

Instability & Patterning of Thin Polymer Films

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Lecture No. # 15

Nano Imprint Lithography (Contd.)

Welcome back. We were discussing soft lithography technique lithography technique for patterning of polymer thin films which is beyond photo lithography and the technique we were talking about is Nano imprint lithography. Today we look into the basic aspects of Nano lithography in the previous class, today's class we propose to look at some other periodical aspects of Nano imprint lithography, and then wind it up and move on to the other set of techniques which have become very, very popular for patterning of polymer thin films that is the soft lithography group of methods.

Of course, some including the inventor of most of the soft lithography methods George Whitesides himself regards Nano imprint lithography or NIL group of techniques also to be part of a wider family of soft lithography methods, but if you look at the classical definition of soft lithography, well Nano imprint lithography is often are in many, many literature, so scientific papers regarded as a separate class of technique or embossing. However, without deliberating too much on to that we will try to understand how exactly Nano lithography Nano imprint lithography, and soft lithography how they are close to each other and what are the their key distinctions.

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Nano Imprint Lithography (NIL)

J. Vac. Sci. Technol. B, 14, 4129, 1996
S. Y. Chou, P. R. Krauss, P. J. Renstrom,
Science 1996, 272, 85.

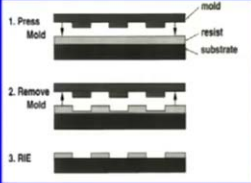
For the original Work, **PMMA** was used as the resist (polymer) layer:

Low coefficient of Thermal Expansion $\sim 5 \times 10^{-5}$ per $^{\circ}\text{C}$

Low Pressure Shrinkage Coefficient $\sim 3.8 \times 10^{-7}$ per psi

Temperature: $\sim 150^{\circ}\text{C}$

Pressure: 30 – 50 MPa



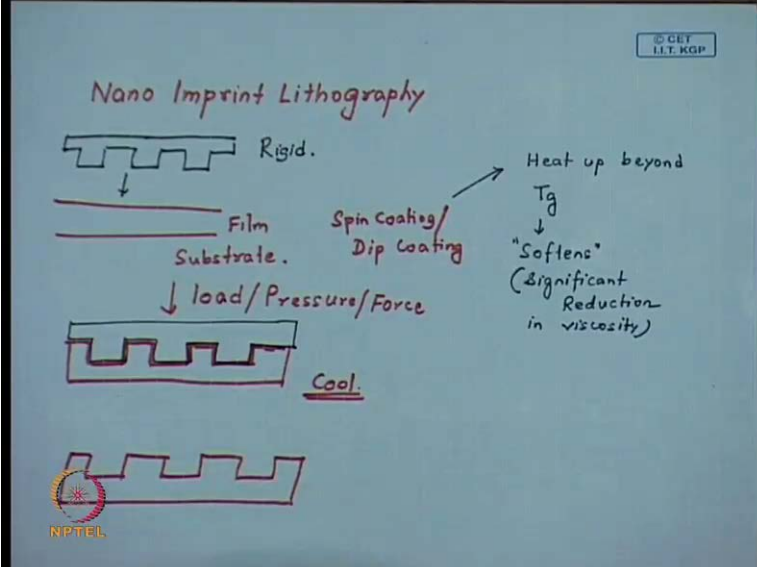
No diffraction
Limitation:
25 nm lines produced in 1998
5 nm lines produced in 2004.

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So, this is what we showed in the previous class the method is very, very simple, all unit do is to sort of take a hard rigid stamp which as the structure, a negative replica of the structure

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Nano Imprint Lithography



Rigid.

Film

Substrate.

Spin coating / Dip coating

Heat up beyond T_g

"Softens" (Significant Reduction in viscosity)

load / Pressure / Force

Cool.

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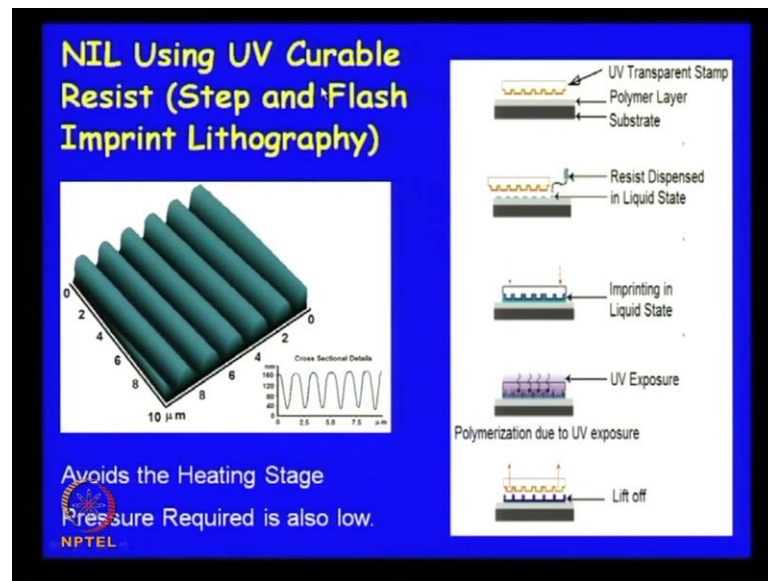
You would like to create you take a film this film is typically can be of any material thermosetting or homo polymer or whatever, so this film we know that it can be created by a many techniques including spin coating or dip coating, and you take a typographically structured stamp. In the classical form of NIL has we have already

discussed this is rigid, today we will talk about what are the likely materials and other related issues.

So, you heat of this film if it is a homo polymer film in the in the thermoplastic homo polymer film, in the most classical form heat up beyond the glass transition temperature of the polymer, where it sort of softens that is more of a common word what happens is there is a significant reduction in viscosity, then you emboss it you emboss it with the application of an external force or external load, and while the stamp is in contact with the film so you emboss it, and then once a pattern replication has taken place you cool it down, so what happens is the polymers structure then gets expose any are sort of its a name of a structure should becomes again the viscosity sort of go up, and then when you withdraw the embossing stamp the structures sort of remain in place, so apparently a very simple technique you really do not no need.

I mean in principally you can implement it any laboratory without any specific instrument like what you need in photolithography which is absolutely mandatory, all you need is a stamp you need the polymer you need the film to be created, you can heat it up and you can emboss it, this is in the simple less form, but today we will see the certain critical issues associated with all most every step, one of the thing is that you can understand the movement you sort of have to have a heating and cooling cycle there can be possibility of several detrimental effects, one of them can be the possible mismatch between the coefficient of thermal expansion between the polymer as a polymer film or the heated polymer film and the rigid stamp.

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So, the other alternative we have already talk about is essential to use the a UV curable resist, again a concept parochially hired from photo lithography which again is good because you typically take a liquid polymer which is UV curable, or in other words it is a sort of cross links once you expose it u v, so you stamp you imprint it not stamp it you imprint at room temperature because it is a liquid at room temperature the viscosity is low, but then two additional components come up, firstly your stamp has to be UV transparent so that the UV light censor of penetrate, and second thing is that you are again resisting yourself to some a specific class of material which are active to u v, in contrast of thermal NIL and classical NIL for there is absolutely no restriction or there is no specific requirement on the photosensitive properties of the polymer you are planning to pattern.

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Thermal NIL	vs. UV – NIL
<ul style="list-style-type: none">+ Less restrictions on template Si and Ni are okay+ Simpler/cleaner process UV resists are more viscous and difficult to handle+ More readily available poly/resists	<ul style="list-style-type: none">+ No thermal cycling+ No possibility of CTE mismatch issues+ Fast (few seconds)+ Usually minimal force needed
<ul style="list-style-type: none">- Temperature May be as high as 200 °C- CTE mismatch between wafer and stamp likely- Require large force, which may result in distortion of alignment and breakage	<ul style="list-style-type: none">- Volume shrinkage due to phase transition- Obtaining uniform layers from spin coating is difficult- Must use a stamp transparent to UV

We also discussed I am doing quick recap. So, that you again sort of you also do a recap and understand the concept they are simple, but my only concern is they are a little new so we will proceed a little slowly.

And we discuss about some of the frozen concept pro thermal NIL and UV NIL. So, less restriction on template as well as in the polymer material simple and cleaner process, we are talking about the thermal NIL and you can sort of work with more readily available are most polymers, in contrast UV NIL you do not have a thermal cycling no possibility of coefficient of thermal expansion mismatch, the pattern replication is much faster and the force required for embossing of this particular force we talk about here is much less in UV NIL, in the detrimental factors in thermal NIL off course you look at temperatures which can be as high as 200 degrees centigrade.

Coefficient of thermal expansion mismatch of course is an issue, and you require large force of which has to be applied externally, and that force actually might lead to possible damage of the stamp at time it is possible, off course UV NIL the critical issues can be volume shrinkage due to phase transition, and as I told that since this UV sensitive pre polymers of polymers sort of or a little high viscosity little tacky at room temperature, so there is a possibility that they are might be some difficulty obtaining an uniform spin coated film, and then off course you need a UV lamp source as well as a stamp which is transparent UV in contrast thermal NIL where they are not no such with requirements.

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Rapid Flash Patterning
Applied Physics Letters, 85, 1794, 2004

typically 60 s with a 500 W lamp, but 10 s with a 10 kW lamp array.

The temperature reached is typically around 260 °C

Does NOT require a UV – curable mold

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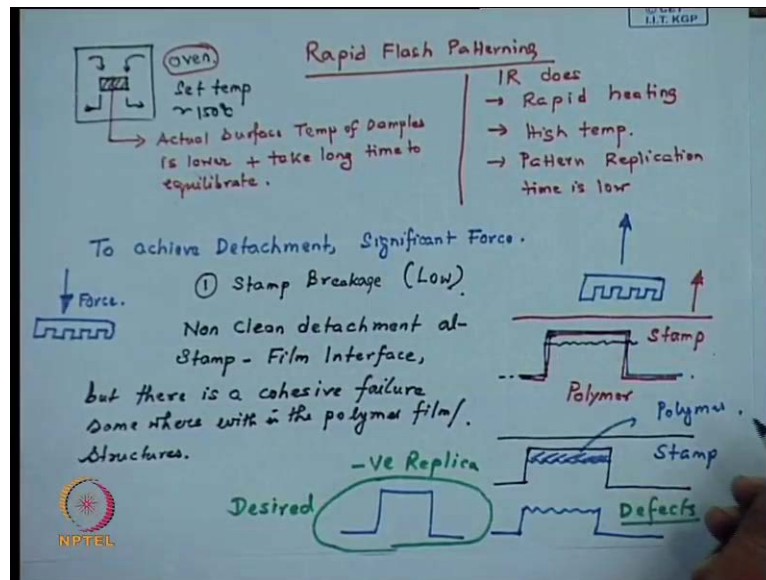
The diagram illustrates the following steps:
1. UV Transparent Stamp, Polymer Layer, Substrate
2. Resist Dispensed in Liquid State
3. Imprinting in Liquid State
4. Infra RED Exposure (Polymerization due to UV exposure)
5. Lift off

In order to overcome some of the technique or as a possible progress of NIL to make it more material independent or to explore are take advantage of other issues, so there is another development which goes by the name rapid flash patterning, here instead of a UV curable mold instead of UV queering of a liquid pre polymer which is liquid at room temperature you sort of go for a I r exposure infrared exposure, and so what in infrared exposure does is unlike conventional convective heating in an oven infrared exposure can sort of lead to very higher or very rapid enhancement in the temperature, and so they can be sort of incentive liquefaction or reduction of viscosity of the polymer you want to pattern.

So, here the technique is pretty simple, there is one small type this particular line UV transparent stamp which is return on the at the first live or word to be written on the right top most corner of the slide is wrong, the stamp does not necessarily you have to be UV transparent you can work with any stamp an any polymer layer. So, what you do is that you sort of bringing the stamp apply a force and then you do an infrared exposure, so infrared exposure sort of here are some typical numbers what is written, so if your power is 500 watt you have the lamp you advise we using is a 500 watt lamp typically you need 60 second for the pattern replication to be complete, but if you are using a 10 kilo watt lamp well 10 kilo watt lamp pad a all you need is ruffle 10 seconds. So, essentially the polymer surface of the polymer reaches temperature of typically more than 250 centigrade in a couple of seconds.

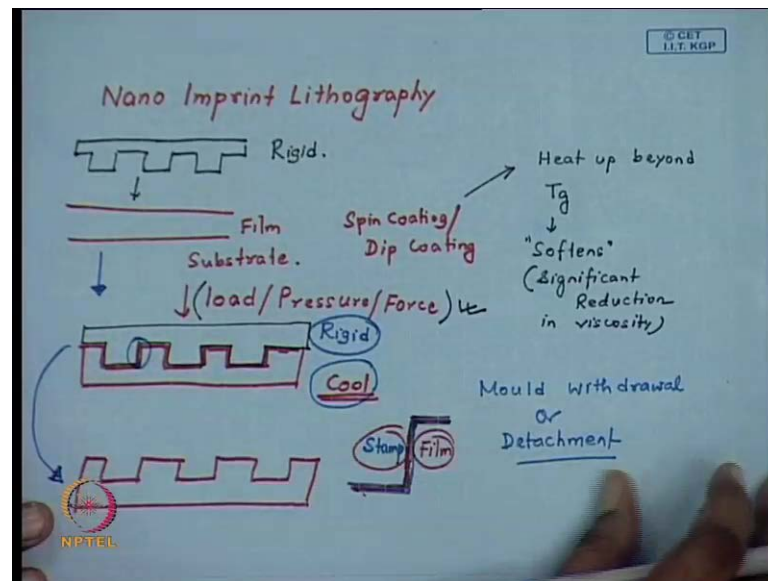
So, this is very close to the classical Nano imprint lithography, the only difference being in classical NIL other thermal NIL you are heating cycle typically achieve to by putting in a convective oven or something like that. So, even if you place it in an oven which has a temperature of say 150 or 160 degrees centigrade there the heat transfer.

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So, the issue is like this you take a oven and you sort of said the temperature to 150 degrees centigrade, so eventually so here your samples are so there will be convection of heat with in the oven and actual surface temperature of the samples it will be firstly it will be lower and secondly it will take long time to equilibrate. So, typically this oven is a sort of hot stage a in which are a hot plate over which you keep your sample and do the NIL embossing are things like that, in contrast what you do is that you rely on an infrared exposure for this heating stage in rapid flash patterning and this what IR does is sort of very rapid heating and high temperature therefore, pattern replication time is low, this is what we are talking about rapid flash patterning, but in other all for all practical purposes the technique equipments pretty much the same as the classical thermal Nano imprint lithography.

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Now, there are couple of issues, so we told that we the when you give you a picture like this apparently you feel the Nano imprint lithography is sort of a very sample easy to execute method which is indeed true, but now we will look into some of the aspects in a little more detail. So, one of them is essentially this particular stage, from here to hear what you do we have to sort of remove the stamp, so mould withdrawal or detachment turns out that this is a very critical step in both thermal NIL particularly in thermal NIL as well as also partial UV n I l rapid flash patterning also suffers from the same problem, a clean release of the resist from the mold is one of the most important characteristics, here there are two couple two microscopic images.

Where the in the first one I am I am coming to what is this anti addition agent a in a little while, from now in the first one you see that the structure the final structures you have obtain have some defects, while in the second one you see that the structure pretty uniform it is a beautiful rating structure, reality is up to this stage that is the embossing or pattern transfer or pattern replication stage, in both the samples in case of both the samples the pattern transfer was equally good, now the reason for the defects for being incorporated is in the first sample or in the on the micrograph shown on the left side is because of the defect in patted during the detachment stage. So, what can be the problem? Problem is the this firstly we have talked about in case of classical NIL as well as rapid flash patterning there is a strong influence or significant effect of the coefficient of thermal expunction.

So, look at this stage again carefully, so you heat up this polymer film so now it is in a liquid form, you bring in a rigid solid stamp which has the relief structures, you emboss it then apply an external force to trigger or ensure that there is an adequate visco plastic deformation within this film layer, and then once you feel you know that your complete pattern replication has taken place then you would cool it.

So, at this surface so this is the stamp surface; and this is the film side, at the stamp wall film interface you have complete contact or in other words between the stamp and the polymer, or in other words because of the strong force you are applying there is a sort of complete wetting or by way of the visco plastic deformation the stamp is causing there is a complete wetting of the stamp surface by the polymer, which itself is a high viscosity liquid sort of heated up to beyond its glass transition temperature, and now sort of you force both of them to cool together, so what happens is after it has cooled down there is the result of a strong interaction or this remains in sort of close proximal contact, I mean this is the polymer in contact with the stamp, so they remain in very close proximal contact. Now, do not forget that in case of classical NIL or UV NIL rapid flash patterning the stamp you are talking about is rigid.

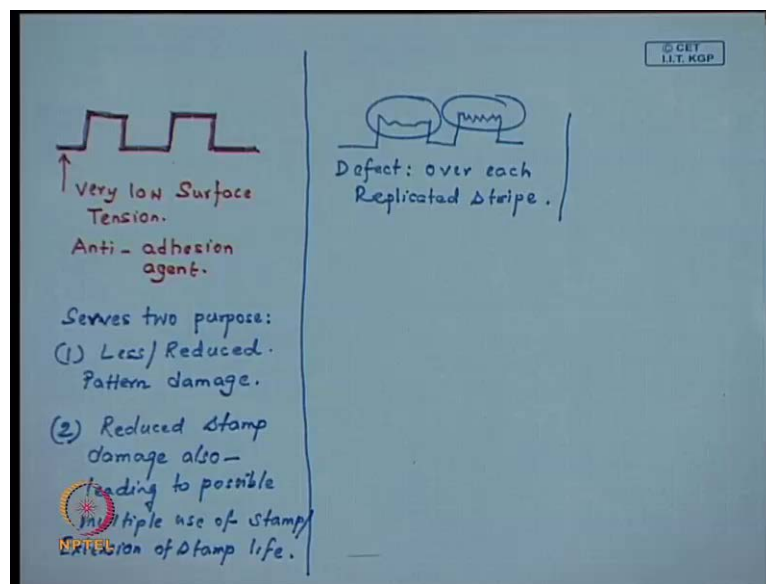
So, now you have to detach, so how do you detach? You have to hold the stamp somehow by robot arm or manually even in some case if you are working in the lab and then you have to pull it out, now since at the stamp film interface the polymer and the stamp material is in a very sort of conformal contact there is a strong possibility, and therefore, in order to detach do not forget that you might have to apply a significant amount of detach force necessary to cause the detachment.

In other words you might need to apply in order to sort of achieve detach detachment you might require significant force, see this force is in the opposite direction for do not forget that while embossing you applied also a force, but it was in the in this particular direction, but here you are now sort of pulling out the stamp. So, as again I repeat since there is very strong conformal contact between the stamp wall and the polymer, and you are applying a strong pull on the stamp with the anticipation that the stamp will detach leaving behind the polymer exactly following the following it is concluded that may not happen, what may happen is that firstly part of the stamp may stick, so during detachment the stamp might actually break which is a rare occurrence with developments are or sort of the instrumentation that a typical NIL instrument uses, but if you have

talked again and again that your stamp is really a costly commodity so you really do not want your stamp to break of.

So, there is a possibility of stamp breakage though reality this is low, but a more likely possible it is that the detachment does not take place cleanly at the stamp film interface, but there is a cohesive failure somewhere within the polymer film or structures.

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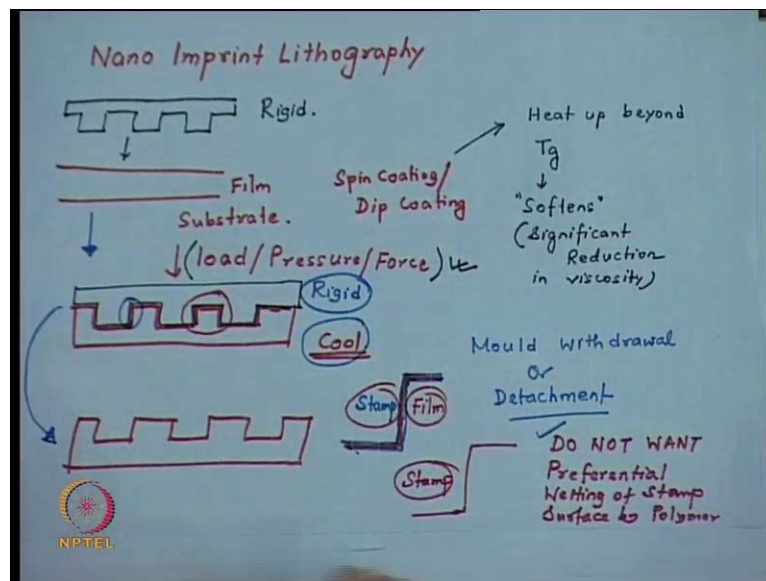
So, what does a cohesive failure mean? It means that well because of this force you are applying to detach the stamp the failure might actually occur here with in the polymer level, so in that case once the stamp detaches this is the original stamp, but once you detach it, it sort of carries away part of the polymer sticking to it, and the on the other side the polymer structure you want to create does not create of complete negative replica as desired by you, but it has some defects in the form of yellow or height or an undulated are a ruff tuff surface and things like that, and also if there is a setting like this you really do not know where what is going to be the nature of the cohesive failure within are below within each channel value or on each of the pattern protrusion.

So, it is going to be a complete waste of the structure because you are going to have structure with lot of defects, may be the defects will be over every... If this was your desired structure you might get some structures like this, so it is very difficult quantify were the defect is going to look over each of the replicated stripe, so defect will be over

may be over each replicated stripe or something like that, so this take it from mean I mean apparently very in significant, but clean detachment is a big problem in Nano imprint lithography. So, in order to overcome this what is typical done is that and anti adhesion agent is typically coated on the stamp.

So, essentially this anti adhesion agent is nothing but a very thin layer of a material which has very low surface tension, or if you are we have talk about heating terms of water, so essentially you would like to impact hydro fabric coating, though hydro febricity is not very important here because this material is not going to come in contact with water, but what you would like to eventually do by imparting this what this adding this anti adhesion agent is that you sort of achieve contradicting sort of effects or any way you want to have contradicting effects.

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So, when you are pushing your stamp you would really want to cause a complete visco plastic deformation within the polymer layer, and you would like to achieve a complete mold filling; however, you would like to achieve this mold filling by due to the deformation and corresponding flow which is induces due to are in order to conserve the mass, but you do not want still do not want the stamp surface that is this stamp surface over here to be preferentially waited by the... Or we will write it of the we do not want preferential waiting of stamp surface by polymer, and this is something that is sort of

ensure by coating the stamp surface with the anti adhesion agent or yellow surface energy coating.

So, that sort of favors and easy detachment and does not disturb, so this again serves two purposes, number one less or reduced pattern damage, and number two is that reduced stamp damage also leading to possible multiple use of stamp or extension of stamp life which is sort of one of the key requirements I must say to sort of implement Nano imprint lithography in a cost effective fashion.

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Solvent Vapor Assisted Nano Imprint Lithography
Applied Physics Letters, 76, 870, 2000

Conveniently Avoids the Heating Stage
Pressure Required is also low.
Residual solvent content a major concern.

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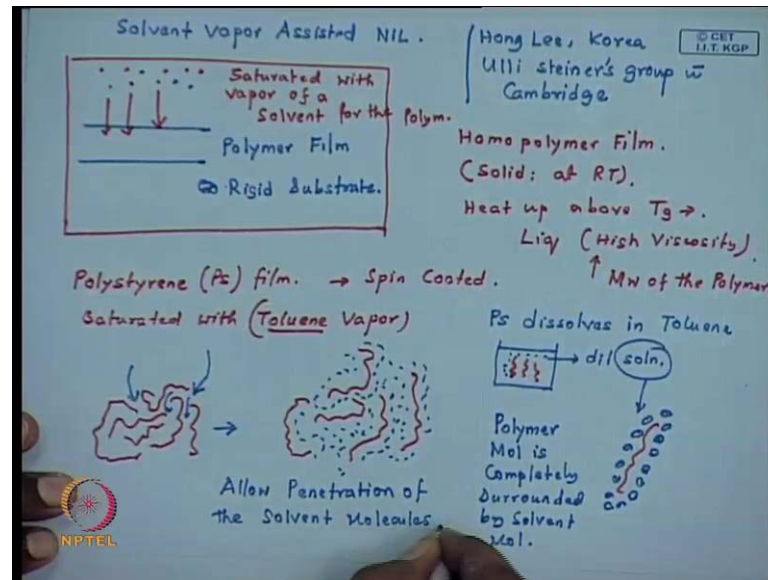
The diagram illustrates the process in three stages:
1. **Solvent Vapor Chamber**: A polymer layer on a substrate is shown above a chamber containing solvent vapor.
2. **Room-temperature imprinting**: A mold (mask) is pressed against the polymer. The polymer becomes a **Swollen Polymer Layer** due to the solvent vapor.
3. **Pattern transfer to polymer (removal of the mold)**: The mold is lifted, leaving a patterned polymer layer on the substrate.

Now, primarily because of this thermal cycling an associated attachment of this of the imprinted polymer or the emboss polymer layer with the stamp, particularly during the cooling stage due to the thermal coefficient mismatch, as well as the possible distortion of the imprinted structure or the mold features due to a thermal cycle of heating and cooling again which is indirectly or directly influence by the coefficient of thermal expansion, because of the two materials add in conformal contact and it is bound to happen that they have some bit of difference in the coefficient of thermal expansion.

So, people started to sort of thing of alternative techniques of what can be done particularly in order to avoid this thermal cycling, and we have seen that one of the possible a probable approaches was to you go for the UV NIL , but then again you are restricting yourself too much to materials which are UV sensitive exactly like photo

resist, so which again was not basic intension of Nano imprint lithography to sort of make it very materials specific.

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So, the other set off approaches that came up were room temperature Nano imprint lithography, there are essentially the two techniques two methods, the first one to see or to get develop is the solvent vapor assisted NIL came from Hong lee grouping Korea, as well as Ulli Steiner's group in Cambridge, where is novel technique all you do are you relay on a specific aspect is that if you have a polymer film coated on a rigid substrate, and usual thing is a concept that we will also be using of talking about a law subsequently when we talk about polymer thin film devoting, **polymer thin film devoting** experiments and things like that. So, this is important to understand till date we have always discuss that if it is a homo polymer film, it is sort of solid at room temperature and you heat it up it sort of becomes a liquid though a high viscosity may be, which again depends on the molecular weight of the polymer you are taken.

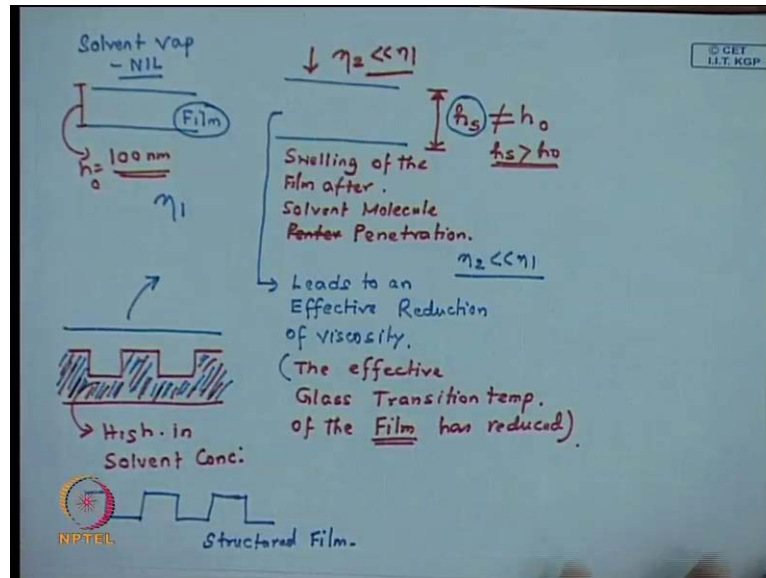
Now, this technique realize on the concept that if you take a polymer thin film and keep it in an environment which is sort of saturated with vapor of a solvent for the polymer, so an example can be that if you have take any a polystyrene film very common example, and you sort of keep it a chamber you have coated a film, you sort of keep it in a chamber which is sort of saturated with toluene vapor, toluene is a very good solvent of polystyrene, so what will happen? What will happen is that this solvent molecules since

it is a good solvent they start penetrating into the polymer matrix, so suppose after spin coating you have molecules which are in entangle state like this within the film this a molecular level picture and this solvent molecules now comes in.

So, since it is a good solvent thermodynamically these molecules will preferred to be revenge surrounded by the solvent molecules this is a concept that we will talk in a little bit detail later, but when you know that let us say p s dissolves in toluene what does it mean? That if you take a if you want to make a dilute solution this will be toluene, so you will have molecules of toluene everywhere, and all the polymer molecules will sort of be dispersed or dissolved or even distributed within the solvent solution.

So, in other word if you with in this solution if you take a molecular level picture this is one polymer molecule and which is entirely surrounded by solvent molecules so this is the picture, so from this we know that a good solvent the at a molecule level the polymer thermodynamically prefer to get surrounded with the solvent molecules. So, here now coming back to this particular setting you have abundant of solvent molecules which go everywhere because it is gaseous state which the molecules are undergoing (()) motion, and this molecules when they come to the surface they are now free to penetrate, penetrate within the polymer matrix, so eventually what happens it does not dissolve a formula dilute solution off course like this, but these molecules sort of allow themselves to get surrounded by the solvent molecules, or in other words they allow penetration of the solvent molecules.

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So, what is the consequence of this penetration? There are two consequences, first consequence is since you have allowed the molecules to penetrate of course how where do you accommodate this molecules, so there is a so if this was your dry film there is an increase in the volume of there is a swelling of the film after solvent molecule penetration, this is number one this from the stamp end patterning straightly documental I would say, because suppose bias spin coating and then by lips metric measurement you now know that your film thickness is lets a 100 Nano meter, and then you sort of expose it to it solvent vapor though you might be knowing the vapor pressure you might be controlling it you might be having a saturated environment, but still the reality is that when you are after you have exposed it to sort of solvent vapor this is let us say some h_s , and this h_s is surely not equal to your h_0 the original film thickness or h_s is defiantly greater than h_0 , but the more I mean from the stand point of understanding it the more complicated parties they are film thickness the precise film thickness is may not be none this is number one.

Number two is that abort from the volume increase or swelling of the film what happens is now these molecules which were sort of entangled with each other and sort of interacting directly or now sort of gets separated from each other, so as they are separation distance from these from each of between the polymer molecules sort of increase their interaction weekends, or in other words the solven film now becomes much more laboyel has compared to your initial as coated film. So, what it mean what it

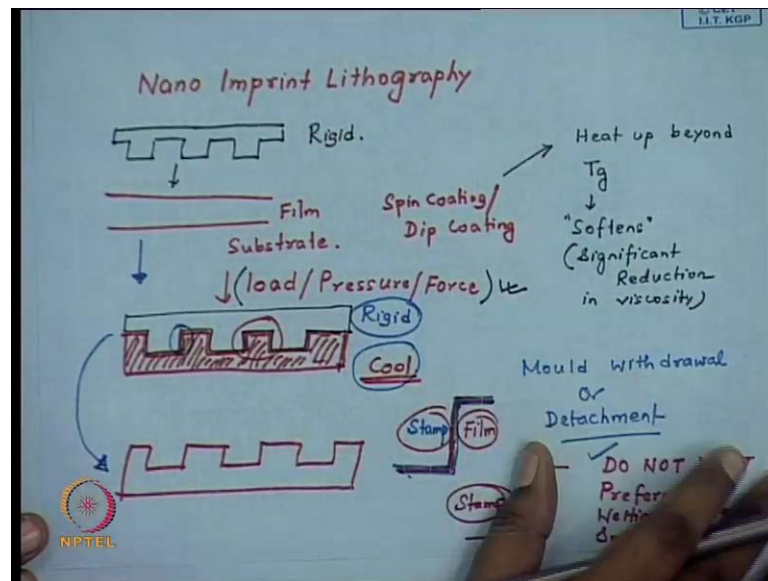
implies that this also leads to an effective reduction of viscosity. So, due to the solvent molecule penetration the film now behaves or exhibits a viscosity which is much lower than this viscosity.

Or in other words this can be regarded as a method by which the effective glass transition temperature of the film has reduced, I repeat it is the effective glass transition temperature of the film which has reduced not the polymer, because you are though this film is now exhibiting a much lower viscosity this film is no longer a film of pure polystyrene by it is a solvent containing film, however, so what from the practical stand point is there is indeed effective reduction in the viscosity and the reduction in the viscosity is the effective reduction on the viscosity of the film.

So, now what you have? What you have that you had a film and by way of exposing it to it is on solvent vapor you have now at room temperature even with bypassing the thermal cycling completely you have been successful in reducing the viscosity of the film, and so now if you sort of emboss it with a rigid stamp and with the application of an external pressure even at room temperature you can sort of get nice structures.

So, this is the key concept of solvent vapor resisted Nano imprint lithography, but the problem is that you need to understand that you are imprinting a film which sort of is high in solvent concentration. So, once your imprint is over two things firstly you need a much lower force may be, and once your imprinting is over the detachment can be also much cleaner has compared to the conventional thermal NIL because of the fact that there is more issue of coefficient of thermal expansion that comes into the picture.

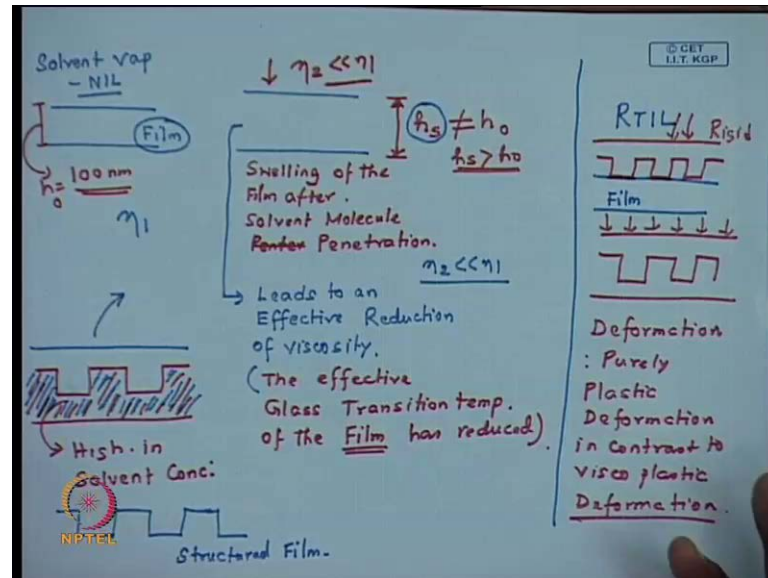
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So, you can imprint it and then you can withdraw and you can get a clean detachment and you can get nice structures, but can you think of any likely detrimental effect of the whole process, if I allowed to think you for a minute you may be may finally come up with answer that after all you are not imprinting a film which only has polystyrene molecules as prove out the molecules of the polymer has you done in case of the classical thermal NIL, you heated heat up it reduced in viscosity, but here in the film you had no other material or molecules other then the molecules of the polymer, because of the thermal heating there was a reduction or the change in the realign of the system, but instead of that here what you have actually imprinted is not a pure polymer film any more, but this contains significant amount of solvent molecules also.

So, while imprinting during imprinting it might be actually easier compare to the classical NIL, they are might actually be some problem after the patterning is over, and what is that problem? That problem is once the patterning is over this solvent remnant solvent will try to escape and that may lead to significant amount of structural damage to the replicated structures.

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So, while this therefore, it is an interesting concept it may not be a very nice technique if your pattern fidelity requirement final pattern fidelity requirement extra is very high, the subsequent there was another development again from Hong Lee's group which talks about the room temperature imprint lithography, this well it is it is truly a room temperature process there is no thermal cycling no thermal exposure, so this is often referred to as RTIL of the room temperature imprinting, so here you take a film by coating so the solvent goes away, and that you apply the stamp of the bring the stamp which is the rigid stamp and you apply very high force to achieve the deformation at the room temperature itself, so the deformation is purely plastic deformation now, in contrast to viscoplastic deformation we have so far achieved or obtain in most of the Nano imprint lithography group of techniques.

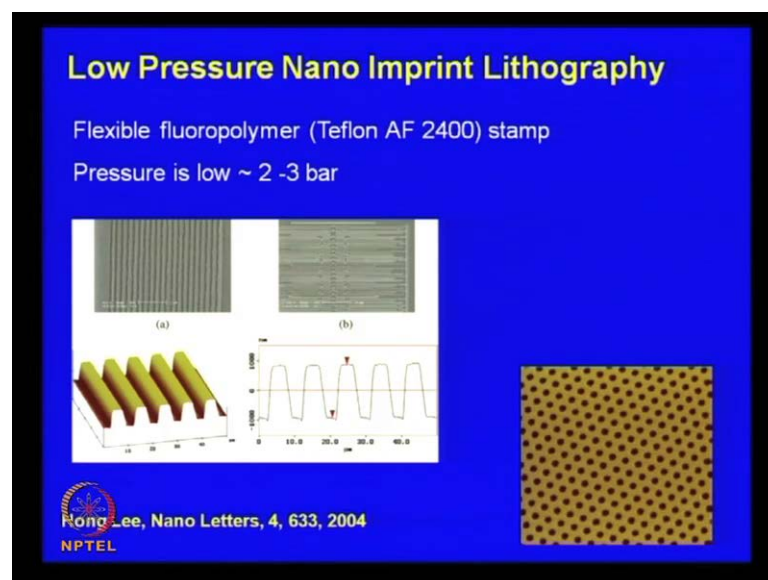
So, the first thing you need that you are deforming the layer in the solid state, the pattern transferred is in the solid state which is very convenient from the stand point of handling, but they first of the immediate consequences you need a much higher force to do that, and achieve directly in the solid state based on plastic flow along with free volume contraction and plastic deformation of the film layer mold release is very easy, of course, the consequences are rather dialed you need a very high pressure so something like 150 mega pascal off course which again is a function of the molecule weight of the polymer, uniform distribution of the pressure becomes extremely important which is very critical, because there is no capillary driven flow of viscous flow to sort of

compensate for the lack of non uniformed of formless of the pressure, mold required is to be very hard because since you are applying a very high pressure your mold should first be able to resist that deformation of that very high pressure that is getting applied.

The final patterns somehow lacks the fidelity you obtain in classical NIL or solvent vapor resisted NIL, because of the fact that you sort of or causing a plastic deformation, so which is always difficult that is no smoothing or flatter effect, and very high accumulation of stress within the structures, because again you are causing a solid state deformation.

So, you can imagine so if this was original film and this is the embossing stamp you are using, so these parts of the film has underground this significant deformation has compare to other parts of the film where the deformation is much less, so not only there is significant accumulation of higher level of accumulation of stresses over these areas, but there is also a periodic special variation in the stress level, which may not be a very good thing to have because of the fact that these stresses might get released eventually rather abruptly during some of the application, this is something we will take up in a little greater detail.

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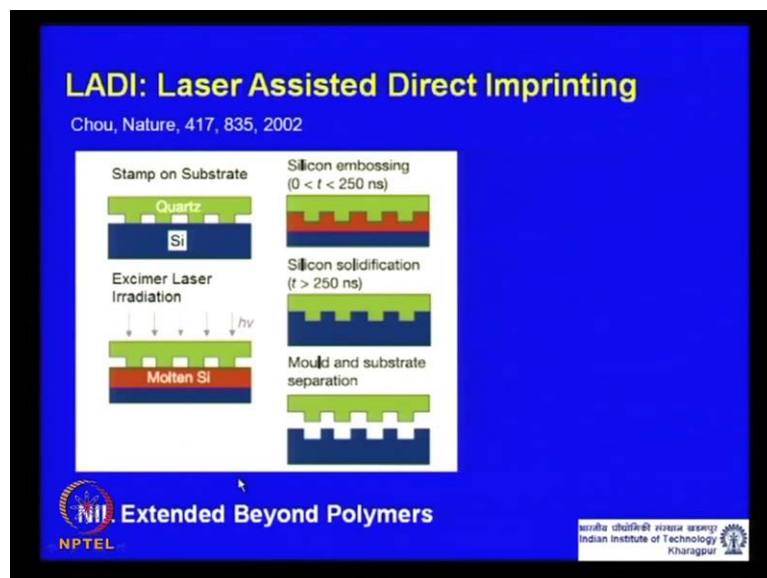
In principle there was a technique which was developed which came out as again a very sort of a popular are very a technique with lot of potential was low pressure Nano

imprint lithography which used flexible fluoro polymer stamp, and the pressure requirement was down to two three bar, but piratical limitation was that this was eventually achieve to very low molecular polymer low molecular weight polymers. So, you sort of compensate try to compensate for your not applying a high pressure by taking at advantage that your polymers are low molecular weight.

So, just like you UV NIL you are again making this technique very material specific, so most of the polymers with higher molecular weight was difficult to sort of imprint, the other thing is that the moment you go for low molecular weight polymer the difficult synthesis if you are purchasing from commercial source there are costly, and also many of the low molecular weight polymers because of a lower molecular weight have lower glass transaction temperature.

So, the structures other structure surfaces if there were sort of getting subject to some sort of a condition which was not at not at ambient, so they are ability to function at higher temperatures was severely limited. So, somehow this method though apparently very promising and established in a very top and jornal Nano known as Nano letters was really has never become very popular.

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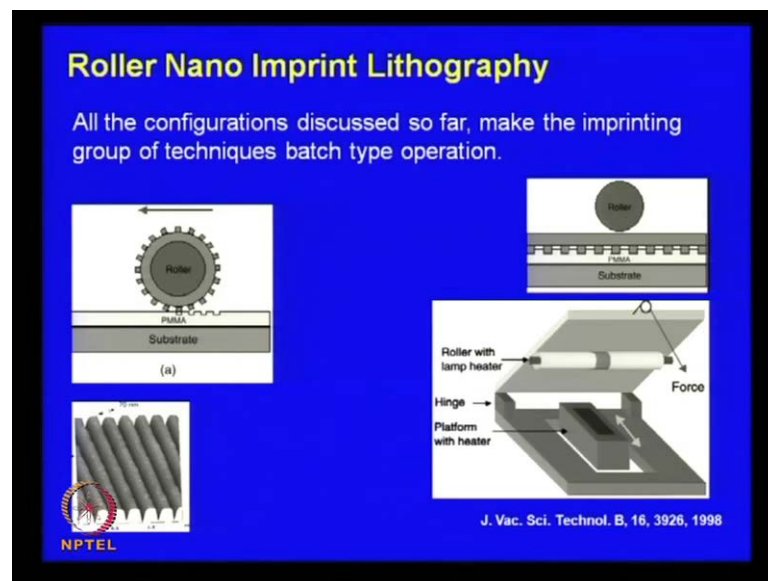


And other major development which un for again which sort of extended Nano imprint lithography for the possible patterning of solid are metallic films straight away again

came from Chou's group, the invention of Nano imprint lithography you should be remembering it by now which is known as the laser assisted direct imprinting, pretty much the same concept, but if you look into this figure carefully there is no polymer film, so all that was taken was a silicon substrate and a quartz stamp which had the relief structures and they were subjected to of course in addition to the pressure.

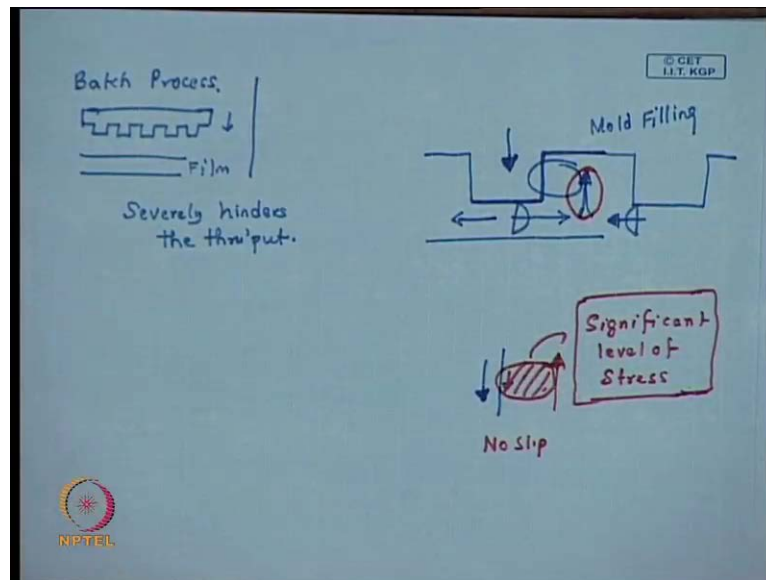
So, there are subjected to the excimer laser irradiation without understanding too much of how laser interact with silicon which is beyond the course of this particular beyond the scope of this particular lecture, all you can understand is that because of excimer laser irradiation the top layer of the silicon surface gets molten, and then at this stage this embossing is achieved following the conventional way, and the times are very fast, so embossing let us say takes typically what was reported this is from a nature paper in 2002 what the time was roughly 250 Nano seconds, and then you turn off the laser, so immediately the silicon sort of freezes in or sort of goes back to the solid state through solid defecation, and then exactly following the what you need to do in Nano imprint lithography you just (()) sort of go for a detachment of the mold, and you can it was therefore, shown in this way that this known has the method of ladi laser assisted direct imprinting, your Nano imprint lithography group of techniques do not remain confine only to polymers, but it is pretty much available to use them for patterning solid surfaces and metals are material like silicon straight away.

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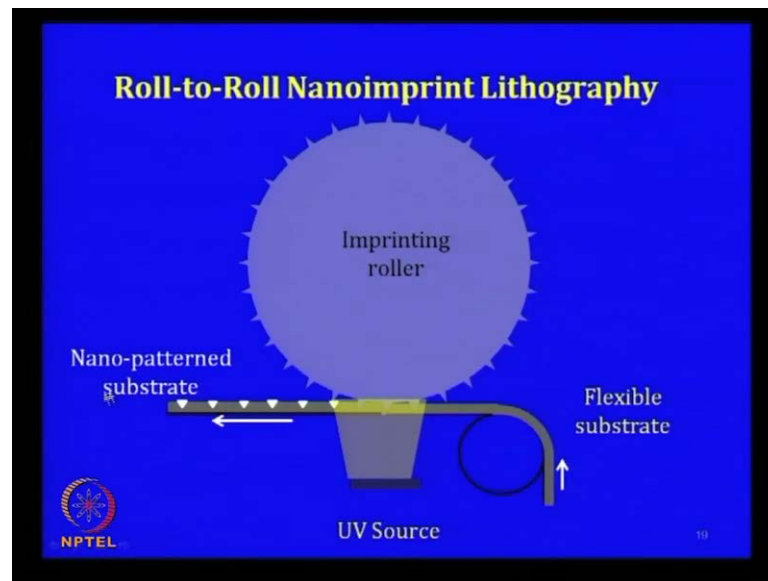
The other thing is that the way we are talking about most of the at least the Nano imprint lithography group of methods including also the photo lithography group of methods the way whatever we have discuss so far, you might have notice one thing that all of them are sort of executed has a batch process.

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So, what you do, you take the film, you put it align with respect to the stamp or the mold, you take the mold, and then you heat it up then you imprint, then you detach, and then you take away patterned film, so this is a batch process, everything is a batch process. So, there is, so this sort of severely you can imagine hinders the throughput, so ((C)) mean essentially to make nano imprint lithography sort of a roller a continuous process, and two configurations were patented to you can find U S patents, so one them is you take a pattern cylinder, pattern cylindrical mold and u sort of have a thermal stage of course there has to be certain extent of automation.

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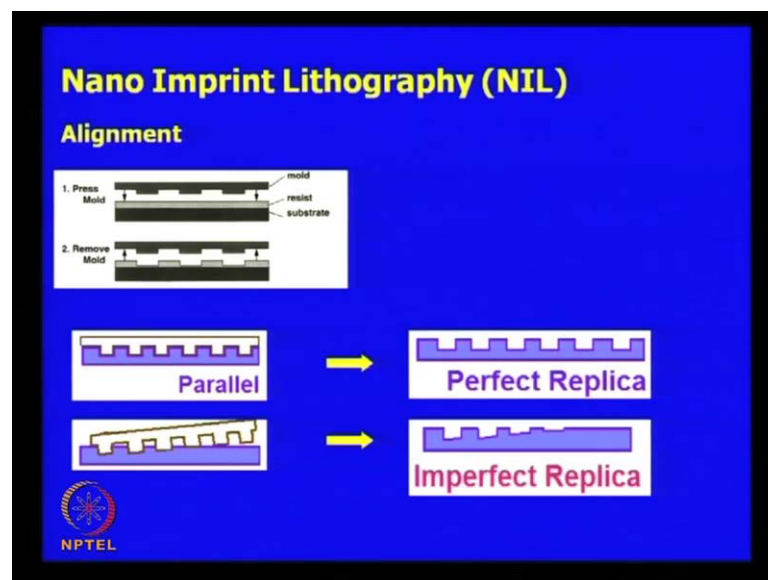
So, you take a film heat it up as it sort of has you can see here, so you sort of have a heating zone or a UV heating zone or something like that, so this is the instead of a flat stamp now you have a cylindrical stamp, so this rotate at specific speed the substrate of the film also as to sort of come at a matching or a common speed, and if there is a localized heating over this particular area each time each of this protrusion of the roller sort of can lead to one imprinted structure on the film, so typically this type of things were very nicely or this type of arrangements sort of this ideally suited when you have a your film is coated on a flexible substrate rather than on a rigid substrate.

Because then you can think of having a role to role patterning, I mean way back in 1998 it was reported that you can create 17 Nano meter structures with roller NIL often referred to as RNIL process, the other method was something similar, but again here it was more conventional I mean this is also sort of considered as a roller Nano imprint lithography technique, but if you look into it carefully what this done is this does is it still uses a flat stamp flat structure stamp, you keep a longish substrate over here and then a roller sort of roles, so this roller with a lamp and heater up sort of roles along with the surface, so what it does the specific zone which is below the roller at again given instance of time that particular part of the polymer sort of subject to heat as well as a embossing pressure.

So, that way it sort of there is a local pattern transfer mission local pattern transfer, or in other words in this particular configuration what you do that you sort of eliminate the requirement of applying a uniform pressure over a large area, which it is can be scientifically challenging under particular settings under certain specific condition, and instead of that you sort of apply a roller along with a heating arrangement which sort of rolls over the glades over this assembly to sort of achieve the pattern transfer in sort of a serial fashion, but this is one of the more ideal configurations where you can really go for a role to role process or have a continuous Nano imprint lithography set up, they are whole lot of engineering challenges associated with such an assembly what would be the speed of the roller; what would the local temperature; what would the local viscosity.

So, critical issues I mean all if all these lecture view are wondering where exactly our chemical or mechanical engineering concepts really coming to such an area these are ideal examples, because the deformation you are resulting in the unit there are appropriate viscosity, you need the appropriate temperature to be sort of there and consequently it has to be the entire system sort of has to be synchronized in a very specific fashion to achieve the desire structure.

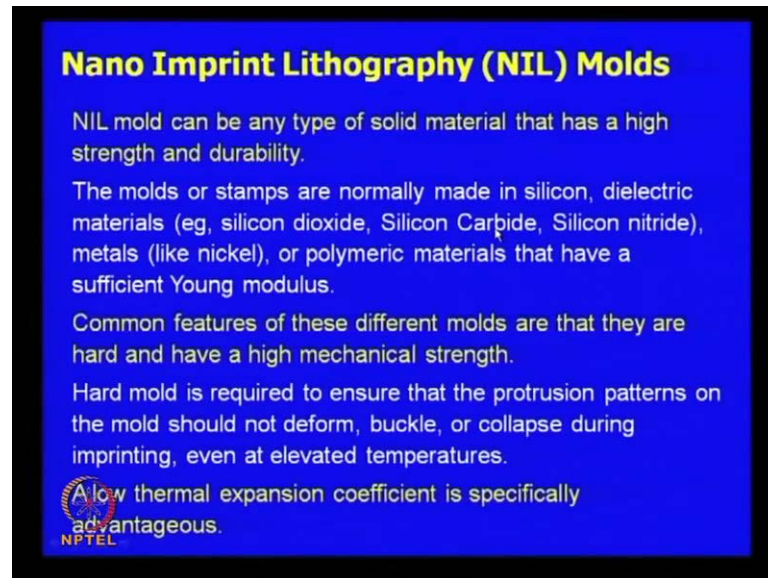
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So, the other important thing in Nano imprint lithography is to sort of achieve the proper alignment between the stamp on the on the film, or in other words you need to sort of insure that the stamp on the film are perfectly parallel, because non parallel

configuration. So, only if there are parallel you will get a perfect replica, if they are not parallel you will get imperfect replica resulting essentially in an edge, so across the sample there will be a variation in the depth of the structure you get.

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Nano Imprint Lithography (NIL) Molds


NIL mold can be any type of solid material that has a high strength and durability.

The molds or stamps are normally made in silicon, dielectric materials (eg, silicon dioxide, Silicon Carbide, Silicon nitride), metals (like nickel), or polymeric materials that have a sufficient Young modulus.

Common features of these different molds are that they are hard and have a high mechanical strength.

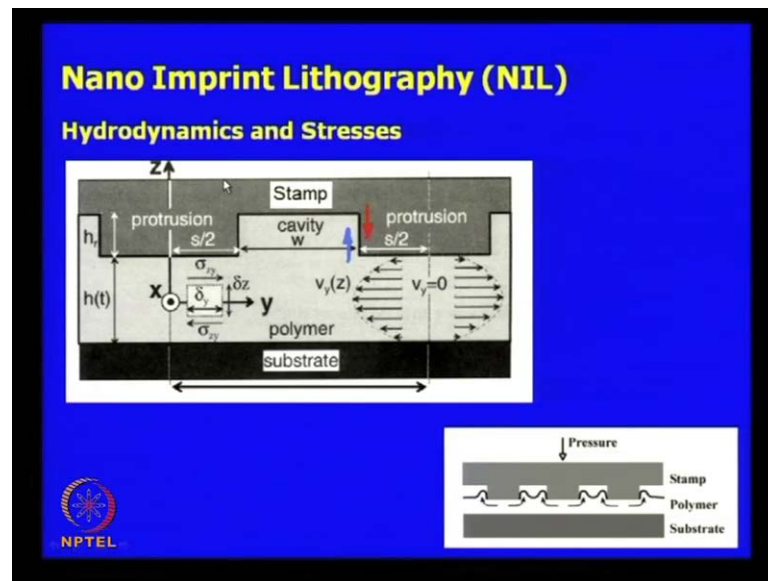
Hard mold is required to ensure that the protrusion patterns on the mold should not deform, buckle, or collapse during imprinting, even at elevated temperatures.

A low thermal expansion coefficient is specifically advantageous.

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The other important thing we need to look at what are the Nano imprint lithography molds, NIL molds can be any type of solid material that has a high strength and durability, the molds or stamp are normally made of silicon and other dielectric materials like silicon dioxide, silicon carbide, silicon nitride, metals like nickel or polymeric materials that have sufficient young modulus, because it have to with stand the external pressure you are applying to achieve the pattern transfer, the common feature of the different molds are they are hard and have a high mechanical strength, a hard mold is required to ensure that the protrusion pattern on the mold should not deform buckle or collapse during imprinting even at elevated temperature, and off course a low thermal expansion coefficient is specifically advantageous and necessary.

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And these requirements do not exclude the use of a flexible back backplane supporting the hard surface of a relief structure, it is so you can actually have a hard pattern which is supported on a flexible backplane, because that type of a mold will be necessary if you are considering system like this; or may be this, so it is actually advantageous for the mold to have global flexibility and local rigidity in many applications, specially, when your patterning a film which is not coated on a flat substrate, as a flexible mold can provide large area conformal contact with the substrate without resorting to high pressure.

Essentially there is a concept which later came up we will skip it in this particular lecture, the rigiflex mold approach the rigiflex lithography approach explicitly exploits this feature of NIL patterning to have a rigid mold sort of support on a flexible backplane, these are other critical issue which is associated with the hydrodynamics soft Nano imprint lithography and which eventually results in a lot of stress within the film itself during the process of patterning, it is because of the fact that you are during the process of pattern replication you are pressing this stamp hard against a heated polymer layer, so there is this visco plastic deformation.

So, how it achieved? It is first achieved by removal of the polymer present below the stamp stripes, so first the liquid sort of moves from this moves or get sort of dislodge in these directions, but the liquid cannot sort of go very far because from the subsequent

protrusion also polymer is coming, so you have a velocity profile over here; you have a velocity profile over here, and the accumulation of the resultant velocity over here eventually leads to a resultant flow in these direction of the polymer. So, this is the flow that is responsible for the mold filling, now if you now look at this particular zone here your stamp surface is undergoing a motion in this direction, you know about the validity of the mostly boundary condition.

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Stresses in NIL

The stresses might eventually release, leading to relaxation and re-configuration of the patterns or structures. This leads to a change in pattern geometry, which in many applications (like an optical application for example) will severely hamper functionality. Sudden release of stresses might also significantly damage the structures.

Advanced Materials, 19, 1377, 2007
 Adv. Funct. Mater, 18, 1854, 2008
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The slide contains two 3D surface plots (a) and (b) showing stress profiles. Plot (a) shows a series of peaks that are slightly tilted, while plot (b) shows a similar series of peaks. To the right of the plots, there are two pairs of images. The top pair shows a transition from a regular array of rectangular pillars to a distorted array where the pillars are leaning and some are missing. The bottom pair shows a transition from a regular array of pillars to a distorted array where the pillars are leaning and some are missing.

So, your polymer adjacent to the stamp is also moving in this direction; however, because of the accumulation of the polymer and conservation of the mass this layer polymer is moving in the upward direction, so over this particular zone there is a significant level of stress, so this is a critical issue in NIL that the structures towards particularly towards the edges have significant amount of stress, and these stresses sort of get frozen in when you cool then down, and it was very recently shown by Kareem's group at Accron NIST that these stresses over the longer period of application can eventually release and can lead to distortion in the Nano imprint lithographically imprinted structure in the form of loss of fidelity or reduction of structure height etcetera.

Again when we talk about these stresses the calculation of these stresses how the velocity profile on the polymer real logy sort of leads to the or controls, the magnitude of stresses you apply a lot in detail your basic engineering fundamentals, this is something

once we discuss soft lithography particularly the capillary best filling and things like that we will like to revise it and have a relook at looking at the level of stresses.