Soft Nano Technology
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Lecture – 20
Soft Lithography – 3

Welcome back, on our discussion on soft lithography. To be more specific we are discussing Nano imprint lithography.

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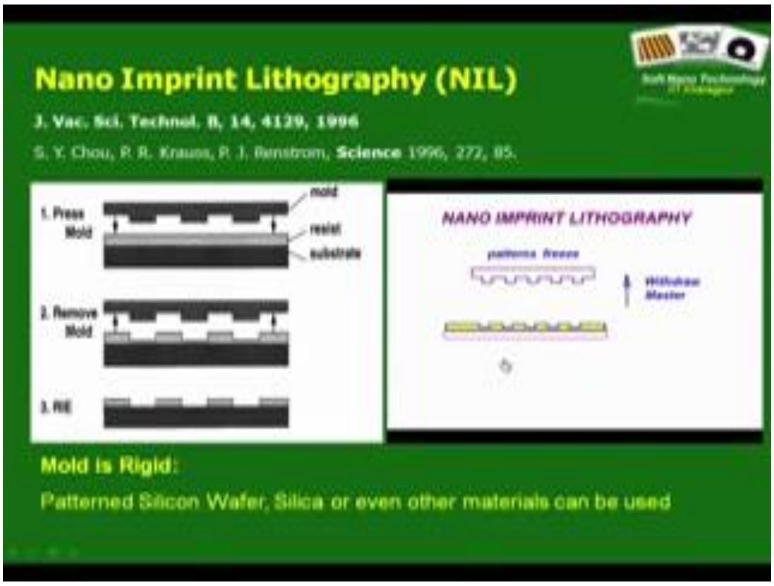

Now, quick recap of what do we have discussed in the previous class. So, this slide this cartoon should make sense to you now. This is a very brief schematic or a very simple schematic of thermal NIL and you understand that you take advantage of the fact that you can soften a glassy polymer by heating it beyond its glass transition temperature. You have a mold which has relief structure at topographic patterns. You simply press it hard against the soften film and you can create negative replica.

There are issues, certain issues we will discuss in this particular lecture and there are other techniques for example, two circumstances

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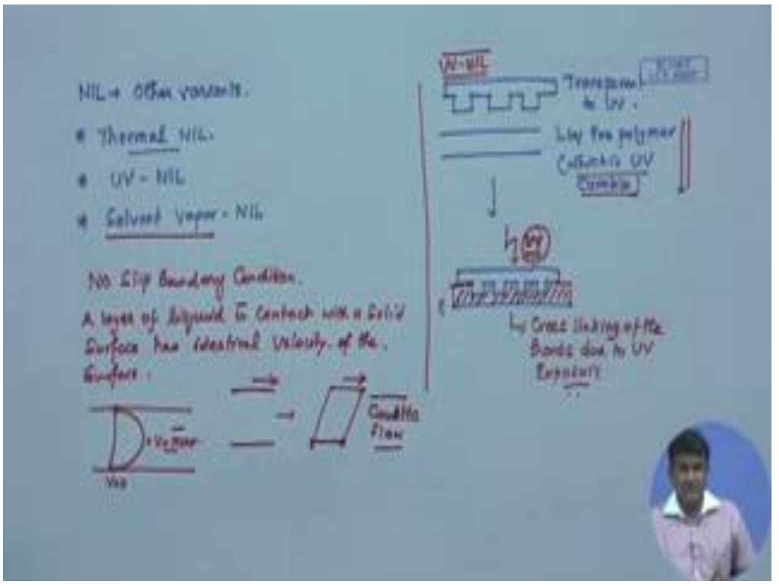

And those problem one of them is UV-NIL which we discussed. Solvent vapor UV-NIL I will discuss a little later, but there are certain very fascinating signs associated with the patterned replication mechanism in Nano imprint lithography, which I would like to highlight. You can consider that to be a limitation, but it is for the sake of understanding the mechanism it is extremely important to understand that.

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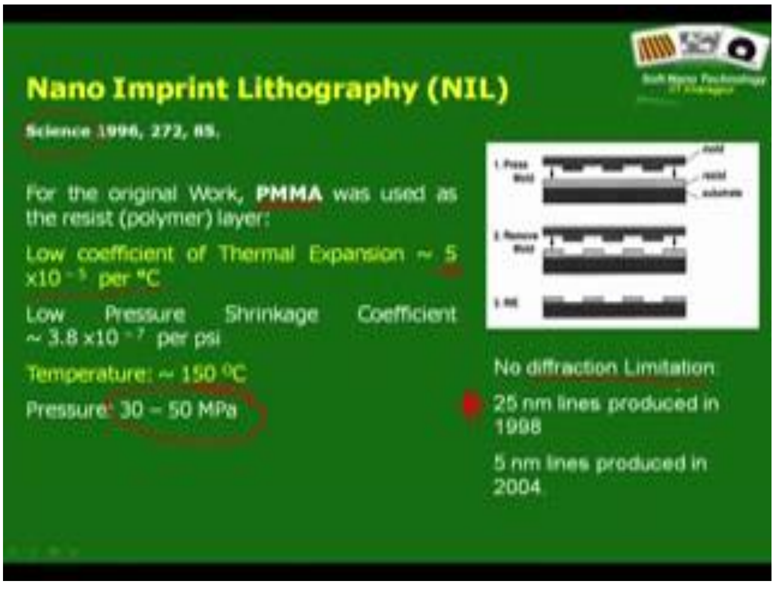

So, this was first reported in 1996 and see in such a simple technique, but such was the elegance and importance of the discovery it was again published in science. There are

PMMA poly methyl methacrylate is used as a wonderful layer as this glassy polymer. It has to have a low coefficient of thermal expansion because this is an issue because you are heating up the polymer; you are also heating up the stamps so the pattern replication takes place at the elevated temperature.

So, if there is a significant mismatch between the coefficients of thermal expansion between them during the cooling step there can be certain problems. So, this is one critical thing you need to check out pressure applied was 30-50 mega pascal which is on the higher side temperature at which the imprinting was done was 150 degree centigrade. Very important note diffraction limitation and see I mentioned I think I was bit wrong in the numbers 25 nanometers was achieved 2 year back in 1998 and 5 nanometers in 2004 that is significant.

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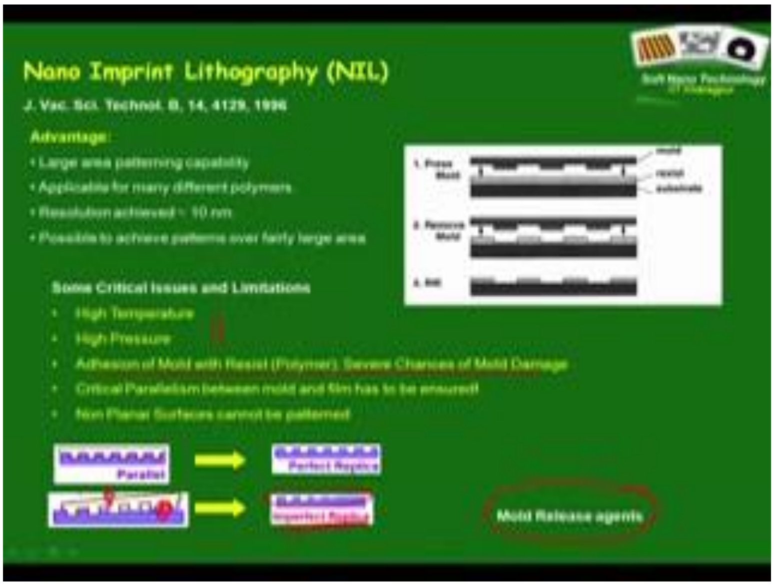

Of course, limitation is high temperature high pressure. There is a severe problem of one of the step we should very easily like you stamp it and you remove the mold there is a problem. Mold release is an issue mold release because it is a digit stamp you cannot peel it the way you had peeled let us say for example, in replica molding so, that is a critical issue and you also need to ensure that there is the mold and the film are maintained in a perfectly parallel configuration because if you are unable to maintain a perfectly parallel configuration, you will get a sort of a gradient geometry or an imperfect replica also dust contamination one has to be very careful.

So, if you have a dust particular over here and you are applying pressure from outside this will lead to significant breakage of the stamp. So, that is a problem and many people who have commercial Nano imprint lithography instruments these days preferred to perform NIL inside a clean room. So, that in fact takes away one of the major advantages of soft lithography in general because one of the ways I try to impress upon you the advantage of soft lithography is that it does not require major infrastructures, but see again you are back to a clean room and stuff like that.

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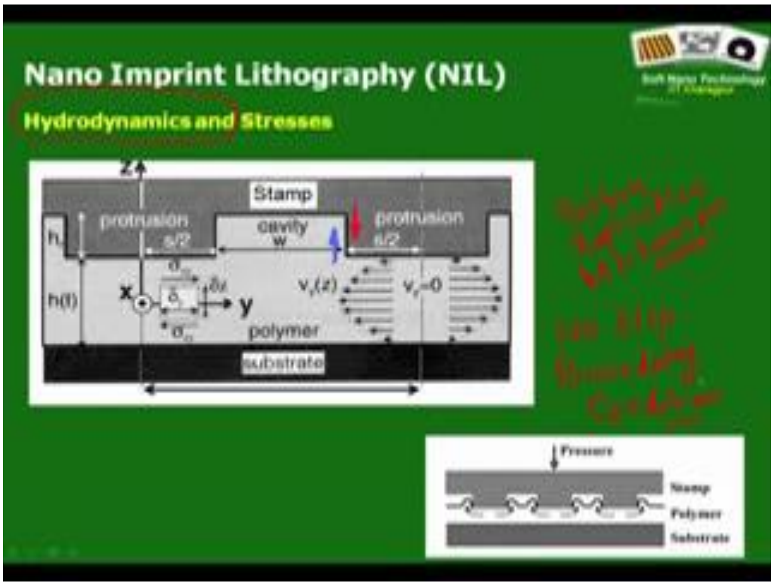

But more importantly let us understand the pattern replication mechanism at the hydrodynamics of pattern replication. So, I will spend few minutes on this. I am assuming our even if you do not know you can just google it out and find it out, all of you understand the meaning of this word no slip boundary condition. What it means that a layer of liquid in contact with the solid surface has identical velocity of the surface; that is why when you draw a flows through a pipe it is a pipe wall you always draw the velocity profile to be something like this because the pipe walls are stationery and therefore, velocity is 0 here and v is maximum at the center.

That is also the reason if you have a some amount of liquid between 2 stationery plates and you start moving the top plate the liquid in fact, deforms like this because the bottom plate remain stationary and the liquid at the bottom as a consequence of that remains stationary and the liquid at the top in contras moves. So, this is also very famous this is known as coquette flow.

So, I am assuming that all of you have some knowledge about fluid dynamics, but even if you do not have these are very simple concepts and either you have already understood or you can just check out in the net to understand this.

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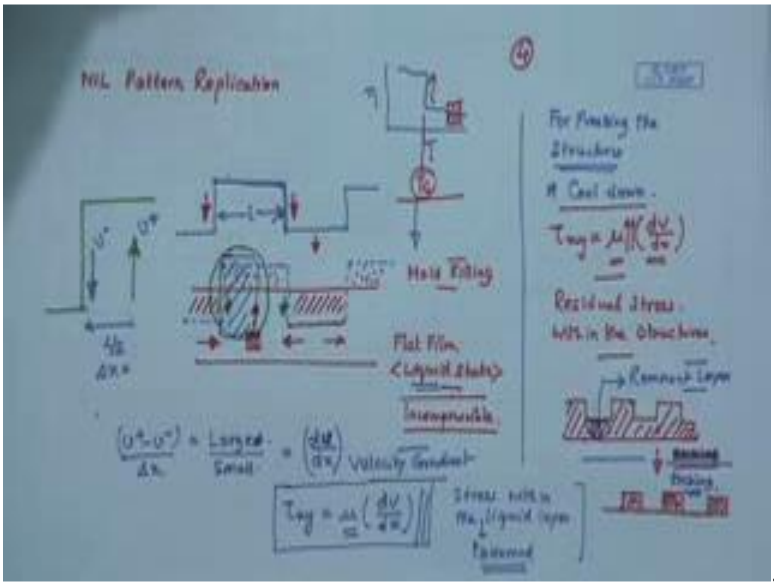

Now you can have a look into what is drawn here this particular picture or I will draw it. This is what it captures is the sort of an intermediate stage, when pattern replication is taking place. Look into it carefully. So, you have a flat film which is soft let us assume it is in a liquid state, it is a high viscosity liquid that does not really matter, but it is in a liquid state and here comes your stamp. So, let us just focusing on one of this stamp features. So, what you do the stamp is coming so, eventually what will happen is the stamp will let us say take a configuration like this and these areas the liquid will sort of work and fill up this area. So, this is what is known as mold filling.

Mathematically you can claim that whatever is the polymer or the liquid that was here as if it is simply displaced to this area that sorry the drawing is not that great, but does not matter, but you are all understanding what I mean. So, that ensure that you are conservation of mass is valid, but physically it is not that simple. How does the transfer takes place? The transfer takes place is based on this area pushes the polymer or the liquid downward but since it has a rigid bottom boundary it triggers an outward flow right and this particular zone in fact, receives liquid from the two sides therefore, it cannot push.

So, in order since the assuming the liquid to be incompressible and most liquids are incompressible. In fact you cannot compress it you apply pressure if the liquid gets compressed it will not flow it simply like air but that is not the case with liquid which most liquids are incompressible. So, this particular zone in fact, it is receiving liquid from both the sides. So, what does it do? It will simply trigger and upward flow so, in fact that upward flow is responsible for the mold filling fair enough, but there is more to the story and that issue is the stamp is or the mold is being pushed down its coming down. So, over these areas the mold is coming down it is in contact with the liquid and because of no slip what we just talked the liquid adjacent to the areas where it is in contact with side walls of the mold they have a downward velocity right? However, at the centre it triggers because of this squeezing out flow it triggers upward velocity.

So, if you are aware so, over this small area let us draw it in somewhat greater detail. So, let us say this is the central part of this feature and this is the stamp wall so, here you have a downward velocity, here you have an upward velocity, you are talking about Nano patterns. So, anyway this L the line width is small. So, this is half of the line width l by 2 or some sort of a delta x which is very small. So, v plus is in the positive direction v minus in the negative direction. So, v plus minus v minus is large. You divide it by a small quantity and what is it? It is in fact, Del u Del x or Del v Del x it is the velocity gradient.

So, you have a very high velocity gradient. So what? What is shear stress as you all know even if you assume this to be a Newtonian fluid scales as the velocity gradient and what did we say? This polymer is in a liquid state, but it is a high viscosity liquid. So, mu is already high the velocity gradient is very high. So, what it leads to? It leads to very high shear stress within this zone and what is this zone? It is actually the area where the patterns are forming.

As I mentioned that this whole process in fact, leads to significant amount of stress within the structures that get generated. Here is this picture in fact, talks about a bit of details but an essential physics I have captured. So, this is the protrusion .Since this area pushes the liquid downward it triggers an outward flow in both the directions and this particular area receives liquid from both the sides and it triggers an upward flow.

And eventually we can see that this leads to very high degree of residual stress within the liquid layer or I just rectify patterned liquid layer. Anything else? Well what do you do in classical thermal NIL to freeze the structures? You in order to freeze the structures what is the step you do? We cool it down why? Because if this is your plot of viscosity verses temperature and you now all understand this is where TG is and you would be doing your pattern replication somewhere over here right.

So, you cool down to solidify the structures right, but what is actually happening what is leading to this so called solidification? It is in fact, significant enhancement in viscosity. So, as you cool down your mu goes up. So, the multiplier goes up this gradient is already very high. So, as the structures get frozen the in fact, have very high amount of stress within them what happens to this stress? The stress does not get released this remains as the residual stress within the structures.

So, it is extremely important to note down that thermal NIL the patterns you make excellent patterns of course, you need to understand that there is some polymer over here remnant polymer for certain applications it is fine, but certain applications you can do additional etching of these polymers or whatever and you can create isolate scripts as such secondary processing, but NIL I mean I think I will just emphasize it. NIL in principle creates a structure like this is a pivot photographic contrast along the film.

It does not guarantee in any way that is not its purpose to create structures like this right? It is not its purpose of course, you can take this and subject it to some sort of plasma etching or whatever what might happen that polymer from all the areas gets etched away at the same rate and as a consequence since the thickness over these area is smaller, it gets completely etched out and along the strips there is still some material and in principle which suitable etching you can create structures like this. It is also interesting to realize that if with suitable etching you can makes structures like this and there is no diffraction limitation. These are now compatible with the semi conducted industry because if this material this polymer can act as a barrier during the doping you are done.

So, all these things people have been trying to do. So, people for some period of time significantly thought that one of the way to circum when this diffraction limitation in photo lithography is to relay on soft lithography techniques and Nano imprint lithography was one of the front runners. It has seen partial success I am really not an expert in that area, but you can in principle do that but please realize that without etching and etching is not part of NIL because etching we have talked in even in the context of photo lithography and we mentioned that it requires separate infrastructure. NIL leads to a film like this .This area one can form as the remnant layer. So, the structures you make by NIL it has significant residual stresses embedded in them or I will freshly write.

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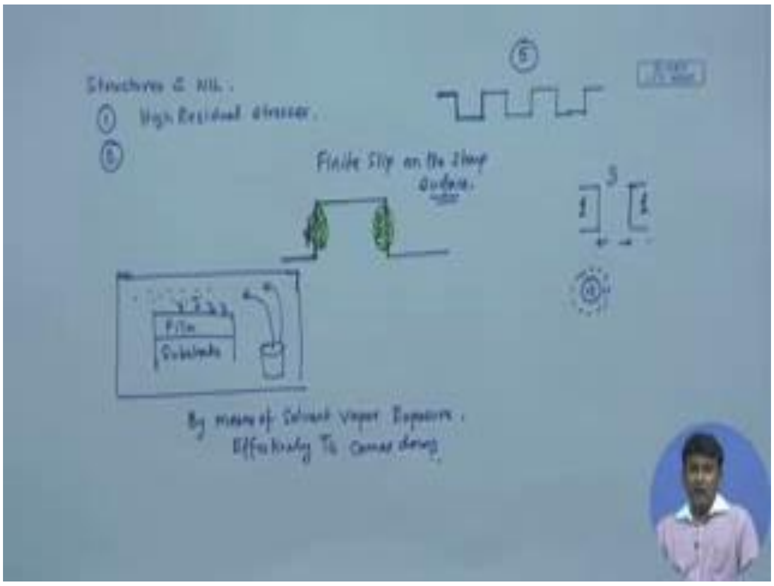

High residual stresses and there also there is some significantly high surface energy penalty. So, surface any area wise so, there are issues related to the Laplace pressure because by way of patterning you are increasing the surface area, but that is far in significant compared to this stresses that are piled up.

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And will anything with stress is not good humans. Doctors always tell you reduce your stress same thing is valid for Nanostructures. So, if you now use it for prolonged usage. One notices that the structures tend to flatten out. One can see this type of tracks or sort of bearing like this which is all signatures of this release of this stresses of course, this flattening is not fully attributed to stresses it is also attributed to the reduction of the surface area or slumping phenomena.

So, this is one of the aspects of one need to realize, these are very new techniques. So, you can come up with the technique, but there might be issues and which might be in an embedded in the physics of the system itself which can sort of an effect or influence of an adversely in the long term stability of the structures and things like that. So, these are thing that you should know and in the physics is also of course, very interesting. In fact, I must highlight that apparently Nano imprint lithography is an Nano patterning technique, but the way you can understand the stress accumulation is related purely to the undergrad speed mechanics you have done either in your in any of your engineering courses. So, see science is pretty seamless I mean everything that happens as I told before also you should be able to explain based on whatever knowledge you have.

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So, these are certain comparisons between thermal NIL and the UV-NIL. I must mention that despite all the limitations thermal NIL is still the most popular technique and there are instruments available which are very expensive again in the commercial market which practices thermal NIL of course, UV-NIL also instruments are available. So, of course no thermals cycling is a very exciting prospect of UV-NIL no possibility of coefficient of thermal expansion mismatch is very fast .Very low force require because the UV curable material is at a liquid state and low viscosity liquid at room temperature.

There might be issues related to volume shrinkage during phase transaction because UV curing is nothing but there is a transition of phase and of course, getting uniform layers which been quoting is difficult at times I would not emphasize this too much because one can control the spin coding parameters getting a new of course, you need severe restriction in the material that you can patterned and you must have a stamp that is UV transparent .Of course, here the limitations of the problems are you need large force you need high temperature .It is viscous difficult to handle and of course, but I will discuss later.

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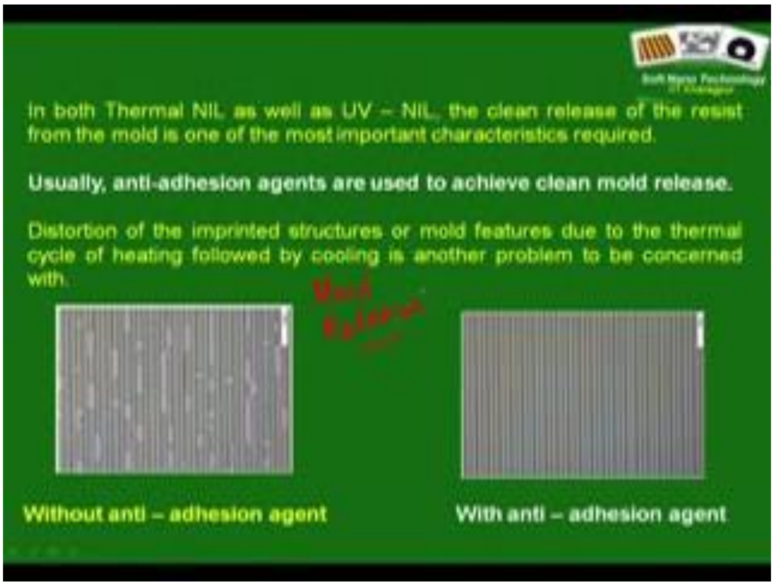

Maybe, I just quickly go their stamp release is a big problems stamp the mold release because you will be surprised again to realize it is in fact, the no slip condition which we talked about and you saw that it is responsible, for this so called generation of high (Refer Time: 20:58) one quick term I just forgot to mention why or what is this flow locally you see along the walls of the stamp which is going down? If you just compare it is nothing but coquette flow. It is because of stamp wall is moving and the liquid layer adjacent to it is also moving downward. Here the bottom is stationary in the classical example of coquette flow here what is happening because of this accumulation over this control volume here there is an upward flow. So, the stress, the velocity gradient is an even higher.

But what is interesting is, the issues related to mold release is during the pattern replication you saw the dis layer of liquid is adjacent to the stamp and it is subject to no slip and it as frozen there. So, the viscosity as increased and now when you want to detach the stamp you are in fact, overcoming this strong adhesion between the liquid layer and the stamp wall at each of the side wall of the mold feature and that is often very difficult to sort of overcome and you In fact, need to come up or quote your mold with some sort of mold release agent.

In fact, this is also situation where if you have finite slip on the stamp surface it is in fact, good because what will happen if there is a slippage this liquid layer adjacent to the stamp will sort of slip and it will not move downward at the same velocity as that of the stamp. So, the effective velocity gradient will be less and why I raise this point is, the movement you actually quote the stamp with this anti adhesion agent which are essentially low surface energy quoting. I have already given you a talked about the spreading coefficient.

I will talk in one of the later classes about one more term which is essentially here in the same terms what is known as work of addition and you will see that the work of addition can be released if the surf substrate surface energy is reduced. So, typically the stamp is quoted with some low surface energy material to reduce the addition which also in most cases enhances the slippage. So, these issues have to be addressed in NIL though the apparently the technique looks very simple.

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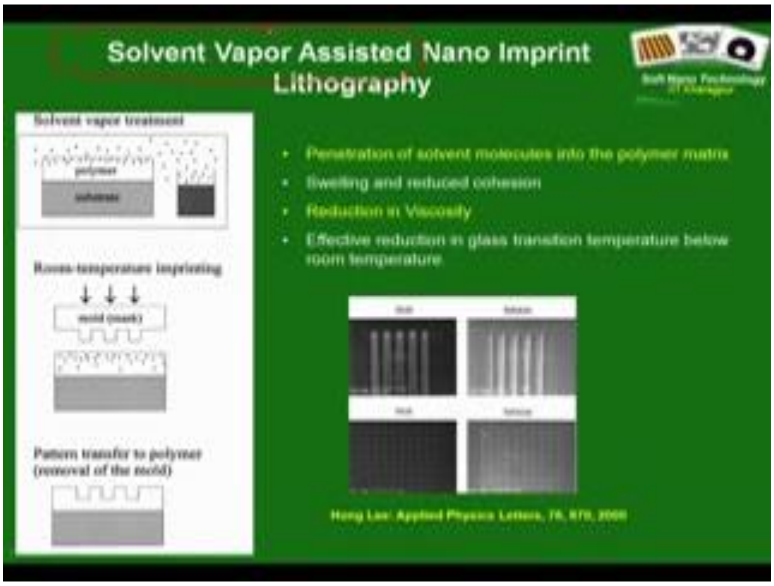

There is another version I mentioned before is the solvent vapor assisted in NIL. What it does is it realize on the fact that if you expose a polymeric film, so this is substrate this is the film you do not dip it in a liquid in a beaker of solvent then it will simply dissolve away, but if you sort of expose it to a chamber which are solvent vapor because these are often rapidly evaporating solvent. So, vapor pressure is pretty high. So, this chamber gets saturated with solve and molecules. Now this film in fact, likes the solvent. So, what is if the necessary condition for solution? I mean if you go back to the example we have talked about in order for just the way in order to have stable colloid one and one in a liquid medium 3 should go away from each other.

Similarly, dissolution is something very similar only issue is every molecule of the solute should be surrounded by a layer of solvent and since it is a good solvent. It is obvious that the molecules want to be surrounded by these solvent molecules. So, what happens is the solvent molecules start benefiting into the film and what it does is that reduces or that first increases the space between adjacent molecules, adjacent and molecules constituting the film or adjacent and solute molecules. As their space increases the strength of their interaction reduces and what it means is there is an effective reduction in their viscosity and therefore, by means of solvent vapor exposure effectively the TG comes down and if the film has up taken adequate amount of solvent it sort of behaves like a liquid at room temperature.

So, you essentially eliminate the thermal cycling again, but please understand that as the film accommodates more and more amount of solvent molecules there is significant swelling of the film you can do a patterning at this stage. In fact, people as done it, but then we need to again frees the structures and what you do you would like to take the assembly out of the solvent vapor chamber and would like to dry it, but then the solvent when the solvent molecules escape there can be some issues related to the shrinkage of the film material and therefore, SV NIL again a nice technique it can be implemented at room temperature, but there are issues particularly with shrinkage of the structures during solvent evaporation.

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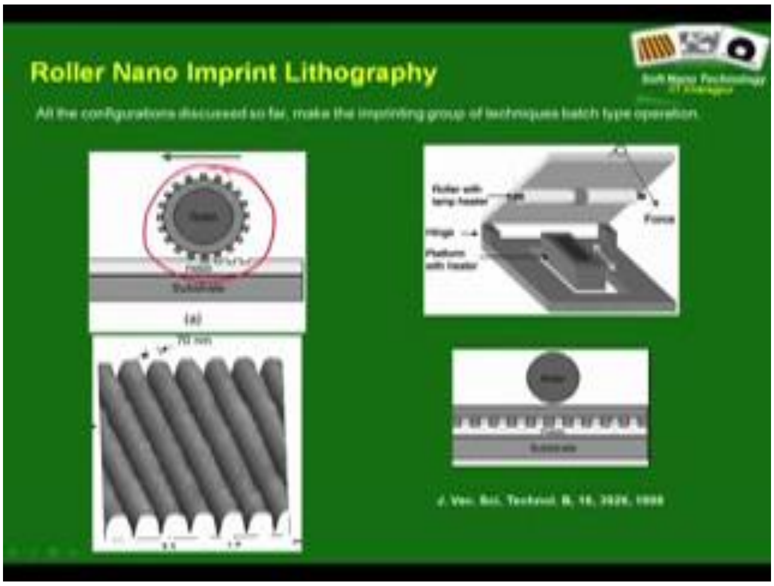

What is next is that all these lithography techniques we had been discussing? So, for they had been implemented in a batch like mode and engineers are very fascinated to have continuous processes. So, people have tried to transfer NIL into a continuous platform with a stamp that is in the form of a roller. This is often called as roller Nano imprint lithography.

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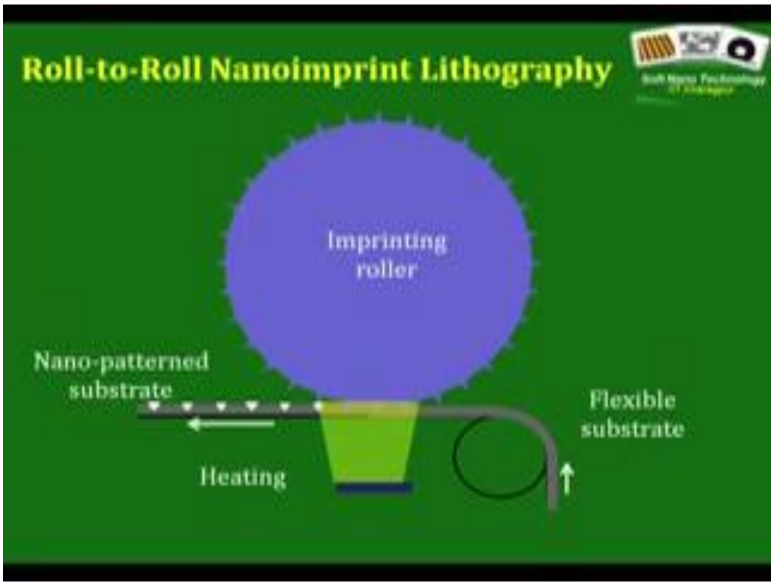

And there are very critical issues, but roller Nano imprint lithography works very well with flexible surfaces, but there are very many critical issues like the temperature as to be very accurately controlled and the viscosity should be absolutely appropriate the contact time should be absolutely accurate here.

So, that you get perfect patterns and then you need to heat up and then cool down immediately. So, that the patterns do not flatten out because of Laplace presser and issues like that. So, these are seen some success and in very specific cases it is probably industrial use, but it is good to know.

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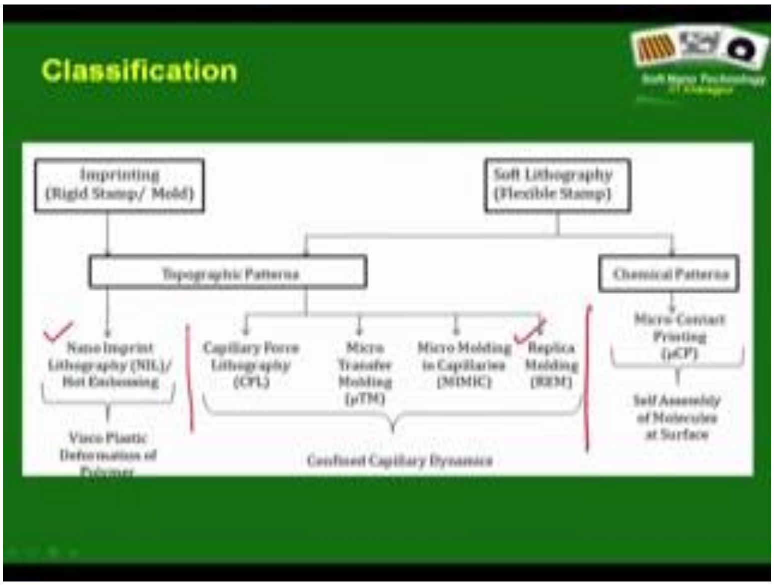

So, with that I think I will stop my discussion on Nano imprint lithography. So, I am back to this particular slide where we now understand that we have learnt two techniques and in the subsequent may be two classes we will discuss the remaining techniques.

Thank you very much.