Soft Nano Technology
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Lecture - 21
Soft Lithography – 4

Welcome back and 21st lecture now. So, we are done more than half way and it a good time for you to check what the new things you have learned are. Quick recap, you now understand you should be understanding surface tension in much better way. You should not be wondering looking at those beautiful tall buildings skyscrapers in all the mega polis cities in India now. You now understand that they content some self leading coating. You should also look at a compact disk or a DVD and should realize why it shows rainbow colors.

So, I am assuring that many of you knew all these before, but I am sure some of you have learnt. Because that my experience with undergrad and postgrad students where I teach at Kharagpur. More interesting phenomena which you can explain with what we have learnt. This can be bit of brain twisters I am just placing them you just start thinking. One of the things most of you have seen as a child is that beautiful so bubbles that float around freely. What you had to do is that you had to add a bit of soap into water. You can never have a soap bubble like thing another the term is soap bubble; you can never have a pure bubble with water. Now you know what is surfactant? So, why you need that bit of soap solution bit of soap in that solution.

A second question you may try to look into and even if you Google it I am sure you will get answer which will be pretty simply understandable you. Is that if you do shampoo of your hair, you tend to see that your hair has become very flappy. Why does that happen? What really makes it like that? In fact, if you are searching for an answer to this question why do not you also try to find out, what is the role of a conditioner, because for the last 20 years so the Indian market is completely filled up with shampoos which comes along with conditioner and which, in fact leaves a here that is properly cleaned, but that is a bit manageable than a shampoo which does not have conditioner.

So, why do not you try out what these are? In addition to this you are now also know that, your latest tablet or your pc or your laptop why its clock speed or the processer

speed is much faster than the one you had seen at your home or you had four years back? And stop admiring great progress by computer scientist. In fact, this is the material scientists who are doing all the great work because; you now know that this progress is entirely due to progress in photo lithography right? You also understand now why on a beautiful rainy afternoon if you are lucky to see rain drop dropping over a lotus leaf and you see that is rolling away. You now know that in fact, the waiting state on the lotus leaf surface is classy. When you also see a beautiful rose which has a drop of water sticking to it respective of whether you turn it up and down.

You in fact, know that the surface has very high hysteresis and therefore, the water does not get dislodged. So, I am sure you are enjoying this course which I will be keener to really hope that you have learned something new and that is the most important thing to me is to learn new things. Then try to somehow use your knowledge in trying to understand and explain things that you see around you.

So, let us move on and continue our discussion on soft lithography is the 4th lecture of lithography over all 20st lectures now.

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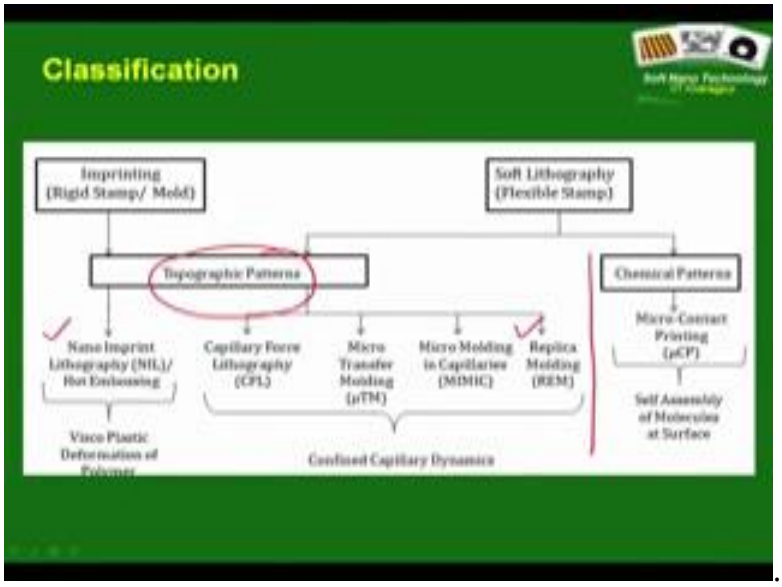

And if we are back to this particular slide, which acts as a very good guide; I love this classification. You now know NIL sorry forgot to turn on the pen. Old people always tend to make mistakes. So, you now know Nano imprint lithography and you now know

replica molding. What about the other techniques of course, all the techniques we have talked so far. They are able of creating topographic patterns right?

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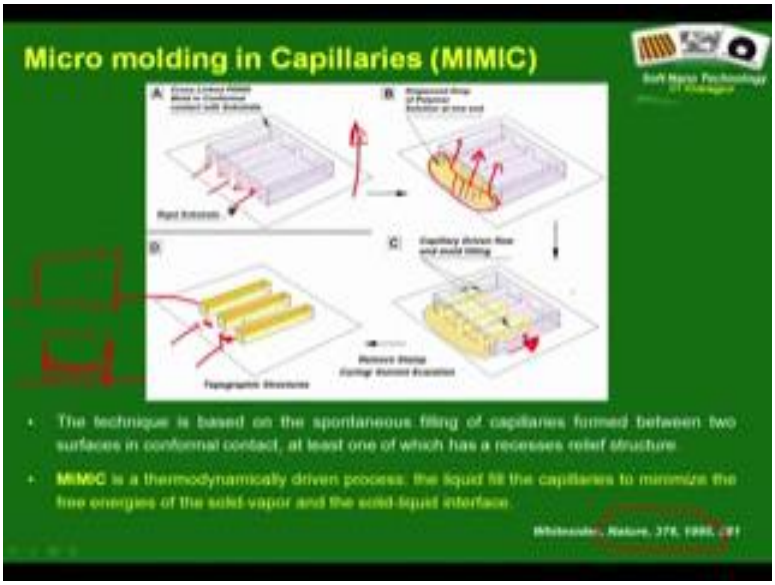

Next what we discuss is micro molding in capillaries and what you do is, in some ways tries to eliminate some of the problems that are being faced.

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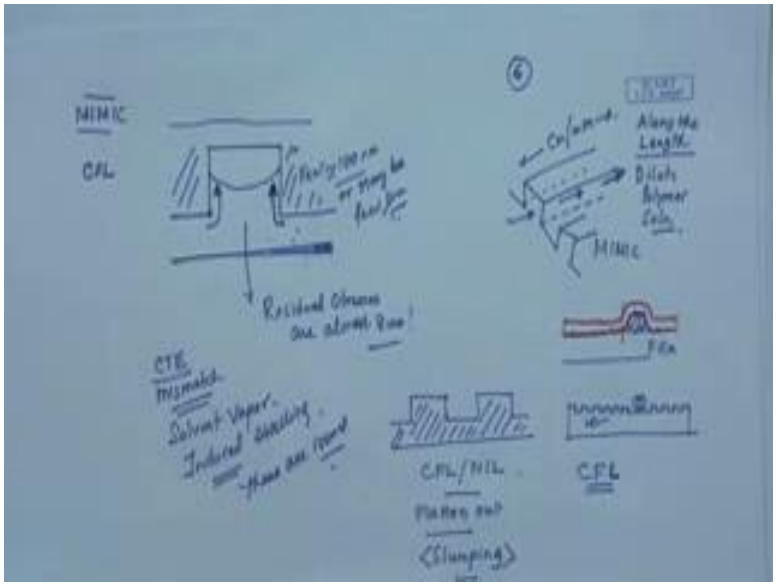

Let say in Nano imprint lithography, it is a very elegant technique, but honestly speaking not very effective. It has certain advantages, certain special capabilities which no other technique can offer but when it comes to routine pattern I am afraid. Nano imprint

lithography is far more popular. So, what you do is you tend to realize that couple of major problems of Nano imprints lithography using a rigid stamp therefore, stamp release is the problem. Also you are trying to pattern a very high viscosity layer, a molten or a softened polymer films straight away. So, the viscose traces first you need a high force to do the deformation and. Secondly, it also leads to very high level of residual stresses.

MIMIC, what you do? You do not start off with the film. You simply take a stamp created by replica molding, so this now flexible. Since it is flexible you simply bring it in conformal contact with the substituent. So you see, if you have a grating pattern stamp on one of the sides, it actually makes zillions of micro channels I have limitations and therefore, what I have shown is only a few of these structures, but you can imagine that if the periodicities of this patterns is let say 1 micron and your stamp dimension is let say 1 centimeter, how many of this channels you make? What you do now is you take a dilute solution of the polymer or the material of with which you would like to create the structures and simply dispense it at the open end right? Now if the stamp wall is weighable and which you can always do by controlling the surface energy, may be I will give you some recipes how to do that later. What will happen there will be capillary driven flow along each of this capillary micro channels.

As a result the liquid meniscus will move. So, eventually all you need to do is, let the solvent evaporate and then what you get is strips of this polymer or the soft materials along the contours of the stamp. Remember this stamp is a flexible stamp. Therefore, you can very easily so, your problem of coating the stamp with release agent, then removing it which has been encountered in NIL is gone. You do not need to heat it up in NIL I like NIL. So, that problem is gone. You also do not require to apply any external pressures. So, that problem is also gone. So, this is what is MIMIC also if you look very carefully, this method is straight away microelectronic or IC fabrication compatible because in principle if your MIMIC is well executed it does not leave behind a remnant layer like Nano imprint lithography.

Why? Because over these areas the stamp was in conformal contact with the substrate and therefore, it did not allow the polymer to get deposited. In reality this is in fact a problem often these liquid lead to some bit of flooding and there is buoyancy force that

leaps up the whole stamp. So, that is a problem but, in principle you can do that. Again such a simple technique originally published in nature in 1995 by White sides.

There are however, despite all the elegance of the technique there are certain issues. One of the issues one needs to understand is that you are replicating a dilute solution of the capillary flow is with the dilute solution. So eventually when the solvent evaporates away you never get a structure with the polymeric material that irrespective of whatever I have drawn that corresponds to the full cross section. So, if this is the cross section of one channel, let say you are very likely to get some structure like this.

Why this may or may not be there this depends on this is sort of an indication that is the stamp wall is wetted well, but you may not have these, but you may have some shallow structure. Why does this thing happen? Because, during the capillary driven flow as shown in this particular step, the flow is taking place with the dilute solution right? Therefore the channels are filled to with the dilute solution which is the case in fact in NIL.

So, once you feel that the capillary dynamics is over and the and eventually the solvent evaporates away is going to be significant loss in dimension because of the shrinkage because of the evaporation. The other major problem is, I will not go to the mathematical formulation, but one can get this formulation pretty easily. The capillary driving force drops away as you go deeper into the channel. So, after a certain point the velocity of mold filling becomes very very less.

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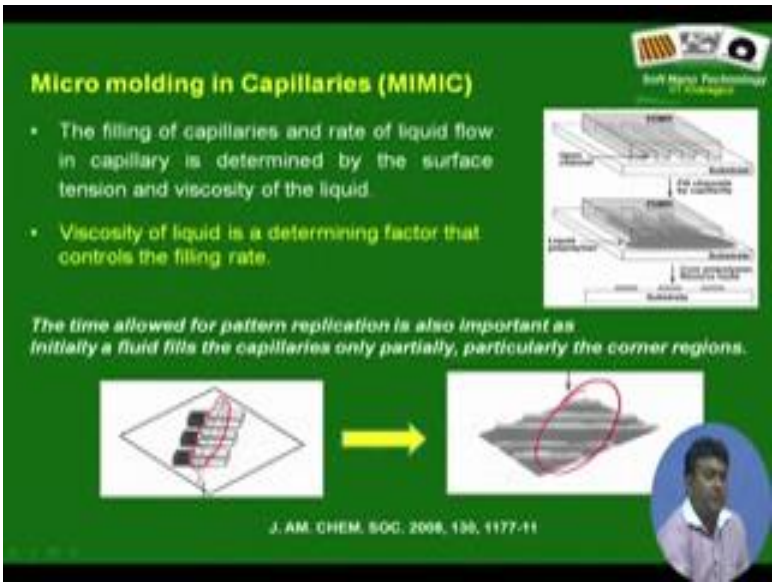

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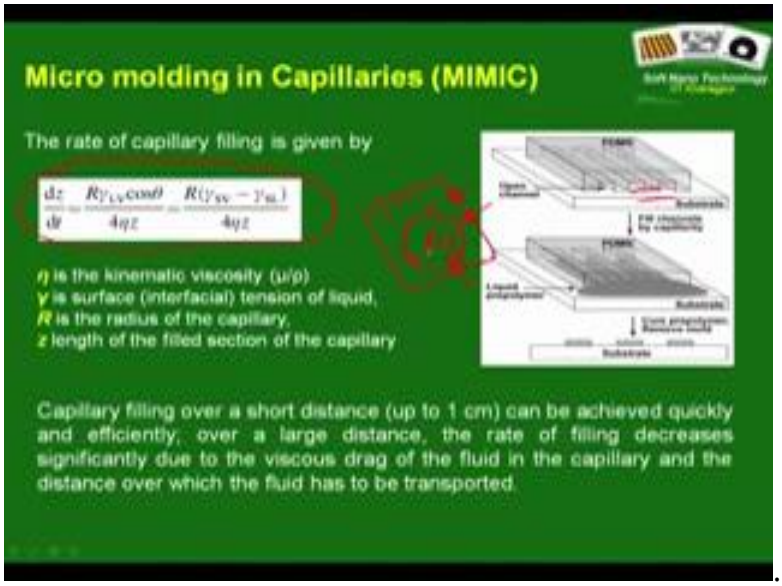

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And therefore, towards the edges you often see this type of incomplete structures taking places. There are some mathematical formulations, but I will probably. In fact, this equation shows why the velocity drops as you go along the capillary channel.

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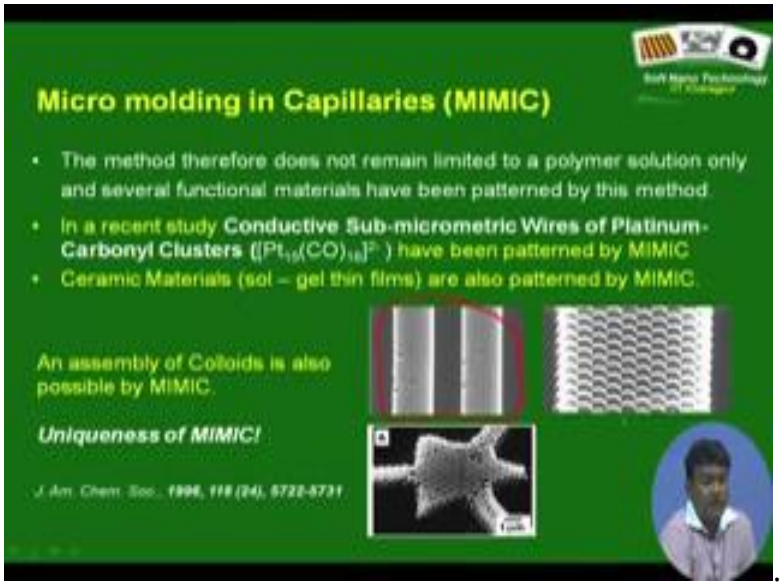

But however, there are certain advantages of MIMIC which know other technique can match and that is something I said that most of the soft lithography techniques have amazing capabilities which cannot be matched.

Look at this a same picture very carefully. You are seeing 2 stripes, but what is important is that they are not made of a polymer; they are made of a layer of colloids that is the advantage because MIMIC does not require a pre-existing film right? It is a capillary driven flow and what restricts instead of a polymer solution, if you dispense a colloidal suspension. The liquid will anyway flow due to capillarity due to preferential waiting and along with that the colloids will go on filling the molds. So, that is exactly what is shown here and these capability is cannot be done or cannot be replicated by any other soft lithography technique.

Earlier in the context of micro lens projection lithography I gave you an example that, you can spin code colloids on a flat surface they form beautiful hexagonal close packed structures, but even if you start off with such a hexagonal close packed structure and try to pattern it, you can never get need structures which are only made of colloids right by Nano imprint lithography. So, this is one of the strengths of MIMIC. One major limitation of MIMIC of course, is that every area below you are stamped so, we have been talking only about gratings like this which is fine, but any complex geometry the whole the entire pattern has to be connected to the sides so that the solution can reach

that area. That is one of the limitations particularly you now realize that MIMIC does not work well or for patterning over large area because the capillary driving force sort of drops too drastically.

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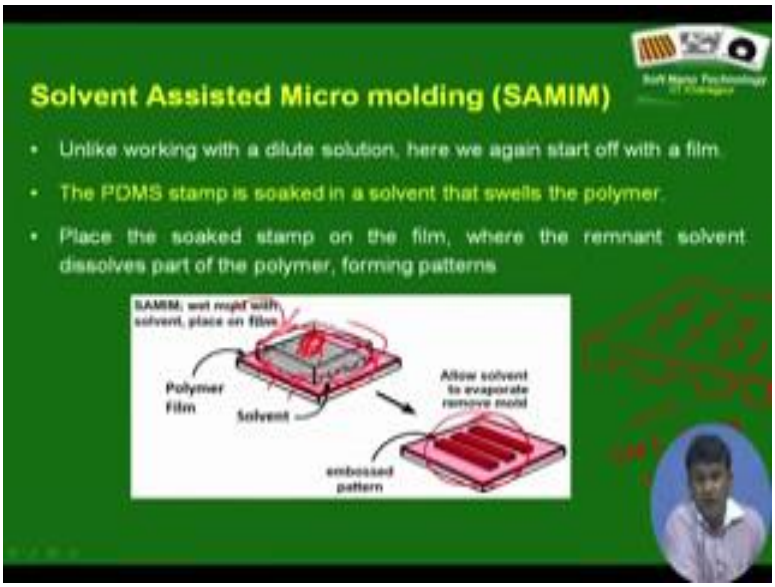

One of the sort of a quick remedy of MIMIC that was suggested bit later was SAMIM solvent assisted micro molding and here is something that I would like to remind you I want you that soft lithography has too many names. So, do not get, parted up or bothered too much about this name thing, but please try to understand. For example, this particular method I am talking now this SAMIM solvent assisted micro molding. It does not figure in my original list. The reason is it is too close to MIMIC. It sort of circumvents some of the elementary problems of MIMIC.

Some other basic problems MIMIC by taking some clue from Nano imprint lithography and other techniques which starts off with pre- existing film. So, what you do here? Instead of MIMIC where you start off with a (Refer Time: 13:32) substrate there is no film. You are back to a spin coated film in SAMIM right? Just like Nano imprint lithography you do that. What you do? You take the stamp wet it in a solvent of the film, you try to wet in the solvent of the film. So, as you place the stamp on the film, locally the solvent that comes along with the stamp sort of reduces the viscosity of the film locally in the periphery of the stamp and since in presence of the stamp due to capillarity

due to any force you are applying the polymer sort of reorganizes along the contours of the stamp pattern and you get some nice patterns.

When the stamp is coming suppose this is the stamp you are bringing in is the wet stamp. So, the wet stamp itself is bringing the solvent. So, therefore, the problems associated with MIMIC that the due to capillarity liquid does not reach at the center of the stamp and at long distances from the edges. These are completely eliminated, but honestly speaking as a concept this is very very good because you still do not need any thermal cycling, you do not need to apply high pressure but then pattern uniformity control is a critically issue because over central areas how does the solvent evaporate away after patterning. I mean the rate of evaporations from the peripheral zone will be much faster as compared to the core area and if the core area content solvent and you withdraw the stamp. What in fact happens is you are leaving behind a patterned polymer layer whose viscosity is too less which is too fluidly.

So, because of surface tension issue Laplace pressure it tends to flatten out. So, the problem again remains mechanism is different as compared to MIMIC. MIMIC areas deep inside the stamp because of very sluggish capillary dynamics pattern do not tend to get replicated SAMIM again often it is seen the central location areas away from the periphery its really flat, but it is not that they were deprive of solvent like MIMIC, but it is simply because of fact the solvent evaporation rate is to slow there and if you do not adjust your stamp withdrawal time very carefully, you might end up doing something where you have removed the stamp, but still it remains too fluidly can eventually it flatten out due to Laplace pressure.

So, all these things needs to be understood and that is one of the reason why soft lithography is preferred by researchers because there is lot of very rich science and more than. So, lot of stuff to sort of examine lot of phenomena that is occurring capillary dynamics Laplace pressures stabilizing effects etcetera, etcetera which are very interesting, but for a bulk fabrication or rapid fabrication these issues might be very difficult to control to lead to reproducible structure.

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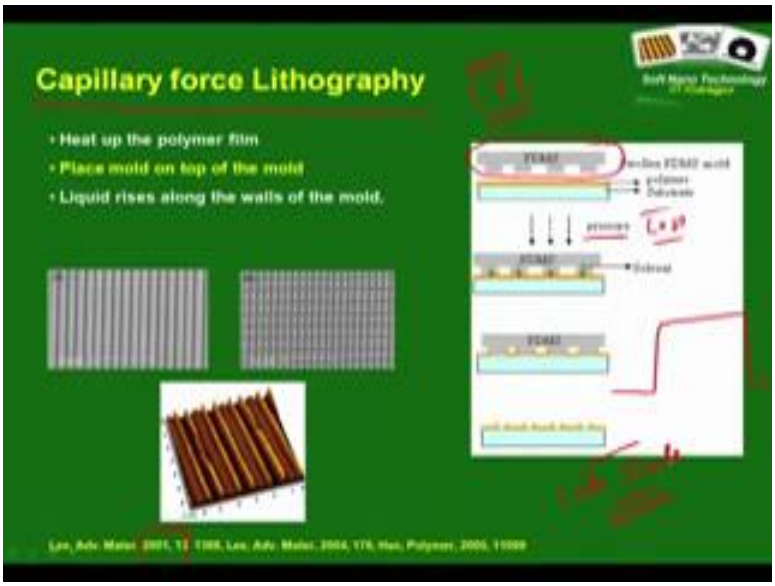

One very elegant improvement over MIMIC, SAMIM as well as NIL is the development of the capillary force lithography CFL. I must very proudly point out well here I am not acting as an Indian, but I am acting as an Asian that this capillary force lithography was not developed. Neither develops by Stephen Chou nor by Whitesides but it was develop in Korea by Professor Hong Lee. A very very eminent scientist in particular area; so what it does it sort of takes the best practices across the different techniques. It does the thermal cycling of the solvent paper exposure like Nano imprint lithography, but it does not take a rigid stamp, it takes soft stamps so that you can peal it off.

The problem associated with the mold removal as observed in NIL is not dominant. What you do is you simply bring a stamp and leave it in contact with and this pressure though it is written is very less very low pressure. Even pressing with your thumb might work. You bring the stamp in contact with the film which is either heated or it is exposing to its solvent vapor. Both has its problem of mismatching coefficient in thermal expansion or swelling as you know because if you know expose to solvent paper the problem is the film swells as well as the stamp swells because it is a seal guard stamp right?

And then you do nothing. In fact, the pattern replication in CFL is again by capillarity dynamics, but unlike in MIMIC, sorry for the bad quality of the drawing. So, this is the capillary driven dynamics in MIMIC. I am just showing one of the channels. So, it relies

on the capillary driven flow along the length of the each of the channel. Firstly the mold filling is along the length and a dilute solution. Instead what happens in CFL is it relies on capillary dynamics of the polymeric film soften polymeric film which in a liquid form along the height of the channel. So, immediate consequence is this height is few hundreds of Nano meter or may be few micron and this is centimeter at least millimeter. So, you are reducing the travel path of the fluid by capillary dynamics.

Therefore, the problem that we had in MIMIC like the velocity capillary driven velocity becomes two layers and mold filling does not take place all those problems are eliminated. Yes it is quite obvious that if you let the stamp remain in contact with the soften polymer layer. If the viscosity is very very high because there is no dilution unlike MIMIC or SAMIM you do not bring in any solvent you just rely on the fact either you expose this film layer to solvent vapor or you do simply hit it up beyond its class transaction temperature.

So, it is a slow process, but then the travel the path that one other the polymer meniscus will have to travel is also less. So, you give some bit of time just need to optimize it might be few hours a couple of hours and you and you get perfect mold filling. What are the advantages? You do not apply a pressure like NIL. You do not use rigid stamp therefore, the issue associated with stamp removal is completely eliminated. You can simply peel off because you are using a cross link seal guard stamp. The structures you see at the pattern replication dynamics, the meniscus rises along the stamp walls unlike in Nano imprint lithography where the liquid adjacent to the stamp wall was actually going down. So, therefore, the residual stresses are almost 0.

Of course, there are issues as I mentioned that you need to liquefy the film so, either you need solvent update or you need thermal cycling. So therefore the coefficient of thermal expansion mismatch or solvent vapor induced swelling. These are important issues, but there are many advantages that CFL offers and CFL has become a very popular Nano pattern in technique. It was developed around early 2000. It is indeed a very very popular Nano pattern in technique and lot of people implement it in the lab scale, because unlike Nano imprint lithography it almost requires nothing. Even you do not require a clean room because unlike NIL you are not using a rigid stamp. So, even if there are some dusts particles here and there, what will happen suppose talking about very practical situation you have a film which is dusty.

Here is the dust particle. So, as I told that if you want to bring in a NIL stamp it will simply break because you are applying a pressure it will form a couple etcetera, ctcetera. Here simply what will happen is stamp will this is of course patterned here go in conformal contact then it will be simply bypass this area. So, after you remove the stamp yes dust has caused damage no doubt, but this area of the film will be neatly patterned and other areas will be neatly patterned.

So, for many applications if you have patterns over some few centimeters or few millimeters square is large in fact in the context of Nano patterning this serves your purpose. So, CFL is indeed an excellent technique. CFL also does not guarantee that your patterns are remnant layer free. So, in order to create self-standing structures you need to do some sort of etching. In fact, it is interesting to note that both CFL and NIL lead to almost identical structures. Both these structures when these structured films are subjected to or liquefied or they are heated up and they are exposed to solvent vapor they tend to flatten out. The reason you now know because a structure or a pattern film has high surface energy and which is not desirable. So they undergo slumping.

I have a question that is bit you can consider it to be before I go to that I let me also highlight one major advantage CFL has remember it is using a flexible stamp. The NIL is again stuck up like photo lithography because it uses rigid stamp and one key advantage is, since is using flexible stamp

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It can now patterned films coated on curved surfaces and this is a non-trivial capability. As I mentioned every technique almost every major soft lithography technique has some major advantage or key advantage or the other and this is indeed one of the major capabilities of CFL of course, MIMIC and all other techniques that use a flexible stamp can in principle be used for patterning curved surfaces, CFL sort of does it very elegantly.

What you see here is another special case that you do multiple CFL with grating stamp and you can create 2D structures. One quick question that I would like to have is related to this in fact

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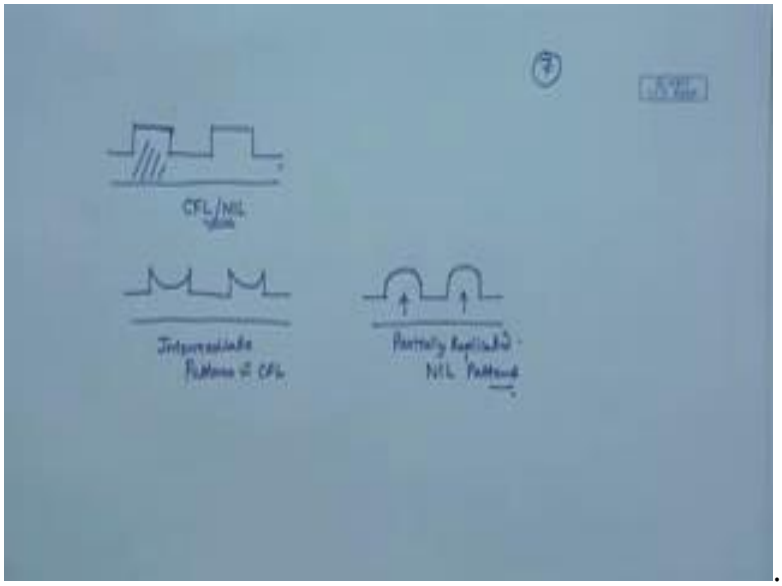

If I sort of give you a profile of a film which you know is a perfect negative replica of your stamp. Can you identify what was the patterning technique? Whether it has been made by particularly I would say whether it has been made by CFL or NIL. Well be practical so do not give me an answer like I will measure the level of stress and come out with the solution that not doable. So, honest answer is that you really do not know. One thing is you can destroy the film. Probably if you heat up the film both the films may be you take 2 films identically structured. One has been made CFL, the other by NIL. Probably the NIL film will undergo slumping faster, because of residual stresses are more.

Important thing to remember that if your patterned application is perfect you cannot identity, but suppose you have tried to pattern and you have stopped at an intermediate level then, in fact very nicely one can look into the profile of the partially replicated patterns and can say what is the pattern replication mechanism. If I now draw this I am sure you can correlate to the mechanism of CFL I was talking 2 minutes back. So, this will be the structure intermediate patterns in CFL in contrast the partially replicated pattern in NIL will have profiles like this because in NIL the rise is not along the walls it is actually through the center.

So, these are I mean you can in fact do that because you know that the advantage with working with the glassy polymer is the moment you reduce the temperature the dynamic freezes and the structure freezes and you can as you will see a few lecture later you can use the wonderful instrument called atomic force microscope AFM which I have promised that I will teach you in detail and you can identify and see all these.

So, with that I stop this lecture and I think I will need 2 more lectures on soft lithography or may be one more lecture to wrap it up and then move on atomic force microscope.

Thank you very much.