Soft Nano Technology
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Lecture - 23
Soft Lithography – 6

Welcome back to the last lecture on soft lithography.

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We get started with the advantages of soft lithography. So now we have a fair deal of idea about both photo lithography and soft lithography and you are now in a position to understand; what are the real advantages of both the techniques? Needless to say even today for the micro electronics industry, photo lithography is the technique. Industry still performs photolithography and all your silicon electronic devices photolithography I think in my opinion is going to be use for long time. But there are as you know there are lots of application areas which are emerging which are coming up where Nano patterns particularly with different types of polymers are required and soft lithography is very effectively catering to the segments.

Let us take a look into some of the advantages. So, it is convenient inexpensive it is accessible to none expert that is a most important thing. You do not need to be a real expert in patterning to perform soft lithography. It might be very likely that you are a material scientist you need some pattern surfaces or you are a fluid mechanics specialist.

You need some patterns surfaces to study behavior of a fluid on a hydro phobic surface. In your lab with minimal facility you can in fact create structures or templates and that is necessary for you. That is one of the biggest advantages.

Photolithography unfortunately you cannot do that. You really need to have at least basic minimum facilities even to create some lines with 5 micron line with those of something like that. There are soft lithography processes are additive and therefore, minimize the waste of materials readily adaptable for rapid prototyping. Isotropic mechanical deformation of PDMS provides routes for complex patterns something I really do not want to highlight it is bit of details. This is extremely important no diffraction limitation and this are wrong again as less as low as 10 nanometers have been fabricated.

We have already seen the structures down to 10 nanometers have been achieved and non planar surfaces. This is another major plus point of soft lithography because most of the techniques rely a flexible stamp or a surface you can create non planar surfaces.

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You can also we have seen that we can create 3 dimensional topographies. Good control over surface chemistry and very useful for interfacial engineering is extremely important. Very broad range of materials can be used. In contrast of photo lithography which unfortunately the direct patterning step is limited to photo resist only. This in fact goes on producing number of copies indistinguishable copies at low cost therefore, it is capable for rapid prototyping and applicable for large area pattering.

So, the step and repeat processes that you need to do with photo lithography because to control exposure because if you want to expose a large area by photolithography, there will be issues with the angle at which the UV exposure is falling. So, that can also be handled by soft lithography. So, you see soft lithography as I mentioned is a suit of techniques, polymer specific techniques and it is really very helpful.

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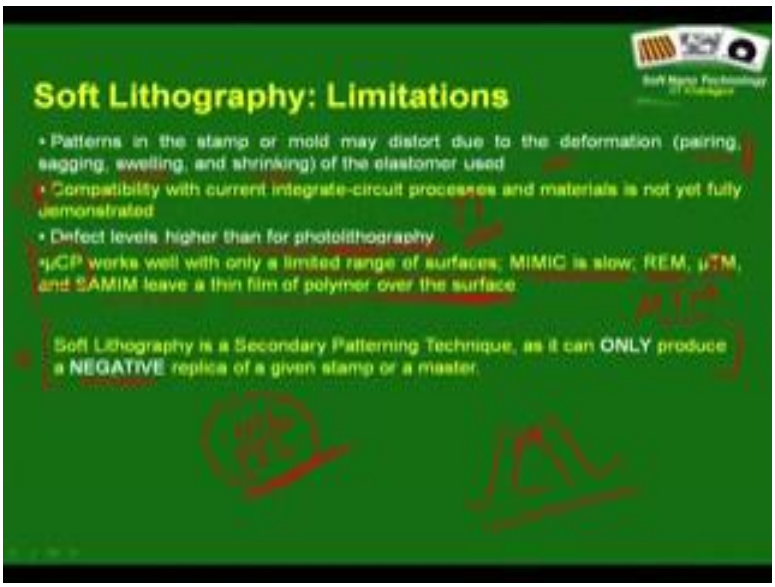

Limitations; there are issues that since in many cases you are making structures with an (Refer Time: 04:01) over particularly for a replica molding and many other techniques. There might be issues like pairing, you have seen pairing like 2 adjacent structures join up like this due to interaction again between them. There can be issues related to swelling shrinking etc. The people are still trying this I always tell soft lithography as a technique for rapid prototyping of different type of polymers then it fix perfectly, but the moment you start talking whether it can be integrated to the microelectronic industry it is becomes it is a big question.

From the stand point of the techniques, it can be compatible there are many techniques may be including Nano lithography with etching. It can create structures that are compatible to the microelectronic industry, but whether technologically it can sustain the through put that to which the industry is used to is a difficult question to ask and the I think it will still say take some time before soft lithography based fabrication goes to the factory.

Of course the defect levels are higher because you cannot achieve that level of control what you have in photolithography. This is important then this you people should now understand that each of the techniques are sort of very specific, so soft lithography as a whole is very wide, but many of the techniques are very specific and they have limitations. For example micro contact printing works on a limited range of surfaces. You just saw that you need to have the appropriate surface so that the silen can bind. MIMIC is slowing not suitable for large area patterning replica molding, micro transfer molding and SAMIM not micro transfer molding. They leave some sort of a remnant layer.

So there are issues and more particularly micro transfer molding also works for only a specific class of a let say UV curable polymers so, it is not each of the techniques what I mean to say or what I mean to highlight that not all the techniques are very versatile. For example some of the most versatile techniques are Nano imprint lithography and capillary for soft lithography, which at least works for a wide range of polymers many almost all glassy polymers, can be handled by this particular method.

These 2 methods, but assuming that that NIL is pretty robust or CFL is pretty robust an under appropriate condition you can implement them nicely for a large number of materials or may be replica molding with silica (Refer Time: 06:56) 4. Here is a major limitation of soft lithography. Soft lithography is a secondary patterning technique. As it can only produce a negative replica under appropriate condition that to of a given stamp or a master. So the moment you

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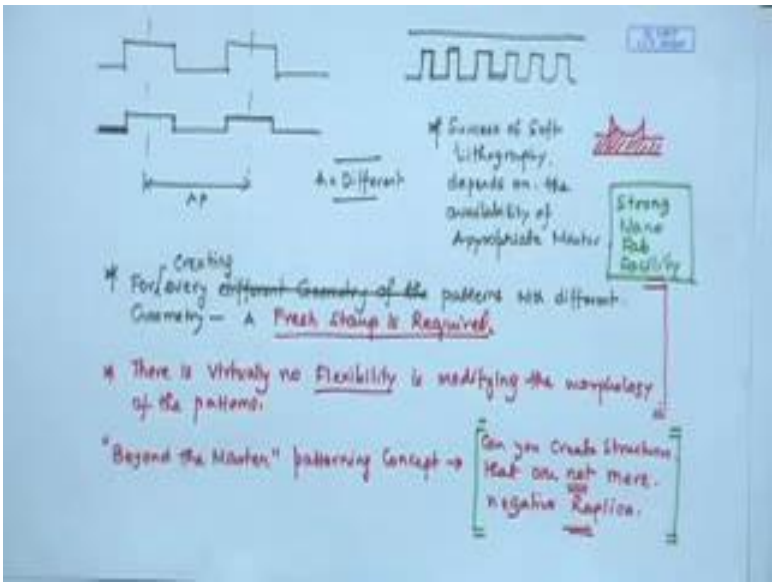

Let say would like to create patterns with two different geometric dimensions. What is the essential requirement you need structures which are you need original stamps that are different without that you cannot work. So this is a major problem. If you would like to create structures like this then you need a stamp which contains a negative replica of this particular pattern. If you need structures like this or may be here it is very interesting they have the same periodicity, but the height of the structures are different and you need different stamps nothing can be done.

So this is one major limitation of soft lithography and recently some I would say significant effort. So that way what happens is the success of soft lithography depends on the availability of appropriate master, which translates to the fact that for every different geometry of the patterns or for every different or every pattern I will just reframe it every pattern with different geometry every pattern for creating a fresh stamp is required. That is the limitation. So, you see that there is no flexibility in modifying the morphology of the patterns. You have a stamp and the best what you can achieve is a negative replica not more than that. Well you can have some incomplete replications.

Let say in CFL and get a structure like this, but then controlling it in a reproducible manner is a big issue. You can still do that, but then it gets limited the periodicity line width etc and determine by that of the stamp. So, significant amount of research is going on for the last few years, in making soft lithography more flexible, not flexible in terms

of like a silica stamp, but can you come up? So, the concepts are what is often called as beyond the master patterning concept. What it means is that can you create structures that are not mere negative replicas?

Why because this way every time you want to create a structure with a new geometry, new dimension you need a original stamp means that for executing soft lithography you are actually depending on a strong nano fab facility. You need that. So that in fact it is a one of the major advantages that it is executable by all and this and that which is not the right case, because you need the appropriate stamp is to be honest that is the fact.

So, this is how where people have been looking at. This is particularly valid for places where you do not have a very good nano fabrication facility, but you have a stamp and can you create structures which are different that then only a mere replica. So, I will give you 2 examples now and much later in the course when I teach you elastic contact instability may be last topic I will cover. I will give you 2 more examples there how these concepts very recent developments are taking place in creating structures which are not limited to a mere negative replica of the original stamp.

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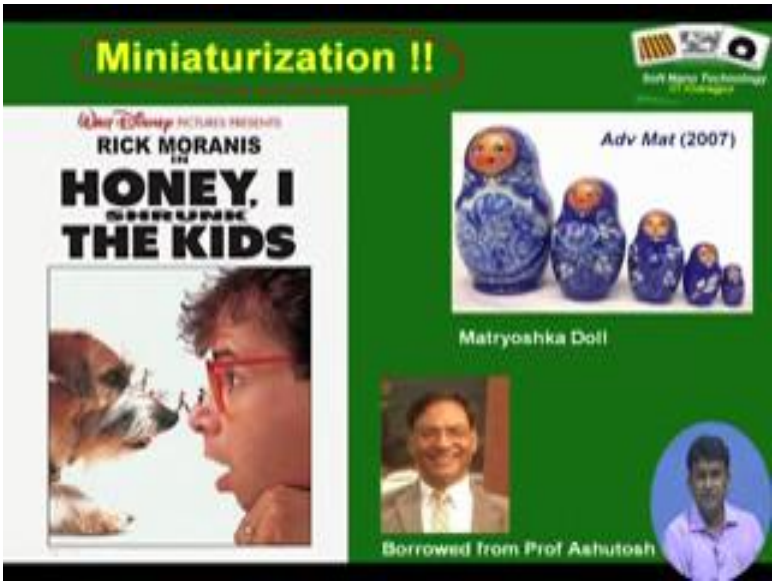

Here is the first example which realize on the concept of miniaturization. So, you start with something big and then you lead to that is something small. You have seen an example of this while we are taking about the use of a reticule in projection lithography, but here this was pioneered by professor Ashutosh Sharma at IIT Kanpur, what you see is

it is very simple use a special type of a material called hydro gel. Hydro gel you can just search what it is? It is special type of gel that contains lot of water.

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and what happens is, as the water evaporates the size of the gel it sort of shrinks. So, water evaporates, size shrinks and professor Sharma always emphasize that his idea was motivated by 90s blockbuster Hollywood movie “honey I shrunk the kids”.

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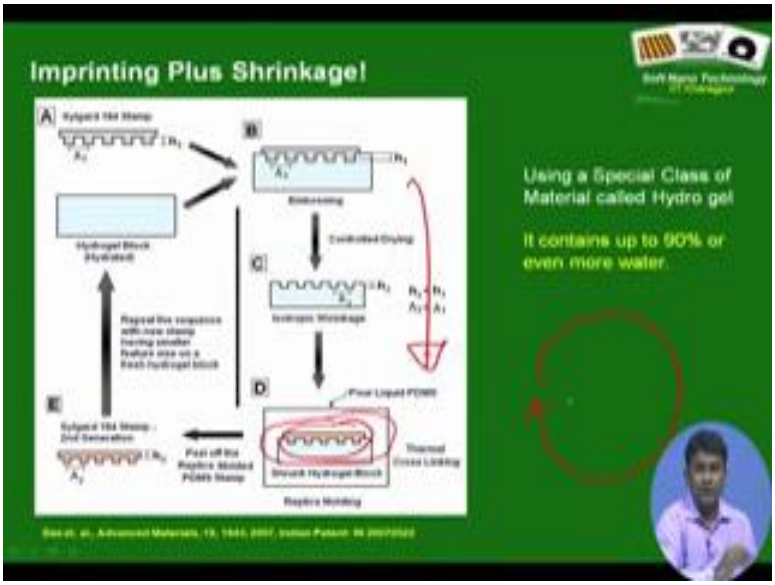

So, any way what it does is, you do a simple imprinting light replica molding or whatever, but you imprint a block of hydro gel and what it means. So, it is a soft material

so you can create the structures and then let the gel block dry. So, as the gel block dries up, it shrinks in size and as a consequence the patterns of a present on the surface also shrink. So, you allow it to shrink up to certain level then you simply replica mold another seal guard stamp from this shrunk gels.

So, what have you done? You have started off with a bigger stamp and then you have allowed the gel to shrink and now you have created a stamp with smaller features. Then you can take another block of hydro gel and which you can emboss with this the second generation stamp run this shrinking process. So it is sort of operates in a loop.

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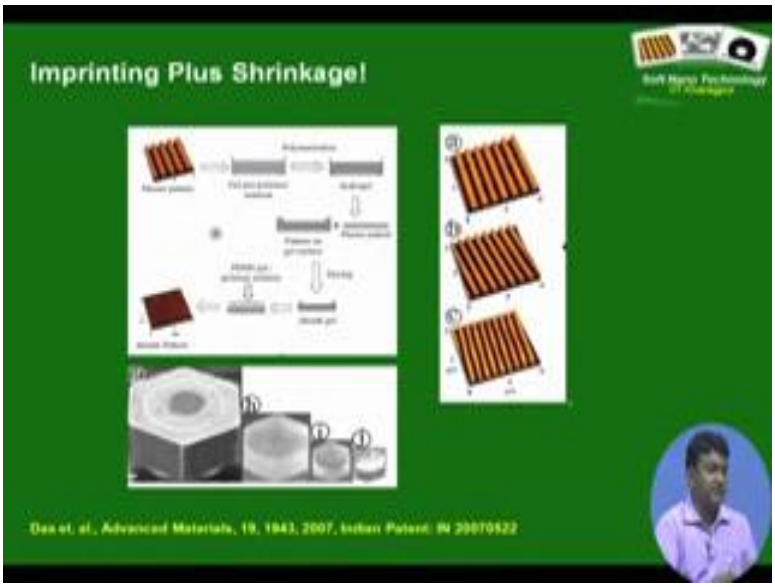

And you can achieve significantly actual reduction. So, you can see here that you have a master pattern you sort of do whatever I we just showed you imprinted a block of gel allow it to shrink and then what you get is patterns which have much smaller periodicity.

So, this is the first generation replica, this is the second generation replica, this is the third generation replica and you can go down significantly for several cycles. Only problem is the shrinkage is isotropic and therefore, there is a shrinkage which is advantage as well as a problem. There is shrinkage in periodicity as well as feature height. If you do not start off with a stamp that has very high features after 2-3 cycles the pattern simply tend to flatten out, but still the concept works and this was one of the first examples where you can create structures which are smaller in lateral dimension lateral size with a larger step.

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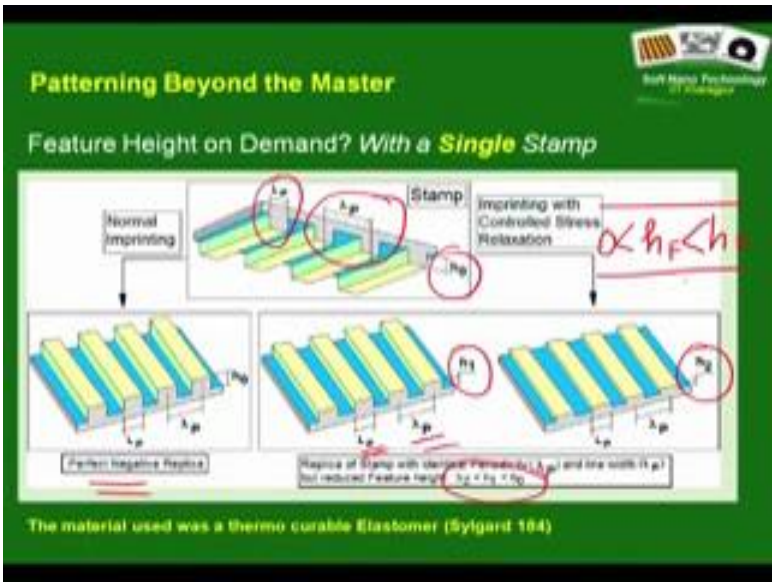

The second idea is this technique is referred to as elastic recovery lithography. So, this is also very nice concept. What you do is you take a stamp let say with periodicity lambda P line width LP and height is h0. So, now, you understand that you can create a perfect negative replica by many of the soft lithography techniques. You can use nano imprint lithography, you can use replica molding, and you can use CFL but the question is to ask is using this stamp is it possible to create structures that have the same line width and periodicity, but have different feature height? Of course, the limitation is the feature height varies between 0 and h0. H0 is the height of the original stamp feature.

What is the difference between this method and the previously reported method based on shrinkage? Here there is only reduction in the height the periodicity does not change. So, you might be interest to do some combinatorial experiment and this will be very very useful. So, how do you do it?

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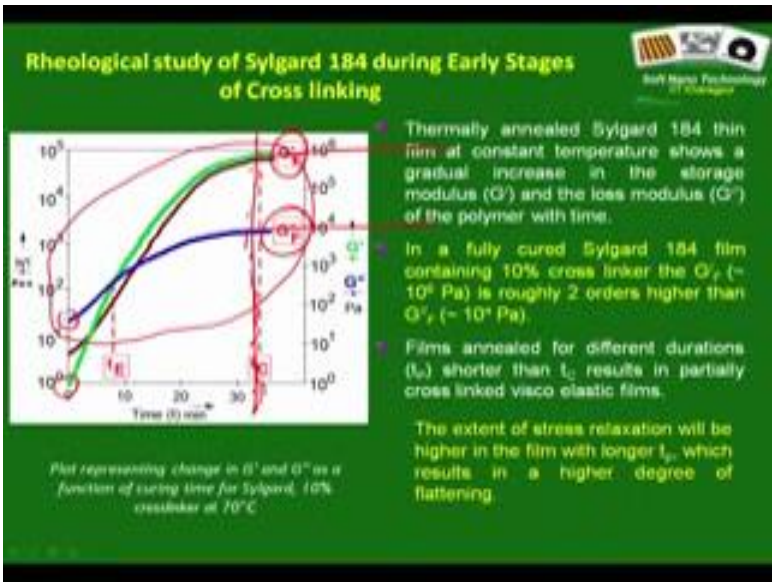

You in fact, do it by using a concept that we have come across during replica molding. What is replica molding? If you remember when we talked about replica molding, we took Sylgard. I mentioned clearly that Sylgard initially even when you makes the oligomer and cross linker part A and part B it is a pure liquid it is in a liquid form. Then you anneal it for some duration some 4-6 hours. It becomes an elastomeric solid. So, rheologically what is happening?

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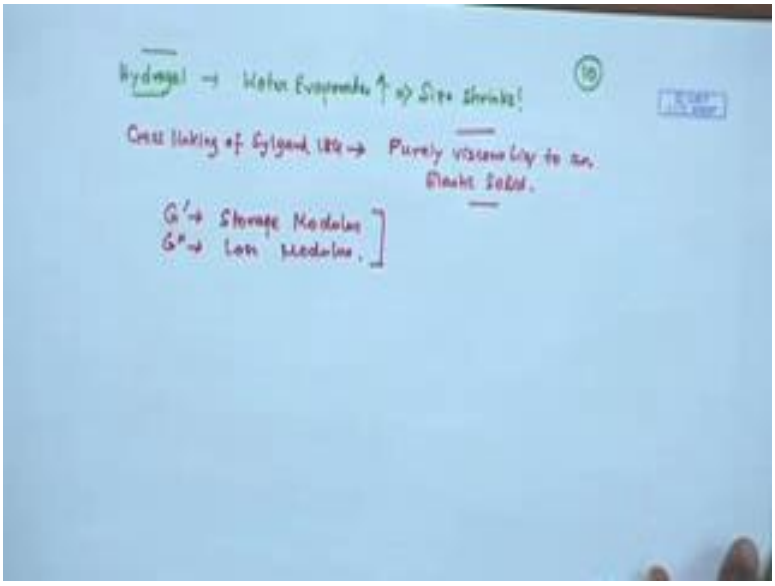

This cross linking process is actually transforming a purely viscous liquid to an elastic

solid and therefore, if you now look at the transience between these two stages what is happening? This transition has to be two different levels of visco elasticity. Which one can clearly see if one does geometry during the transformation process.

So, what it means that, if you now take two Sylgard blocks or films none of them are fully cured. It turns out that you actually do not need those 4 or 6 hours roughly 30 minutes the thing film fully cross links. However, you pick up a film some over here let say one is pre cured for 10 minutes one is pre cured for 20minutes. These two films are different levels of visco elasticity. Obviously the one that is pre cured longer as higher level of elasticity as compared to the one which has been pre cured for a shorter duration. This is particularly what has been utilized in this is the particular idea that has been utilized in this concept.

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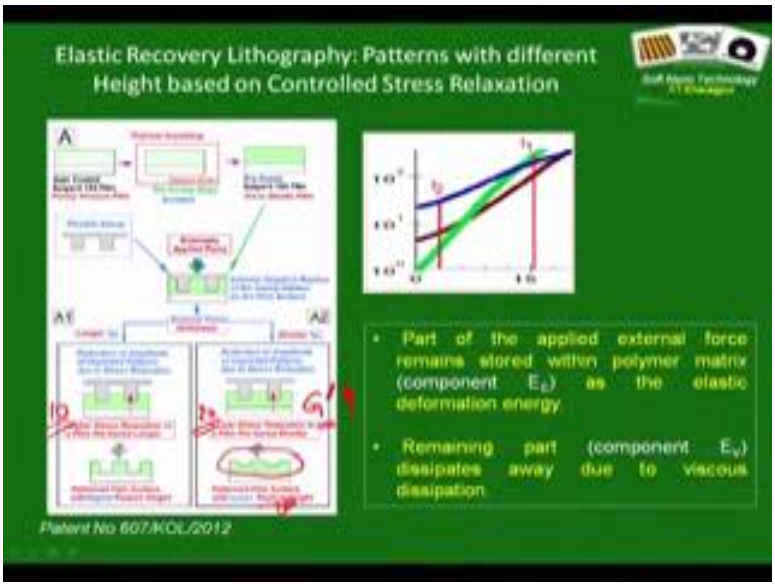

What you do is you take two identical Sylgard 184 films. I am again giving a very simplified picture not going much in to details of what is happening. You pre cured them for different durations. Let say we have two films here and one is let say procured for 10 minutes and one is let say pre cured for 20 minutes. So, what is the immediate thing you can tell? You can tell that this film has higher level of visco elasticity as compared to this film. G dash is known as storage modulus.

So, if you have done some course on complex fluids you can immediately get an idea, but otherwise also you can find out in the net what is storage modulus and this is loss

modulus. So, these two parameters or rather the relative values of these two parameters give you an idea about the extent of the exact rheology of visco elastic material.

So, what you do now? You emboss both the films with the same stamp. It is a weightless stamp for some reason we will realize. You apply some force like nano imprint lithography and you achieve an intrinsic negative replica, but what you do is that what we must understand that you are embossing a visco elastic film unlikely a pure viscous in nano imprint lithography. So, the energy was spending part of the energy is stored within the elastic matrix as a elastic deformation energy; however, since the materials of visco elastic part of the energy is dissipated.

So, next step is a very clever one which is not done in a nano imprint lithography and you with draw the external force. So, what you now have? You have two embossed films or imprinted films, but there is no external force to sustain this deformation. You simply have taken it out. So, the now film tries to relax back to it is original flat configuration, but the energy that has been consumed in deforming the film is not fully stored because if you deform any elastic film and withdraw the load that exactly what happens when you stretch a rubber and just simply release the load, the rubber relaxes back to it is original configurations, but this is not a pure elastomer. It is a visco elastic material. So, it will recover or relax back due to stress relaxation, but only partly. The extended of stress relaxation now becomes a function of the elasticity of the material.

So, the film that has been pre cured for a longer duration in fact relaxes more and the film that is given for a shorter duration relaxes less so what is the manifestation of this relaxation? The only manifestation of the relaxation is it will push up the stamp and that is the reason you would like to use a very very lightweight or almost a weight less stamp like a foil stamp or something like that. You do that therefore, eventually what you will get of course, you then subsequently place the films for subsequent cross linking to make the structures permanent that is an important criteria.

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And simply what you get is simply by wearing the pre curing time. So, here you see you have this different pre curing durations. You get structures with different feature height. You just look into the this number here in the vertical scale, but these are all atomic force microscopy images and therefore, it is extremely important for you to realize that I mean since you are getting this height then you can say that your technique has worked perfectly

But how do you get it and this feature height the vertical height is something that only an AFM can give no other microscope can give that to you. So, that in fact sort of paves us the way to take up atomic force microscopy very seriously which we are going to do from the next class itself. No pre curing so that is a limiting case that means that the film is in a pure viscous stage. There is no elasticity and then there is no restoring effect and therefore, the film fails to restore. So, with a stamp which has a depth of 120 nanometer you get a perfect negative replica which many times we refers to be a PNR nothing to do with railway PNR of course, you get a perfect negative replica, but you see you pre cure for different durations that the times you need to control very carefully.

So, essentially the visco elasticity of the film during imprinting actually changes and you get structures with different feature height. You can get similar type of behavior with long chain molecules even in a glassy polymer because of the fact that I will something I will avoid for the timing because due to the entanglement effect they are results in or the

entanglement of the long chain molecules even in a glassy polymer sort of results in some bit of visco elasticity.

If you anneal such a film for a prolong time there is stress relaxation. So, you can sort of utilize that and can use this technique with a bit of variation in protocol for creating differential heights structures even in a glassy polymer, but it works beautifully well for elastomer of course, here you see that with roughly 27 minutes of pre curing the structure is nearly flat only 7 nanometers. So, you cure it for it even for longer you get completely flat films. That is another limiting case so this is one limiting case where the film while it was patterned was purely viscous and on this side while the film was pattern it was purely elastic.

So, it results in a completely in a flat film and the reason why this 27 or 30 is because what you see in the aerometer. So, see after roughly 30 32 minutes the film sort of becomes fully cross linked. It is purely elastic. How do you get that? G dash is roughly toward as then G double dash and they do not change with time. So, if you do this experiment or run the aerometer longer then these two lines become parallel. Initially you can see the g double dash is high compared to the G dash and therefore, the film is in a viscous state.

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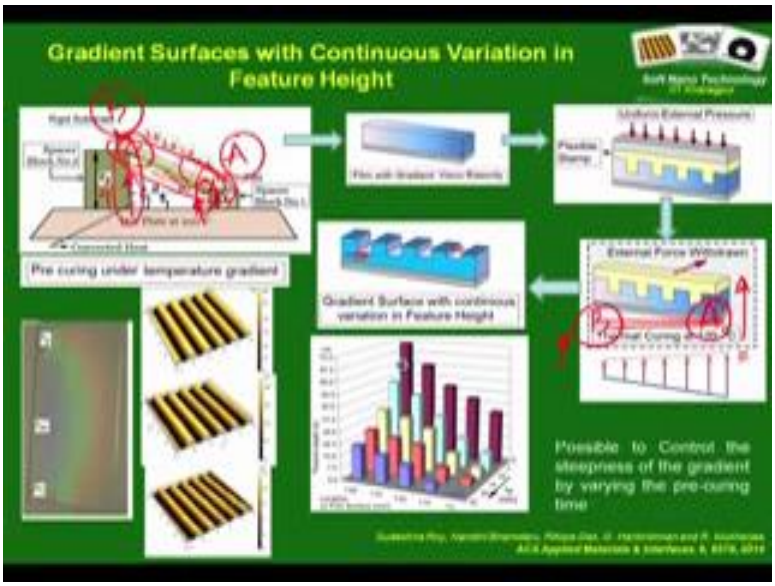

This method has been very cleverly used to create topographic gradient surfaces. So, you have topographic patterns, but the heights of the patterns sort of vary from one end to the

other.

So, when one talks about this pre curing of the films typically what one means is the film were put inside a oven to do the pre curing, but instead of that what was done was that you do the pre curing on a hot plate. So, you take a hot plate lab scale hot plate and you keep the film upside down film side is facing the hot plate, but what you do is that you take two blocks of different height and place the film in a slanted configuration. So, this part of the film is closer to the plate and this part of the film is further away from the plate. What it means is this part receives more heat flux as compared to this this part for a definite duration of pre curing for a particular for any duration of pre curing. What does it mean that this part the Sylgard over this part cross links more and this part cross links less and intermediate areas exhibit intermediate levels of cross linking.

So, what does it mean? This way you can very easily create a film with a visco elasticity gradient along it is length; now do the same repeat the same techniques. What now happen is different areas of the film exhibit different levels of stress relaxation. So, this part let us mark this as part A point A and this as B. This is a so this has higher level of elasticity. So, this will undergo most stress relaxation. This is B lower level of elasticity this will undergo less level of stress relaxation. As a matter as a consequence here the stress relaxation is more the feature height is less here the feature height is more and you can create topography gradient surfaces.

Most interestingly you can vary the time duration of pre curing and you can control the stiffness of the surface. So, all this can be done. So, these are some of the recent developments that are taking place and with let say a bio (Refer Time: 27:40) stamps or stamps with feature height. This way you can in principle creates structures which exhibit not only topographic gradient, but a weight ability gradient along it is length.

So, we talked about hydro phobic surface, hydrophilic surface. So, in principle it becomes possible to create structures that exhibits hydro phobic waiting state on one side and may be hydrophilic state on the other side. So, I stop here and that is sort of the discussion I wanted to have on soft lithography and next thing that is start in from the next lecture is a discussion on atomic force microscope because all this characterization we have been seen are done by AFM.

Let say techniques like where you create features with different heights if you do not get

an idea about the feature height you do not even know whether your method works or not. So, that is why the utility of an AFM comes in. So, see you in an AFM class next.

Thank you.