

Soft Nano Technology
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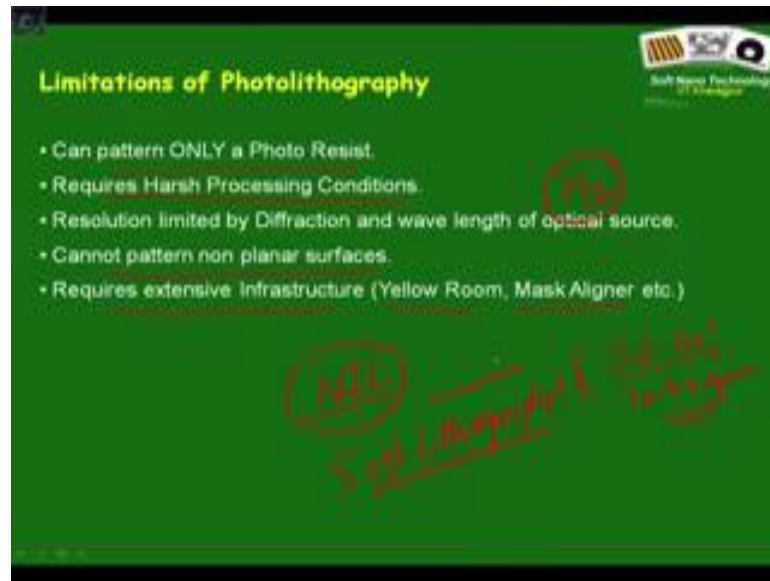
Lecture - 18
Soft Lithography-1

Welcome back. We just completed our discussion on Photo Lithography and according to the content syllabus of this particular course we will now move on to Soft Lithography. Maybe, this is another term that is going to be new to many of you, but we will slowly learn and I am sure you will appreciate that, you are learning something new because this is not what we have been discussing, we have been discussing is not something that is very routinely covered in the under graduate curriculum what you have studied. So we are approaching also roughly the midway stage.

So, it is not a bad idea to recapitulate the team you are quite well conversant with me my face by now, but if you want to sort of drop me a mail, here is my mail id; however, any discussion related to the course I will prefer to take it at the discussion forum and not in a personal mail. You can find out my home page by best option is to key in my name and you can just the first search will take you to my home page.

Also for one of the reasons one more reason you might have to search, the internet and that is if you want to use the NPTEL resources that we already have for my course theme film in stability, patterning an instability of theme polymer films, which covers large part of what have been discussing here, you can go to you tube straight away and find them out of course, you can also find them first slide, first lecture I have given you the numbers, course members in NPTEL website which also you can use. TS will be Nandini Bhandaru and Anuja das and they will be replying to most of your question in the discussion forum, but I will also be online I am a online and I will be checking what is going on.

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So, moving on I am assuming that we have now all understood photolithography at least in its basic form, and let us try to find out a why we need some additional techniques or Soft Lithography. One of the motivation of course, is if you look very carefully is photolithography is a technique that is sought of optimize for the microelectronic of the IC industry, but when we were initially discussing about some of the patterning application.

You have seen that apart from microelectronics there are host of other areas, like structural hydro fabrication of hydro phobic surfaces or self cleaning surfaces or let us say structural color, many other applications implied for bio data logical applications. Where you need pattern surfaces, but you really do not need to go all the way down to the doping or you do not really always need the structures to be in the photo resist layer.

So, is photolithography a necessary in those stages or should we concentrate with some techniques, that are compatible or that are more versatile that can handle different types of materials, other than sticking only to photolithography. In fact there are quite a few though photography is sort of an extremely dominant, extremely important technique there are in fact a few limitations of photolithography, and let us take a quick look into some of this.

The most important thing that you should immediately and you should in fact help me a sought of prompt me what had been a class I would have made you prompt, most

important thing first that should come to your mind is, photolithography is a technique can pattern only a photo resister.

If you need structures, which may be other polymers or other soft materials like jell or let say neo organic soft materials some neo organic materials can be processed to the to a soft route and that falls into a very well known area of research, a sol jell a base techniques. This type of materials photolithography as it is cannot handle. Requires very harsh processing condition and therefore, pattern surfaces actually find application in what nano bio tech application. So, bleaching cells and things like that which cannot sustain that harsh processing condition of a newly exposure, not to mention that if you sought of go all the way down to removal of the barrier layer, you use a extremely harsh agent in the form of hydrogen fluoride or plasma.

Of course, there is a resolution limitation, due to the diffraction and wave length of optical source and though there are, I am sure most of you are well conversant with this factor now. Though there are methods to circumvent this problems in the form of lecture projection lithography or emersion lithography it still very combisave.

Certain thing I almost we none of us almost discussed or realized is that photolithography. Since it use a pin coding platform, it cannot handle patterns on non planer surface, Of course you do not need pattern on non planer surfaces for the IC industry, but you think of. So, it cannot neither it can handle non planar surfaces nor can it handle fixed surfaces, but see now you have display devices, which are not even big TVs which are not perfectly played they have curvature for better enhance viewing comfort, you have flexible display like, you can fold your display and stuff like that and photolithography fails in all of right and of course, it requires extensive infrastructure you like a yellow room, mask aligner, etcetera, which we have already talked.

Now all these very stringent requirement are perfectly for the IC industry, where sort of pattern fidelity and numbers of defects I mean the structure should be absolutely defect free in order for having desired performance because of a one single defective on a chip is going to spoil the whole chip, but there are host of bulk nano segments as we call; I mean where you need nano the skills structure, but there well the requirement is not so the requirement of the defect free nature is not so strong, you can some effects here and there you need to have these structures a much lower cost.

So, there is a huge segment, for example self cleaning coatings you want to have. You really cannot spend money for coating some windows for the type of money you spend for buying a consumer durable micro electronic device. So, there has to be some alternative route for catering to this bulk nano fabrication segment where patterns can be sought if we produce easily, without so much extensive infrastructure and more importantly they can handle variety of materials. So generically soft materials or materials that can be handled in the soft form can be handled by them and they are not limited to some photo sensitive material like photolithography.

So all these considerations gave rise to a group of techniques that led to the development of group techniques, which we go by the name soft lithography. In fact, another important thing that you must realize at this point of time is photolithography refers to a very specific technique set of technique, there might be certain variations here are there like you can have positive or photo negative photolithography, but overall or you can towards the end you can either you have (Refer Time: 07:47) of, but overall photolithography is a very well defined technique. In contrast of lithography as it is no technique at all. It is a suit of different techniques that are capable of handling or patterning different types of soft materials which includes polymers, which includes elastomers, gels, sol gel films, even colloids and stuff like that.

Pioneering development in this area was primarily done exactly about 20 years back by professor G.M. Whitesides. He was at Hayward and so he and one of his graduate students at that point of time Jiya, they are the 2 key players who developed most of the techniques. Some techniques as you will realize that, some techniques have been developed later. But almost simultaneously Stephen chow initially at (Refer Time: 08:41) and eventually he moved on to Princeton, came up with another technique which goes by the name nano imprint lithography. There is a debate and as will see from the classification, whether nano imprint lithography should be considered into the Soft Lithography technique or not, because there are arguments in favor and arguments against.

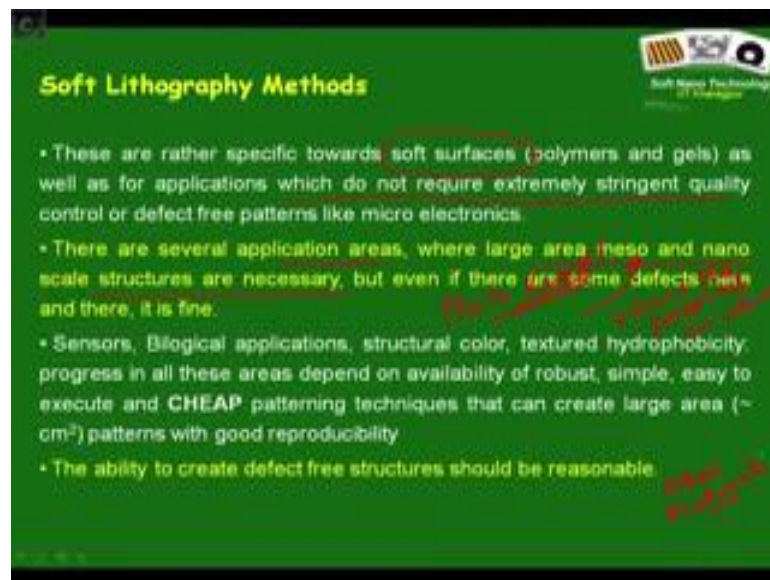
One of the key reasons why people feel that it is not a part of a Soft Lithography method is of course, it was not invented Soft Lithography is a technique, that was a phrase that was coined by Whitesides too, but it had a different genesis and there are some issues,

but the way we will I visualize this, I prefer to include nano imprint lithography as one of the soft lithography techniques.

Why this discrimination comes? We will discuss when we talk about classification of Soft Lithography and as I already hinted soft lithography obviously covers a lot of different techniques, I must also say that each of the technique has their own advantages and certain unique features also let me sort of give you a subtle warning there are too many names available in the Soft Lithography literature. So, anybody who has developed some technique has sought of filed a patent with a specific name. Some of them are genuinely new, but some of them are essentially extension of existing techniques.

So, it is not possible for anyone, forget about a condense course like this in which to talk about even to identify all Soft Lithography methods what are which are there, but I have tried to do is I have tried to pick up some of the key techniques, these are sort of the pioneering techniques initially developed and extensively practiced now and these techniques as you will realize each one of the techniques we will be discussing have certain specific capability which none of the other techniques have.

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So based to this introduction let us move on in understanding a Soft Lithography in some greater detail. So, as I have already told the Soft Lithography is sort of groups of a technique those are specific for soft surfaces like polymers and jells. Particularly for application which do not require extremely stringent quality control, several application

areas where large area nano and micro structures are necessary, but even if there are defects here and there it is and more importantly there is absolutely no need why the structure should be on a photo resist. So, you in fact want the patterns on other materials. And that is a capability that is severely limited in classical in photo lithography not even classical.

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Soft Lithography

- ↳ Capability of Handling Soft Materials - Generality.
- ↳ Non-Planar Surfaces - Flexible Surfaces
- ↳ Processing Condition - Gentle.
- ↳ There is NO diffraction limitation.

Stone / Mask / Master.

PDMS → Poly dimethyl siloxane
Inorganic Polymer

(A) Oligomer
(B) Cross linker

Thermally Heated

Silylation
Cross linker PDMS

Area: 10³ - 10⁶ cm²
4-6 hrs

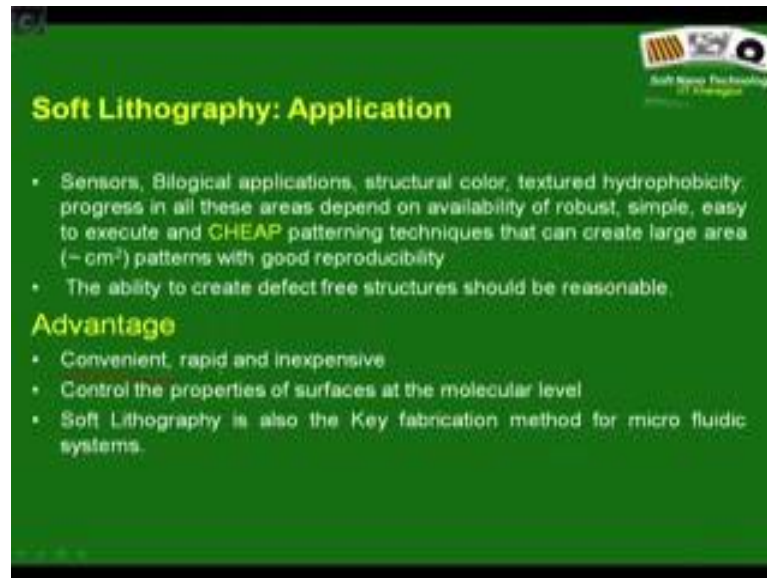
Liquid → Elastic Solid

- C - C - C - C - C -

Si-O-Si-O-Si-O
Si-O-Si-O-Si-O

Let me just quickly highlight the key points. So, capability of handling soft materials generically; well we will see that its capability also includes patterning of let us say non planer surfaces, flexible surfaces and also situations where processing condition is very gentle. You tend to rely more on, there are techniques which tends to rely more on let us say subtle forces like that capillary force (Refer Time: 13:14) not really on brute forces externally applied high pressure, which also is there certain techniques relay on that or let us say UG exposure on things like that. So, you can in principle pattern biological samples living cells everything by stuff like that.

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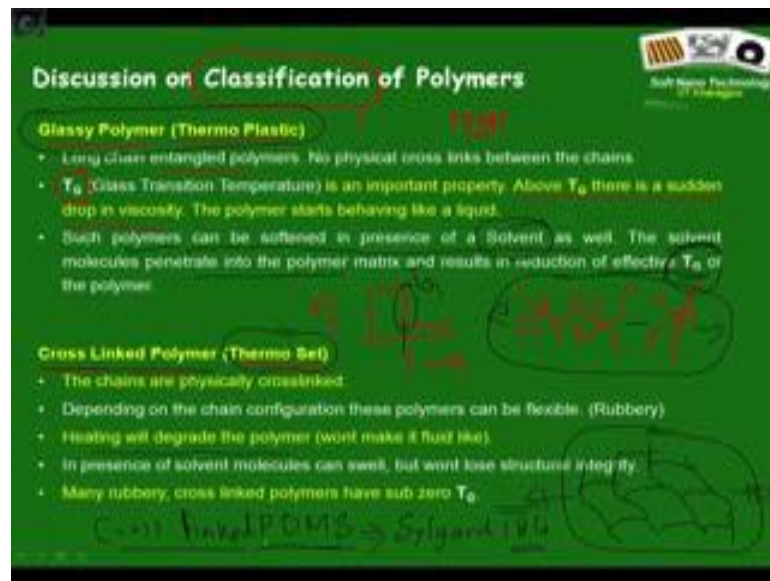
Moving on these are advantages, we already discussed convenient rapid inexpensive, also another very important issue in Soft Lithography is, there is like Fraction limitation. Way back in 1997 I think 10 nano littoral resolution was achieved and I think by 2001 or 2002 by nano imprint lithography 5 nano littoral resolution was achieved. So, that is a big advantage, there are disadvantages or but that disadvantage is also there in photolithography. If you think very carefully, photo lithography is not a primary patterning technique. What I mean by this prime? This word primary patterning technique is photo lithography as a method cannot create it its own pattern. It is capable of only reproducing the pattern that is drawn on the mask.

So, the original patterned actually is created on the mask by whichever technique you make the mask that is say primary patterning technique and we briefly mentioned in the last class about this next generation lithography techniques like focus tern, beam electron, beam lithography etcetera which are the ones which we can which sort of kind right a pattern.

So very similar to that you will also realize, very similar to photo lithography, Soft Lithography is a parallel processing technique, however it is not a pattern takings. So, just the way photo lithography requires a mask Soft Lithography requires a stamp mold or a master. In fact, this these three words sort of are interchangeably used one can say in Soft Lithography literature, some techniques sort of specifically refer to the same thing

with name for example, nano imprint lithography will always refers to the stampers the mold, but they serve the same purpose this is where the original pattern is engraved and Soft Lithography is sort of a very rapidly Xerox machine it goes on producing replicas of this structure. In principal lithography also does the same thing, but it is much more cumbersome technique and induce the photo sensitive property of the photo resist to achieve that.

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Before I move on further, we need to sought of have a very quick an, this is not a course on polymer physics these are issues that I have a completely avoided in fact, but I think we sought of need a bit of this discussion is a quick a classification of the basic types of polymers and it turns out that a one can divide the polymers into 2 categories, most of you will agree that polymers are most of you know that, most of the polymers are amorphous material. There are certain rare examples of semi crystalline polymer, but those are special cases and we are not talking about that type of complicated stuff.

So, one can sort of distinguish polymers as glassy polymer or so called thermo plastics and the crosslink polymer or so called thermoses. So, these glassy polymers are long chain entangled polymers and there are no physical cross links between the chain, but they can remain entangled. So, it is essentially when we talk about in the context of surface and attention, the different components these are ideal candidates so are you in fact have a strong effect of steric interactions right. Though in order to keep things

include we did not talk about the mathematical expression of steric interactions, but we all understand that steric interactions are there important and these are essentially the classic examples.

One can also say that higher is the molecular weight of these polymers, longer are going to be their chain lengths, higher is going to be the steric interaction and that is manifested in terms of higher viscosity. Many of these polymers including for example, the cover of this pen or many components you see in our daily life they are plastic made, but they behave like solid at room temperature and how is it possible? The fact is these polymers have; there is a specific property of a polymer that is called the Glass Transition Temperature. Below that their viscosity is extremely high. So, the polymer does not flow and it behaves like a solid.

So, that comes the thing that TG of this polymer is an important property and above TG all we need to understand there is a certain drop in viscosity. So, the viscosity if you sought of heat of polymer slowly and you record its viscosity you will see a plot like this and I do not think I need to tell anything more you people are quite knowledgeable by now. So this is the temperature which corresponds to the glass transition temperature right. This is a TGN from our stand point the only thing we will know above TG is that above that glass transition temperature there is a certain drop in the viscosity of the polymer.

Many of the polymers like polystyrene and PMMA and what we are going to use, they have TG in the range of 100 to 110 degree centigrade. So, at room temperature material made out of them behave like (Refer Time: 19:12) they are solid. More importantly as we will discuss atomic force microscope, we will realize there are excellent candidate for performing experiments because you can heat them up, they behave like liquids. So they are soft now. So, you can pattern them you can have instability with these soft films whatever and then you simply bring down the temperature. So, the structure sought of gets frozen in and therefore, there in a solid state. So, you can simply analyze them using an atomic force microscope, which we will learn probably next topic after a few classes 5 to 6 classes, but you will realize that a (Refer Time: 19:48) can only characterize a solid sample. So, these behave like perfect solids.

And such polymers this is something I will discuss in greater detail such polymers can be softened in present in presence of a solvent as whole. What happens is the solvent molecule penetrates into the polymer matrix and reduces the effected TG, something I will discuss.

So, this is one set of class polymers glassy polymers and you will realize that in most cases we will be talking about Soft Lithography techniques will be talking about patterning these polymers right. We will be actually taking advantage of glass transition temperature in many cases we will see that the polymers are being heated be on that glass transition temperature patterning is done there, then they are sort of they are either cooled or they are taken out of the solvent chamber to enhance their viscosity. So, you get structures which are stable at room temperature. So, these things will be routinely done.

There is another class of polymer which polymer people will call as thermoses, but let us stick to the term cross link polymers. Here the polymer change, are physically crossing and depending on how much gap is there between this changes, and these actually leads to flexible or rubbery behavior. So, that is a factor almost all the rubbers have are crossing and since they exhibit excellent amount of elasticity often they are referred to or this a very simplified picture.

Please do not use this term as you say you know what elastomer is, but many of this crosslink polymers are essentially elastomeres. There are courses available on polymer physics and you can look into them what exactly are an elastomer. But well, our purpose elastomer, what we will understand the one of the necessary condition is the elasticity comes from the deformation of this cross link chain is very simple. So if you try to elongate these polymers, there is no physical bond or anchoring between the adjacent molecules.

So, when you deform the energy you spend in deforming is not stored any were it is lost due to viscous dissipation, but when you have an a entangled network even it is flexible if you now deform by apply external force, part of the energy or the entire amount of the energy that you that you spend in deforming remains stored within this flexible matrix as the elastic de formation energy of the material and that is exactly why you see that when you stretch a rubber and withdraw the force the rubber relaxes to back to its original

configuration. So, this is this is actually due to physical cross links present within the polymer matrix.

So, heating this polymer of course, since the chains are cross link it cannot flow. So, there is a no analog of a glass transition temperature here. This statement is not fully correct the better way of putting it most of the elastomers have very low glass transition temperature. Like one polymer we will be talking very frequently now onward it is PDMS, cross link PDMS, there is a very famous commercial product brought out by Dow Burney Sylgard 184 or even other varieties of Sylgard which is a crosslink PDMS. PDMS is also very special from another stand point is, it is a poly dimethyl may be I will spend some time on this or I will just use it here, what makes it really special its see locks in this polymer.

So, most of the polymers you know the backbone is a carbon backbone and therefore, polymers fall in to the category of o organic material, but what is there is a SIOSI backbone is (Refer Time: 24:12) 4 points with SI. So, this is an example of a inorganic polymer. So as it is PDMS is liquid at room temperature because its glass transition temperature is close to minus 50 or minus 60 degree centigrade, but this Sylgard 184, it is a commercial product I think we have the details somewhere here.

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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

The slide features a green background with a white text box containing the bullet points. To the right of the text, there is a chemical structure diagram of a PDMS chain segment, showing a backbone of silicon (Si) and oxygen (O) atoms with methyl groups (CH₃) attached to the silicon atoms. Below the diagram is a photograph of two white plastic containers, likely the two-part Sylgard 184 kit, with a red circle highlighting the larger container. In the top right corner, there are logos for 'Soft Matter Technology' and 'Dow Corning'.

This is the Sylgard 184 it is in fact, it comes it is a cross linkable PDMS and it comes in two parts, the part A is called the Oligomer the main polymer and you can search the net

which Sylgard 184 you can get the datasheet and you can get all other details about it and the part B is crosslink.

So, what is typically done is some proportion of part B is mixed into the part A, it can be 5 to 10 percent or 15 percent and then thermally heated. So as you thermally heat, what happens is bonds form between at the same chains. So, these bonds form and it forms this type of a crosslink network as we were talking about. In fact, one can very carefully notice that in fact the unlike carbon because of its structures silicon needs an oxygen between that there has to be an oxygen molecule present between two adjacent silicon and therefore, the gap the silicon, silicon gap is more which in fact, provides more flexibility to Sylgard.

Therefore this is one of the excellent candidates all that is done is it comes as a liquid you mix it at a room temperature and cure it or anneal it for some time at a liberated temperature; temperature typically of 100 to 120 degree centigrade for 4 to 6 hours. Some people cure it for a longer duration and from a liquid it transforms to an elastic solid. So, this type of a material falls into the second category of polymer crosslink a polymer. And it actually has a rubbery filling and as we will see in the subsequent lectures this is very this particular material is extremely important in the context of soft lithography.

Now, if you expose this to its solvent vapor, this material again does not flow like a glassy polymer, but it sort of swells and that is another advantage one can take in control in the dimension in the block of whatever.

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So, with this brief introduction we are now in a position to take up a Soft Lithography or discuss Soft Lithography in some big detail and from the next class I will start from classifying the Soft Lithography techniques which itself is an important topic and you need to understand based on what methodology you are going to classify.

And there are different methodologies; different thought either the type of patterns you are creating can be one of the criteria or the nature of the stamp or the mold. You are using one of the criteria or the type of force you are using can be one of the criteria. We will start from there.

Thank you.