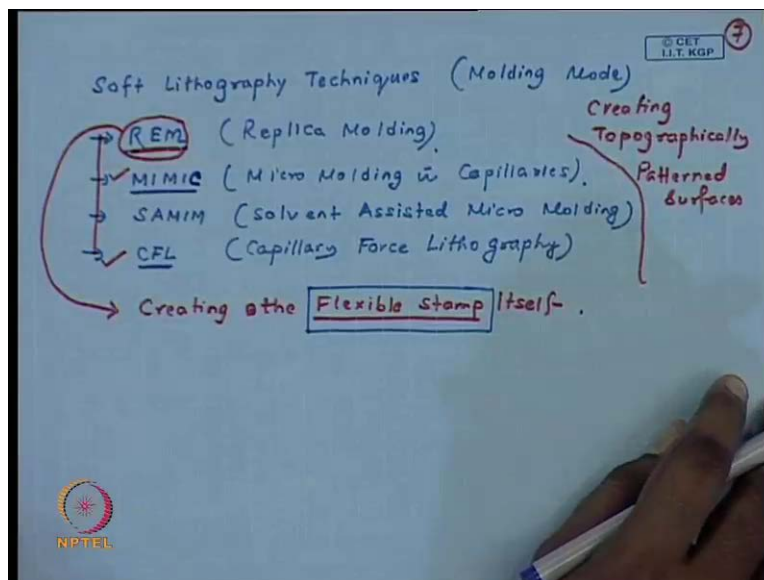


Instability & Patterning of Thin Polymer Film
Prof. Rabibrata Mukherjee
Department of Chemical Engineering
Indian Institute of Technology and Kharagpur

Lecture No # 18
Soft Lithography - III

While talking about soft lithography in some details, it is now time that we actually look at some of the techniques in greater detail. What exactly is the pattern replication mechanism and associated issues?

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So, we have already talked about some of the methods in which some of the patterning methods or some of the advantages of soft lithography over let us say something like Nano Imprint lithography, where we have already shown what are the what can be the some of the advantages of using a flexible stamp.

And now, it is time that we look at the precise mechanism how soft lithography technique works. First we will be discussing in somewhat detail, these four major soft lithography techniques which are primarily the molding mode techniques or you use them for creating topographically patterned surfaces. And out of them you will find that these two are the key techniques or Micro molding in capillaries and Capillary Force lithography, of course, R E M

that is Replica molding is also very **very** important. Often you may want to remember that the Replica molding is the technique one uses for the creation the flexible stamp itself.

Now, one question you may ask that how exactly do we create a flexible stamp? Well this is actually something you need to realize that this is where soft lithography depends on some other lithography techniques. So, typically what is done is that you take a rigid master or a mold which can be made by photolithography. We talked about this previously, which can be made by photolithography or which can be a sort of a Nano Imprint lithography mold. And then you would like to replicate that structure replicated you get a negative replica essentially of that structure on this cross link P D M S matrix or material which you then subsequently go on using as your soft lithography stamp.

And in most cases, it is now time that we talk about it in detail. The replica molding is actually the technique that is used to create the flexible stamp. Often that is also part of your entire soft lithography process. So, first if you have to create the stamp you desire and then once the stamp is ready, then you are in a position to sort of implement soft lithography.

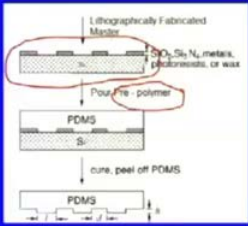
And in this particular class we will talk about R E M shortly which is very simple technique nothing much is there having talked about the composition and the nature of sylgard or a cross link P D M S typically it is a liquid in at room temperature. So, you have to mix the two parts. One part is the is the oligomer and second part is the cross linker and having mix that.

So, understanding all this R E M is not going to take time. But, we are going to spend some bit of time in understanding MIMIC in detail. Solvent assisted micro molding in is again in many ways a sort of an extension a nice extension of micro molding in capillaries and then once you are through with this group of techniques the MIMIC group of techniques, we will spend again sometime on capillary force lithography, which is again, a very, very novel pretty recent and very useful addition, to the soft lithography group of techniques.

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Replica molding (REM)

- The features are transferred by solidifying of a liquid pre-polymer mixture in contact with a master. The liquid pre-polymer conforms to the form of the master and exposure to UV radiation or suitable temperature induces the crosslinking, making the polymer solid. Removal of the master creates an inverse replica, referred to as the mold.



Typically when UV cross linking is performed, the method is referred to as UV – Molding.

In many cases, the stamp for Soft Lithography Techniques is fabricated by REM

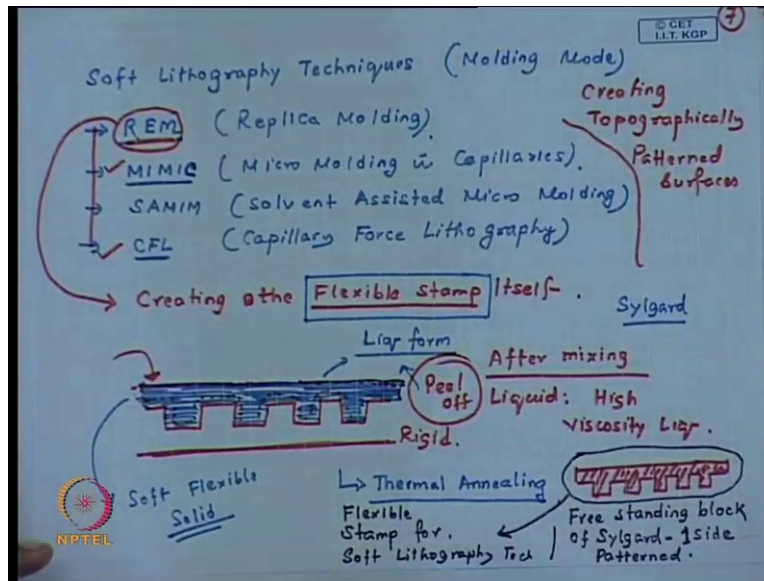
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So let us, have look at replica molding, here in this technique the features are transferred by solidifying a liquid pre polymer mixture in contact with a master. So, what does it mean? That you take a rigid stamp as what we have said, you essentially take a rigid stamp here which can be a photolithography stamp or a Nano Imprint lithography mold or whatever.

So, this is lithographically fabricated and then you take the pre polymer. So, it is essentially if you are talking in terms of P D M S and let us say you are talking of sylgard, I am talking from a practical stand point. So, sylgard is most likely the material or the chemical you are going to use for fabricating your stamp.

So, you mix part a and part b in desired proportions we have talked about it in couple of lectures back. So, please refer to the lecture number 16 I think where you talked about what is the nature of sylgard it comes as a two part pack. So, part a is the actual polymer part b contains the catalyst or the cross linker. So, if you mix them at room temperature they typically behave like a very high viscosity liquid and then if you leave it over period of time are you sort of heat at up thermally at any temperatures between let us say 60 degree to 150 degree, it cross links into a soft solid matrix.

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So, here we are talking about the pre polymer which is let us say, that is liquid mixture at room temperature. So, you just pour it on this lithographically fabricated stamp or master. So, if you pour it what is going to happen? So, this is the original stamp this is rigid again let me remind that, you have taken you pour a liquid. So, what is going to happen? The liquid is gradually going to fill up this voids it is simple going to flow.

And sort of you also know that it is also going to attain a uniform level. Because you know that liquid surface is horizontal and things like that. So, eventually you pour and you allow some time for the liquid to reconfigure itself or reorganize itself on the surface, by actually filling in the stamp completely or the mold completely. And you need to give some time because of the fact that typically after mixing it is a liquid, but it is a pretty high viscosity liquid.

So, because of the high viscosity it might take some time for mold filling and sort of leveling out or flattening out. So, once that happens. So, this is now the rigid stamp or the mold is fully submerged now under the, cross linked P D M S cross likeable P D M S not here cross linked in the liquid form.

So, now what you can do? You can leave this pre polymer for a long time or you can put this whole assembly now into for thermal annealing. So, if you now thermally anneal the stuff let us say at elevated temperature for desired duration which can vary from 2 hours to 24 hours,

These are certain protocols even if the top scientific papers you read, you will find that every group sort of has their own protocol.

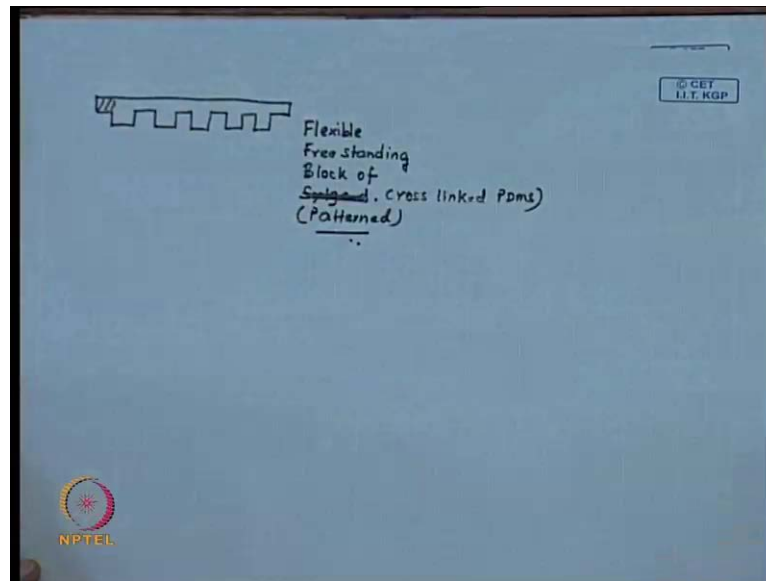
But pretty much rheological using a rheometer one can measure and see that may be 3 to 4 hours of curing is more than enough. And after that if you cure the rheological properties do not change. So, there is no further cross linking or the elasticity of the material does not change. So, you have reached the sort of optimum value of optimum amount of cross linking you can achieve for a particular composition or the ratio of part b to part a, what you have taken.

So, I mean those are things you can just search in the literature and find out what is the exact experimental protocol. But if you do a thermal annealing or you leave the whole stuff for a few days, what will happen? This liquid pre polymer which was in the liquid state now gets cured. Or in other words what it means? That it is now fully cross linked. And then once it is cross linked, so it is no longer a liquid it is now a soft flexible solid. And you know what to do, simply peel it off.

So, what you have? You now have a free standing block of sylgard. One side of which is patterned. So, you are now ready and what is going to be the utility of this material? So, this is going to be your stamp flexible stamp for other Soft Lithography techniques.

So, you have been able to make it and this is something very, very simple. I mean you really do not need to know that this is replica molding to do this. (()) Even from your common sense you can simply do this and that is it. But so, this is what replica molding is one of the simplest form of soft lithography and often the stamp that you require for pursuing of soft lithography techniques itself is made by one of the soft lithography methods which is replica molding.

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So, once you understand, what is replica molding? So, that sort of allows you to have a flexible free standing block of sylgard, which is patterned of course or of cross linked P D M S and one side is patterned.

The other thing is that if your detachment or typically that is what is done if your detachment during the peel off is neat you have a neat detachment then, after you have peeled off you again sort of would and this is something that sort of make soft lithography cost effective. You would like to use the same rigid stamp again and again for replica molding and to make multiple number of soft lithography stamps with only one single rigid stamp. Often what is done to sort of ensure the reusability of this stamp in replica molding or after replica molding or this rigid master after replica molding is often the surface of this master is coated with a low surface energy chemical.

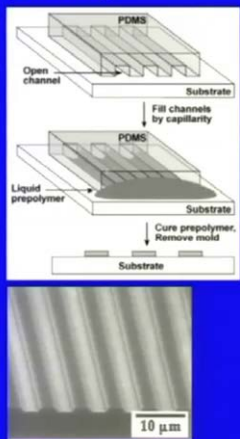
It can be a mold release agent or in some cases it can be a silen layer, what is silen layer? we think I think we will talk in a little bit detail when we talk about the printing mode soft lithography techniques. So, that the addition between the cured cross linked polydimethylsiloxane and the master itself is not very great not great and therefore, the peel off is clean which not only ensures that your stamp, the soft lithography stamp which you have fabricated does not have defects in terms of fidelity or roughness, but it also means that the master the same master once you have peeled it off can be used again and again for replica molding.

This is one of the key practices that one uses in soft lithography. So, depending on the pattern you want to create you just get one you have to fabricate or get one rigid master from somewhere by some high other high and soft lithography techniques or wherever which can be photolithography which can be electron beam lithography or whatever. And then you try to use it as many number of times to produce flexible stamps which will be subsequently use for subsequent soft lithography methods.

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Micro molding in Capillaries (MIMIC)

- The technique is based on the spontaneous filling of capillaries formed between two surfaces in conformal contact, at least one of which has a recesses relief structure.
- **MIMIC** is a thermodynamically driven process: the liquid fill the capillaries to minimize the free energies of the solid-vapor and the solid-liquid interface.

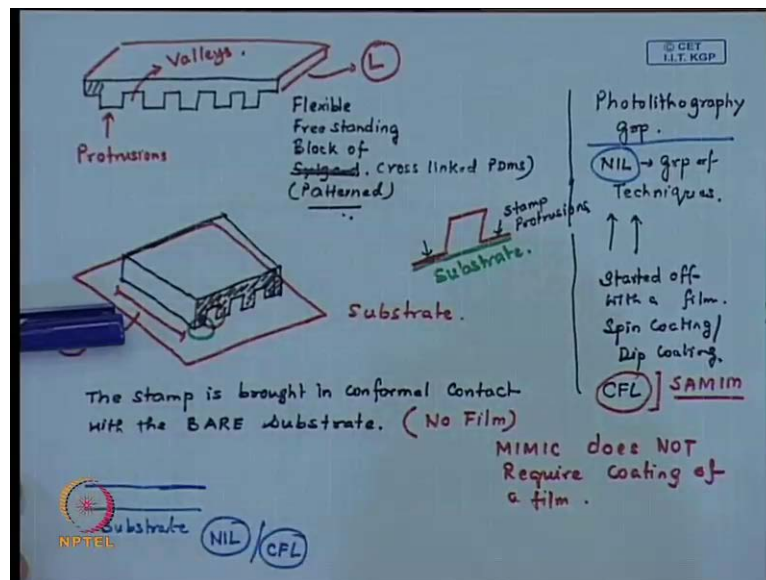


The diagram illustrates the MIMIC process in three stages. The first stage shows a PEMS (polymer) layer on a substrate with an open channel. The second stage shows the channel filled with a liquid prepolymer. The third stage shows the prepolymer cured and the mold removed, leaving a patterned substrate. A scale bar of 10 μm is provided.

Wentzides, Nature, 376, 1995, 581
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So, having said that now you have a flexible free standing block of polymer, which you are planning to use as a stamp or in for your subsequent patterning and the first technique that we are going to discuss is micro molding in capillaries.

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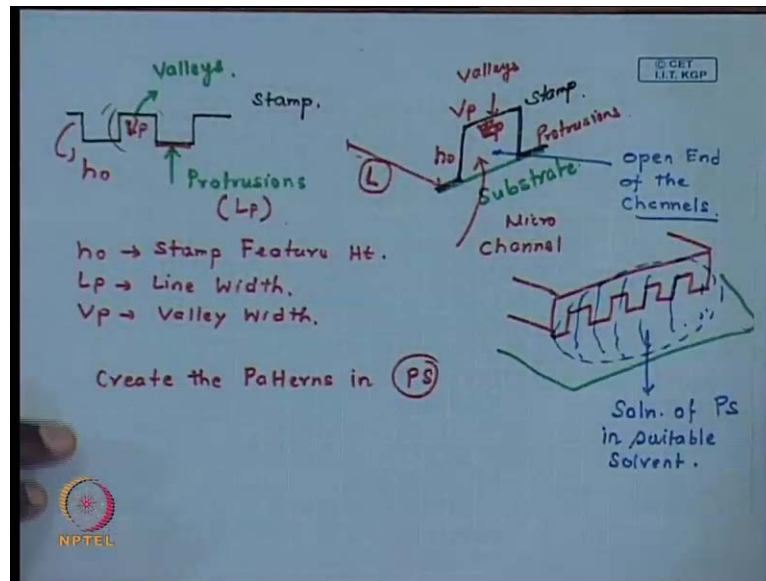
Now, in comparison to all the techniques we have discussed so far, that is mostly the photolithography group of techniques as well as the embossing or the Nano Imprint lithography group of techniques. There is a significant implementational difference I would say in the way micro molding in capillaries or MIMIC is executed. In all these techniques if you remember we actually started off with a film and we talked about a technique either like spin coating or let us say dip coating to create the film.

Now, in contrast I mean there are other soft lithography techniques like let us say C F L which we will subsequently discuss may be later half of this class or in the next class where you also start working with a you initial it quote the film the C F L as well as in SAMIM you quote the film. But please do remember that, in micro molding in capillaries you do not start off with a film. So, all you start off is with a substrate like this which is substrate often and then you place the stamp on the bare substrate this is very, very important to realize that in MIMIC you bring the stamp not in conformal contact.

So, the stamp is brought in conformal contact with the bare substrate this is extremely important and one of the key difference of MIMIC as compared to most other soft lithography as well as N I L and photolithography group of techniques. So, please remember that at the beginning there is no film or in the classical form MIMIC does not require coating of a film.

But then, how do you get the structures? Well, if you now look carefully this once the stamp the flexible stamp has been brought in conformal contact with the substrate, each of the stamp feature or if we regard these as sort of protrusions and these areas to be the valleys. So, if this is in contact with the substrate, this is the area that corresponds to the stamp protrusions. I think I will just redraw it.

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So, here you have a stamp you see that these are the protrusions and these are the valleys. Now, what you have done? You have brought the stamp in conformal contact with the substrate. So, if you look into it in detail if you look at a contact zone let us say in detail. So, this is the substrate and this is the stamp we are looking at one feature of the stamp let us say this area. So, this is the stamp.

So, what you can what you immediately realize looking at the figure in somewhat detail that actually the stamp protrusions sort of come in conformal contact with the substrate and the stamp valleys actually form each stamp valley forms a channel or a micro channel. And each of this and channels; so each of these areas sort of correspond to one micro channel and the channel length is limited or is identical to length of the stamp. So, if this is the stamp and this is L so, each channel now has a size or dimension.

So, if you look at the channel dimension this is let us say h_0 , this is let us say L_p and on this side let us say it is L . So, while h_0 corresponds to the feature height on the stamp, L_p is the valley width or let us say V_p , L_p let us say is the line width or the width of the protrusions V_p

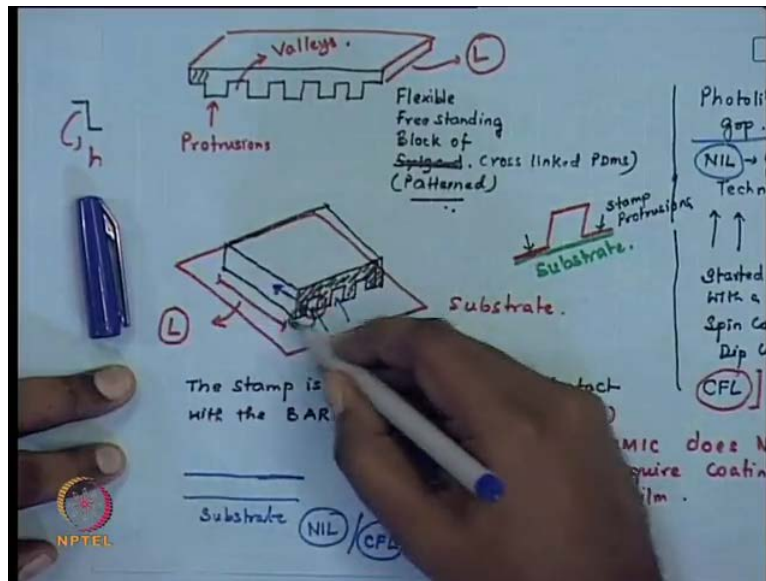
is the valley width. So, here are the parameters h_0 valley width. And this L : is the length of each channel which is nothing, but the length of the stamp or it is limited by the size of the stamp. So, essentially by bringing this stamp in conformal contact with the substrate you are making very long micro channels or so, each of these channels eventually will act as capillaries capillary tubes we will see that. So, once this is achieved or in other words your stamp is now in conformal contact with the substrate forming these open channels or micro channels.

What you do? You dispense the liquid pre polymer and this pre polymer do not confuse this is not silygard or cross link polydimethylsiloxane this is actually the polymer material a solution of the polymer material in which you would like to create the patterns. So, let us say if you want to create the patterns in polystyrene. So, what you will be dispensing here is so, this is on the substrate it is in conformal contact. What you will be dispensing here is a dilute solution of p s in suitable solvent. Otherwise, had you been starting off with any other techniques off course photolithography you cannot directly patterned a polystyrene film.

But let us, say in Nano Imprint lithography you can pattern poly styrene film directly. So, in N I L what would have been the equivalent step? The equivalent step would have been to dispense the polystyrene same polystyrene solution for the spin coating process itself, but here you do not I repeat that in micro molding in capillaries you do not start off with a film. So, instead of dispensing it is for spin coating and then in. So, something like a N I L this would be your substrate. You would have dispensed the polystyrene containing solution or polystyrene dissolve let us say in good solvent like toluene or whatever over here to get the film.

Here you do not do that so, this would be the setting in N I L and also you will see this is again the setting in C F L subsequently we will see. Here you do not do that, what you do? you dispense the drop at the edge of the stamp where it is in conformal contact with the substrate or at the open ends of the channel. So, each one is a this is an open end of the channels which have formed due to the conformal contact between the stamp and the substrate. So, once you dispense that what happens? Depending on the wettability if **your** you all know what is capillary motion or capillary dynamics we have talked quite a few lectures back about capillarity in the initial part of this course.

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So, what can happen? What can happen is that along the channels the liquid may flow in the direction of each of the open channel due to capillarity like this.

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Micro molding in Capillaries (MIMIC)

- The technique is based on the spontaneous filling of capillaries formed between two surfaces in conformal contact, at least one of which has a recessed relief structure.
- MIMIC is a thermodynamically driven process: the liquid fill the capillaries to minimize the free energies of the solid-vapor and the solid-liquid interface.

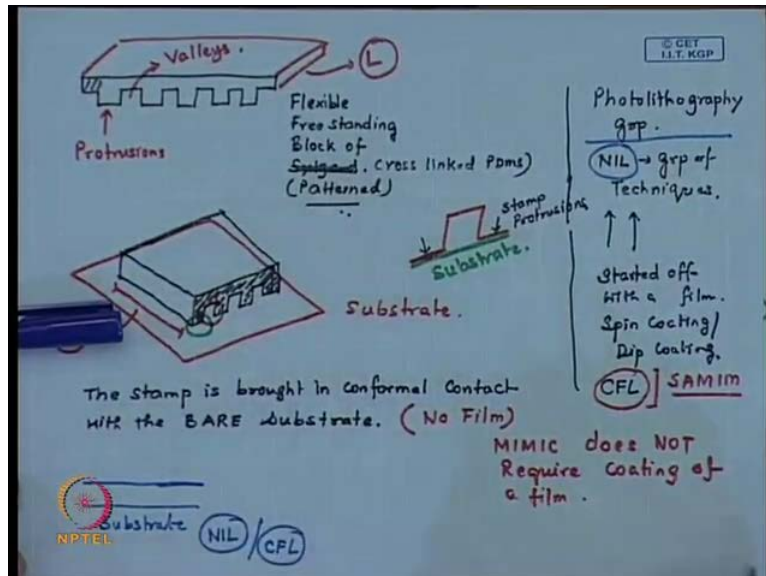
The diagram shows the MIMIC process in three stages: 1. 'Open channel' showing a 'PDMS' stamp and 'Substrate' with an 'Open channel'. 2. 'Fill channels by capillarity' showing 'Liquid prepolymer' filling the channel. 3. 'Cure prepolymer, Remove mold' showing the final 'Substrate' with the patterned structure. A scale bar indicates 10 μm.

Wentzides, Nature, 376, 1995, 581
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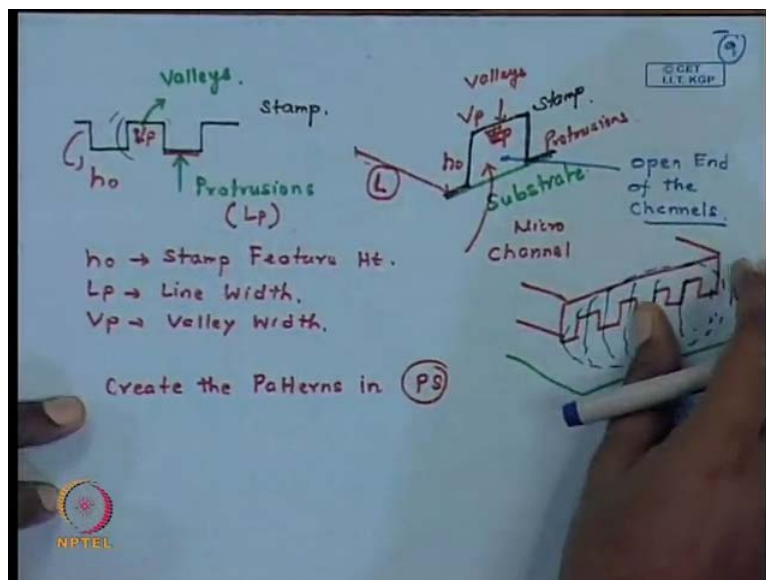
So, here this is the direction of the capillary driven motion or in other words whether the liquid will penetrate through the channels or not or to what extent to it will penetrate depends. You do not have a pump or any forcing any external mechanism to sort of impart any pressure to this liquid to trigger this flow. But this flow will be entirely triggered and

control by capillary dynamics. Now, having realize that and knowing the very basic idea of what capillary driven motion is.

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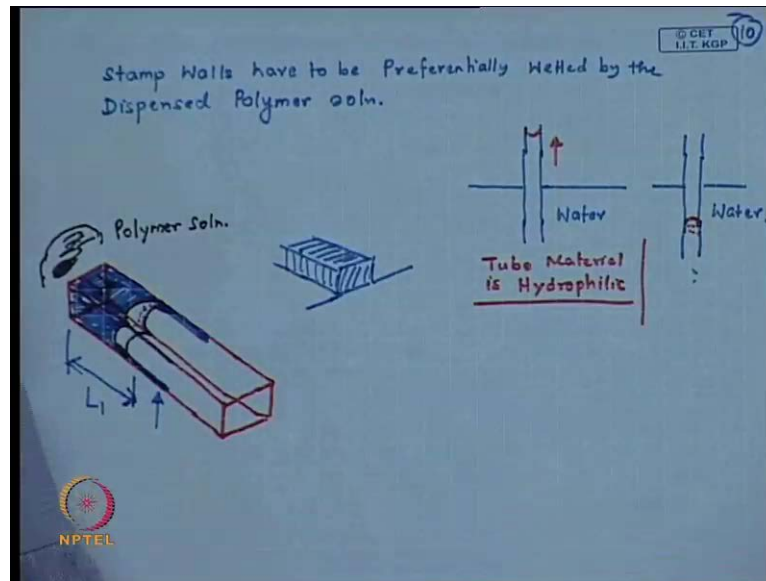


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So, what would be the fundamental requirement for this?

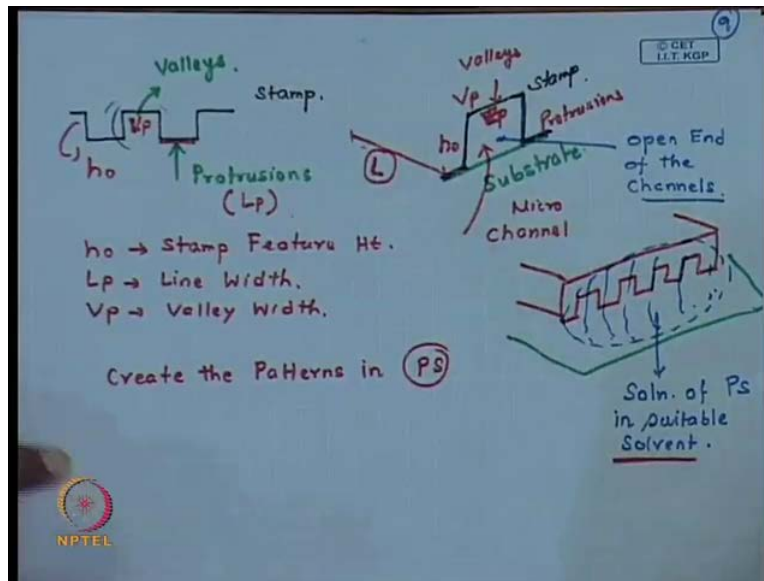
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The fundamental requirement of course is to be that the stamp walls have to be preferentially wetted by the dispensed polymer solution. Because if you think of a scenario. So, it is now let us consider, the geometry which of with which you are more well accustomed, we are always well accustomed.

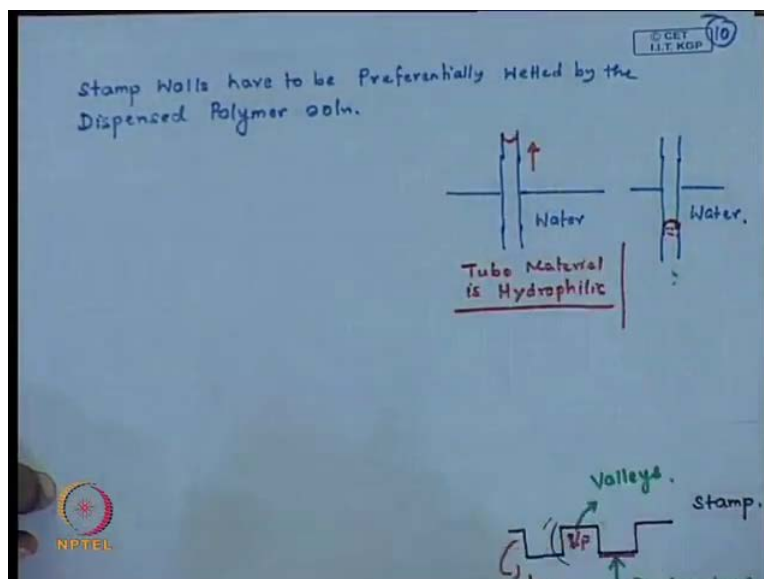
So let us, say this is water and we immerse a capillary tube a narrow tube into that. So, you know that there can be we have discussed it in detail I think we have covered a derivation also. So, you can have two configurations either the configuration can be like this or the configuration can be like this. So, you can have a capillary raise only when the tube material is hydrophilic. If the tube material is hydrophobic, instead of seeing a capillary raise you will actually see a capillary depression we know that.

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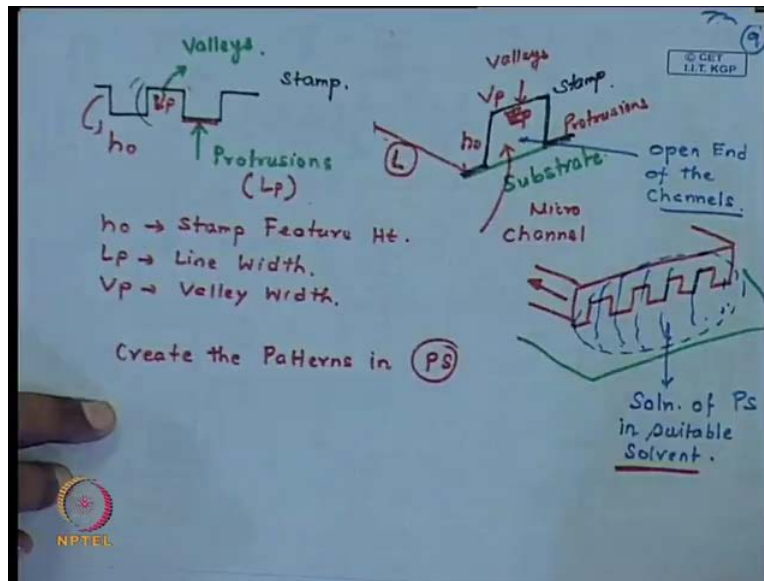
So, similarly here when you dispense the solution the polymer solution you are not using water. So, hydrophobicity or hydrophilicity really does not matter, but what matters is whether the stamp wall the material of which the cross link polydimethylsiloxane which we are using here for making the stamp whether the stamp wall is preferentially wetted by the solvent mainly the solvent of this solution.

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So, if it is preferentially wetted exactly in similar fashion as you see a capillary raise, which defies gravity I must say.

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Here there is sort of typically the experimental configuration is such that you do not have to sort of flow opposite to the gravity, but that sort of also does not limit to what extent the liquid will sort of flow.

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Micro molding in Capillaries (MIMIC)

- The technique is based on the spontaneous filling of capillaries formed between two surfaces in conformal contact, at least one of which has a recesses relief structure.
- MIMIC is a thermodynamically driven process: the liquid fill the capillaries to minimize the free energies of the solid-vapor and the solid-liquid interface.

W. J. Koros, Nature, 376, 1995, 581
NPTEL

But the liquid flows inward through the channels filling in the channels. So, as that is done what eventually happens is all these rectangular channels sort of get filled up with this polymer containing solution, replicating the structures. So, eventually what you will do that after sometime you will show the channel filling ideally the channel filling will be over. So,

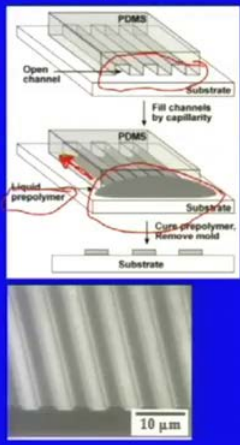
eventually you wait for some time and then withdraw the stamp and you sort of allow the solvents to evaporate and you are left with the final structures which are pretty good high fidelity.

So, MIMIC essentially. So, this is in principle what is MIMIC. So, you break first bring in a soft lithography a flexible stamp in conformal contact with the substrate. You dispense a polymer solution at one of the edges where you have the opening of the channels or the micro channels which are made which forms due to conformal contact between the stamp and the substrate. And then these liquid or the pre polymer sort of flows through these channels because of the capillarity replicating the structures. So, essentially you are creating a negative replica here of the stamp patterned with the by channel filling with this polymer solution that it is important to realize.

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Micro molding in Capillaries (MIMIC)

- The technique is based on the spontaneous filling of capillaries formed between two surfaces in conformal contact, at least one of which has a recesses relief structure.
- MIMIC is a thermodynamically driven process: the liquid fill the capillaries to minimize the free energies of the solid-vapor and the solid-liquid interface.



White sides, Nature, 376, 1995, 581
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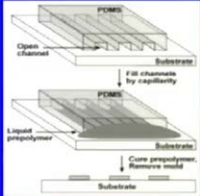
So, this is MIMIC in the simplest form which was discovered around 1995 by white sides by Whitesides and look at the significance I mean this work apparently such a simple work, but it was a much ahead of time when it was discovered about exactly I had taken it a half back and in got published in no other journal, but the top most journal which is nature. So, MIMIC essentially is a thermodynamically driven process the liquid fills the capillaries to minimize the free energies of the solid vapor and the solid liquid interface. You know from why how the capillary driven flow occurs. So, it is essentially the free energy minimization that takes place over here.

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Micro molding in Capillaries (MIMIC)

- The filling of capillaries and rate of liquid flow in capillary is determined by the surface tension and viscosity of the liquid.
- Viscosity of liquid is a determining factor that controls the filling rate.

The time allowed for pattern replication is also important as initially a fluid fills the capillaries only partially, particularly the corner regions



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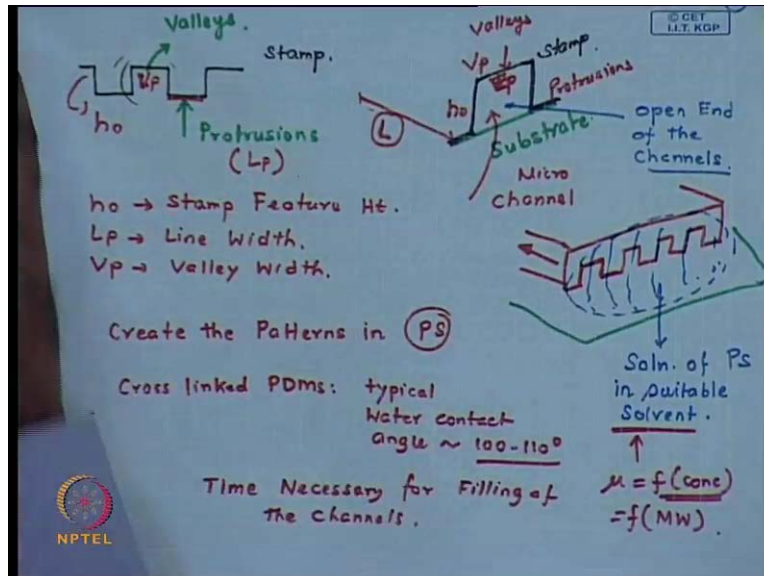
The filling of the capillaries as well as the rate of liquid flow within the capillary; so here is the physical parameters that come into play. Flow in the capillaries is determined by the surface tension and the viscosity of the liquid, why surface tension is important? Because of the fact that the surface tension of the liquid that is primarily the solvent and the stamp material the relative magnitudes of the surface tension will decide whether the stamp walls or the channel walls are preferentially wetted by the solution or not. So, that is where surface tension becomes important. If the stamp wall if the surface tensions such situation can be that if you have a very low surface energy stamp let us say, it might not be preferentially wetted by the liquid at all.

So, in that case they are will be no thermodynamically driven or capillary driven flow. So, liquid will just refuse to sort of get in into the channels because of non wettable repulsion hydrophobic repulsion had the liquid been water something analogues to hydrophobic repulsion. So, one of the key requirements for successful implementation of MIMIC is that you must have a stamp material or the walls of the (Refer Slide Time: 28:49) each of this channels which are be made should be preferentially wetted by the by the polymer solvent.

So, one other things is that we are talking that you make this (Refer Slide Time: 05:55) stamp mostly with cross link polydimethylsiloxane, which typically as a surface energy roughly of the order of 20 Millijoules per meter square. This generally with in contrast to water in contact with water exhibits a weak hydrophobicity. So, typically the water contact angle I

repeat it is the water contact angle nothing to do with the polymer solution you are using, but that is of water contact angle gives you a reasonable branch mark about the surface energy.

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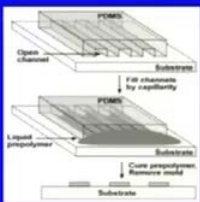
So, silygard exhibits a weak hydrophobicity with a water contact angle varying somewhere between 100 to 110 degrees; so, for cross linked PDMS typical order of 100 to 110 degree; so, which might be slightly on the lower side. So, in order to sort of ensure a good capillary driven flow or good channel filling driven by capillarity, you might have to sort of ensure that your surface energy of the stamp walls is slightly higher. So, that you have a significant amount of driving force how that is tailored? I think we will discuss in one of the subsequent slides how viscosity. So, that is essentially the role of surface tension over here.

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Micro molding in Capillaries (MIMIC)

- The filling of capillaries and rate of liquid flow in capillary is determined by the surface tension and viscosity of the liquid.
- Viscosity of liquid is a determining factor that controls the filling rate.

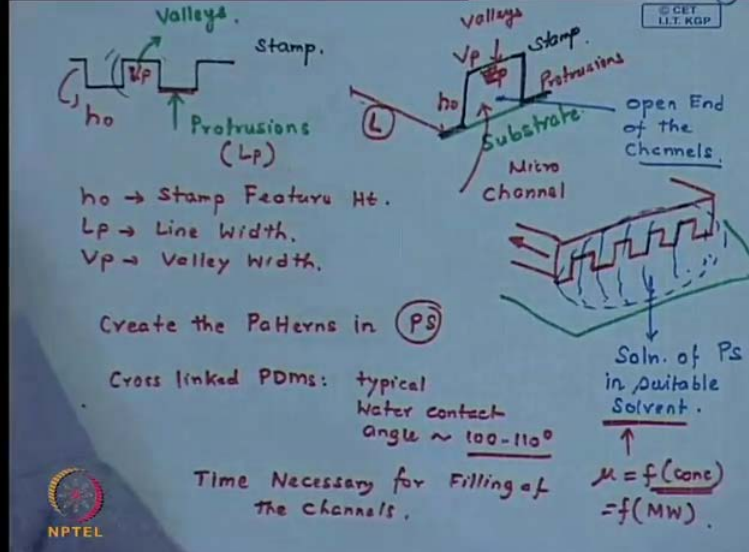
The time allowed for pattern replication is also important as initially a fluid fills the capillaries only partially, particularly the corner regions



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Now, as far as viscosity is concerned how viscosity becomes important we need to look into. So, viscosity is essentially in the simplest form, viscosity is the parameter with sort of gives you a back of the envelope idea or gives you an idea about the resistance of a liquid towards flow subjected to an external driving force. So, here the driving force is the surface tension driven capillarity or it is a thermodynamic driving force and the viscosity of the liquid will determine that even if you have a thermodynamically favored situation how fast or slow the capillary filling is going to be.

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Valleys, Stamp, Protrusions (L_p), h_0 , V_p , Substrate, Micro Channel, open End of the Channels, Soln. of Ps in suitable Solvent, $\mu = f(\text{conc}) = f(\text{MW})$, typical Water contact angle $\sim 100-110^\circ$, Time Necessary for Filling of the Channels.

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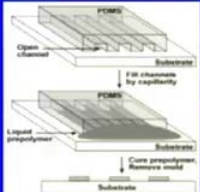
So, you might depending on the viscosity of the solution of the polymer solution you have taken and again viscosity is going to be significantly a function of the concentration of the solution, as well as the function of the molecular weight of the polymer. So, the viscosity is eventually going to determine the time necessary for filling of the channels.

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Micro molding in Capillaries (MIMIC)

- The filling of capillaries and rate of liquid flow in capillary is determined by the **surface tension** and **viscosity** of the liquid.
- Viscosity of liquid is a determining factor that **controls the filling rate**.

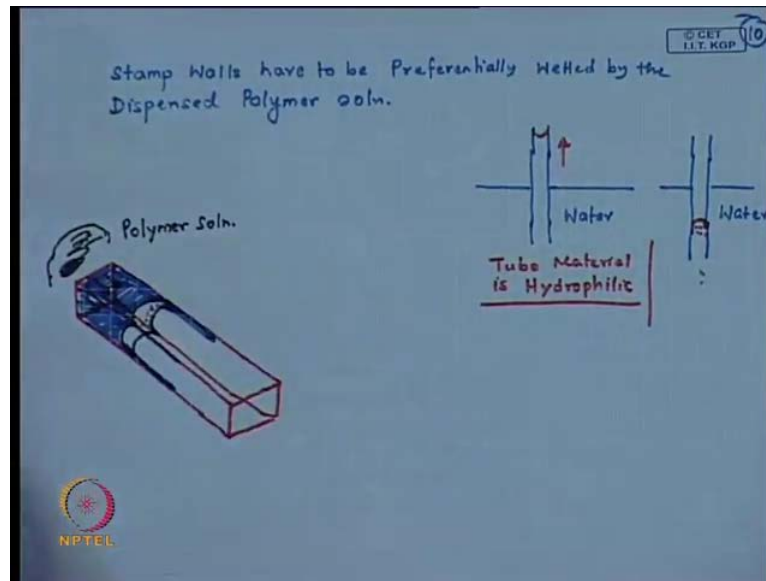
The time allowed for pattern replication is also important as initially a fluid fills the capillaries only partially, particularly the corner regions



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So, it essentially controls the filling rate. The time allowed for pattern replication is also important, as initially a fluid fills the capillaries only partially. So, this is another important concept (Refer Slide Time: 35:05) that the filling is sort of not uniform **the** because of the edge effects.

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So, this is let us say one channel let us say, this is the channel. So, here you have dispensed on this side you have dispense the liquid, the polymer solution, which sort of is filling from this side. Now, what happens is you typically would be seeing a liquid meniscus like this. So, this is all filled up with the liquid.

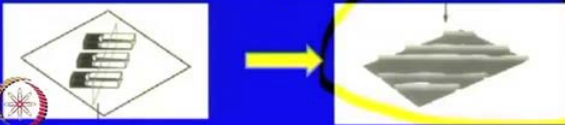
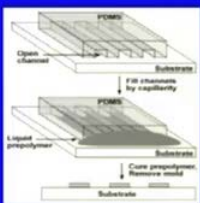
This is remember we are considering only one channel. So, this is liquid and this is also liquid So, the drawing is the little difficult, but what typically happens that you will have a much longer range advancing meniscus along the edges and the subsequent major meniscus or the complete filling it might take significant amount of time.

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Micro molding in Capillaries (MIMIC)

- The filling of capillaries and rate of liquid flow in capillary is determined by the surface tension and viscosity of the liquid.
- Viscosity of liquid is a determining factor that controls the filling rate.

The time allowed for pattern replication is also important as Initially a fluid fills the capillaries only partially, particularly the corner regions

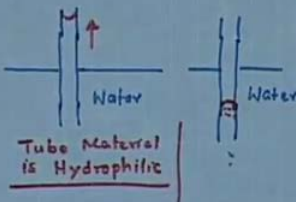
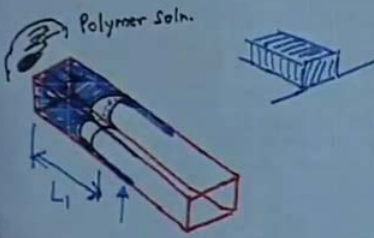


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So, what it implies that if you do not allow and how long it is going to take for this meniscus to travel and fill up the. So, you might.

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Stamp Walls have to be Preferentially Wetted by the Dispensed Polymer soln.



Polymer soln.

Water

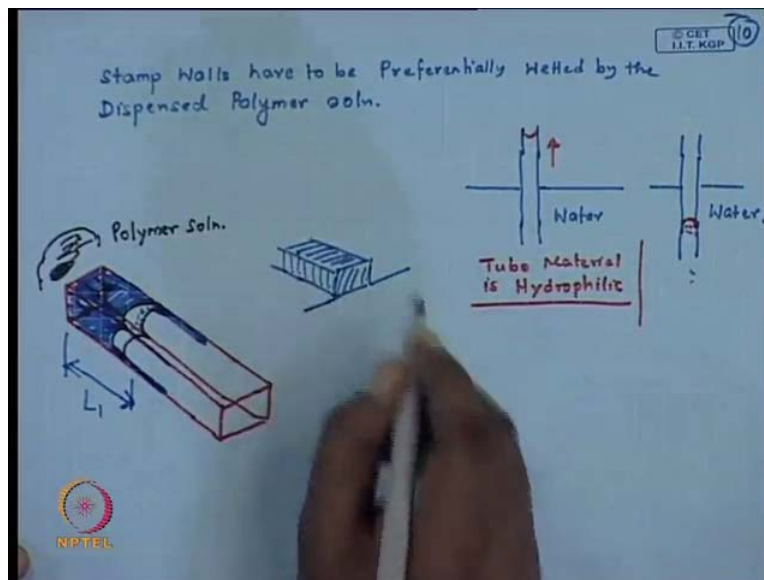
Water

Tube Material is Hydrophilic

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So, in other words let us say at location L one at any given if you are sort of in the earlier stages of the pattern replication process you might not be having a complete bore filling.

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So, if you freeze the pattern replication at that stage you might not (Refer Slide Time: 37:44) have get a sort of structure like this what you were let us, say expecting like a grating or a protrusion.

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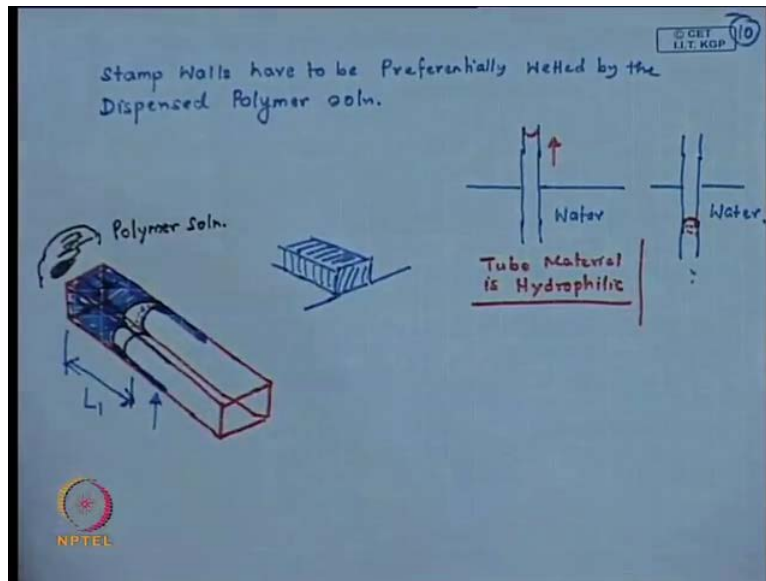
Micro molding in Capillaries (MIMIC)

- The filling of capillaries and rate of liquid flow in capillary is determined by the surface tension and viscosity of the liquid.
- Viscosity of liquid is a determining factor that controls the filling rate.

The time allowed for pattern replication is also important as Initially a fluid fills the capillaries only partially, particularly the corner regions

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So, this is let us say, the structure you are expecting, but instead of that you might get a structure like this which sort of corresponds to the only the advancing part of the capillary meniscus. So, (Refer Slide Time: 37:44) that is where your viscous effects become very very significant. How long it is going to sort of take to fill up the channel completely is something that is governed entirely by the viscosity of your system.

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Micro molding in Capillaries (MIMIC)

The rate of capillary filling is given by

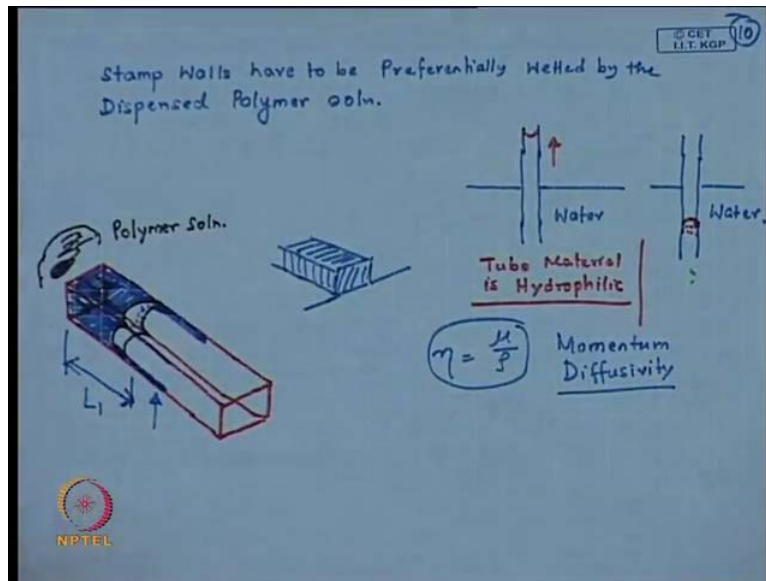
$$\frac{dz}{dt} = \frac{R\gamma_{LV}\cos\theta}{4\eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4\eta z}$$

η is the kinematic viscosity (μ/ρ)
 γ is surface (interfacial) tension of liquid,
 R is the radius of the capillary,
 z length of the filled section of the capillary

Capillary filling over a short distance (up to 1 cm) can be achieved quickly and efficiently; over a large distance, the rate of filling decreases significantly due to the viscous drag of the fluid in the capillary and the distance over which the fluid has to be transported.

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The rate of capillary filling can sort of be given or is given by this equation where $\frac{dz}{dt}$ is $\frac{R \gamma_{LV} \cos \theta}{4 \eta z}$ or $\frac{R(\gamma_{SV} - \gamma_{SL})}{4 \eta z}$ where η is the kinematic viscosity and it is $\frac{\mu}{\rho}$. So, this is also referred to some times as the momentum diffusivity. So, this is sort of an idea a clear idea this gives clear idea how fast or slow your dynamics is because of two two of its intrinsic properties that is one is viscosity and other is density.

(Refer Slide Time: 39:34)

Micro molding in Capillaries (MIMIC)

The rate of capillary filling is given by

$$\frac{dz}{dt} = \frac{R \gamma_{LV} \cos \theta}{4 \eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4 \eta z}$$

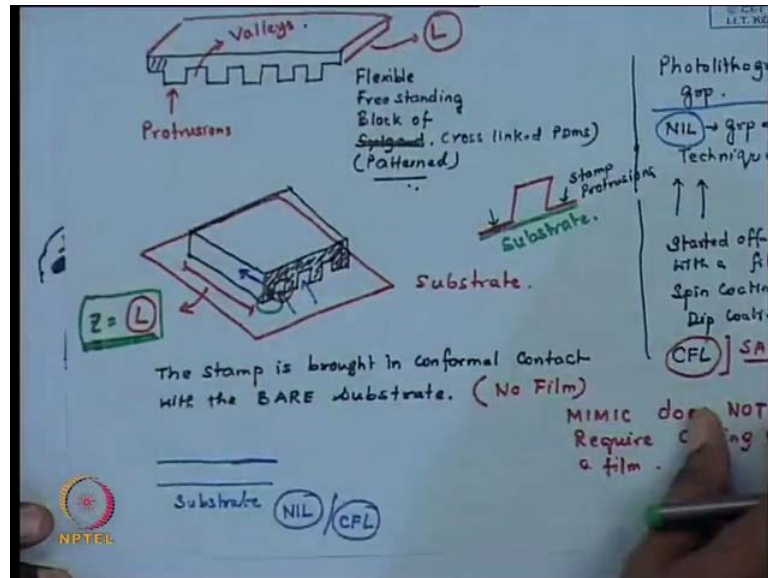
η is the kinematic viscosity (μ/ρ)
 γ is surface (interfacial) tension of liquid,
 R is the radius of the capillary,
 z length of the filled section of the capillary

Capillary filling over a short distance (up to 1 cm) can be achieved quickly and efficiently; over a large distance, the rate of filling decreases significantly due to the viscous drag of the fluid in the capillary and the distance over which the fluid has to be transported.

So, you see the equation and look at the functional it is. So, γ is usual the surface tension, r is the radius of the capillary which if you have a non circular (()) you can think of

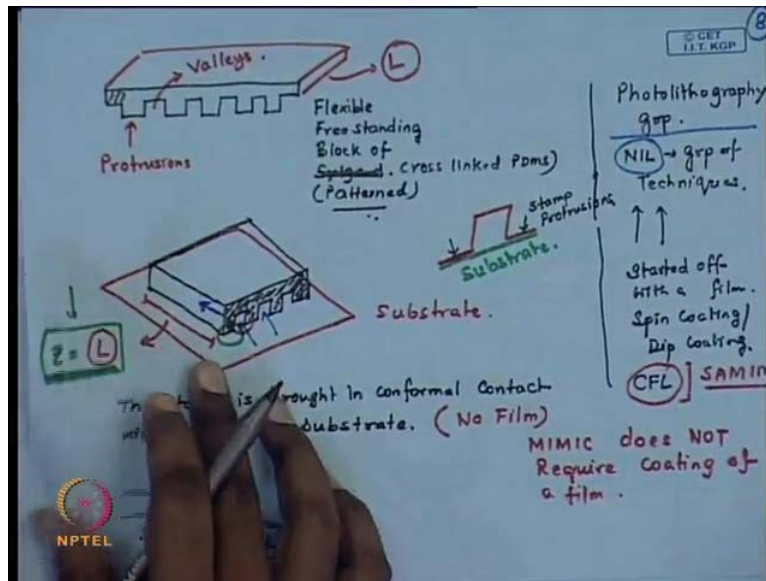
the equivalent diameter or the hydraulic radius, z is the length of the filled section of the capillary.

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So, essentially a scenario like this where you your stamp is in conformal contact with the substrate Z is essentially the you are final objective would be to essentially figure out the, essentially fill up the entire length. So, your final L will be final Z you want to fill up is L , but this equation sort of (Refer Slide Time: 39:34) gives you an idea about the time dependence of the filling rate. So, if you solve it you will get an idea that what is the time that is necessary to fill up the length of L viz a viz at any given instance of time up to what length the capillary filling has sort of occurred.

(Refer Slide Time: 40:30)



So, that is the utility of this equation. (Refer Slide Time: 39:34) However do not forget that, if you have very void stamp that is L is very, very long there can be some difficulties in terms of the filling.

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Micro molding in Capillaries (MIMIC)

The rate of capillary filling is given by

$$\frac{dz}{dt} = \frac{R\gamma_{LV}\cos\theta}{4\eta z} = \frac{R(\gamma_{SV} - \gamma_{SL})}{4\eta z}$$

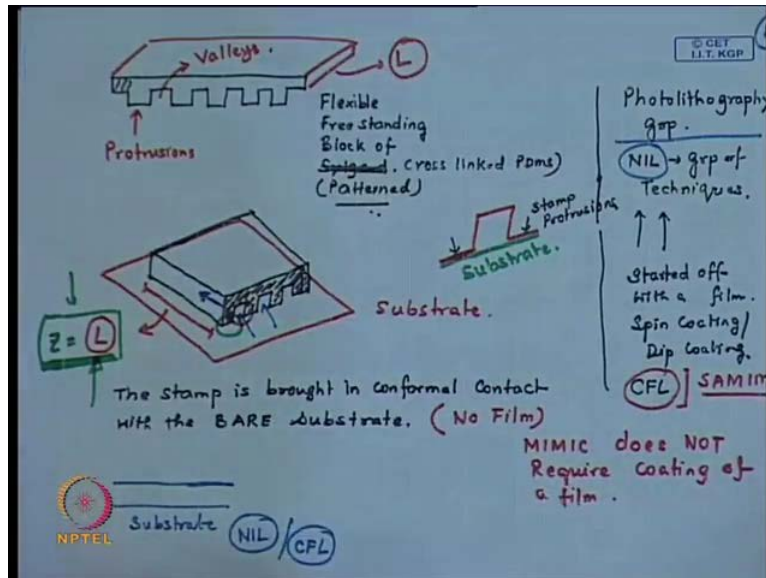
η is the kinematic viscosity (μ/ρ)
 γ is surface (interfacial) tension of liquid,
 R is the radius of the capillary,
 z length of the filled section of the capillary

Capillary filling over a short distance (up to 1 cm) can be achieved quickly and efficiently; over a large distance, the rate of filling decreases significantly due to the viscous drag of the fluid in the capillary and the distance over which the fluid has to be transported.

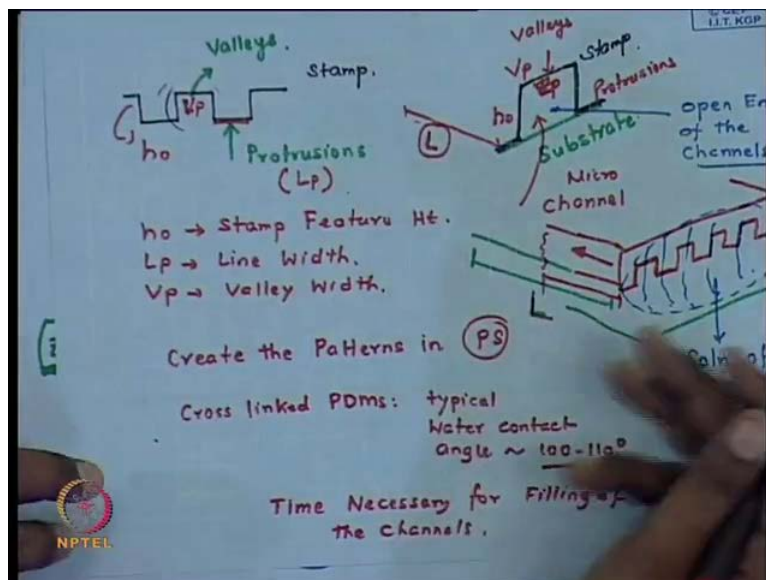
Because it has been observed that capillary filling over a short distance let us say up to above 10 Millimeters or let us say, centimeter can be achieved quite quickly and efficiently. But over large distance the rate of filling decreases significantly due to viscous drag effects,

primarily of the fluid in the capillary and the distance over which the fluid has to be transported.

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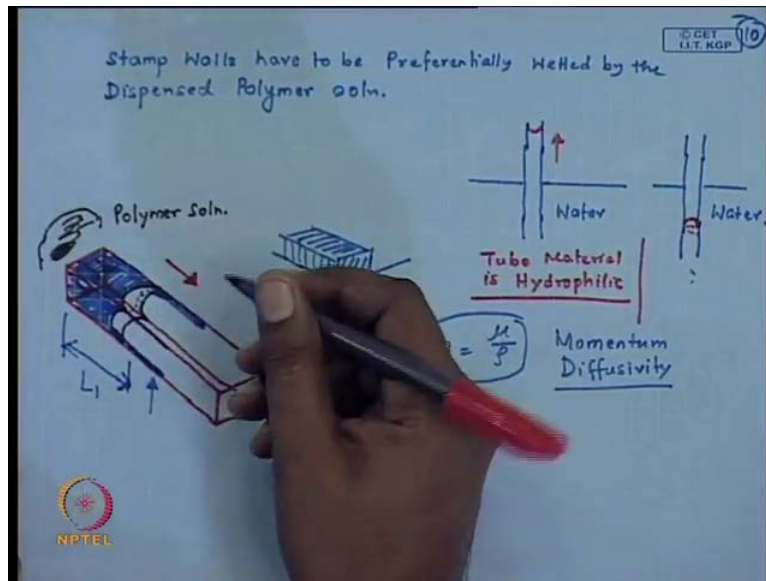
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So, in other words that if you have L to be very, very large since. So, this is one of the limitations or constraints of the micro molding in capillary process we are now actually referring to that you are actually you are dispensing the polymer solution at one of the ends and it has to in order to sort of make a perfect negative replica of the entire stamp, it has to travel all the way along the entire length.

So, what it means what is written there in simple term it means that if the initial section or let us say the first 10 Millimeters or about a Centimeter that if wettability and other conditions are favorable, the channel filling is not a problem is pretty efficient. But if you sort of have a extraordinary long length which has to be filled and do not forget that here the only driving force you (Refer Slide Time: 39:08) have is essentially a passive driving force or passive mechanism that is the capillarity.

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So, you might actually because of viscous dissipation there is significant loss of energy as the liquid fills of these channels. So, the capillary driving force over a very long length might not be adequate to sustain the complete filling or in other words the dynamics might eventually, at longer enough distances might become very, very sluggish. So, that might eventually prevent a proper pattern replication.

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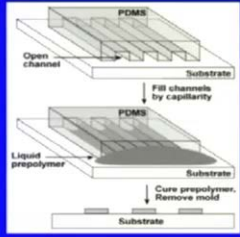
Micro molding in Capillaries (MIMIC)

In MIMIC, the distance flown by the solution inside the channel is given as

$$\text{Re} \cdot f \cdot \frac{\eta \cdot w}{2 \cdot D_p^2} \cdot z = \frac{2 \cdot \sigma \cdot \cos(\theta)}{D_p}$$

where

- Re:** is the Reynolds number,
- f:** a geometrical factor,
- η :** viscosity of the solution,
- w:** velocity of the fluid along the main stream,
- σ :** surface tension,
- θ :** the contact angle of the meniscus,
- D_p :** the wet perimeter of cross-section.



The diagram illustrates the MIMIC process in three stages. The first stage shows an 'Open channel' in a 'PDMS' layer on a 'Substrate'. The second stage shows the channel being filled with 'Liquid prepolymer' by 'Capillarity'. The third stage shows the 'Cure prepolymer, Remove mold' step, resulting in a solidified channel in the PDMS layer.

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But if you are talking in terms of let us say something like a millimeter a Centimeter width. So, from let us say here to here up to a few millimeter up to let us say about a Centimeter is perfectly fine. So, this itself shows that the whole methodology of or approach of MIMIC is essentially ideally suited for lab scale thing, you want do something 1 millimeter 1 Centimeter by 1 Centimeter stab. So, 10 millimeter square 10 millimeter into 10 millimeter area its perfectly fine.

So, something else you also may want to look in MIMIC the distance flown by the solution inside the channel is given by this particular equation, which has functionality of Reynolds number fiction factor f kinematic viscosity again, this is the velocity D p is the wetted perimeter of the cross section, Z is the length up to reach it has flown, sigma here is the surface tension typically we refer to this is gamma, cos theta is the equilibrium contact angle of the liquid on the stamp material and D p is the wetted perimeter.

So, if you solve this equation of course Reynolds number is also a function of the velocity of the liquid, but you can still solve this equation and this will give you an idea about the velocity of the capillary filling. So, at the velocity at which the micro molding filling is going on you can obtain that by solving this equation, because everything else is a physical parameter of the geometrical parameter. So, theta gamma eta these are fluid properties D p is a dependent of the geometry of the system or the configuration of the stamp and stamp. So, f is a geometric geometrical factor so, which sort of assumes some specific value depending on

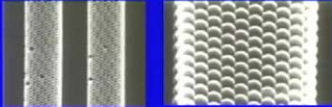
the scenario and then Reynolds number also contains $D v \rho$ by μ and so you have v that is velocity w here.


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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.



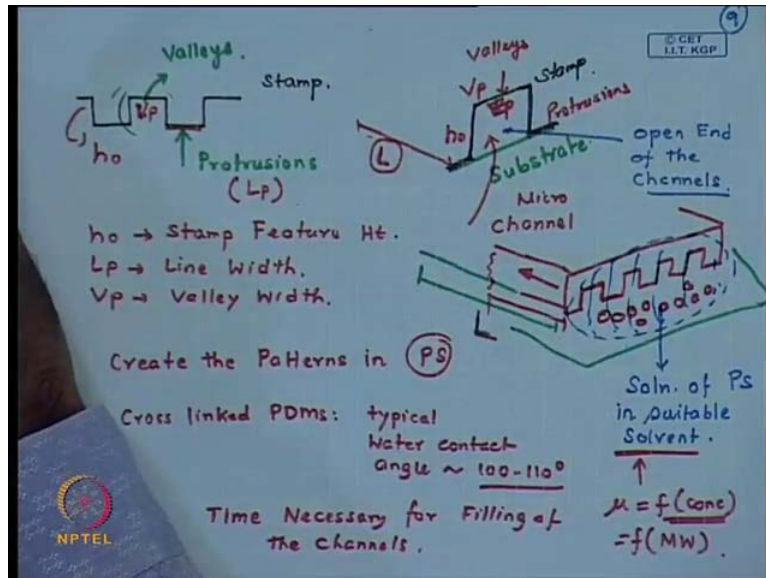
 Am. Chem. Soc., 1996, 118 (24), 5722-5731
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So, you get an equation essentially in terms w square and which you can solve for w to have an idea about what is the filling rate or what is the velocity at which the filling is going on. Since, it sort of realize on dispensing a solution essentially and the subsequent capillary filling. So, there is no reason why this technique remains limited only to a polymer solution and several functional materials including dispersion which is very very important, including dispersion, colloidal suspension etcetera has also been successfully patterned by MIMIC which is one of the key advantages of this technique. There has been a recent study of conductive sub micron wires of platinum carbonyl clusters some complicated stuff you do not have to worry too much about the chemical composition all that have also been patterned by MIMIC.

This method has also been extended for patterning ceramic materials by this or this which has there is specific processing technique which known as sol gel technique, where you sort of start off with a precursor solution, but it is in solution phase. So, you can those ceramics are hard we would all know that. So, you can actually allow a pattern or allow the patterning by MIMIC of this film which is still in the solve in the solve performance or in the low viscosity form and then you can have a sol to gel transformation and subsequent thermal annealing can

give you the desired ceramic phases. Also instead of using a polymer solution one can we have talked about nano sphere lithography briefly in one of our previous lectures.

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So, instead of using a polymer solution one can also use or dispense a colloidal dispersion over here. So, which contains dispersed particles in a liquid solution and. So, stable dispersion and this dispersion then under goes a capillary dynamics through the these channels and eventually you can get narrow strips of perfectly ordered colloidal particles arrays. So, this is also possible. So, a self assembly of (Refer Slide Time: 45:15) micro spheres it can be 2 D or it can be 3 dimensional arrays also 3 dimensional crystals which can be colloidal crystals as they are conveniently refer to as or also possible to make by this technique of MIMIC.

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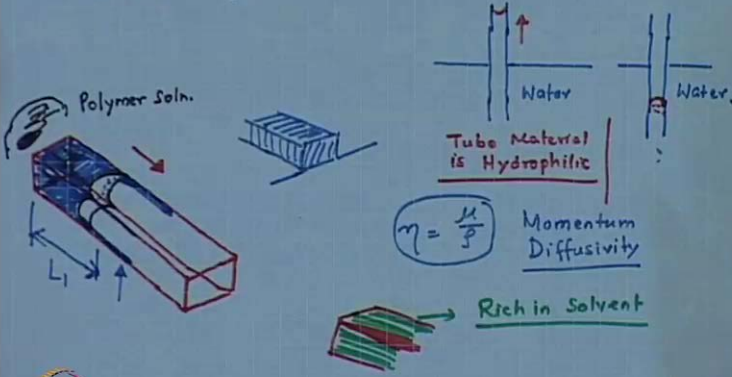
MIMIC

- The replicated structures are rich in solvent, and therefore there might be significant volume reduction after patterning, when the solvent evaporates away.
- Achieving large area patterning is not easy, as the flow through a very long capillary tube is difficult.
- There might be variation in the cross sectional variation along the length of the channels




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Stamp Walls have to be Preferentially Wetted by the Dispensed Polymer soln.



Tube Material is Hydrophilic

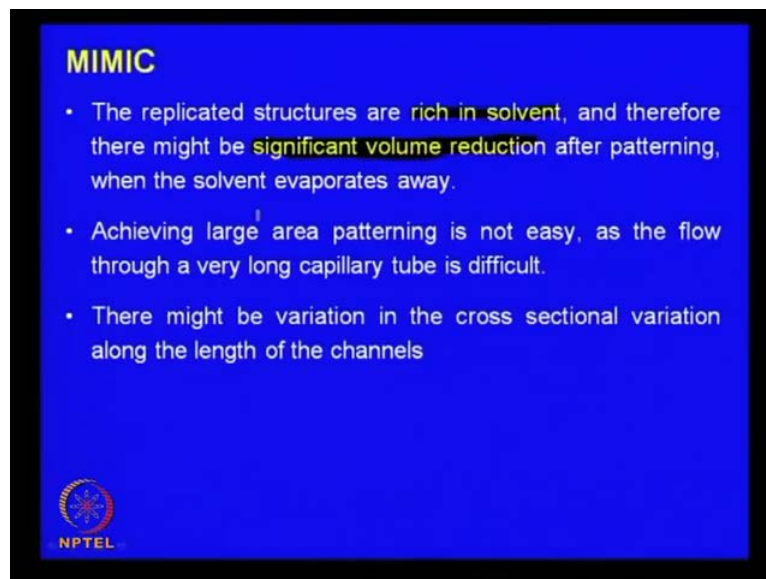
Momentum Diffusivity

$$\eta = \frac{\mu}{\rho}$$


Having talked about MIMIC and the simplicity as well as its elegance of course we should not forget the that there are certain limitations of MIMIC as a patterning technique as well. Since, your pattern replication is not only film, but is primarily due to the flow of a polymer solution in the liquid form. So, the final structures that you make essentially are very rich. So, this is the structure you are making after pore filling. So, the structure you actually make by the pore filling method is not in pure polymer, but this is very rich in solvent.


So, that is again if you can imagine. So, that is not very desirable thing because eventually the solvent will evaporate and there will be significant amount of reduction in feature size this like significant likely amount of reduction in feature size once the solvent evaporates. So, unlike the Nano Imprint lithography or some other lithography techniques where you actually patterned a film, you do not pattern a film here, but what you do is you get structures of a polymer or something, but which is very rich in solvent.

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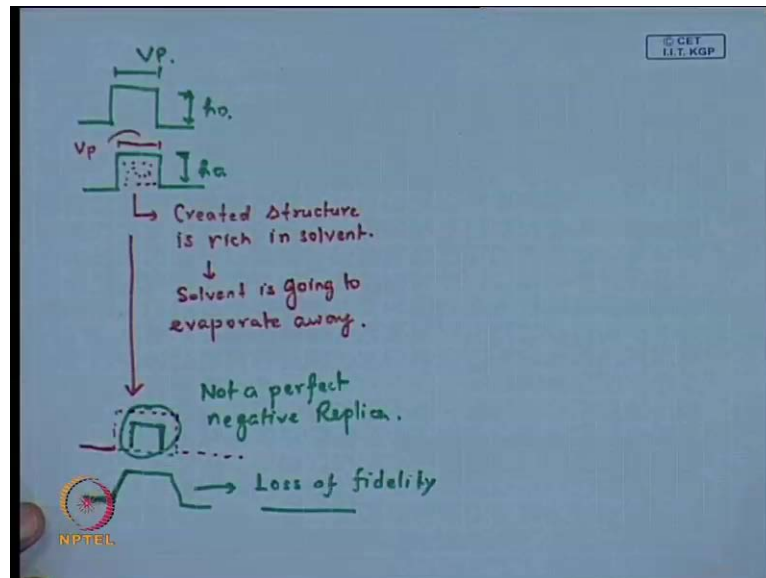
MIMIC

- The replicated structures are rich in solvent, and therefore there might be significant volume reduction after patterning, when the solvent evaporates away.
- Achieving large area patterning is not easy, as the flow through a very long capillary tube is difficult.
- There might be variation in the cross sectional variation along the length of the channels

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So, there is a significant possibility that when the solvent there might be significant volume shrinkage or volume reduction after patterning, when the solvent evaporate away. So, this might sort of hinder severely the resolution you want, because you the controlling factor of the resolution is essentially your stamp geometry and you get a negative replica of that, but the replica you get is rich in solvent. So, eventually you not be. So, the solvent will eventually evaporate away.

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So, the final structures though might be after replication. So, if this let us say, your stamp geometry your final replicated structure might be a negative replica of that. So, it dimensionally matches let us say, this if this is the width of the valley this is h_0 . So, you might actually be able to create this. But what is the problem? The problem is this structure, what you have created rich in solvent and typically these are polymers. So, this is organic solvents so, the solvent this likely to evaporate away. So, as the solvent is going to evaporate away once the solvent evaporates the structure which this was let us say the original dimension, it might shrink isotropically or may shrink even anisotropically and. So, this mightily to reduction in feature geometry or feature dimensions as compare to you do not show if you look at this you do you get some nice structures, but this is not a perfect negative replica. If your scenario is like this, it is even words, because there is loss of fidelity.

So, these are the things that you have to consider one can off course do the experiments in pretty controls. So, you exactly what type of shrinkage you are going to get after the solvent is completely evaporated away which again the level of evaporation and subsequent structural (Refer Slide Time: 47:00) sort of shrinkage is also function of the concentration. So, you may want to sort of start off with a higher concentration polymer solution. What it is going to lead is that higher concentration of the polymer solution is going to increase the viscosity and is going to the make the dynamics a little sluggish, but that might be preferred in favor of having significant reduction in the structure.

The other issue is that as we have told (Refer Slide Time: 49:25) that up to a let us say centimeter its find to have a capillary to even flow. But large area patterning is not easy as flow through a very long capillary of a capillary tube might be difficult and there might be cross sectional variation of the patterned morphology along the length of the channels.

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It is something similarly like this, what we have discussed. So, if you are thinking of very long area or something like that you may not get a perfect negative replica all along and also the concentration might be different in different areas. So, there might be some difficulties. So, with that I think, I will wind up today's class here and in the subsequent class we will talk about the other soft lithography techniques primarily if you refer to the list we have talked about. So, we still need to discuss about SAMIM and capillary force lithography and subsequently we will be shifting on to the printing mode soft lithography techniques, that is micro molding in capillary and micro transfer printing.