Instability & Pattering of Thin Polymer Films

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Lecture No. # 20

Soft Lithography - V

Welcome back we will continue our discussion with soft lithography, and we had been talking about capillary force lithography, when we finished our last lecture. So, we will continue with CFL, but what I introduced you right now, what I will take of couple of minutes to highlight to you that right now, we have up till now we have learned quite a few pattering methods some of which follow under the category of classical soft lithography.

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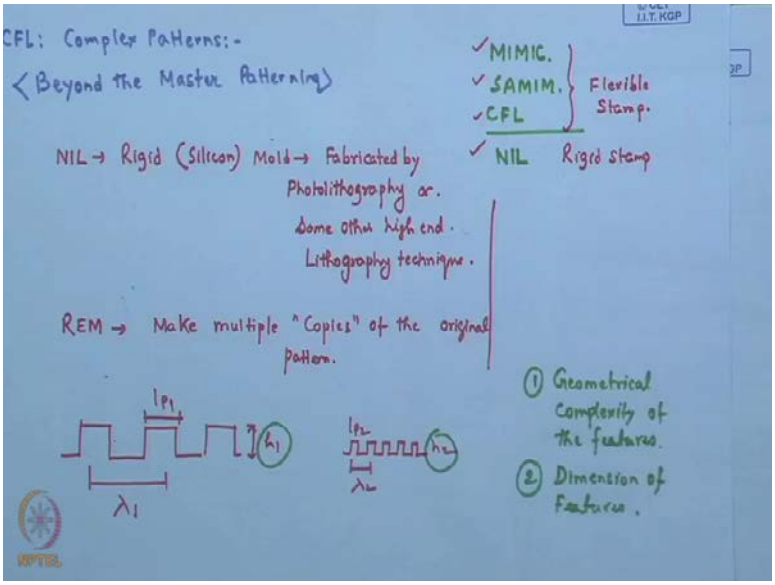

And some of the methods at least three of the methods that, you should be able to recall are MIMIC, SAMIM, and CFL in addition we have also learned nano imprint lithography, which due to historical prospective, because it was discovered by Stephen Chow at Minnesota not by wide sides it uses a rigid stamp if you remember, your our discussion. So, historically it was not part of the soft lithography group, but many people now consider that NIL is also one of the soft lithography methods, without going into

that argumetraly what we can definitely conclusively conclude is that both NIL as well as this other soft lithography techniques, they fall into the category of non photo lithography techniques for patterning, and the generic nature of the techniques make these methods rather useful or easy to implement for polymers soft materials, and you do not require complex materials like photoactive or photoresist or things like that. They can be very easily use for simple structure polymers with a little bit of tuning of glass transition temperature to either room temperature or by a little bit of heating or things like that.

So, that way if you now contrast the methodologies we have talked about nano imprint lithography as well as MIMIC, SAMIM, and CFL and you compare it with what we have already discussed few lectures back about photolithography. You can immediately understand the processing steps as well as the hardware requirement in these methods is much less compression, less complicated as compare to what you require in photolithography. So, that is why these methods are really very simple photolithography of course you have optical exposure, then you have several developing stage then you have doping exedra.

So, that is why these methods are much stable, much easy to implement, and you require much less infrastructural requirement therefore, these structures also the patterns made out of these techniques can be fabricated at much lower cost, which we have talked in probably first couple of lectures of this course itself which makes these methods ideally suited for bulk nano application where you mean high fidelity, large area structures in large numbers rather than maintaining absolute critical requirement in terms dimensional tolerance as is necessary in micro electronics.

However if you have carefully been following the lectures you might have noticed one specific things, and that issue is that in all these methods we have mention so for, you are actually producing by some what different techniques or mechanisms or method or protocol, a perfect negative replica of an original stamp or a mold. In soft lithography lecture, you refer the original thing as a stamp, a nano imprint lithography literature you talk to you refer to it as a mold, but real it is respective of that what you are always able to achieve is a negative replica therefore, one of the limitation and then comes the question, How does or where does on produce this original mold or stamp? A nano imprint lithography group of methods, you know that you require a which is silicon

master which often is fabricated by photolithography itself or some other high end lithography technique.

In soft lithography group of methods, in most cases you use flexible PDMF stamp, but that PDMF stamp has to be made by or is generally made in most cases by replica molding, which is another soft lithography technique itself the simplest one I would say, by replica molding, again still lithographically fabricated master. So, what are the limitations now? the limitations of soft lithography that emerge including nano imprint lithography that they require a primary structure which contains a perfect negative replica of the desire structure, that is important.

The structure you want to make it contains a negative replica of that, that is the stamp, because ultimately what you are making by any one of these methods is a negative replica of what you have already in your master mold or wherever, and for to produce this, you have to relive on some other lithography technique. So, the that way soft lithography is to a largest extend dependent on some other lithography method. The other critical issue that immerges, so, even if you start sort of producing, let say in most soft lithography group of methods since you use a flexible stamp. So, once you have a one lithographically fabricated master you can then go on producing by replica molding as we have sort of make multiple.

This is a method by which you can make multiple copies I can say like a xerox machine may be of the original pattern, but then again you have to understand one specific thing. For every deign of structure, you want to make, suppose you want to make these two type of structures by soft lithography, let say this as a periodicity of a lambda 1, line width of l p1, and height of h 1 verses, so generically both of them are let say gratings, but you would be needing two different stamps to make these two structures originally some were done the line you need to have two photo lithographically or some other made by some other lithography two distinct original masters, which then you can go on producing or mask produce following any one of the soft lithography techniques.

So, that way, so you can understand that since this original master have to be fabricated by photolithography or some other ion lithography it is costly, and every new design you want to make could essentially require or will force you to get an originally fabricated stamp and the other thing to realized that we have shown some structures which are

simple grating structures. The cost of a stamp lithographically fabricated stamp sort of exponentially increases with two things, number one is the geometrical complexity of the features, and number two is the dimension of the features.

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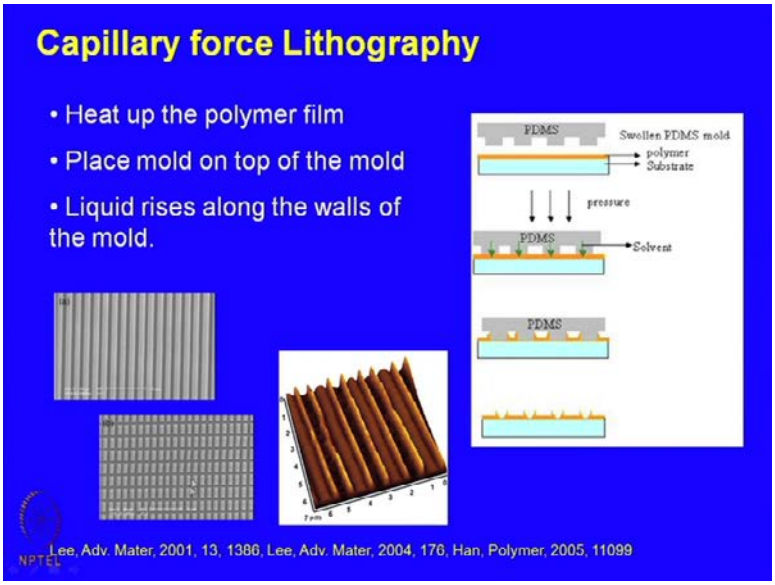

By geometrical complexity we mean the simplest structures probably the gratings more complex structures like ordered array of something like this 2-D pillars or rectangular pillars or something will then it becomes more and more complex. Similarly, the smaller the feature size is it becomes more and more difficult to fabricate, let say if you want to make simple gratings with 5 micron line with (( )) 50 nanometer line with may be you will be ending up pain, 10 times higher price for in the in the later case. So, the third aspect also that sometimes really effects the cost of a of a lithography, lithographically fabricated stamp or a structure is how over how much amount of area you want it, because photolithography is a parallel process, but many of the directorate methods like electron beam lithography focused I am beam we have an covered these techniques in detail, but you can always look into the literature and find out, what they are.

So, they are serial writing methods. So, creating this structures they can produce features with extremely low literal resolution line to down to let say a 20 nanometer, but if you want to have this structures over few centimeter square area, that might actually take few days to write the whole area, because the tip has to physically raster at every location go come back and dislodge the material, burn of the material to create the structure.

So, the larger area is requirement you have for original stamp that is also going to sort of increase the cost of your hardware or the stamp. So, therefore, there has been significant research particularly in the area of soft lithography, is what is known as beyond the master patterning what it means is that you produce final structures which are not only a perfect negative replica of your stamp or master, but it can be more complex patterns. It can be different in the periodicity, it can be different in line width, it can be geometrically different something like that.

So, then what happens is that you might be having a simple stamp let say you have a grating, and the idea is that using a simple grading stamp can you make structures which are let say I have 2-D complex order. So, that will be very interesting and significant amount of research is actually aimed at those directions recently. We I am I mean, as I have told right at the beginning that the whole business of soft lithography patterning it is an extremely advanced area, so, lot of developments also take place even now. So, every new issue of some of the many of the top journals you find newer techniques which are coming up, but one has to realized that most of these so, called new methods are essentially extension nice extension I would say of majority of the existing techniques.

So, it is not possible in a course to cover all the methods that are available, but to give you an idea about how this beyond the master patterning concept can be implemented I have a picked up a few case studies which are all sort of came into existence in the last 5 to 10 years, to impress up on you how with the simple stamp let say you can go on creating more complex structure which can have significantly higher degree of complexity, and it can be used in other higher functionalities. So, capillary force lithography had been one of the major techniques which has which offers extreme flexibility to the user in terms of the fact that you can go on you can go on making complex structures using simple stamps.

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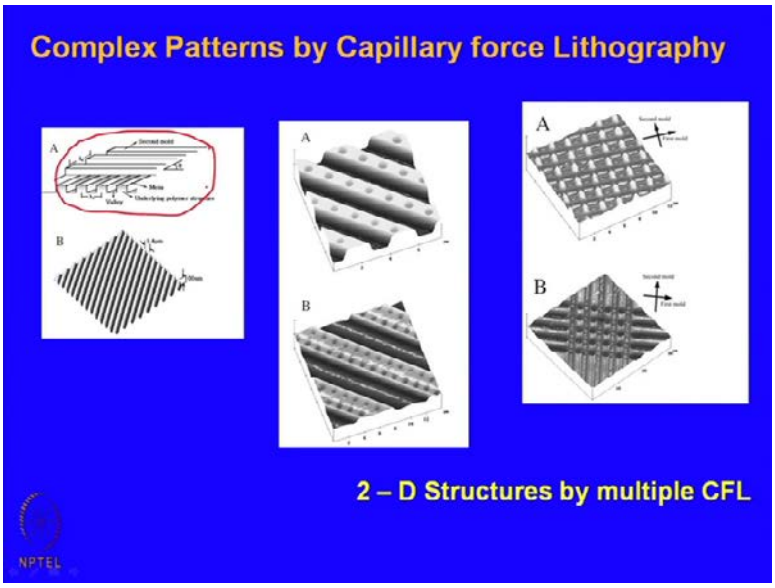

So, some of such developments we will discuss one of the developments is to or one of the methods that in this regard that came was actual to use to moles of stamps by CFL.

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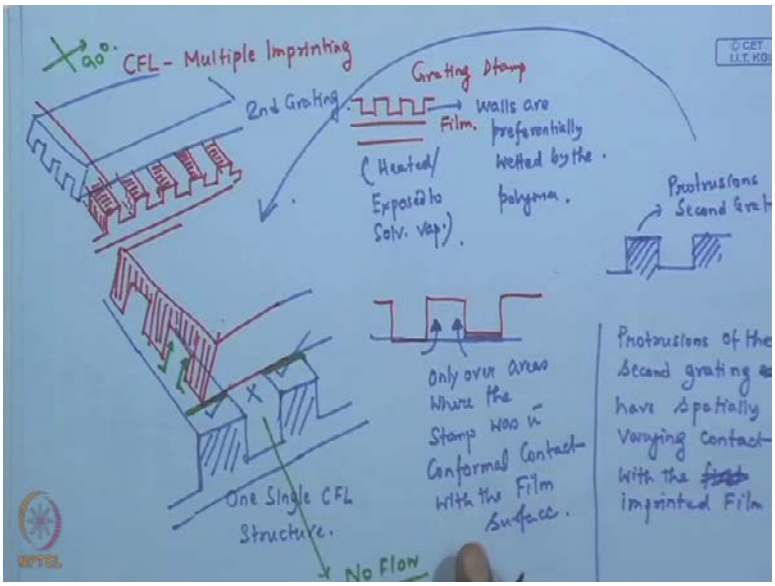

So, what you will do? You first generate a negative replica of your first mold by CFL. So, you had taken a polymer Film usual you have implement imprinted it or perform capillary force lithography with a grating stamp to obtain a perfect negative replica. So, this I guess with the level of understanding you have it is essay for you to understand how this can be implemented. So, all you need is a stamp, the walls of which are

preferentially wetted by the polymer, which is in either heated or exposed to solvent vapor. So, that it is in a it is in a liquid stage, and you can simple get a grating structure if you remember carefully the pattern replication took place due to confine capillary dynamics that is flow capillary ravine flow of the polymer along the stamp walls or in other words this flow was possible only over the areas, where the stamp was in conformal contact with the Film surface.

Now, in this approach one of the easiest things that can be done is that once you have a pattern Film. So, this is all the polymer, but now it contains a negative replica of the first grating, what about this? You simply place another grating may be the same grating, grating with the same geometry add some angle with the already created structures. So, now what happens what you can understand if you take a detail view of one replicated structure let say, so, this is one CFL structure, and let say we take a cross section at this particular plane. So, here is the second grating that is paste. So, what you can immediately understand, this is the structure polymer Film now.

So, this second grating is now in contact with the pattern Film not all along its length, but only at these locations, over these location where the reseed portion or the protrusions of the second grating. So, these are protrusions of the second grating. So, this grating you go place here. So, the protrusions of the second grating are in contact with the pre pattern Film or the let me write it down. So, the protrusions are grating have spatially varying contact with the first, with the imprinted Film or in other words you can you can see that it is only over these specific areas, where the protrusions are in contact with the already imprinted Film and over these areas there is no contact.

So, here over these areas again there will be a capillary driven flow, which will be doing the second mold Film, but below this zone since the protrusion are the higher zones or the hills on the pattern Film or not in contact with the protrusions of the second grating, there will be no flow, I hope it is clear to you. The way the second grating is placed on the pre pattern stamp. So, are to make it even simpler we take a first grating we create a perfect negative replica of that first grating on the surface of a polymer thin Film by capillary force lithography, and then we take a second grating and place it with its protrusion facing towards the pattern Film in such a fashion. So, that the direction of the stripes on the Film on the of the pre pattern Film and the directions of strips of the grating are at 90 degree with each other.

What this results is in a spatial variation in the extent of contact between the second grating stamp and the pre pattern Film surface. So, you can see that there is going to be spatial variation in terms of the contact. So, you have contact over here you have contact over here, but no contact on these zones and therefore, if you again allow capillary force lithography, capillary driven flow to take place the mold Film will only occurred over the areas where the second baring stamp is in contact with the pattern bottom layer Film.

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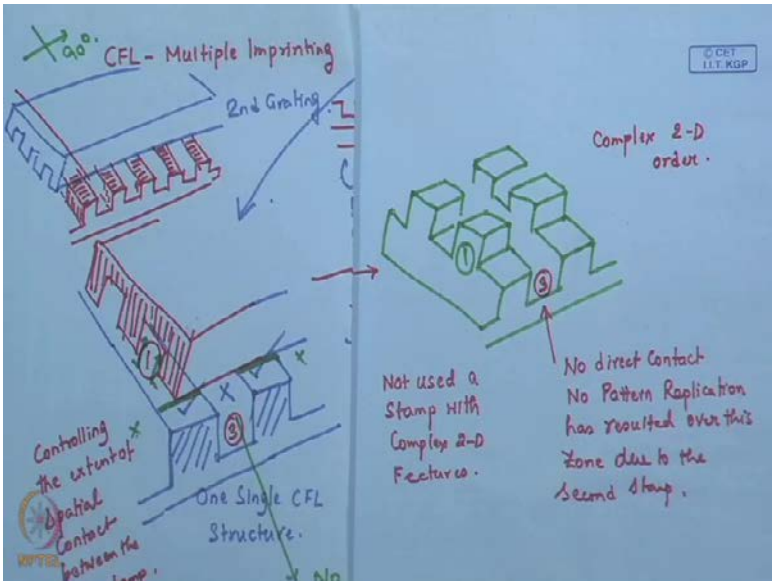

So, what this will imply, this will result in some structures like this. So, you can immediately understand that if I mark this is the same zone 1 in this particular picture where you have a second capillary raise below the second grating, and here over let say zone 3, the stamp and the pre pattern Film there was no direct contact and therefore, no pattern replication has resulted over this zone due to the second stamp. So, therefore, what the structure you see now has a 2-D order, but what is the real novelty behind this approach that though you have created a pattern which has 2-D order you have not used a stamp with complex 2-D features.

As we have already mentioned that stamp with complex 2-D features will be more expensive, as it will be more difficult to fabricate either photo lithographically or by any other ion lithography technique. Instated of that you have used all you have done is to use two grating stamps in a slightly clever fashion. So, you first use grating stamp to generate a CFL negative replica, and then placed another grating stamp on that pattern

Film at an angle where the strips not parallel they might some angle each other it can be 90 degree, it can be some other angle to generate these type of structures.

So, all your doing that you are, where you are controlling the extent of spatial contact between the second stamp, and the pattern Film second stamp and the. So, this is an example by which you can use CFL other methods also, but CFL is very simple to handle in this way, because if you if you compare it with the other methods what you have to understand that in CFL you are not brining in any solvent. So, same thing can also be done with nano imprint lithography you can do a perform second embossing after already existing structure, but that also been done it as not that it has not been done, but CFL as its unique advantage in the fact that compare to SAMIM or micro molding in capillaries you do not brining any solvent, because the moment you brining solvent, what might happen during the second imprinting step, the solvent might actually distraught the first structure, the structure originated from the first imprinting and therefore, a technique like MIMIC or even SAMIM might be pretty difficult to use in this mode to generate beyond on the master structures.

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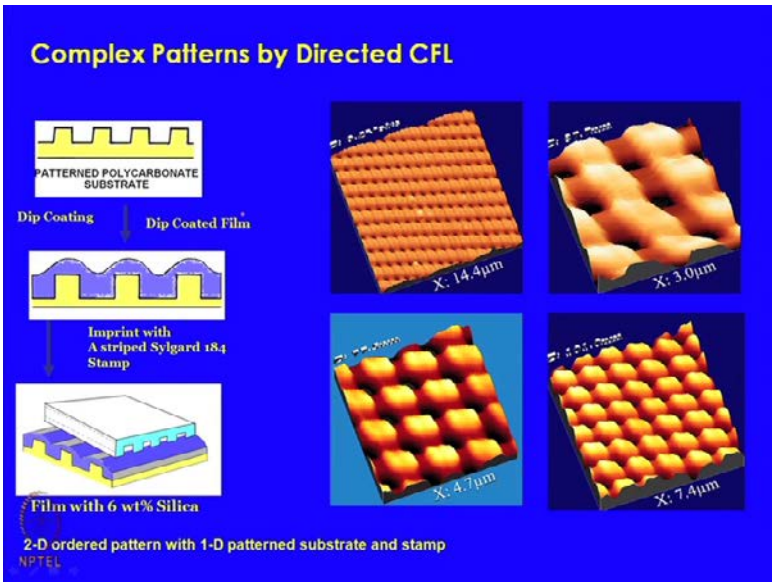

The other approach which is pretty similar to this one, but which we did recently and can also be regarded as a nice technique for making more complex structures in by using simple stamp or simple hardware is to use not to use two gratings as stamps.

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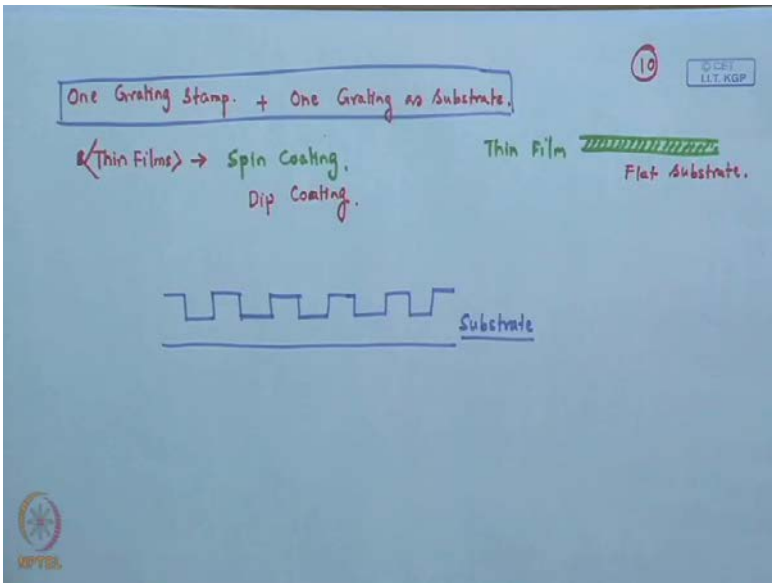

But to use a one grating stamp, and the other grating has a substrate. So, this is now interest in all the methods we have been talking for the last few classes now they use very thin polymer Films. So, we have talked in while talking about photolithography that one of the preferred method, particularly with polymers are making thin Films is the method of spin coating. So, in all the methods we have discussed so for this thin Film was deposited on a flat surface or flat substrate. So, if you remember the basic methodology of spin coating you dispensed a polymer solution on a flat substrate which was held on a chart by some vacuum or other holding devices, and then a high RPM was given.

So, it started to rotate and this centrifugal force sort of allowed the solution to spread uniformly over the entire Film surface, and simultaneously the solvent also evaporated away living behind the solute which is nothing, but the polymer on the Film surface resulting in ultra thin Films, and I think I have an also mention by that by this method of spin coating it is pretty easily possible to fabricate or generate polymer thin Films defect free polymer thin Films with very low feature or very low thickness which can be as low as 15 to 20 nanometer.

Spin coating one can also use for making structures which are let say few 100 nanometer thick for thicker Films spin coating can still be implemented, and industrially it is also implemented, but there is another nice technique that sort of can easily result in few 100

nanometer to few micron thick Films, which is known as a dip coating, but for the timing we will keep our discussion limited to spin coating. So, in this particular... So, all this CFL some in MIMIC all this we have implicitly assume that we understand spin coating, and the thin Film we have been talking about have been spin coated.

Now, in this particular method or technique we are going to discuss, we take a grating stamp and grating substrate. So, now the difference is that instated of coating the polymer on a flat substrate which we have been doing so far, we now are going to coat the film itself on topographically patterned substrate, which is let say grating. So, this is now your substrate.

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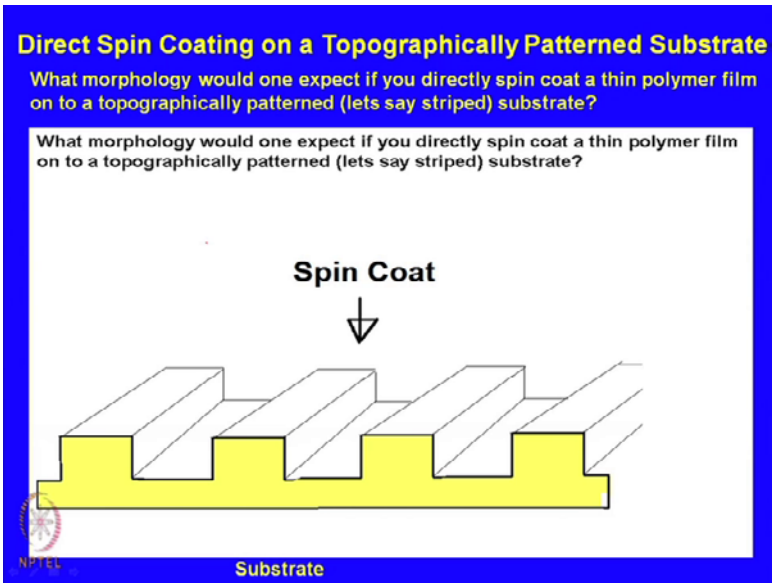

So, this is where the problem statement lies down, so you are going to spin coat on topographically patterned substrate which let say is of the order of like a grating.

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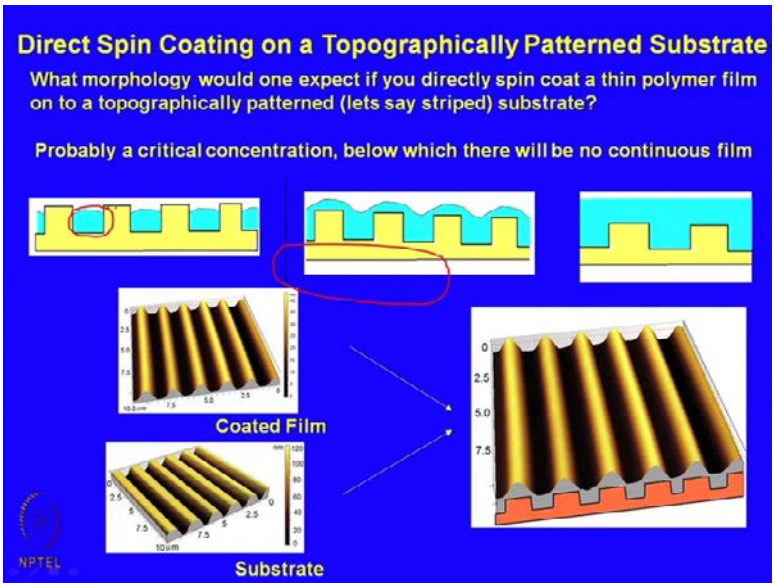

So, what would you expect? You would probably expect that if your polymer concentration is too low you would not even get a continuous Film you probably expect that your polymer will get deposited within the groups if the polymer concentration is very low.

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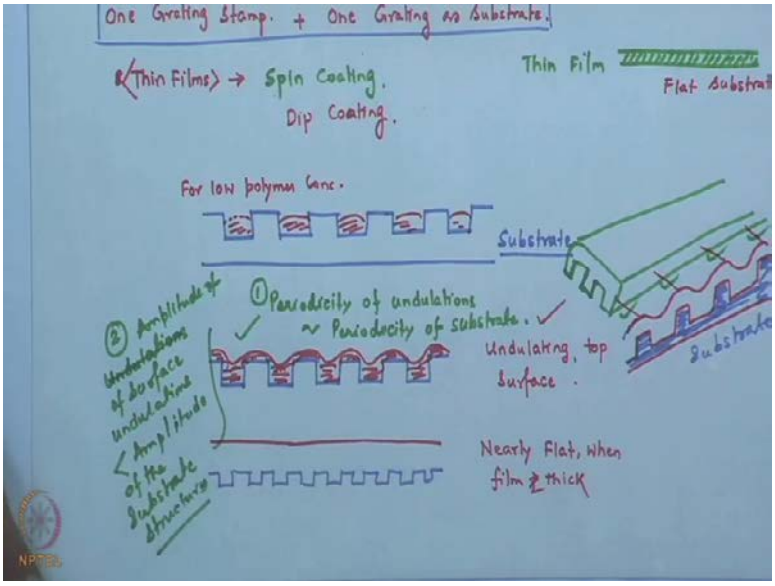

So for, it will get deposited within the groups, and if your polymer concentration is high enough probably you will get a Film which is fully covered, but still you have an undulating top surface, and the undulations are likely to be, so, Film with undulating this

is how the Film should look like, and if your Film is very thick as compare to the depth of your surface features, then may be you will again have a Film which is nearly flat. So, flat Film is thick. So, this is the general notion we had, and so, eventually in this case what would happen is that once you get to this configuration let say then if you now place a stamp which is at a direction or let say the second the grating is perpendicular to this direction of the undulations.

So, the Film would be looking after putting will looking, something like this, and so, this is the substrate, and this is the Film with the undulating top surface. So, now, if you place the stamp like this well you are essentially back to the (( )) now you again have a spatial variation in the extent of contact between the Film surface and the grating stamp. So, over these zones there will be contact, and over the other zones there will be no contact.

And therefore, in this process it becomes possible to use a grating stamp and a grating substrate to generate structures like this are this with square pillars this is interesting to notice this is not an a polymer, but this is on a silica and silica titania sol gel Film that we made all this structures by varying the initial thickness as well as the geometry of the stamp, and the substrate it now becomes possible to taller the exact picture size also this is the intention is to give you some sort of an idea I do not have any intention of going into great amount of detail. But one thing is that this mechanism what people things is based on this fact that if you have a reasonably thick Film, then you would be having a undulating Film surface with the undulations where the undulations are in face with the substrate pattern, but very recently.

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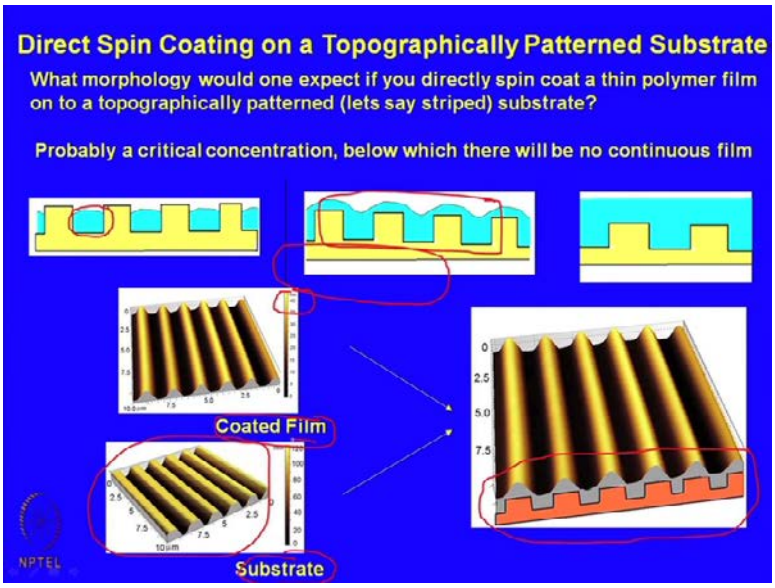

So, if you have if you have been doing an automatic force micro scope of the substrate incidentally we will take up atomic force microscope as our next topic as soon as we finish soft lithography, I will give you some basic idea about how and atomic force microscope are in AFM works. So, that you understand what you see how it is correlated to the surface structures.

So, you do an AFM of the substrate you get a structure like this you get an AFM. So, then you do the spin coating and then you. So, this is the AFM of the coated Film. So, if you supper impose that to I do not think many of you have a doubt that probably this is the this is how the thing is arranged. So, you have an undulating top surface were the periodicity of the undulations. So, important thing to note is periodicity of undulations matches the periodicity of the substrate. The amplitude of the undulations here you can see it is 40 nanometer is the maximum height here you can see the maximum height is 120 nanometer. So, the undulations this is the first thing to note, second thing to note is, undulations of the amplitude of the surface undulation sorry, the amplitude the substrate structures.

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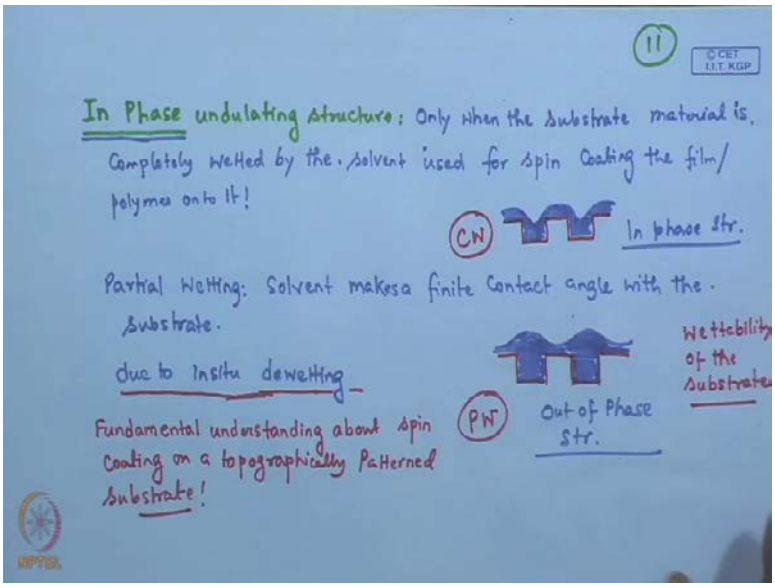

Very recently it has been shown that this configuration is valid only when the substrate is completely wettable by the solvent. So, in phase I will highlight this is important here, because you get an undulating structure any way you get an in phase undulating structure only when the substrate material is completely wetted by, the solvent used for spin coating the Film or the polymer on to it. This is an important revelation I will skip all this details.

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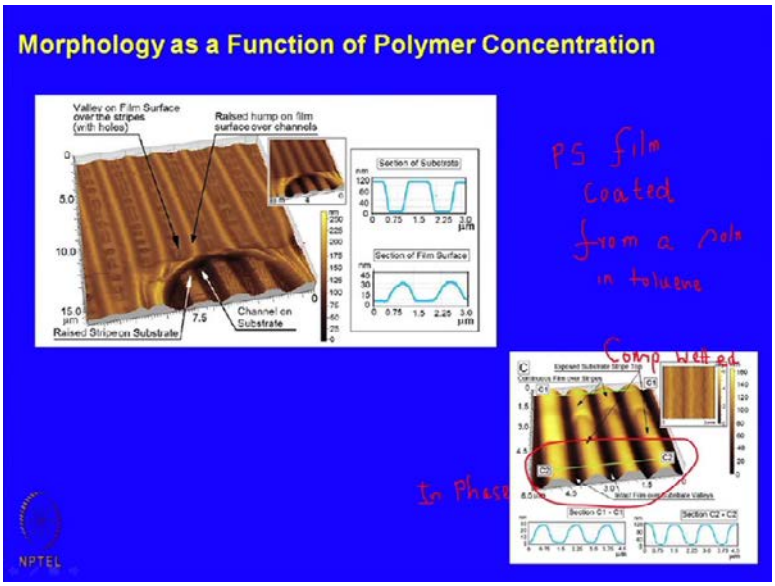

So, this is a surface which was. So, this Film has been coated the Film which has been coated is a poly stir Film. So, it is say PS Film, coated from a solution in toluene. So, this is a situation where the substrate was completely wetted completely wetted by the solvent that is by the by toluene and this clever atomic force microscope image where you can see the substrate. So, this part is the Bayer substrate this part is the Film. So, you can see that the Film is surface is also undulated just like the substrate, but the Film undulation, but and the Film undulations are in phase with the substrate pattern. So, this I will highlight as the in phase structures.

However, when the substrate is partial wetted. So, that is the solvent makes a finite contact angle by partial wetting we mean that, the solvent makes a finite contact angle with the substrate, then what happens is due to intrinsic or insitu dewetting, and this is another word which we will talk in very great detail in one of our some of our subsequent lectures. So, for the timing please keep this key word in mind due to insitu dewetting, but I will skip going into the details right now, because we will be talking about dewetting in much greater detail, but what you can see very clearly over this particular zone that the undulations on the surface of the intact Film. So, this is the undulation here you can see a hum here you can see a hum, but this hum sits over a substrate value.

So, here the final morphology indeed resemble what we anticipated. However, here the result is slightly counter in dewettings, so you get a structure like this. So, the only difference is the dispense polymer concentration is the same so, I would say this is the out of phase structure, this is in phase structure. So, the only difference between the two cases were the wettability of the substrate. So, in this case this was a partially wettable substrate I write it is a PW, this case it was a completely wettable substrate depending on CW.

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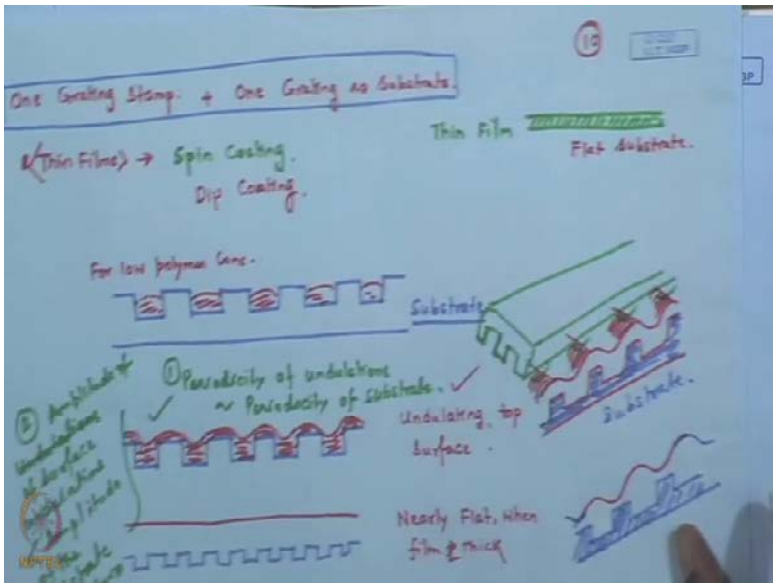

So, the reason I highlighted this particular finding is that now when you try to place a second stamp on a Film with an undulating top surface it becomes also important understand whether this is the geometry or the undulations or the higher locations on the Film surface or actually sitting on the on the on the substrate values. So, the other possibility can be the Film is like this. So, this is very important and this will also affect the final morphology of the of the final structures, but well depending. So, we have already shown two examples I mean this is one.

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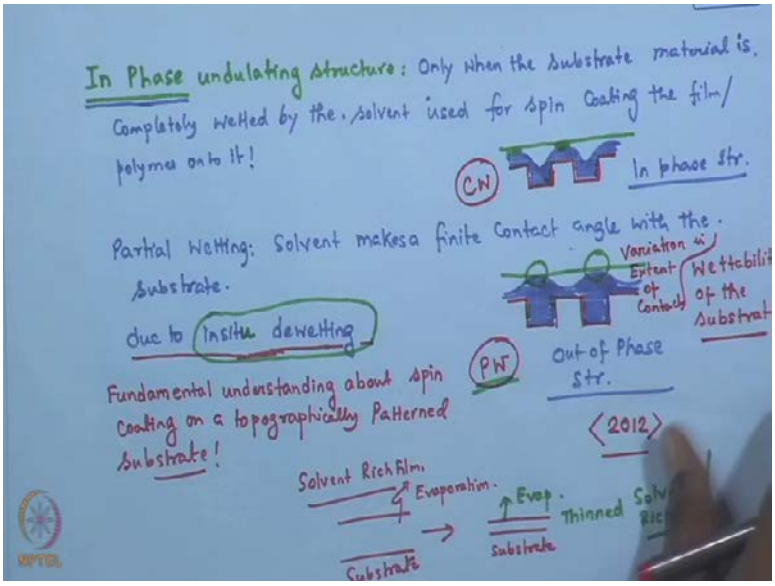

I would say fundamental understanding about spin coating on a topographically patterned substrate, and in addition to that last couple of examples we have already shown that indeed becomes possible to achieve beyond the master patterning or implement beyond the master patterning concepts two examples we have picked up is both of them are. So, for we have limited our discussion or kept our discussion limited to CFL base techniques or capillary force lithography base techniques.

And the first approach we shown was the used use of two stamps or two masters each having a grating geometry, first one is used to generate a negative replica of the stamp pattern and then the second stamp is placed on that pattern Film at 90 degree at a right angles to the first set of structure. The second example that we have picked up is instead of using two pattern, two gratings as stamps we use one of the gratings as a stamp, and the other one as a substrate. So, we had to address the issue of direct spin coating or coating a Film on to a topographically structure surface, and in this case it was a grating, and I in the process I introduced to something that is a little counter inflictive, because one would invariably thing that if you are coating topographically patterned substrate.

And if you your Film thickness is adequately higher then you will always get a Film which might have an undulating top surface, but the surface undulations will always be in phase be if the substrate pattern, but I show to you that it has been very recently understood and this is I gone telling you that this area is still very active. So, this whole understanding came in 2000 as let is in 2012 were people realized for the first time that the structures can be in phase or can be out of phase depending on the wettability of the substrate you are using with respect to the solvent of the polymer.

So, what happens is as you spin coat there is significant evaporation of the polymer solution the polymer remains back on the substrate, and the solvent evaporates away. So, as the solvent evaporates the thickness of the solvent Film. So, I would say this is the solvent rich Film which contains. So, initially let say it is like this is on the substrate, this on the substrate and then there is evaporation, and gradually there is thinning of this solvent rich film, during the process of spin coating itself and once. So, this layer is now become thin, but still it is rich in solvent, so, its entire hydrodynamics is govern by the hydrodynamics of the solvent that is the wettability of the substrate by the solvent and all these things are still dominate.

So, now, if you if you have a substrate which is partially wetting by the solvent what happens is due to insitu dewetting you get structures which are out of phase with respect to the substrate. In contrast, if you have a substrate this so, I have decided we talk that insitu dewetting we will be talking latter when we discuss dewetting in greater detail, but for the timing we need to understand or that if you have a partial wettable substrate then by direct spin coating it is one gets structure or a Film surface which is undulating, but the undulations are out of phase with respect to the bottom substrate.

In contrast, if one has a surface, substrate which is completely wetted by the by the solvent then on still gets say in phase structure, and then a combination of these or these surface undulations if now one places a stamp like this which is perpendicular to the direction of the undulations or 90 degree with the direction of this these undulations then what happens is now there is you can see very clearly, in both the geometry it is valid that there is a variation in the spatial contact, and now if you if you allow CFL to take place. So, let me just draw it neatly.

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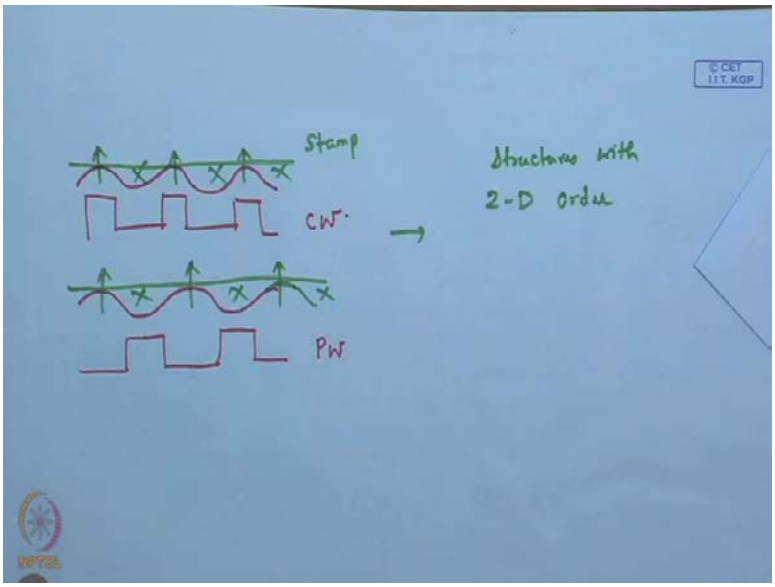

So, you have a undulating surface like this let say so, whether which of the geometries you have depends of the wettability, but irrespective of that irrespective of that, if you now bringing a stamp from the top, you can now see that there will be capillary rise only over these areas, because these are the zones only where the film, and the stamp are in direct contact. So, this will also lead to structures with 2-D order; as there will be a

spatial variation in the extent of contact, which will transfer into a spatial variation in the extent of capillary rise.

So, today's lecture I will stop here. I give you some examples where we could we solve how beyond the master patterns or patterns with complex geometry can be obtained by capillary force lithography using simple stamp in one case and a combination of a simple grating pattern stamp, and a grating pattern substrate in the other case. We will continue our discussion and soft lithography with two more things, there are going to come up; one is how to make chemical patterns that is the micro contact printing in little bit detail, and couple more examples beyond the master patterning where other than creating 2-D structures you control other parameters to make more distinct structures from the original stamp, thank you.