Instability & Pattering of Thin Polymer Films
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Lecture No. # 19
Soft Lithography – IV

Welcome back, we continue our discussion may be last couple of lectures on soft lithography, we have been talking about different patterning techniques for a while, first we got started with photo lithography. And then for the last three and half three lectures, we have now been talking to the more polymers specific soft lithography methods. If you remember in the last lecture, we talked about a specific technique, which you goes by the name MIMIC or micro molding in capillary's which is a very very versatile technique, discovered around mid 90's by white sides group. And one of the things that I mentioned has advantages; one of the key advantages of MIMIC which majority of the other patterning techniques are unable to handle.

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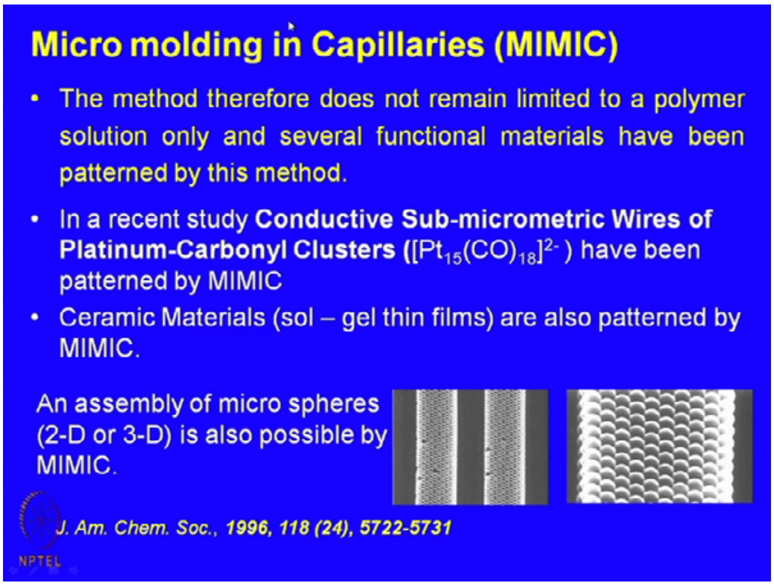

Micro molding in Capillaries (MIMIC)

- The method therefore does not remain limited to a polymer solution only and several functional materials have been patterned by this method.
- In a recent study **Conductive Sub-micrometric Wires of Platinum-Carbonyl Clusters** ($[Pt_{15}(CO)_{18}]^{2-}$) have been patterned by MIMIC
- Ceramic Materials (sol – gel thin films) are also patterned by MIMIC.

An assembly of micro spheres (2-D or 3-D) is also possible by MIMIC.

J. Am. Chem. Soc., **1996, 118 (24), 5722-5731**

Let me just focus on that before we move on to certain anything that is new is the ability of MIMIC to pattern not only a polymer film or a polymer, but also the ability to pattern colloidal assemblies or colloidal particles.

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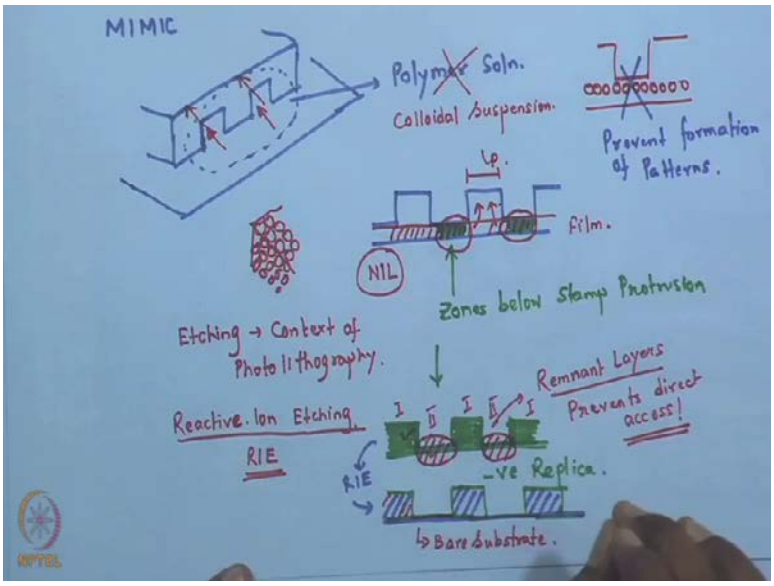

The key advantages, that since if you remember the process by which way you implement, you essentially bring in a PDMS stamp which has the desired structure, the negative replica of the desired structure. First, you bring it in to a conformal contact with the substrate and then typically what you do; you dispense a polymer solution over here. So, it is it contains the solute which is the polymer. So, in normal MIMIC it is polymer solution, which contains the polymer has the solute and the solvent. So, because of the capillary driven flows though this micro channels, that is a pattern replication or that is gradual mold filling, because of the flow of the solvent.

Now, the way this can be utilized or has been extended for colloidal particles is instead of a polymer solution. If you now dispense a colloidal suspension, then essentially the dispersing media or the liquid in which the colloidal is suspended, place the same role as that of the solute and that starts to flow along with the micro fluoric channels performing or undergoing the mold filling operation and eventually what you can get is a nice array of colloidal particles which get deposited only the locations at which this flow has resulted.

So, eventually if you or if you dispense a colloidal solution over here, what will happen? The colloidal solution will flow only over these resumes and you will have isolated zones or stripes containing colloidal particles like this. Let me remain that whatever soft lithography or lithography techniques we have discuss so far, none of the methods has the potential to use or to pattern colloidal particles. Because of the facts that most other methods forget about photo lithography, which requires a significantly different hardware even soft lithography techniques, which we have already discuss. Like nano imprint lithography, you initially require a film and you pattern only by embossing on that film. So, the moment you are talking about colloidal suspension for example, the best you can do is to spread it on the surface of a substrate.

And then when you bringing the stamp, the problem will be that there will be some particles; colloidal particle which will be at the locations, where the stamp protrusions come or try to come at a conformal contact. So, these areas will act us hindrance and will prevent formation of patterns. So, that way MIMIC offers this unique advantage in the form of allowing the ability or offering the ability to pattern colloidal suspension. The other real advantage is that we have already talked about the presence of the remnant polymer layer in while discussing nano imprint lithography, that is when you bringing the stamp in contact with the film depending on the galaxy, that is the line width periodicity height of the stamp.

Of course, there is mold filling due to the visco plastic deformation. So, please do not confuse we are now just cross referring to nano imprint lithography, which we have already discussed and you already know, but the critical issue is even if there is mold filling and there is flow of polymer from these zones, now why these zones are unique because these are the zones which fall below the stamp protrusion zones below the stamp protrusion. So, inspire of having a significantly nice pattern replication, in most cases what happens is this you have. So, these are let us saying the replicated patterns or structures were depending on the geometry of the stamp, a negative replica has been formed.

But, if you now remember or try to correlate back with photolithography or if you really want this non photolithography techniques to be used for let us say microelectronic application, one of the thing is during the doping stage and all you would like to have access of the access directly to the substrate. So, these remnant layers of polymers prevent that direct access. So, that is a hindrance. So, you have to do some secondary processing to remove these remnant layers and which is typically done by a specific etching technique. We again have already talked about etching in the contest of photo lithography. But there we have the advantage of working with their exposed polymer, which means that parts of the polymer had already becomes stiffer or have already worse in depending on whether you are using a positive or a negative photo resist layer.

In contrast, if you look a carefully in nano imprint lithography physically there is no difference in the property of the polymer of these zones. So, if I mark the zone 1 and zone 2 let us say zone 1 is the area in which the pattern replication has taken place and zone 2 is the area, where from where the liquid the polymer actually flown out, but physically these areas there is no difference in the in the property of the polymer. So, the advantage that we had using the develop a solution that it preferentially removes only areas or photo resist from areas where it has degraded. That advantage, now get missing in this particular case and there is a specific technique I was not going to the details, that is beyond the scope of this particular course.

But, I would encourage you to have a look at it in internet or consultation literature is a specific method which is known as RIE reactive ion etching, which can be used to remove these remnant polymer layers. And you only on that circumstances, you have a possibility of using embossing group of techniques has a violable alternative to photo lithography are possible application in microelectronics. So, this is how it looks like if you perform in RIE now. So, from this step to this step, if you do an RIE you will get something like this. So, this zone will be bare substrate, and then if you recall may be our lectures 13th, 14th or 15th lectures, when we talked in detail about photo lithography.

Then you can have a similar situation, that this can now be exposed for the doping the only condition, being that the polymer in which you have not perform the nano imprint lithography, which now remains in the form of these strip or stripes whatever that has to with stand the doping conditions. So, they do not they should not degrade when you are performing the doping, but if you have this picture in your mind that you need to have an access to the bare substrate and parts. So, that this now becomes sort of equivalent to a partially develop photo resist layer and can sort of find application in micro electronic processing, that way from that stand point MIMIC also is uniquely advantages.

Because if you look at the basic configuration of MIMIC, ideally theses areas of the stamp are in conformal contact with the substrate and the liquid should only flow through these micro channels or micro cavities formed three sides of which is the stamp and the fourth side is the substrate itself. And ideally, there should be no reason why liquid should penetrate below this stamp or the zones over which the stamp is in conformal contact with the substrate.

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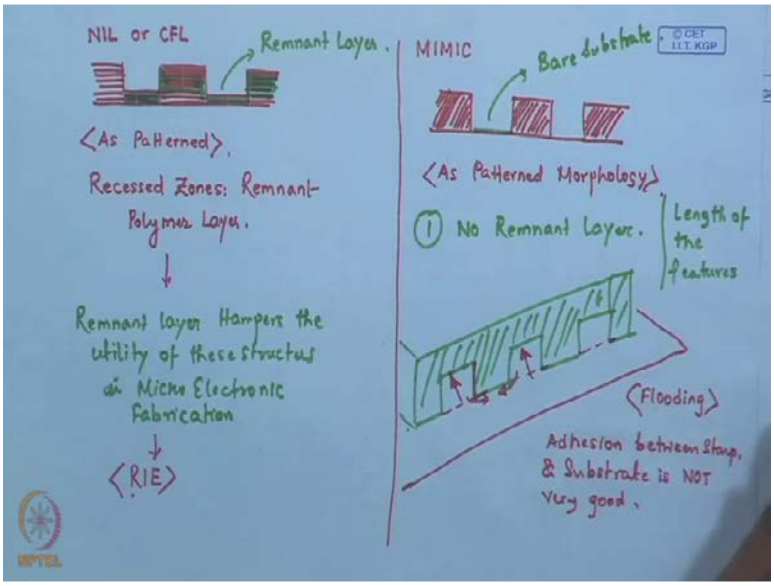

So, that way we have already discussed that a MIMIC structure, even if you are working with a polymer should be like this. So, these are polymer features and these zones are of course, bare substrate. So, in a well performed MIMIC experiment, this is already you can find the advantage that there is no need to sort of go for a secondary processing like RIE. So, there is a possibility. So, let us write it down neatly that in NIL or as we will also see that the same thing is valid in CFL, which are going to discuss today may be in this lecture or in this next lecture as patterned structure is like this. So, you form a negative replica of the stamp no doubt about it, but the recessed zones they contain the remnant polymer layer which is find for some application, may be if you are we already have talked about structural super hydro febricity.

For example, and applications like that or structural color where we see rainbow color due to optical refraction, this type of a structure is perfectly fine. But so this is let us smart this is the remnant layer, but this remnant layer hampers the utility of these structures in microelectronic fabrication and in order to enable there utility in microelectronic fabrication, this has to a company with the stapes of reactive energy. So, that is limitations you are adding another complicated hardware element to your whole process, which makes the process completion costly, all these associated problems are there.

In contrast, if you now look at MIMIC carefully again so, here is the possibility now what MIMIC offers you and only MIMIC offers no other technique has we already known nano imprint lithography and we will discuss other lithography methods can offer. That is this is the as patterned morphology and you already have access to the bare substrate. So, one key advantage would be no remnant layer, of course in our previous lecture itself, we have discussed one of the critical disadvantages of MIMIC that is in the length of the feature. Because, longer the capillary length is the driving force for the capillary flow will gradually reduce and there will be a dearth of driving force for mold filling.

But, if you forget that in principle there is a possibility that MIMIC and give you standalone isolated polymer structures or isolated structures with no remnant layer. But this is important to note that this is easiest said the none, because under practical conditions what many times happen is the liquid, if the contact between the I will take fresh if the. So, we review at the configuration. So, this is the stamp which is in conformal contact with the substrate and here you dispense the liquid. So, here this zone sort of access the liquid pull, now if the adhesion between the stamp and substrate is not very good, then what happens is liquid in addition to flowing along the micro channels also sort of starts priding through the bottom of these stamp or in other words, it sort of this larges the stamp from the substrate and sort of fills in the zone between then.

So, this is often refer to as the case of flooding. This is very commonly uncounted, if you do not have your solvent concentration or if your processing condition is too humid, which sort of prevents a good conformal contact between the stamp and the substrate. If you have impurities; impurities in the form that along the so, this some dusk particles or some irregularities are there which prevent conformal contact between the stamp and the substrate and sort of a micro cavities through which this type of a cross flow is encouraged or take place. Then what happens is that the whole idea of having a remnant layer fee pattern from MIMIC gets spoiled.

So, this is something one has to very carefully examiner keep in mind, while performing micro molding in capillary’s and so here are the… So, thus the final winding up, so this is one of the very nice, very novel techniques which can be used for polymers. But it is utility is not only limited to polymers, it has been extended for various other types of jells or any materials that essentially flows and can sort of be made solid like by either evaporation which is the case with a polymer solution. Or let us say by other techniques, like cross linking or reaction, let us say and MIMIC therefore, has been rather extensively also been used for in organic jells or sole jells for making nano, and measure scale structure and ceramics films and surfaces and what we have highlighted write at the beginning of this particular lecture is that MIMIC has also found utility in patterning of colloidal suspensions.

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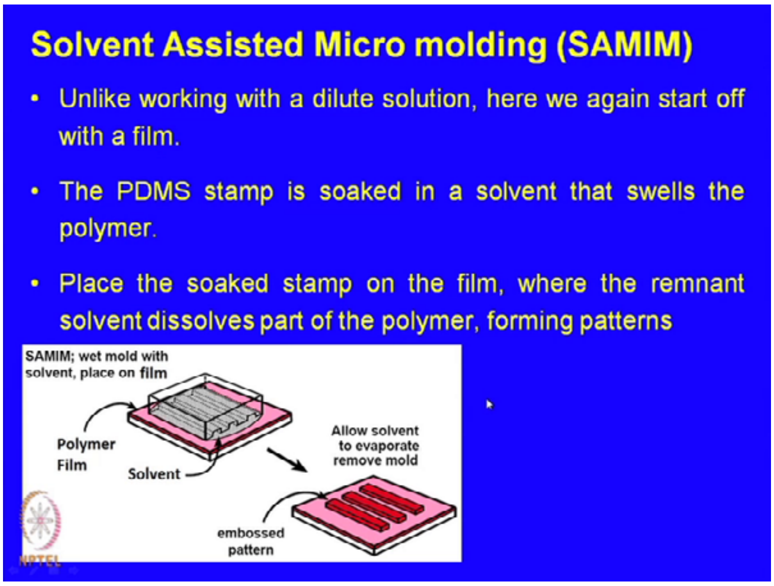

Solvent Assisted Micro molding (SAMIM)

- Unlike working with a dilute solution, here we again start off with a film.
- The PDMS stamp is soaked in a solvent that swells the polymer.
- Place the soaked stamp on the film, where the remnant solvent dissolves part of the polymer, forming patterns

So, with that we sort of move on to the next technique, which is one of the extension of MIMIC you can say which is known as solvent assisted micro molding. Here, if you look at the experimental configuration it is quite similar to MIMIC, but the key advantage or the key difference between MIMIC and the SAMIM is the fact that MIMIC you bringing your stamp with direct contact with a bare substrate as we have already shown here. And you dispense the solvent as well as the polymer over this open size of the stamp geometry. So, the other thing if you remember in the previous class, we talk that in order to implement MIMIC, it is absolutely essential that every part of the structure, you want to make is somehow interconnected. So, that the liquid or the solution can flow from the edges write down to the central of the pattern you want to make.

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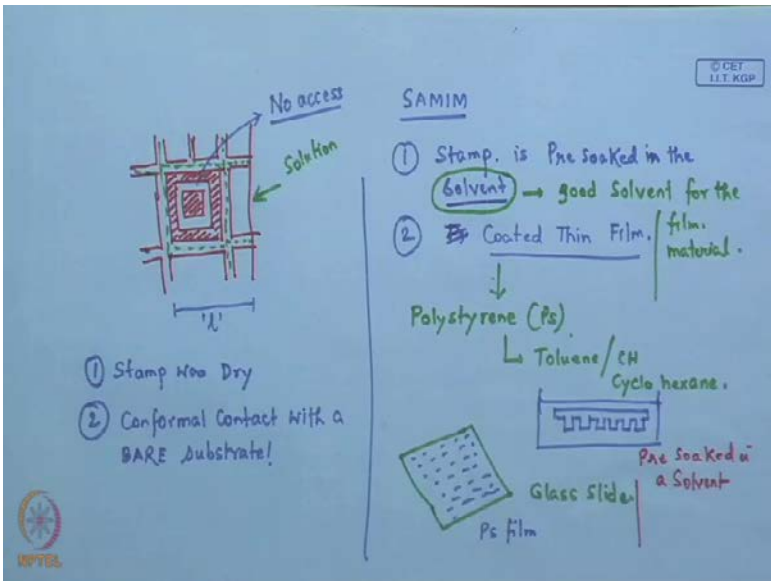

① Stamp Was Dry
② Conformal Contact with a BARE substrate!

SAMIM

① Stamp. is Pre soaked in the Solvent → good Solvent for the film. material.
② ~~By~~ Coated Thin Film.
↓
Polystyrene (Ps)
↳ Toluene/CH
Cyclo hexane.

So, quick example can be let us say you want to make some structures like this; the central part is let us say closed, you cannot really replicate this pattern by MIMIC, because of the fact, that MIMIC will fail in this particular case in replicating the structure. Because of the fact, that if you make a reservoir over here or dispense your solution from this side other, solution due to favored capillarity will probably fill up all these zones, but it does not have any access to the central zone. So, here there is so, the pattern replication will not take place. Of course, you can think of using some other pattern technique like nano imprint lithography or other techniques suitable. So, and the second limitations of course is that depending on the how long, you want to sort of make your channels is the flow pates of the driving force.

We have already shown the equation in the previous class, the driving force sort of ran solve on the rate of film becomes extremely sluggish. So, in order to overcome that what SAMIM does, the method of SAMIM realize it resembles MIMIC very closely, but the key differences is difference number one is the stamp first is sort of pre soaked in the solvent, now solvent for what will coming to it, and instead of taking a bare substrate, now we take a pre coated or a coated thin film. So, in MIMIC if you contrast it and write it down again to avoid any possible confusion, the stamp was absolutely dry and it was brought in conformal contact with a bare substrate. Here, what is done is the stamp is already pre soaked with a solvent and it is coated with a film.

Whether question, natural question that will come to your mind is that it is pre soaked to the solvent of what it is pre soaked in a solvent in a liquid, which is a good solvent for the film material. So, let us say if you have one two pattern, let us say polystyrene a very well known polymer, which is commercial available it is a very easy to dissolve in solvent like toluene or cyclohexane. So, in that case if you want to implement SAMIM, better idea would be provably to better the idea would be that you take a substrate; a rigid substrate which can be as simple as a glass slide coated with polystyrene film and you have the stamp somewhere and this is now pre soaked or immersed a simplest form in a solvent and now since we know the polymer we can be more specific.

So, it can be let us saying toluene. (Refer Slide Time: 19:06) So, what you do now you can see, you have if you look at the cartoon, we have a weight mold with the solvent. So, we have a weight mold and placed on the film. So, you already have a film, polymer film as we have talk about and the solvent. So, as you transfer the weight stamp it carries a little bit of solvent. Now, what happens is this solvent or the polymer film that is already coated on the glass slide, now comes in contact with the solvent. So, there is sort of a local dissolution that express. So, locally a sort of a solution which is very reach in polymer now is meant or in other words we have already talked about the glass transition temperature of the polymer.

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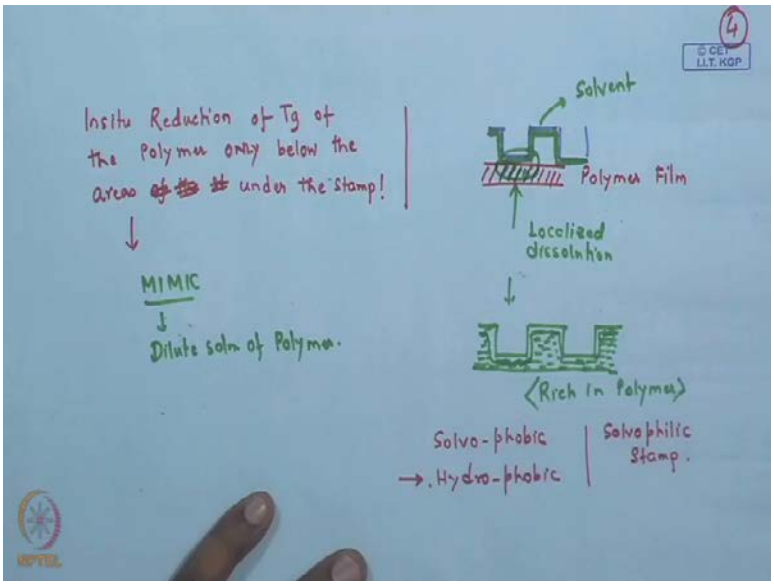

Insitu Reduction of Tg of the Polymer only below the areas ~~of the~~ # under the Stamp!

↓

MIMIC

↓

Dilute soln of Polymer.

So, what happens is because of this contact with the solvent layer locally, there is an incentive reduction of the glass transition temperature of the polymer only below the areas under the stamp. So, we have already talked about this glass transition temperature and what is the manifestation of this glass transition temperature on transfer properties, there is an intrinsic reduction. So, this results for our purpose what we understand that a reduction of glass transition temperature means, that there will be a drop of viscosity of the polymer, even may be at room temperature.

So, now what happens is the polymer film which you have taken by coating, which was solid like at room temperature sort of a frozen in solid frozen in liquid, now it comes in contact with a rigid stamp which is sock. So, sock with a solvent with a liquid which is a solvent for the polymer? So, this solvent now comes of the polymer now comes in contact with the solvent, it sort of locally dissolves and once it. So, now, it is like more like a locally it is in a liquid state. So, what happens now is this polymer in the liquefied form tries to do a mold filling and then also most of the cases these are inorganic, these are organic solvent so, they are pretty high volatile it evaporates away and eventually it forms a negative replica.

So, if you compare this is imprinciple the method of SAMIM. So, essentially what it says that allow the solvent to evaporate, remove the mold you get a negative replica. (Refer Slide Time: 19:06) Advantage and disadvantage, if you sort of contras this technique with MIMIC, there can be couple of advantages. One of the major advantages is that unlike MIMIC, where in order to sustain the flow one typically takes a dilute solution of the polymer. Because if you take a very concentrated solution then what will happen is that through this force, the flow itself will be sort of hindered. So, in order to sustain the flow or sort of have the flow achieved in realistic time scales, the solution is often taken to be dilute.

So, what is the problem of that we have discussed in the previous class itself, that since after mold filling the structures you have is reaching solvent and when you allow the solvent to evaporate, there might be significant shrinkage of the feature dimension. The features can sink literally, the features can sink vertically this can be a significant problem in certain cases like particularly in sol jell systems; this can also lead to porus structures so, the density of the structures. So, the structures may not be that dense. Again, sol jell you have a multi component system so; there can be associated issues like face aggregation, during this evaporation stage.

In contrast, what is happening in SAMIM is that you are working with a very concentrated solution polymer solution, which as just dissolve locally below the stamp. So, therefore, your concentration is very high. So, the patterns you get the insitu as transfer patterns, they are very rich in polymer and the solvent content, this is now sustainable because of the fact that you do not require this long flow of the liquid, as what is necessary in MIMIC. In contrast, your liquid flow path is only limited at the length scale of each feature, which can be a few hundred nanometer may be maximum couple of microns of few microns has compared to microscopy length scales at time, let us say five hundred micron one millimeter five millimeter even one millimeter width of a stamp is too less to handle.

So, for realistic things you might be actually making a stamp which is ten millimeter long. So, the liquid has to travel ten millimeter, in case of MIMIC to achieve mold filling and therefore, you would like to keep the viscosity of the polymer solution as low as possible by reducing the concentration of the polymer. In contrast, here you do not control the polymer concentration, you all you do you take a thin film and you place the stamp.

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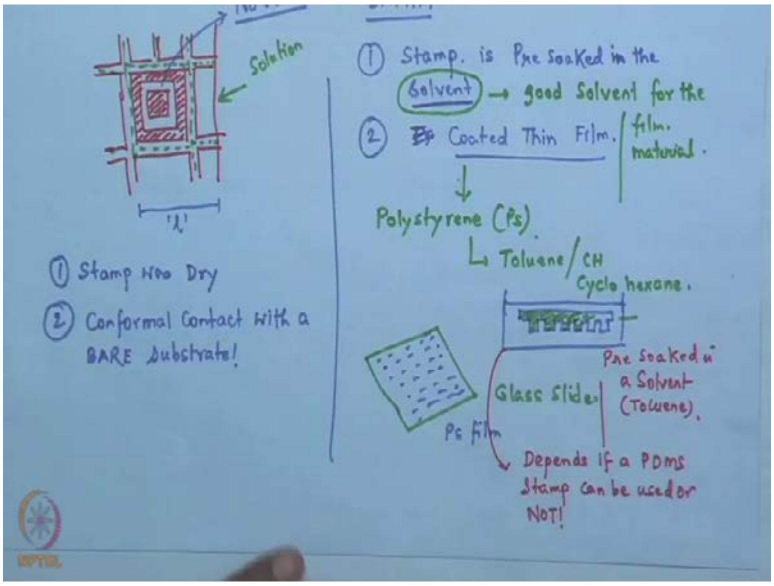

① Stamp Now Dry

② Conformal Contact with a BARE Substrate!

① Stamp. is Pre Soaked in the Solvent → good Solvent for the film material.

② Coated Thin Film.

↓

Polystyrene (Ps).

↳ Toluene/CH Cyclo hexane.

Pre Soaked in a Solvent (Toluene).

Depends if a PDMS Stamp can be used or NOT!

What is important here, couple of additional things you needs to be understood that when you perform this emotion. It depends whether you can still use a PDMS stamp or not. Because, most of the soft lithography techniques it is taken for granted that cross link PDMS stamp can be used, but here it is a straightly difference scenario. Why because you are taking an organic solvent, which is a good solvent for the polymer film. But many of these solvents for example, cyclohexans toluene also to a significant extant and chloroform for example, if you are using as a solvent this swell PDMS. So, why during this pre soaking stage, the stamp if you are using a PDMS stamp, the stamp itself might get damaged.

So, that becomes a critical limitation now and based on that you might have to use or implement SAMIM with a stamp of a different material which is completely in or to this solvency for which can be a silicon stamp or it can be let us say something like a fluro polymer stamp, which is which exhibit more inactiveness has compare you PDMS. So, these are few of the limitations of SAMIM, but the real advantage is that the since the flow path now becomes very limited you and you have very little amount of solvent in the replicated structures. So, the shrinkage induce damages, the possibility of shrinkage in dues damages which is predict common in MIMIC, is now significantly reduced.

The critical parameter here to control apart from the material of constriction of the stamp, whether you can use you can still use a polymer stamp or you like to use a silicon stamp or any other rigid stamp, is the immersion time and the surface energy of the stamp. Because, eventually that will dictate how much amount of solvent, the stamp is going to carry into your system from this immersion stage to when it is placed on the film. So, if you have a stamp surface which is extremely solvo phobic. So, this is something it should mention to you now because you understand this particular term a surface that does not like water. So, solvo phobic would be a surface that does not like to be wetted by the solvent in which you are immersing it.

So, if you have a solvo phobic surface for example, that will sort of allow you that will result in very little amount of solvent getting transferred from the immersion bath, let us say we mark this as immersion bath. So, very little amount of solvent will be transfer from the immersion bath on to the film. So, if very little amount of solvent comes this will be able to locally dissolve, very little amount of the polymer and therefore, your pattern replication might be significantly hindered.

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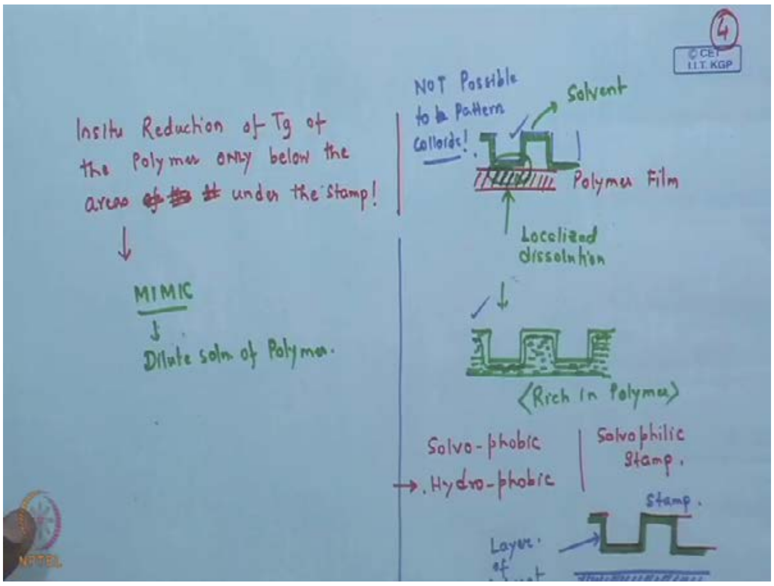

In contrast, if you take a solvo philic stamp, that is the stamp surface prefers to remain weight by the polymer, by the solvent you are using then it is perfectly fine. Because, when you transfer the stamp from the immersion bath on to the film surface, it will it is likely that there will be a nice layer of the solvent and this solvent will then coming contact with the polymer film. So, this is the stamp if you one to understand it once more greater detail, this is a layer this is not a polymer layer of the solvent and now this comes in contact with the polymer film.

So, once these two are in contact then this entire amount of the solvent that is present here that is that has been carried from the immersion chamber on to the film is utilizing locally, diluting the polymer film and which then prefers are helps in the pattern replication process. So, the critical thing to control under actual experimental conditions is the wettability of the stamp or the duration over which you would like to keep your stamp immersed in the immersion bath, so that indirectly you control how much amount of solvent, you intrinsically want to transfer on to the film surface which is available for the insitu pattern replications. So, this is a very nice concept that has it origin in MIMIC, but sort of removes several disadvantages which are associated with MIMIC.

But then looking back, we highlighted one of the specific aspects of MIMIC right at the beginning today, is that it is a ability to pattern colloidal suspension if you now think of the protocol of SAMIM for example, it is almost impossible to handle colloids. So, they this is how the full thing goes I am in every method has it is some advantages and some disadvantages which we have to understand. So, that depending on your specific requirement you can pick up the method of your choice.

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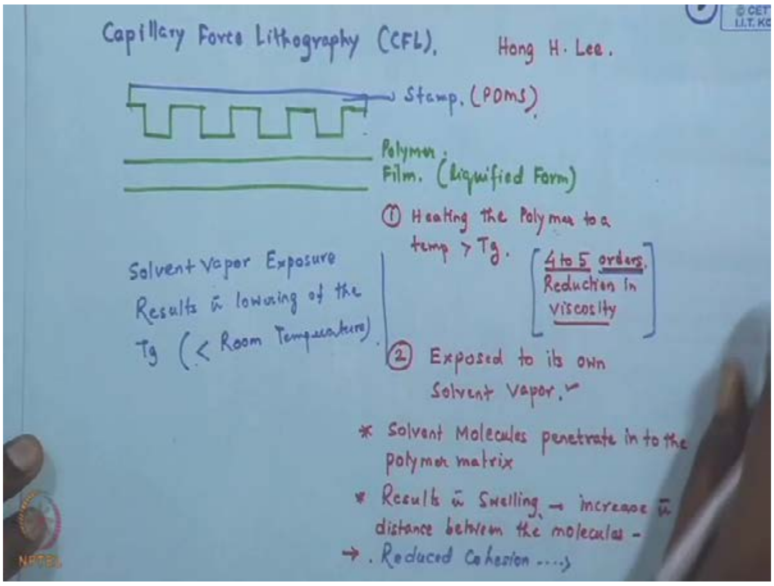

Capillary Force Lithography (CFL). Hong H. Lee.

Stamp. (PDMS)

Polymer Film. (Liquified Form)

① Heating the Polymer to a temp $> T_g$. [4 to 5 orders Reduction in Viscosity]

② Exposed to its own Solvent Vapor.

Solvent Vapor Exposure Results in lowering of the T_g (< Room Temperature).

* Solvent Molecules penetrate in to the polymer matrix
* Results in Swelling → increase in distance between the molecules –

→ . Reduced Cohesion ....)

The subsequent method which was which is a some way it is unique, because of the fact that though it is an extremely popular soft lithography patterning technique now and is pretty well utilized and also it is very easy to implement. This method was not discovered by white sides group, is a rare method and this is a very strong Asian origin this was discovered by Hong lee's group in Korea around early 2000. So, similar to micro molding in capillaries, which also takes advantages which realize on capillary driven flow, CFL also realize the pattern the hot of CFL realize on capillarity, but it is utilized in a completely different fashion? In a way, the way we have discussed makes much more sense, because of the fact that C F L is closer to SAMIM in many ways.

But SAMIM, one of the real implementation problem if you look carefully was the step involving the pre soaking of the stamp, because the amount of solvent that is made available on to the film surface for the pattern replication is entirely govern or is entirely due to the stamp, I mean. So, you wait the stamp you take it out from the immersion chamber, you place it on the film. You have no direct control and how much amount of solvent is going to get transferred from the solvent chamber or the pre soaking chamber on to your stamp surface, which is a big problem. Because, ultimately the amount of solvent that is available to you is going to decide in many ways, has to how much amount of film is getting sort of dissolved and (Refer Slide Time: 36:13) what will be the local viscosity of the system and whether what type of the structure, you are going to achieve.

So, in other words if you have very little amount of solvent that is getting transferred, very little amount of polymer will get dissolved and consequently there might be inadequate poor filling or mold filling on the pattern property or the pattern quality might be effected has a consequence of that. CFL tries to remove some of these problems, which are associated with SAMIM and what it does is that, it sort of realize on the fact that you have a stamp, it is not pre soaker anything like that, it is brought in contact with a film which is already in liquefied form. So, by film we mean a polymer thin film, which is already in a liquefied form and this liquefaction or liquefication is achieved as we all know it can be achieve by two approaches. One can be heating the polymer to a temperature greater than the glass transaction temperature, which sort of results in 4 to 5 orders reduction in viscosity.

It is important to note is 4 to 5 orders not 4 to 5 times so, 10 to the power of 4 to 10 to the power of 5 times reduction in the viscosity. So now, a polymer let us say simple linear chain homo polymer, which is Stephan solid like at room temperature may be something this plastic cap of this particular pen, which is also a polymer. So, you heat it up this can be some polymer, which has a glass transition temperature let us say somewhere between 100 to 110 degree centigrade, you heat it up what happens is does not burn of directly.

So, polymer in most cases the constituents are carbon and hydrogen so, if you burn it of eventually, it will burn of giving producing carbon dioxide and water that does not happen if you moderately heat it to some temperature let us say 120, 130 degree centigrade, instead what happens is that it becomes soft and this softness is associated with nothing, but this reduction in viscosity what we are talking about that. But the moment you need to understand from this very simple practical example, that the moment it is in a soft state you can now imprint it or you can if you bring it or improximaty to a surface, which is waited which is preferentially waited by the polymer.

This polymer can actually start flowing and that exactly, what we have been enthusising is this is the processing condition at which capillary force lithography is implemented. So, what is done this is a stamp and here you have generally have no restriction of using a PDMS stamp and you have this polymer film, which is either heated beyond it is glass transition temperature or is exposed to its own solvent vapor. This is another technique I think, we in one of our earlier classes of already discussed about this specific method. Solvent vapor exposure, what it does is that the solvent molecules penetrate in to the polymer matrix. This results in swelling; swelling means the physically the polymer molecules are for their away apart from each other.

So, this also means that there is an increase in physical distance molecules, this now results in a reduced cohesion and consequently there is a reduction of viscosity or in other words, if you want to look in to from the stand point of glass transaction temperature. In many cases, solvent vapor exposure results in lowering of the T g often to sub room temperature, but either way either of the two methods you adopt here you have a film, which is now already in a liquefied form unlike SAMIM (Refer Slide Time: 36:13) where the film remains in fully intact high viscosity form and you bringing the solvent along with the stamp only to achieve localized liquefaction or dissolution of the polymer in to the solvent. In contrast here in CFL by the time in stamp comes in contact with the film it is already in a lower viscosity state.

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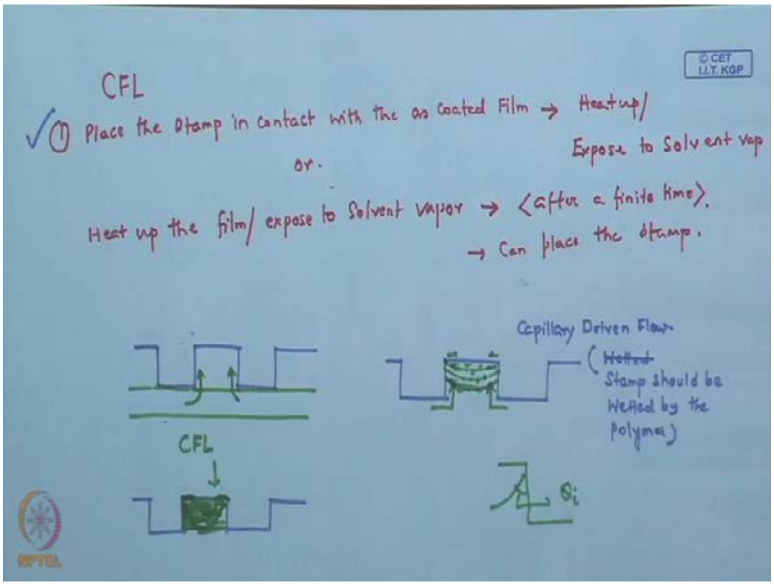
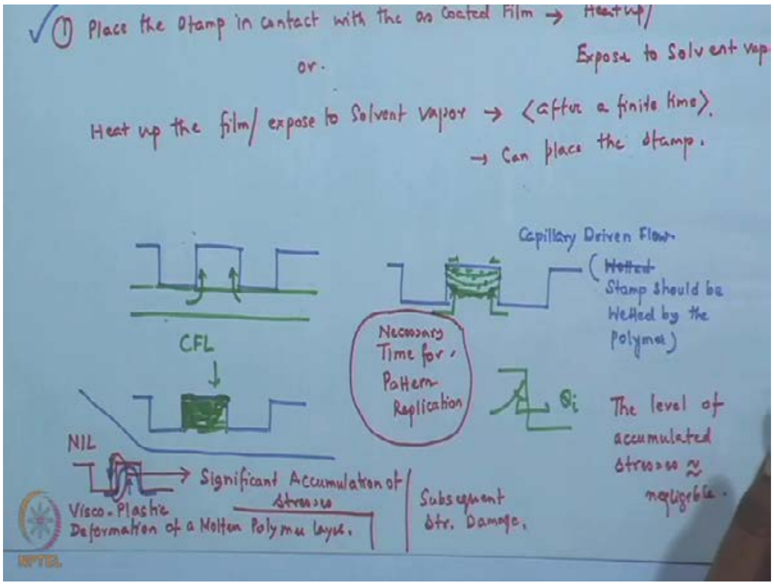


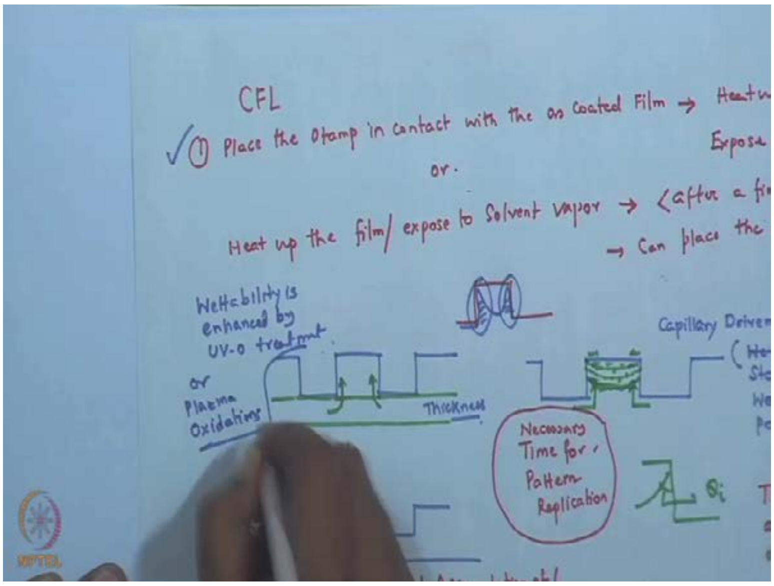
CFL

✓ ① Place the stamp in contact with the as coated Film → Heat up/ Expose to Solvent vap

or.

Heat up the film/ expose to Solvent vapor → <after a finite time>.
→ Can place the stamp.





Experiments can be performed in both the modes, one can have place the stamp in contact with the as coated film and then heat up or expose to solvent vapor or one can heat up the film or expose to solvent vapor and then after a finite time interval can place the stamp. Important thing to remember is that CFL can be implemented with high degree of automation with a automatic positioner or and devices like that or it can also be implemented with simple hand. So, if you are implementing it with your hand, I would strongly recommended that this first protocol is much favored, because if you do not have a precise poisoning device for the stamp and one to place it on to a already liquefied film, then there can be significant vibration in dues to damage to the structures when you try to keep the stamp.

So, once you have place the stamp now let us see what happens. So, if your stamp material now is waited by the polymer; the polymer will start climbing through the voice of the stamp. And eventually, so the pattern replication will be through different stages, like first it fills up the walls and then once the walls are filled up it starts (()) from the top and eventually if there is adequate amount of polymer, then complete mold filling takes place. I will repeat the pattern replication sequence depending on the wettability of the stamp, first the polymer or the liquid starts rising along the walls.

This in order to have this flow is a passive flow, it is a capillary driven flow it starts depends on the or the preferred is the wettability the stamp should be wetted by the polymer and first it starts rising from the sides, then eventually it takes a meniscus like this; this particular angle this intrinsic theta, here can you imagine on with this will depend on the contact angle of the polymer on the stamp material, that detects the shape of the meniscus. So, it first fills are completely and then it starts priding these direction eventually, resulting incomplete mold filling.

If you now remember, we just get back quickly to NIL; NIL the pattern replication was due to visco plastic deformation of a molten polymer layer and therefore, the pattern replication, if you now refer back to some of the older lectures stated like this. So, the flow us from the centered, because the liquid was sort of pushed away from both sides, because of the stamp which was getting pushed in and the stamp if you remember the stamp was moving in this particular direction, the liquid because of mold filling was moving in the opposite direction. So, there was one significant negative side of NIL that we have highlighted to some extent, was significant accumulation of stresses resulted it NIL, which could also lead to subsequent structure damage.

In contrast, so in capillary force lithography the level of stresses is negligible and therefore, the long time stability of the structure is much higher, only thing you have to worry is that you have to sort of work out the accurate timing that is require for because you have to understand that you are dealing with a only a polymer melt and you do not you are not applying any external pressure from outside like NIL. So, that you sort of force your liquid out. So, all you are relying is a capillary driven flow of a high viscosity liquid at room temperature. Therefore, the time requirement of NIL for CFL can be significant it can run into several hours for example, and only then you can have a proper mold filling or you can get a perfect negative replica of the stamp pattern.

In other wise (Refer Slide Time: 38:01) what might happen is that you might get some structures like this. So, this is a polystyrene film which we try to implement or pattern by capillary force lithography in our lab and what you can clearly see that the time that was provided for this particular case was not adequate. So, you see very clear signature of the rise, capillary driven rise of the polymer along the walls of the stamp. So, what you actually see is an incomplete replicated structure and you see these sharp edges in the atomic force microscope picture over here. So, probably given longer period of time, this could have resulted in to a perfect negative replica.

Of course, the other thing you need to understand is the thickness; film thickness is also very important and if the film is not adequately thick, what we mean by not adequately thick there is not enough polymers to achieve complete mold filling. Then also one can get incompletely replicated structure and incompletely replicated structures invariably contain sharp edges like this. This is a clear signature of the pattern replication mechanism itself, that the pattern replication has taken place based on capillary driven flow or preferential waiting of the stamp wall by the polymer.

Before, you when the just like to remain that in most cases PDMS stamp is used for capillary force lithography also and PDMS by itself crossly PDMS or cell guard is a low surface energy material. So, very often it is it exhibits partial wettability, not very good wettability towards many other polymers. So, that you understand that for CFL one of the key requirements is the stamp should be as wettability by the polymer as possible. So, in many cases what is done is these PDMS stamp or stamps are made more wettability. So, the wettability is enhanced by either UV oxidation treatment or plasma oxidation, what exactly physics leads to this wettability enhancement, we will discuss in one of the subsequent classes, we as I will talk to you about this UVO treatment.

So, this is in a not cell what the process about of capillary force lithography is that it realize on the pattern replication due to preferential waiting. In the subsequent lectures, we will take up some more application. So, orientation how CFL can be used to generate more complex patterns and in CFL as well as SAMIM we have used a thin film. So, we need to discuss a little bit about this thin film coating procedure which is spin coating has we have already talked, but in greater detail. Thank you.