Micro Transfer Printing (μTP)

Recently, mu TP in conjugation with metallic thin film deposition has been extended to result or create 3D structures 3D topographic structures. So here you see that though, we sort of are talking about it distinction between whether it is a printing mode or a molding mode etcetera, but you will see that now with advancement of in this area many of the methods have sort of got marched and they are I mean used interchangeable. Some of the concepts from let us say soft lithography are implemented in advancing in some of the advance nano imprint lithography methods. Some of the concepts of Nano imprint lithography are now sort of used in soft lithography group of methods.

For example, though we write that though we say or in the classical form, the pattern replication in soft lithography is due to capillary driven flow. Reality is that, there is something called a pressure assisted capillary force lithography which is one of the finest method in terms of pattern fidelity is concerned, and pressure assisted CFL you can imagine that this application of an external pressure, that idea itself comes from Nano imprint lithography.

Similarly, there are some nano imprint lithography group of methods which now talk of using a flexible stamp. So, that you can imagine now that instead of using a classical using a rigid stamp as necessary in a in a or as was designed in original NIL from where the concept of this flexible stamp has come in. It has come in essentially from the development in the field of soft lithography. So, these non photolithographic platform is sort of is sort of seeing tremendous expansion; that is lot of hectic activity in this area; lot of activity in terms of material, in terms of processing, in terms of creating structures which are novel, exotic structures going in for multilevel 3D structures as well as, there is lot of keen interest in understanding the mechanism that is responsible for the pattern replication both in NIL group of techniques as well as, the soft lithography group of techniques

Frankly speaking, these are all pretty high and research areas and it is not really possible to covered in one course, but some of the major exciting highlights and major results I will sort of showcase as a part of this lecture in may be this as well as, two more to subsequent lecture which are we are going to spent on soft lithography. And finally, as I had already told that we will do a comparison or we will look in to the scientific as well as, the hardware aspects what really makes NIL, and the soft lithography based the molding techniques particularly both of which lead to non photolithography topographic structures what makes them difference and what makes them similar.

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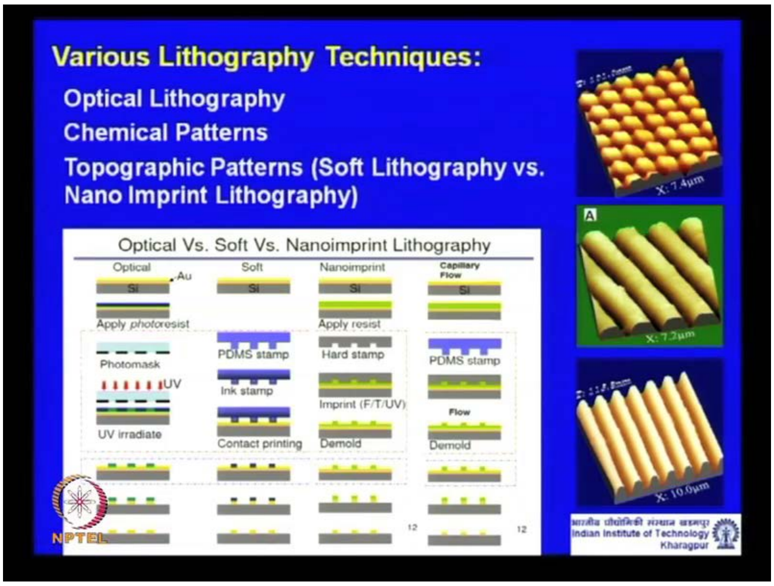

Various Lithography Techniques:

Optical Lithography

Chemical Patterns

Topographic Patterns (Soft Lithography vs. Nano Imprint Lithography)

So here again, exactly what I just told the sort of a glimpse of the various lithographic techniques. Of course, you have good old optical lithography or photolithography, then you talk about chemical patterns or soft lithography in the printing mode, and then topographic patterns you have soft lithography in the molding mode and the nano imprint lithography group of techniques. And this is where, I am repeatedly telling that there is a keen feeling amongst many of the researchers that well NIL is also nothing but a molding mode soft lithography or it can mean corporate. But anyway, for a for the course we will regard that NIL is not part of a soft lithography technique, and it is it is something distant. So, here is quickly what you have you have an optical lithography, so the key hardware requirement is a photo mask, you also needed UV exposure, and then the associated (( )) etcetera, etcetera resulting in topographic structure, and then if you do the decision, you get a chemical structure having different domains of doping.

In a printing mode soft lithography, you need a flexible stamp. I am going to just going to take up this issues; you need an ink, we will again see it may be in the next class and you do a contact printing to get a structure which is chemical patterns. So, you have alternate let us say hydrophilic and hydrophobic domains like this. Nano imprint lithography, you need a hard stamp with relief structures; you need to heat up the polymer so that it goes to a liquid state or maybe you sort of expose it to it is solvent vapor or do something so that you now over take a liquid pre polymer which can be UV curable or cure by IR exposure which is liquid at room temperature.

You emboss it many times you sort of apply an external force, freeze the patterns or either by cooling or by UV exposure or whatever and demold or remove the stamp to get topographic structures. And forth technique, the molding mode technique what we are going to discuss today; it is pretty similar to NIL, but you do not really going for a thermal processing or you do not use a rigid or hard stamp and typically by your pattern replication is not by viscose plastic deformation, but it is triggered by a capillary driven flow, and the final result is very same as NIL. So, NIL as well as the molding soft lithography methods gives you both give you this that is a topographically structured surfaces.

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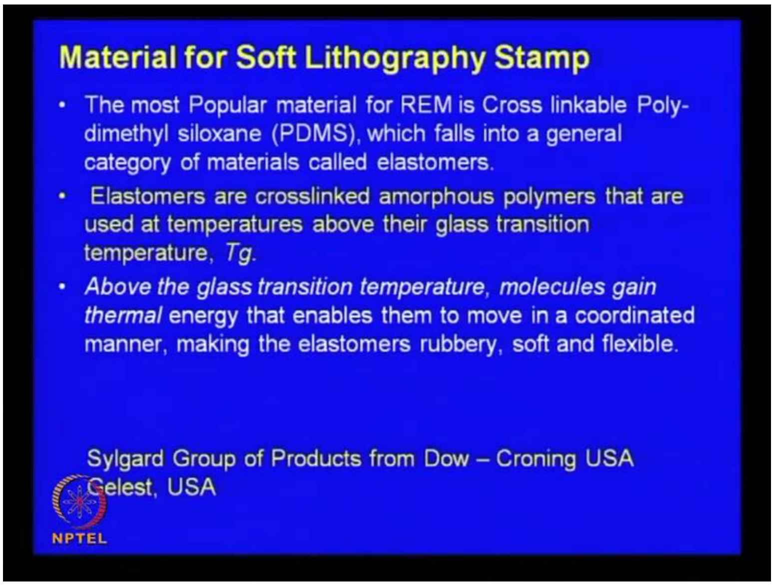

Material for Soft Lithography Stamp

- The most Popular material 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
Gelest, USA

Now, here is one important thing you need to know now that is the material for soft lithography stamp. The most popular material for not for REM, but for most of the soft lithography stamp is an elastomer. What is an elastomer? We just come in to it, but remember the most prefer material is what is known as PDMS or to be more precious cross linked PDMS; it is polydimethyl siloxane. A cross linked PDMS is something that which falls into a general category of material called elastomer. We will not going to too much of the details, but we will just have a very brief outlook about what exactly elastomer. You can remember that, the you can understand; you can sort of regard it to be some sort on an elastic flexible material which give it is a room temperature elasticity like let us say flexible, rubber band or something like that. Reality is rubber brand of course is some sort of elastomers indeed.

So, elastomers are cross linked amorphous polymers that are used at temperatures above their glass transition temperature Tg. So, this is important. So, if a material is exuviating room temperature elasticity or is flexible at room temperature so, the first thing you need to know that of course unlike a homo polymer film we have been talking so for, where you just have the entangle molecules, but there is no physical binding between the individual molecules.

In contrast to that, an elastomer will in were lively have the molecules will be sort of cross linked. So, there is physical cross linking between the molecules like this so that you cannot really sort of flow away an elastomer like a you can a typical homo polymer film, and we talked about the solvent vapor penetration where the solvent molecules sort of simple penetrate in and you can sort of it it it is sort of goes in a in a liquid form. That is not possible with elastomer because of the fact that the molecules are sort of cross linked with each other the. So, first thing to note is elastomer are cross linked amorphous polymers and the second thing is that, if you see that a that a material is sort of exuviating a room temperature elasticity. It is typically of an elastomer, you are bound to assume that is above their glass transaction temperature.

Above the glass transaction temperature, the molecules gain thermal energy that enables them to move in a coordinated manner making the elastomer rubbery, soft and flexible. Well, indeed they have the thermal energy to move, but also interesting is that they cannot move beyond a certain level because, they are sort of physically tired to each other. In other words, if you take a block of let us say elastomer, we say we say block of a homo polymer which is where the molecules are not cross linked, and if you deform this surface with a load and suppose this is heated. So, this anyway is above Tg. So, this you heat above Tg or something like that and then you apply a force.

So here, this is appear only viscose liquid. So, if you apply the force, the deformation energy is sort of dissipated away by viscous dissipation. However, here if you apply a force that definitely supplies the thermal energy to the molecules so they are fee to move, but the energy were giving sort of remains it is not dissipated away, but they remain stored in the form of elastic deformation energy with in the cross linked polymer matrix.

So, what it means? That this energy that you have applied to cross the deformation here it is completely dissipated. So, you have embossed it, it has taken the emboss structure. There is no energy so that energy is dissipated this energy is lost to the surrounding. So, once that externally applied force is withdrawn, there is no energy available to restore the deformation on the film surface. In contrast, this is what gives the flexible properties. So, you stretch an elastomer you are applying deformation, but so that leads to stretching of the molecules, but the force you applied sort of is stored within the elastic matrix. So, it is not dissipated to the surrounding. So, the moment you you you withdraw the stretching low what happens is, those forces sort of triggers the retraction or the attraction of the entire block to which original configuration.

So this energy sort of stored as in the form of elastic deformation energy with in the cross linked polymer matrix and once the external deformation force is withdrawn, this stored elastic energy gets or is responsible for relaxation of the structure to it is original configuration. The… What you would see if you if you read even little bit of literature on soft lithography. That cross linked PDMS is the most favored material and once specific brand which is widely used is the sylgard group of commercial products sylgard group of commercial products. That is extensively used for fabricating stamps, soft lithography stamps or in many cases creation of patterns itself which comes from Dow Crooning, USA.

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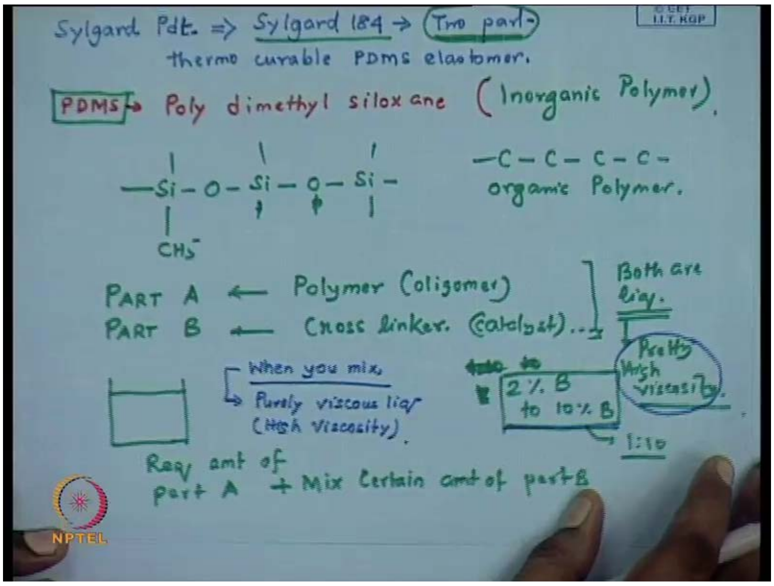

Sylgard Pdt. => Sylgard 184 → (Two part)
thermo curable PDMS elastomer.

PDMS → Poly dimethyl siloxane (Inorganic Polymer).

—Si – O – Si – O – Si –
CH3

—C – C – C – C –
organic Polymer.

PART A ← Polymer (oligomer)
PART B ← Cross linker. (catalyst)..

Both are liq.

When you mix,
→ Purely viscous liq
(High viscosity).

2% B
to 10% B

1:10

Pretty High viscosity.

Req amt of part A + Mix Certain amt of part B

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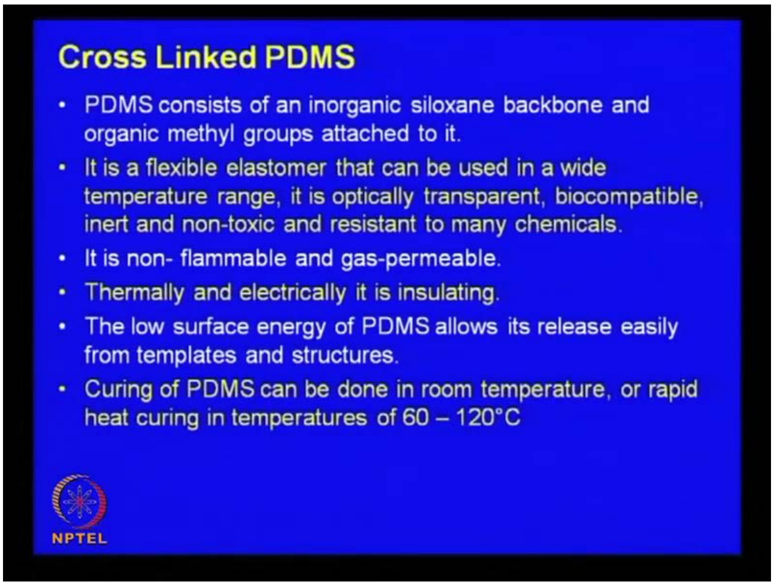

Cross Linked PDMS

- 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

Of course, there is another company called gelest valsom commercial elastomers. But particularly you will find in most soft lithography papers or general articles is some sylgard product or the other; the most popular it of it being sylgard 184 which is a two part thermo curable PDMS elastomer; the something and again as I said that most micro fluidic circuits are made of sylgard 184. So, cross linked PDMS essentially and PDMS is also interesting from another stand point if you look into its name poly dimethyl siloxane. This is rare example; this something interesting you may be remember without knowing too much of chemistry. It is rare example of an inorganic polymer. Typically, we understand an organic polymer has a carbon carbon backbone typical. This is what makes an organic polymer. Of course, you can have unsaturation somewhere does not really matter.

In contrast, a siloxane group and with this silicon methyl groups are attached. So, this backbone is the one which sort of gives the molecules it is flexibility like an like an polymer, and you have methyl groups attached here which sort of lead to further cross linked. So here, the basic backbone of the molecule is not a carbon carbon organic backbone, but it is a silicon or Si O Si inorganic backbone and therefore, PDMS is rare example of an inorganic polymer. So PDMS consists of an inorganic siloxane backbone and organic methyl groups attached to it. It is a flexible elastomer that can be used in wide temperature range. It is optically transparent, biocompatible, inert, non toxic and resistant to most chemicals. It is a non flammable material and gas perm it gas permeable to this material. It is thermally and electrically it is insulating. PDMS also offers very low surface energy so that sort of makes it suitable for two things direct fabrication of hydrophobic surfaces as well as, if it is been used in soft lithography particularly in molding mode molding techniques.

Big it is low surface energy sort of makes it very, very easy to detach from the patterns you have created in a polymer. And curing of PDMS, this is we are talking of cross linked PDMS now like sylgard 184 which we have already discussed. The curing of PDMS can be done in room temperature or rapid. So, if you if you… So, this it if you look into this carefully, it is a two part thermo curable elastomer. So, if you open a container of sylgard 184, it will say part A and part B. Typically, this is the main polymer which also with affect to as oligomer times and part B is essentially the cross linker.

So, ideally contains the catalyst or whatever; I mean, we will cover this detail, but may be when you are little bore more conversant about PDMS and all this things. So, all you have to do is you take requisite amount of part A and mix certain amount of part B. At room temperature both of them are liquid then, part A is pretty high viscosity. So typical percentages would vary from let us say 1 is to 10 to let us say or let us say down from 1 is to or may be 2 percent B to 10 percent part B to part A ratio. So, 1 is to 10 B is to A here down to 0.2 is to 10 or something like that.

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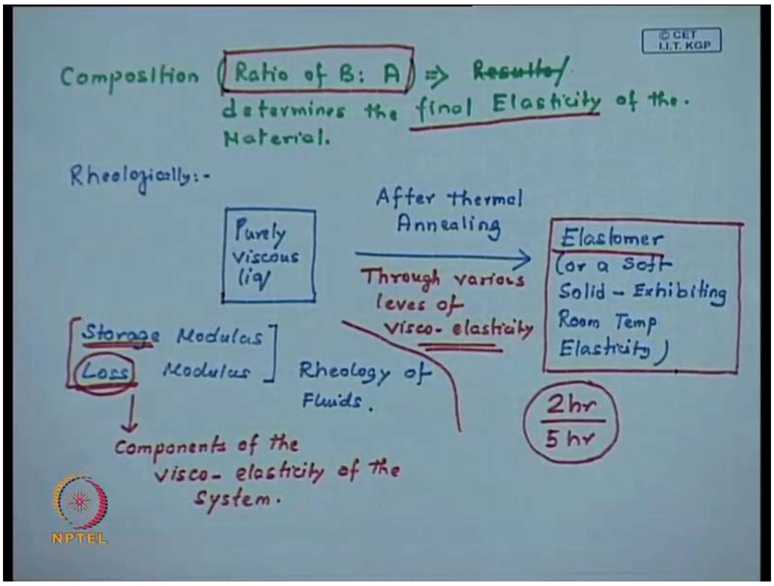

Composition (Ratio of B: A) ⇒ ~~Results~~/ determines the final Elasticity of the. Material.

Rheologically:-

Purely viscous liq

After thermal Annealing

Through various leves of visco- elasticity

Elastomer (or a Soft Solid - Exhibiting Room Temp Elasticity)

[Storage Modulus
Loss Modulus] Rheology of Fluids.

Components of the visco- elasticity of the System.

2hr / 5 hr

The composition that is the ratio of B to A sort of results or determines I want to use the what results. It determines the final level of elasticity of the material. This even if do not understand fully at this point of time does not matter we will revise it. So, coming back all you have to do that you have to mix part A and part B in requisite proportion. What this proportion is like; what determines the proportion and all that we will talk about it and we will understand the very very simple concept. And, if you just mix them and put it in a weaker it will cross linked. So once it cross links, it will form a soft flexible mass transparent block. If you if you sort of leave it inside a weaker, it will take the shape of the inside of the weaker itself.

However, so this might if you leave at room temperature, the cross linking might take some time. It might be 7 days before it fully cross links. However, you can expedite this cross linking process by heating up this part A to part B mix in an oven and typically, it varies from people to people, group to group. But typically, at any temperature between 60 degree centigrade to 120 or may be 140 degree centigrade and any duration between 6 hours to 24 hour is good enough to achieve complete cross link.

So, this rapid heat curing as it is written here. So, this thermal annealing states sort of facilitates the cross linking process. Now rheologically, if you look at this A to B mix once you mix it, we have say that is pretty high viscosity material that is that part A. Part b is low viscosity, but typically looking at the composition since the proportion of part A is definitely is going to be higher. So, the final mix also is a pretty high viscosity material when you mix. So, you have a purely viscous liquid may be with high viscosity, but when you sort of allow it to remain in place for long time or you thermal rapidly thermal anneal it, it eventually results to and elastic elastomer or a soft solid exhibiting room temperature elasticity and this as this transformation has occurred from a purely viscous liquid.

So, if you care to look into Wikipedia or if you already know from your courses on fluid dynamics, if you look at the terms of the storage modulus and loss modulus, these are related to rheology of complex fluids or rheology of fluids. Ideally, these two modulus sort of combination of these two modulus is very simple put; this is something we are not going to talk in detail in this particular course at least. The combination of the relative magnitude of these two modulus’s which can be determine determined using an instrument call rheometer gives you an idea about the visco elasticity idea about the visco elasticity of the system.

So, for a purely viscous liquid, the lost modulus is much, much higher the storage modulus and for an elastic solid, the storage modulus is higher than the loss modulus. So, this in anyway is to in some way is correlated to this picture. When we talk about the deformation in a elastic material, the deforming energy is sort of stored in the form of elastic deformation within the matrix. So the elastic part of the rheology is sort of referred to as the storage modulus. So, this is actually a very simplistic way to define the storage modulus; we are essentially talking about the storage modulus.

In contrast, when we talk that we are deforming causing deformation to the surface of purely viscose film and energy is completely dissipated by viscose dissipation so the energy is essentially lost. So therefore, or consequently the viscous component is refer to as the loss modulus. So, what I intend to say I mean, this would be more than enough if you if you remember this or understand this that, this thermal annealing step the way you process it. So, you mix part A and part B, you have a viscous liquid at room temperature. When you mix the two and heat them up due to thermal annealing, what you are performing is from rheologically you are transforming a purely viscous liquid to a elastomer to a soft solid exhibiting room temperature elasticity.

Or in other words, there is significant transformation of the loss and storage modulus of the material. So initially, the loss modulus is high; storage modulus is negligible. Once the thermal annealing is achieved, you have a system which give it is a much or the storage modulus is higher than the loss modulus. It is predominantly elastic and this transformation you may note down through various levels of visco elasticity or in other words, that at this intermediate stages of this transformation, you have the various stages of visco elasticity; the the the the material under goes this transformation through various stages of visco elasticity.

Now, once the material is fully cross linked, annealing it further does not alter its level of elasticity. So, if you are curing for annealing for 2 hour or 5 hour really would not matter much in determining the final level of elasticity which is effected only to a to a large extend on the or by the ration of B is to A. What is important that, why is some people cure it for 2 hours; why is some people cure it for 5 hours etcetera; that you would actually try to cure or anneal your system for a period of time which is certainly higher than the period of time which is actually necessary to achieve complete cross linking.

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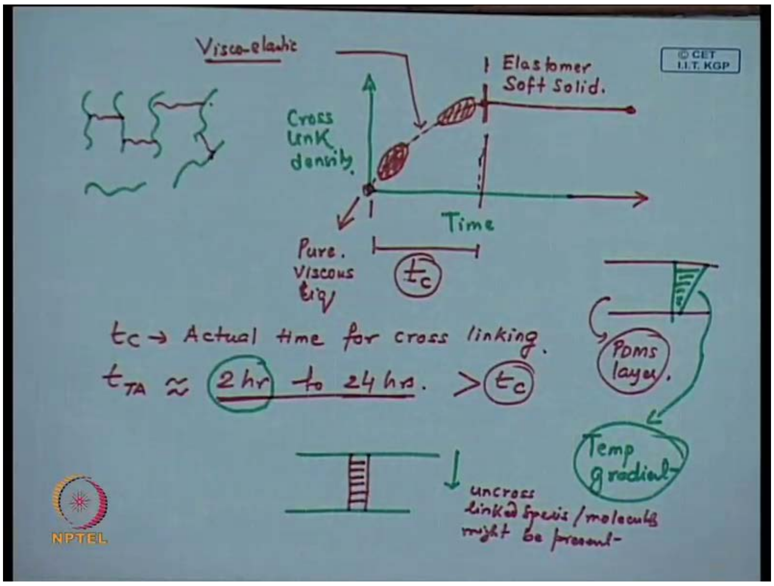

$t_c \rightarrow$ Actual time for cross linking.

$t_{TA} \approx$ 2 hr to 24 hrs. $> t_c$

What I also did not mention is that from the stand point of cross linking. So, rheologically this transformation is to various level of visco elasticity, but the other side of the picture is initially when you take the reaction mixture, you have isolated molecules of PDMS roaming around like this or within the systems. So, you have isolated molecules. So, if you leave it for longer period of time after you add the part B or if you do a thermal annealing what happens is the physical cross links between the molecules grow, and depending on what is the ratio of B is to A you have added, the final level or the final amount of cross links.

So, if you define as the number of cross link number of cross links for unit areas something like that; that is sort of determine by this ratio, and the intermediate stages what happens is at intermediate stages what happens is while from the molecular picture the with progressive annealing, the number of cross links sort of gradually increase or in other words, if you sort of plot with time the cross linking density initially, it is zero and it reaches a final value which after it has reached the final value with the time of annealing, it does not change and the intermediate stage is where with time, it gradually or there is gradual increase in the cross link density.

So here, at the beginning it is a pure viscous liquid. Once it is fully cross link, it is an elastic or elastomer or soft elastic or soft solid and this intermediate stage visco elastic. Note on this side, it is a visco elastic liquid with high levels of viscosity; higher up over here it is visco elastic liquid with more solid like behavior or high level of elasticity. So typically, the annealing time so, this is the actually time. If you define this is t c to be the actual time for cross linking and typically, the thermal annealing time which can vary between 2 hour to 24 hour is kept higher than t c.

Of course, there are number of issues; that is that with the time is not completely in significant because, there are certain cases where there is a gradual; I mean, the heating within the layer this is the PDMS layer. The heating may not be uniforms so they are might actually be a temperature gradient. So, if you sort of do a low duration annealing, this temperature gradient might remain and so within the along the depth they are might be significant number of uncross linked species or molecules might be present. In contrast, if you sort of this is simple heat transfer problem that in contrast, if you sort of heat it for a prolong duration probably, you have much more patter profile and the cross linking density or the cross linking density variation along the depth of the film will be less which is off course setting that you would like to have.

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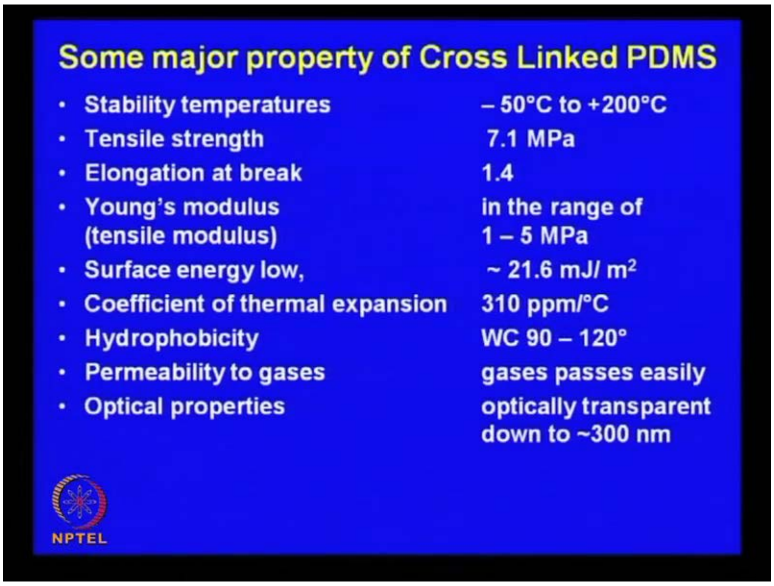

Some major property of Cross Linked PDMS

• Stability temperatures	– 50°C to +200°C
• Tensile strength	7.1 MPa
• Elongation at break	1.4
• Young's modulus (tensile 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

So here, are some quickly some major properties of cross linked elastomers. Stability temperature is between minus 50 to 200; tensile strength is about 7 mega Pascal;

elongation at break is around 1.4. So, you can sort of stretch it by almost 40 percent. Young’s modulus in the range of 1 to 5 mega Pascal and this is something that also depends on the ratio of part B to part A. Surface energy is low around 20 milli joule per meter square; coefficient of thermal expansion also is extremely low; hydrophobicity it shows a water contact angle of roughly between 100 to 120 degree roughly 115, I would say; permeability to gases, gases can pass easily.

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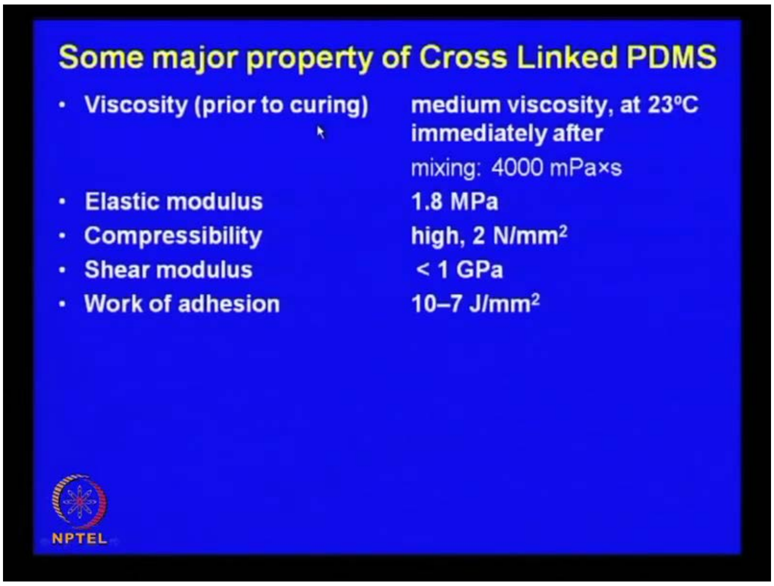

Some major property of Cross Linked PDMS

• 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^2
• Shear modulus	< 1 GPa
• Work of adhesion	10–7 J/mm^2

Optically transparent down to 300 nano meter viscosity prior to curing is after mixing that after you have mix the part A and part B as we have discussed here is roughly 400 milli Pascal second. Elastic modulus is about 1.8 mega Pascal again something that depends on the ratio of the part B to part A. Shear modulus is about less than a giga Pascal and work of adhesion is 10 to power of minus 7 joule per milli meter square.

So, I think we will stop here in this particular class and pick up from what, how this cross link sylgard can be or sort of easy used our is extensively used as the stamp for most of the soft lithography techniques.