Soft Nano Technology
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Lecture - 22
Soft Lithography – 5

Welcome back, now on to the 22nd lecture of the course, we are roughly still in the middle of the course. We are discussing soft lithographic methods; this is the 5th lecture on soft lithography in fact.

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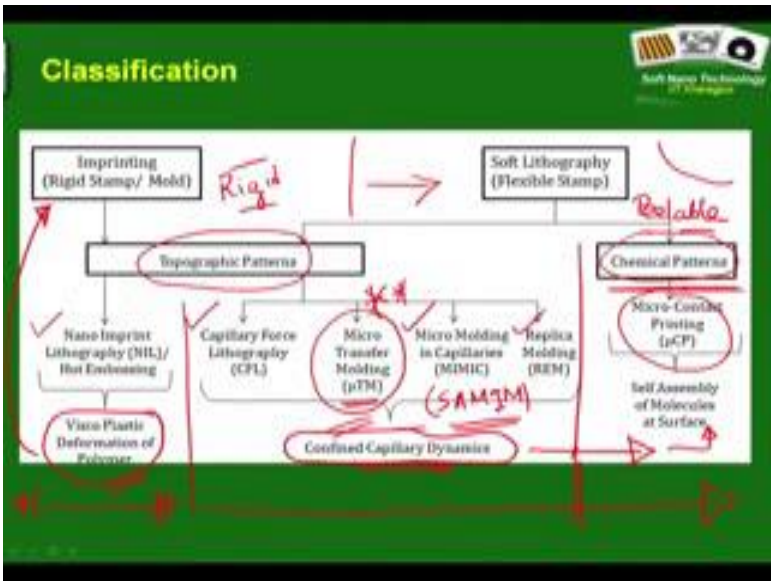

Classification

Imprinting (Rigid Stamp/ Mold)

Soft Lithography (Flexible Stamp)

Topographic Patterns

Chemical Patterns

Nano Imprint Lithography (NIL)/ Hot Embossing

Capillary Force Lithography (CFL)

Micro Transfer Molding (μTM)

Micro Molding in Capillaries (MIMIC)

Replica Molding (REM)

Micro-Contact Printing (μCP)

Visco Plastic Deformation of Polymer

Confined Capillary Dynamics

Self Assembly of Molecules at Surface

So, let us continue. We are back to this slide again which sort of classifies the different techniques and now let us re look into it. So, we do not now know firstly, some of the techniques. We now know Nano imprint lithography, we now know CFL, and we now know micro molding in capillaries. We of course, know replica molding and we have also talked about another technique which is sort of very close to micro molding in capillaries SAMIM. Just to give you a flavor how many names are there? How different techniques are present which vary some bit from the original technique.

So, now we see that we have not talked about micro contact printings which is in fact, a method for creating chemical patterns and another technique that sounds very similar to it is micro transfer molding, but that does not give a chemical patterns it creates topographic patterns in fact you will find that this technique is very special. Why it is special? Let me tell you now because typically Nano patterning results in patterns on a film or on a surface. So, these are primarily 2D structures, but this micro transfer molding with invent of micro transfer molding people have tried to use soft lithographic methods or Nano patterning methods in a limited way for creating 3D structures. So, we will see that. I would also like to emphasize one more thing that the classification we have had so, far topographic patterns and chemical patterns that we understand. We also had a classification based whether you are using a flexible stamp which can be pealable that is the most important aspect or a rigid stamp that we understand.

However, one more thing is written over here which I did not highlight till now and now you are in a position to understand that, is the dynamics is this particularly valid for different topographic techniques. In fact, it turns out this is also valid to a large extent for micro molding in sort of micro contact printing. Is that the pattern replication in almost all these methods expect may be micro transfer molding because which is a very special technique it is just bracketed there because it also creates topographic structures. They are not 2D structures they are in fact, 3D structures we will see that. In all these techniques on this side of the diagram, the pattern replication takes by means of confined capillary dynamics and therefore, you typically do not apply a huge amount of excess pressure or force from outside.

In contrast Nano imprint lithography is actually a brute force method. You apply lot of force to do the deformation and the deformation of the polymeric clear is actually a visco plastic deformation, it is not a capillary driven flow and that is in fact, this mechanism as I mentioned once briefly necessitates you to use a rigid stamp because since you are applying significant amount of excess force to cause deformation of a softened or molten high viscosity polymer layer. You need lot of pressure to cause deformation and unless you have a rigid stamp, you apply the pressure over a flexible stamp and the stamp is simply going to collapse it is not going to lead to pattern application. So, these are the issues. So, anyway today we will concentrate or focus in this lecture on learning the process of micro contact printing or mu CP.

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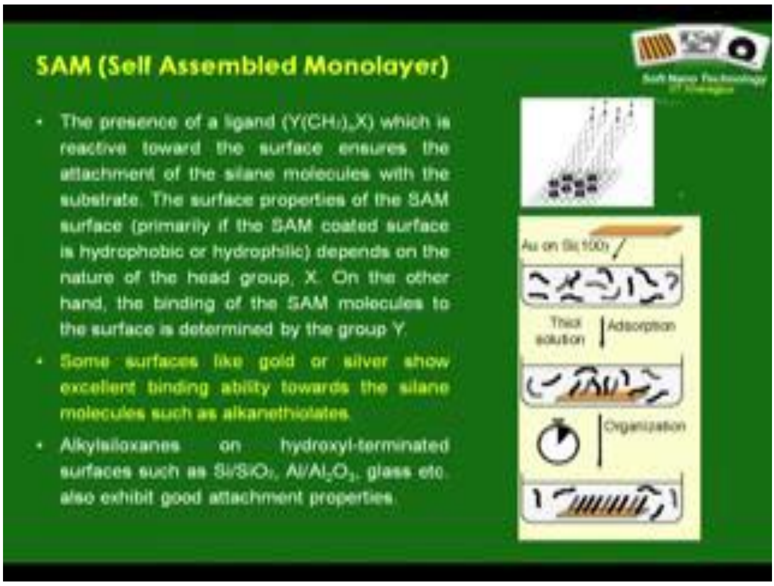

SAM (Self Assembled Monolayer)

- The presence of a ligand ($Y(CH_2)_nX$) which is reactive toward the surface ensures the attachment of the silane molecules with the substrate. The surface properties of the SAM surface (primarily if the SAM coated surface is hydrophobic or hydrophilic) depends on the nature of the head group, X. On the other hand, the binding of the SAM molecules to the surface is determined by the group Y.
- Some surfaces like gold or silver show excellent binding ability towards the silane molecules such as alkanethiolates.
- Alkylsiloxanes on hydroxyl-terminated surfaces such as Si/SiO_2, Al/Al_2O_3, glass etc. also exhibit good attachment properties.

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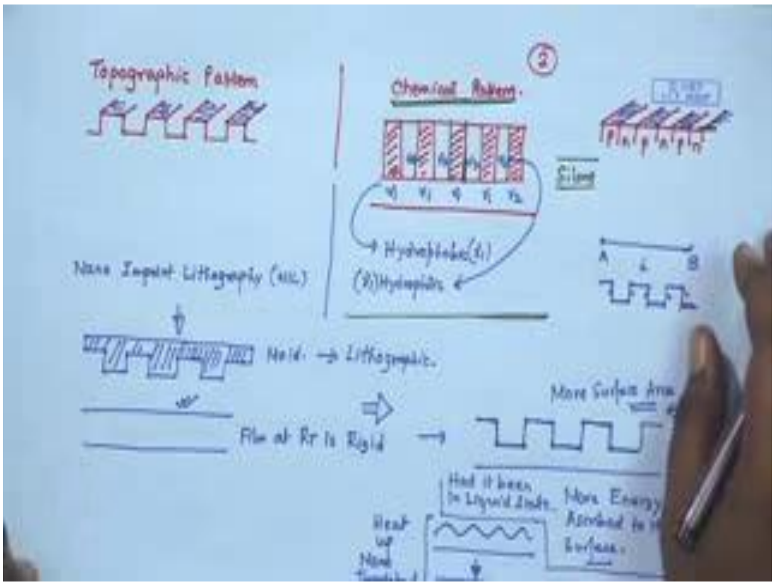

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Let us just recap quickly, what we mean in the context of soft lithography as a chemical pattern and this in one of the initial slides on soft lithography I had clearly highlighted that, in the context of soft lithography a chemical pattern typically means alternating patches of more and less weighable domains. So, how do you create that? Well in order to create that of course, some of the things match very closely to other soft lithography methods like you use a flexible stamp seal guard stamp, but you need to in order to create this weighablility domains, you need a special type of a molecule called as Silane molecule.

It is another type of a surface active molecule. Not exactly a surfactant because the geometry and the chemistry is slightly different. In fact, there is lot of work that goes on in Silane chemistry. I will not focus too much on that I will just give a very brief idea about this so called Silane molecules; they have a structure like this. So, they have 2 groups.

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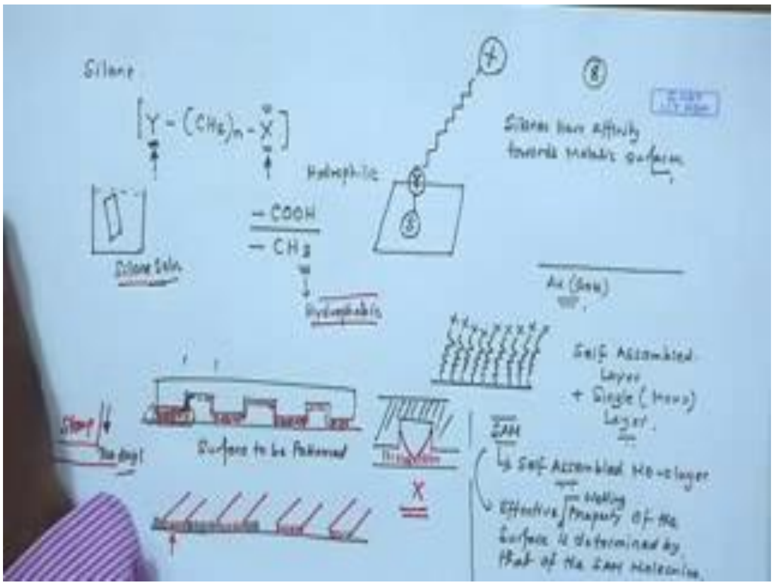

So, if you look carefully, this is the structure of a Silane. This is somewhat different from a surfactant because the surfactant has this hydro carbon tail but it has only one head group. In contrast a Silane molecule is sort of attached to 2 n groups on the 2 sides; and these 2 n groups actually have different roles to play, which you can see from this particular slide, this particular figure shown over here. In very simple terms the group Y is sort of again let me sort of tell you that this picture you are getting is a very simplified picture, Silane chemistry is very complicated the self assembly process is very complicated and lots of people do research on that.

We just pick up the essential concepts for patterning and therefore, I will only limit my discussion to that, what is necessary in the context of soft patterning. So, this group Y is sort of its function is to bind this molecule to a surface. So, let us say this is a surface molecule to which this Y binds itself. Now of course, it does not bind to anything and everything. It binds to only specific molecules. Most cases Silanes have affinity towards metallic surfaces therefore, the original paper on micro mold micro contact printing as well as subsequently many other papers or what you see here people use gold coated substrates.

It works with silicon also, but mostly people use gold coated substrates because this Y group, I am not even telling you what this is (Refer Time: 08:19). So, what is the exact chemistry of this Y or X group? I am not even telling you that it is also not important to you. So, this Y end attaches to the surface. So, now, the structure of the molecule is something like this. This is the hydrocarbon tail. And, on the other end you have this group X and this X you can have different types of end groups. So, you can have groups like COOH or CH3 and it turns out this is acid. So, this is hydrophilic in contrast this is your hydro carbon. So, this is hydrophobic.

So, what is the consequence? Consequence is that if you have a surface like this over which the Silane molecules attach very closely depending on the concentration things like that. The surface is now fully covered with a layer of these silane molecules. What determines this covering it is a self-assembly process just like the formation of surfactant and (Refer Time: 09:38). So, you see it is a self-assembled layer and it is a single layer. So, this whole process is called a SAM. This thing this type of a coating is called SAM. Its what is known as a self assembled mono layer.

Only thing that you need to ensure that, you provide the appropriate surface (Refer Time: 10:29) the appropriate Silane group. Why you need the appropriate surface because you must take a surface to which the n group Y has a preferential affinity. If that is not there it will not take this structure. The molecules will be simply scattered over the surface and the functionality will be lost. So, what can you say once the self assembled mono layer has formed? All you can say that now the effective property of the surface, effective what property in fact, waiting property of the surface is determined by that of the SAM molecules.

At this point you should not make a comment that well you have a self assembled mono layer coating and they are therefore, the surface is behaving like hydrophobic or hydrophilic. Why you should not jump to a conclusion because it depends whether the surfaces effectively behave like hydrophobic surface or hydrophilic surface will depend on the nature of the group X. So, if you have a hydro phobic silane well anything now dispensed on the surface a drop of water let us dispense on the surface will not see the actual surface, but it will sort of see this end group X. So, and depending on what type of silane you have the surface can either behave as a hydrophobic surface or hydrophilic surface.

So, self assembled mono layers are in any way even without micro contact printing very widely used to tell us the effective property of a surface. So, you have a surface, you need some hydrophilic property of the surface for certain application. All you do is you take a silane solution, immerse the substrates into the silane solution take it out. Let the solvent evaporate. As long as solvent is there the molecules will re-orient and self assemble on the surface and this will lead to effective change on the surface.

So, this was known, but how do you create patterns with alternate patches? So, this is what we would like to achieve. What we have talked that you have a surface with surface tension gamma s. You silanize in it, that is the term. You end up having a surface which has very similar mechanical properties and all other properties because silane layer is only one mono layer thick. However, the effective surface energy will be reflected of that of the silane molecule, but from there how do you get these types of patterns patches?

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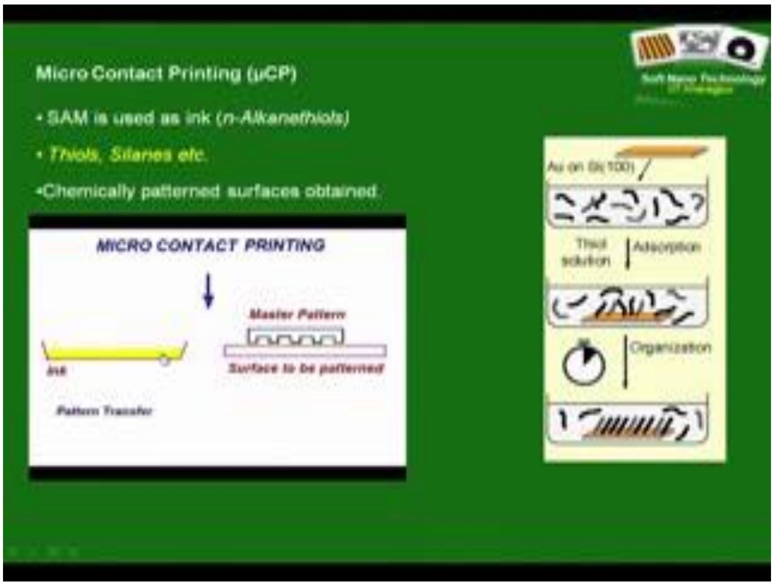

Micro Contact Printing (μCP)

- SAM is used as ink (*n-Alkanethiols*)
- *Thiols, Silanes etc.*
- Chemically patterned surfaces obtained.

And the philosophy that was adopted is very simple. In fact, I will just take a minute to run the. So, this movie will give you an idea about how it works so, before I start let me just tell you what we have.

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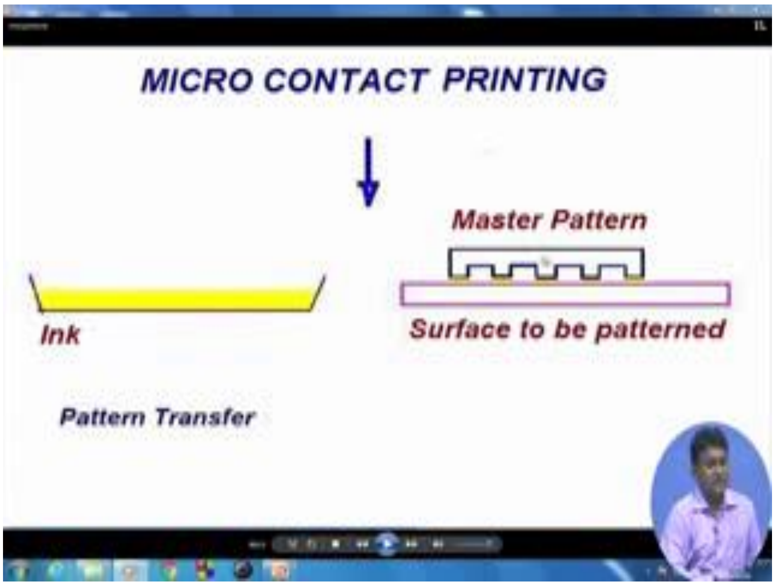

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So, this is the surface that needs to be patterned and you have a master which is nothing but a replica molded seal guard 184 stamp. Here you take the ink which is nothing but a silane solution. So, all you need to do is initially you immerse the stamp into the silane solution, the stamp becomes wet. You can recall that there is another technique in which you have used a wet stamp that is SAMIM. So, there you wetted the sealed stamp at a pure solvent. Here instead of a pure solvent you are wetting the seal guard stamp with a silane solution. So, this wet part of the stamp of course, please understand this is a cartoon I have drawn therefore, it shows as if only these areas are wet, but it does not happen like that the whole stamp gets wet. All you need to do is you simply bring it in and press the stamp against the surface to be patterned.

What is the idea? Idea is very simple. Idea is unfortunately the movie is not working from here, it is working great so idea is that, but anyway you had a exaggerated view which is good. When you bring in and place it in contact so, here is your surface to be patterned. Here you bring in your stamp which is wet with the sinale solution so, here is the critical step. So, it is already wet all over and so, when they are in contact in fact, these areas the liquid is in direct contact with the subtract so, ideally the silane molecules present over these areas should bind should get an opportunity to bind to the surface.

While other areas it will not bind and therefore, you end up getting patches which are alternating with alternating weighablility regimes. Whether this silanised patches is hydrophobic or hydrophilic again will depend on the nature of the silane molecule you are using. So, if you are using let us say hydrophobic silane and had hydrophilic base you can create a surface with alternating weighability domains. You can also start off with a hydrophobic surface and take a hydrophilic silane to achieve at the same, however, there are certain critical issues that one need to understand is that the viscosity of the silane solution is very very important and the contact time during this transfer because what happens by the time you wet the stamp, bring it into in contact with the surface to be patterned.

If by the time the stamp has become too dry then what will happen there is not adequate amount of solvent to form the bridge between the stamp and the substrate. If it is too dry then unfortunately the silane molecules are completely stuck on the stamp surface and they actually need this liquid meniscus through which they can sort of migrate and undergo the self assembly, but if the liquid meniscus is absent if like the stamp comes and it is too dry then the transfer does not take place.

On the other hand if it is too dilute, if it is too wet so, what will happen? It will transfer the silane molecule will transfer, but if it is too wet then, liquid tries to drain off from these areas. As a consequence these patterns will try to smear out and you will get transferred, but you will get additional transfer of molecules which are beyond the width of the original stamp pattern. So, your feature size becomes large. This is not a very controllable technique. So, you cannot control it, smearing is dangerous like you try to write with an ink pen on a blotting paper you cannot control the width of the paper, your writing spreads out. So, something similar, but there it spreads because of the fibrous nature of the paper.

Here it tends to spread because the solvent is too wet there is too much amount of the excess solvent which is trying to spread out. What is the danger of this technique? I mean if there is too much danger of course, these are small patterns. If there is too much amount of spreading there is a possibility that the meniscus from 2 adjacent so, these are 2 adjacent tooth of the stamp so, the molecules are transferring which is spreading. It is spreading up to here this one spreads up to here they join up and your whole purpose is lost why? You achieve salinization, but not only below the protrusions of the stamp. You get a full coverage of the surface with the silane molecule.

And therefore, your whole purpose of using a pattern stamp to bring in silane molecule and buying the preferentially the whole purpose is lost because this you could have anywhere done by simply immersing the substrate into silane solution. There was no need for you to take so much amount of trouble.

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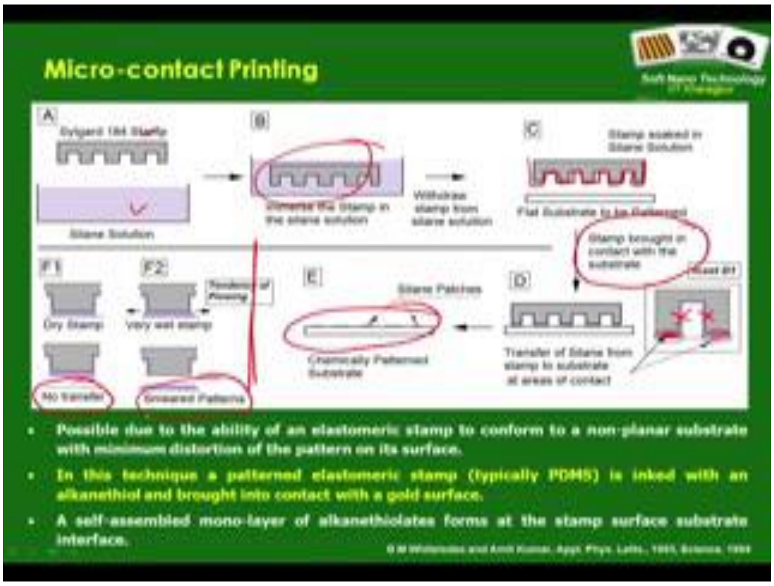

Micro-contact Printing

- Possible due to the ability of an elastomeric stamp to conform to a non-planar substrate with minimum distortion of the pattern on its surface.
- In this technique a patterned elastomeric stamp (typically PDMS) is inked with an alkanethiol and brought into contact with a gold surface.
- A self-assembled mono-layer of alkanethiolates forms at the stamp surface substrate interface.

So this is micro contact printing. This is another schematic that tells you of the details roughly the same thing say good capitulation for us. So now you understand this is the stamp, this is the silane solution you immerse it. So unlike the cartoon you now understand the silane layer is adhering conformally through all the surface and therefore, the possibility the later possibility this particular possibility is very high. So therefore, this particular possibility is very very high.

\Therefore, it is very important to control the drying time and the exact condition of how wet the stamp is. So it is possible that after you wet you might wait for some time for the solution to dry a little bit. Therefore often salinization is or micro contact printing is performed inside a lap box or something like that which has controlled humidity, because humidity again affects it in a very big way because even if you give the same amount of waiting time between waiting and imprinting your embossing depending on humidity the amount of solvent actually sticking on to the surface is going to be different.

So, you transfer it this is the inset this is what you want to achieve. You do not want this layer to drain off and spread on your surface. This is the chemically patterned surface and here are the problems. If it is too dry there will be no transfer if it is too wet there will be smeared patterns.

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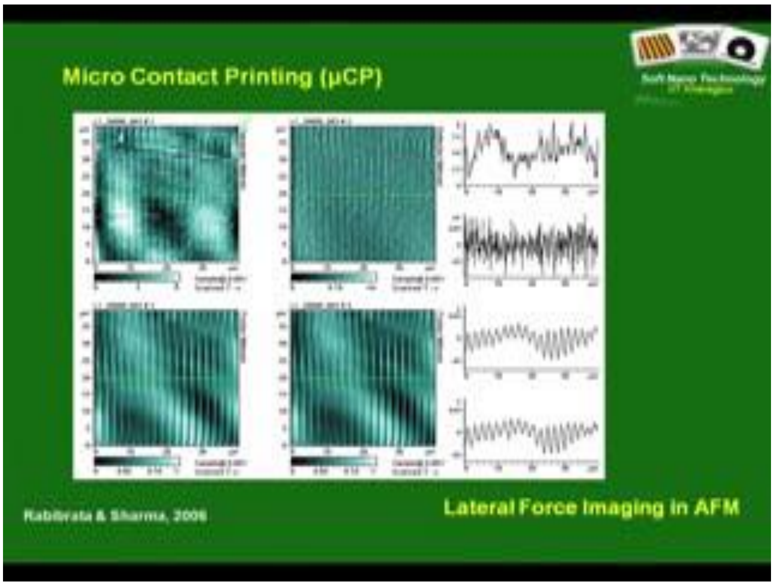

Micro Contact Printing (μCP)

Rabibrata & Sharma, 2006

Lateral Force Imaging in AFM

Now I thing you understand the problems and there is one singularity that comes out silane molecules even over here they have formed a single mono layer. Their height may be is of the order of a Nano meter maximum. So question is how do you visualize such a surface? I have not yet thought you AFM which I will start in 2 lectures.

Within just about 2 lectures or so and then you will realize that a regular atomic force microscopic imaging will not help you to achieve this. So you need some special technique for that which I will also cover with reference to this particular picture. This is something that we will come up later.

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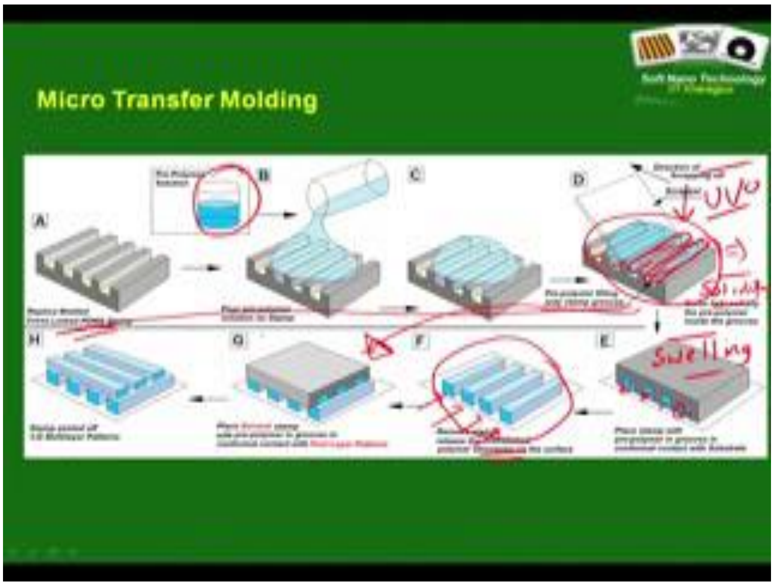

Micro Transfer Molding

The last so called conventional soft lithographic technique is micro transfer molding a very allegiant technique. As I have already mentioned that this is this technique is capable of producing 3D structures. So let us see what is done. You initially take a cross linked PDMS stamp as usual. You take a special type of a pre polymer which is (Refer Time: 22:48).

So what you do? You pour it just like replica molding, but then after you have dispensed the solution with a doctor’s blade or even a simple scrapper you just throw away the excess amount of liquid that you have dispensed. So, all you have is this stamp and this is filled up with this pre polymer. Now this pre polymer is actually a special type of a pre polymer. It is typically (Refer Time: 23:22) material.

So we have talked about this is so called UV curable material in the context of UV NIL. So we know that these materials solidify upon (Refer Time: 23:32) exposure. So, you do that you shine UV they might I would have been better off to UVO one more frame which I missed out due to whatever reasons. You shine UVO. So, each if this polymer stripes within the grove sort of cross links and they solidify which is good.

Now all you do is you turn the assembly so these are now solid. Each one of them is now solid, they are no longer liquid. You turn them upside down keep it on a flat surface and you would like to release them from the stamp. Now a simple peeling of the seal guard stamp as you have done in the replica molding or something like that is not going to work because this is the stripes are adding here too closely to the seal guard stamp. So, what do you do? You take advantage of one specific property that I have mentioned and that is solvent paper exposure of this seal guard block.

You remember when you do a solvent paper exposure of a glassy polymer, it starts to flow because of its reduction of its apparent glass transition temperature to room temperature or even below, but I mentioned that when you do a solvent paper exposure to a cross linked polymer it fails to flow because of the physic the presence of the physical cross link which sort of prevents the flow, however since it is a polymer and you are exposing it to a solvent a good solvent of it therefore, you still have this liquid penetrating into the cross linked polymer matrix, but it does not flow or it does not lead to reduction in TG, but it leads to swelling.

In contrast by this method what you have done, you have created the structures within the seal guard stamp and you have simply placed it over here and that in fact pays a way for creating 3D structures by means of stacking let us say one layer after the other. So, if you can do this transfer once, what prevents you from repeating the process up to here and then straight away now place the stamp at an orthogonal direction to the initially existing structure. So, you build the second layer, you build the third layer and you go on building your structures like this which demonstrates that under certain conditions and of course there is material restriction here because you cannot work with all sorts of polymers you can in fact use soft lithographic methods also up to certain limited extent for creating 3D structures.

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Advantages of Soft Lithography

- Convenient, inexpensive, accessible to chemists, biologists, and material scientists
- Basis in self-assembly tends to minimize defects
- Many soft lithographic processes are additive and minimize waste of materials
- Readily adapted to rapid prototyping
- Isotropic mechanical deformation of PDMS mold or stamp provides routes to complex patterns
- No diffraction limit; features as small as 30 nm have been fabricated
- Nonplanar surfaces (lenses, optical fibers, and capillaries) can be used as substrates

So, that sort of brings us to the end of our discussion on soft lithography. I will pick up some very unconventional and new techniques that are coming up along with that advantages and limitations of soft lithography.

In the next class which is going to be the next last lecture on soft lithography.

Thank you.