

Soft Nano Technology
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Lecture- 38
Spin Dewetting

Welcome back, now on the 38 Lecture of the course. We have been discussing a how to coat or what happens when one tries to coat a thing film on a topographically pattern substrate.

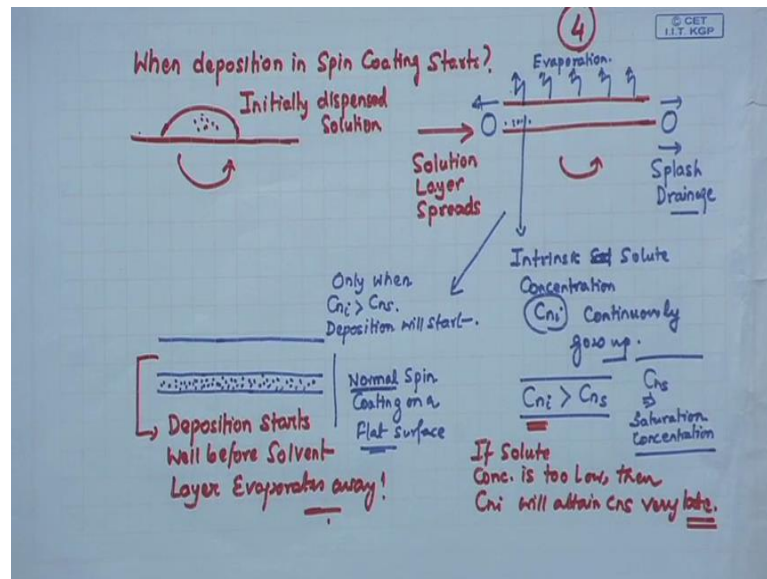
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And we have just realized that there is in fact, a critical concentration only above which a continuous film might form. Even there are additional complexities like even if a continuous film forms whether the substrate to what extent the substrate is waited by the casting solvent that is an important criteria important criterion.

The waiting in the sense whether the equilibrium contact angle is of the order of 30 up to 35 or less when you get a film where the undulations of a continuous film or in phase with the substrate pattern. However, if it is higher than that if it is weights less then you actually get a continuous film where the undulations are out of phase.

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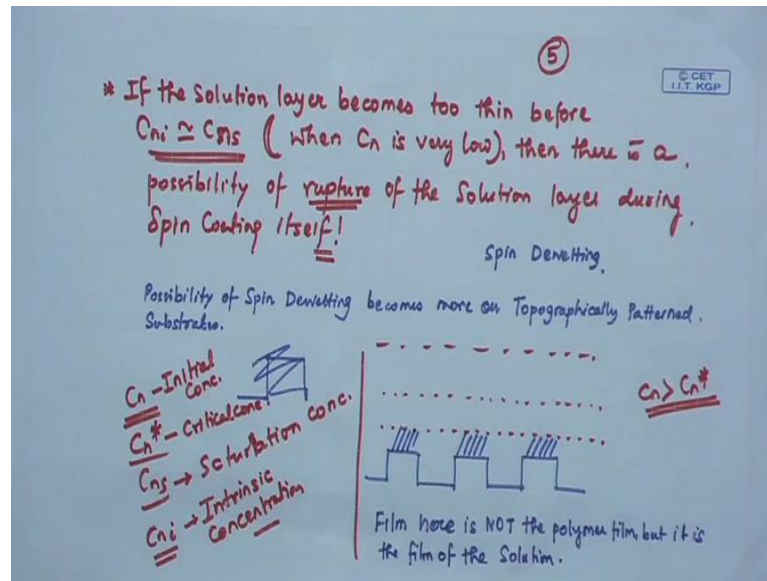


More interestingly, what we were discussing is how you get to this discontinuous film during spin coating itself? And what we realized is a bit certain issues related to spin coating is that in spin coating, deposition of the solute does not start instantaneously as soon as you start the rotation. In fact, the deposition of the solute only starts when your intrinsic concentration matches the saturation concentration. Under regular circumstances when you get continuous film what happens is, this deposition starts well before the solution layer or the solvent fully evaporates away. Or in other words the solution film is adequately thick.

But if you are trying to coat a film where the concentration of the solute is too less then this happens at pretty late stage that the intrinsic concentration matches the saturation concentration. This itself happens at a pretty late stage. However, your solvent is going away continuously, so what happens is your film the solution films, the solution layer which is rotating above the substrate becomes two thing and if incidentally it is thickness becomes in the range of 100 nanometer or less then all the physics that governs dewetting polymer thin film, now starts to trigger dewetting of this solution layer.

Do not forget this has solvent significant amount of solvent. So, it is viscosity is much much lower than a polymer melt and if thermodynamically there is reason for disjoining pressure to amplify the fluctuations then immediately it ruptures. And in fact, under this condition what may happen is that the solution may layer may rupture during spin coating itself leading to dewetting and what you lead to this phenomena is known as spin dewetting.

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The probability of spin dewetting or possibility of spin dewetting becomes more on topographically patterned substrate. Simply because of the fact, I write here that if you have a Nano patterned substrate, its height may not be very large, may be out of the hundred nanometer. So, initially the thickness of the solution layer is much much higher. But then as the solvent evaporates away, it becomes thinner and thinner. At this stage, if you have adequate C_n that is C_n is greater than C_n^* . C_n^* interesting thing is C_n^* and C_{ns} at two other parameters.

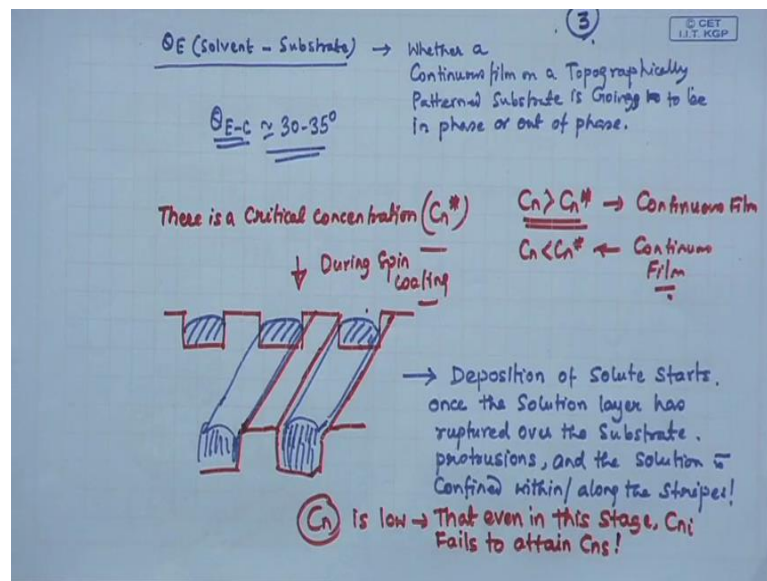
C_{ns} is independent of the substrate geometry because it is the saturation concentration. It is a property that simply depends on the solute and the solvent nothing else. However, C_n^* in fact, depends of the wettability depends on the pattern periodicity geometry and whole lot of things. Then you have C_n which is the initial concentration of the solution which you are dispensing and you also have C_{ni} which is the intrinsic concentration at any instance of time.

So, please do not get confused; it is a bit of many many things because we are learning it in a very easy way, but the physics is really complicated. But anyway I never would like you to feel that your learning something very difficult and everything should be explained very very in very simple terms anyway. So, what happens is if the solution layer becomes too thin which happens when your initial concentration is very very less. Then

of course, over a topographically patterned substrate there is possibility that over these areas the local thickness becomes too less.

And the film here is not the polymer film. Film here I will probably write it down to avoid confusion of the solution that undergoes rupture over these areas. And this spin dewetting in fact, leads to localization of the polymeric threads along the grooves.

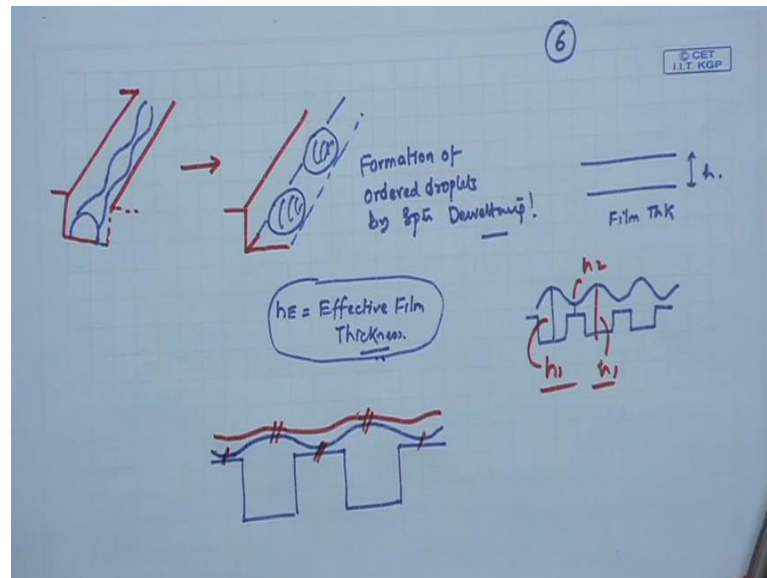
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Now, interesting to note that if so what is typically expected when you not expected in fact happens is when you get this type of morphology like you get threads, polymeric threads along the substrate grooves. Based on our discussion so far what you realize that the deposition of solute starts once the solution layer has ruptured over the substrate protrusions and the solution is confined within or along the stripes.

Well, what happens if your concentration of; so this is the substrate geometry and here is your polymer threads solution threads. What happens if your initial C_n is so low that even in this stage C_n fails to attain C_n^* ? Talking about a situation where your initial concentration of the solution you have taken is so low that even in this stage C_n fail to attain C_n^* . The problem is these are long polymer threads and therefore, they are also subject to Rayleigh instability and that is precisely what happens if the solution concentration is so low that even after the first rupture of the film over the substrate protrusions deposition does not start covering the entire substrate groove then in fact, these solution threads now, rupture within the substrate grooves.

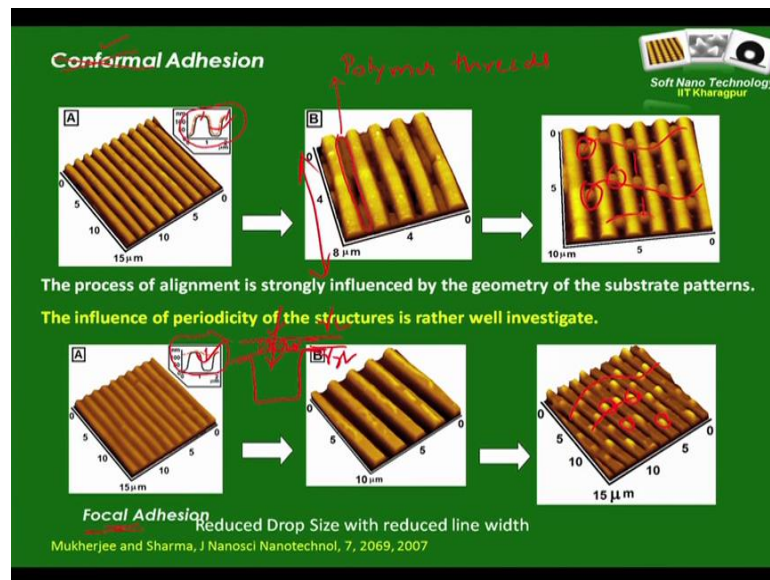
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Let me see if I can draw one. So, here you have a solution thread and this solution thread becomes unstable following Rayleigh instability and it results of course, you have this here it results in isolated droplets of the solution layer were eventually finally, solvent evaporates away and the solute deposits. And did you observe it anywhere? Yes of course, you have observed it.

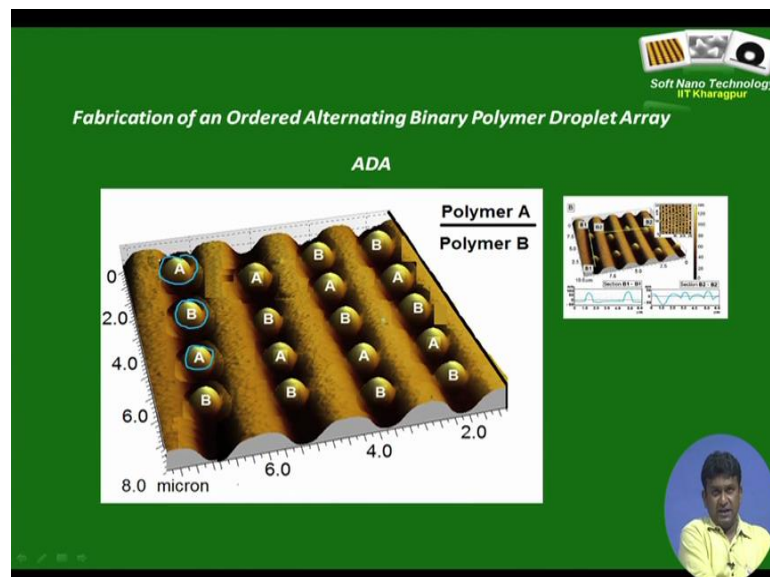
So, when you say that you get a structure like this this is precisely what has happened. And this is in fact, formation one can say formation of ordered droplets by spin dewetting. In fact, this also highlights the strength of spin dewetting because all these happened in a fraction of a minute during the spin dewetting. And have you seen a structure similar to this one?

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Yes, indeed you have seen and you have seen the structure an identical structure over here. And when you actually floated transferred or even dewetted a film for a long time over a topographically pattern substrates. So, this took six hours and in contrast to that spins dewetting in fact, can make the same structure in minutes time.

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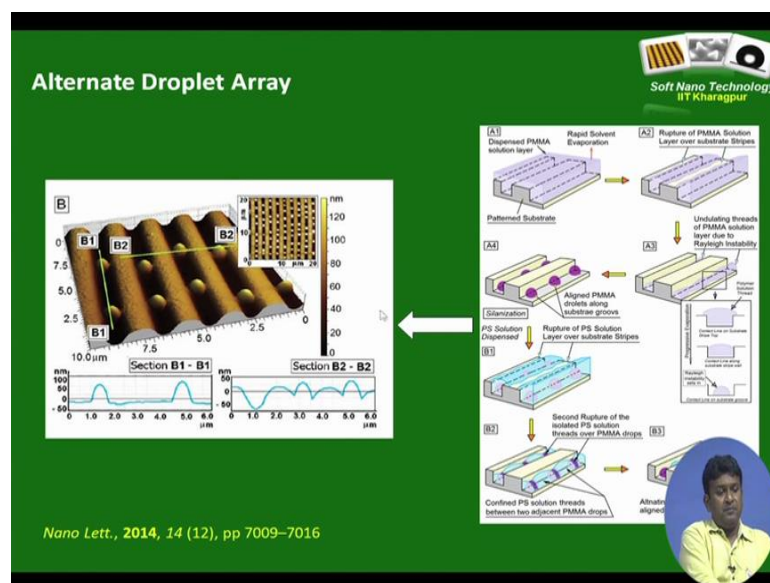


So, that is the advantage of spin dewetting which a very very recent development and it is going to become a very popular rapid nanofabrication tool for sure. In fact, spin

dewetting has been utilized to create a wonderful alternating droplet array. So, you would sort of get to see.

This is in fact, a morphed image. You get to create an array of nearly equal sized polymer droplets, but each alternating droplet is for a different material if you look into the schematic here, you will see that. So, this was shown with PS and PMMA and all that was done was in fact, to used spin dewetting over a topographically pattern substrate down to the formation of droplets twice.

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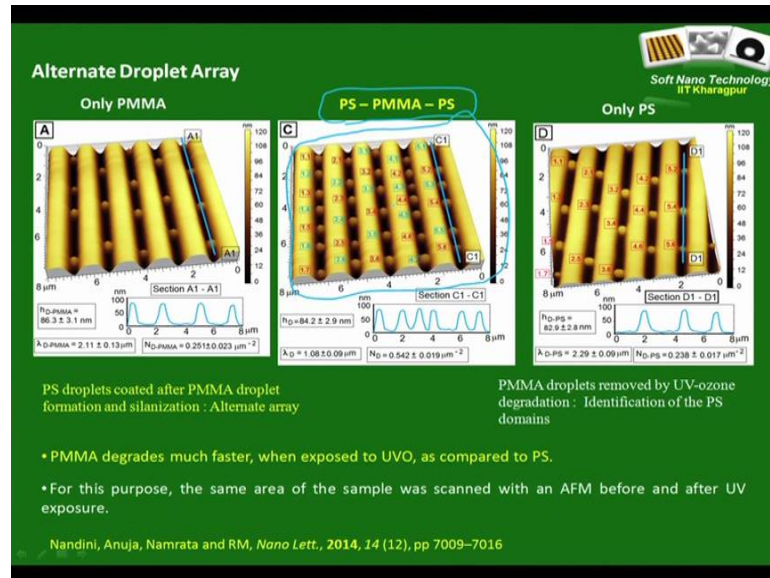


So, first time you use spin dewet of course, your solution layer ruptures over the substrate protrusions, concentration is too less. Therefore, even when the solution layer is confined within the grooves, deposition does not start Rayleigh instability sets in. It leads to formation of droplets of the first polymer which in this particular cases PMMA. Then over this you start coating polystyrene from a solvent which does not dissolve PMMA and all you want to happen or all you ensure; these are all self-assumed. So you do not have to do anything.

In fact, what you ensure is again similar to this step the solution layer first undergoes a rupture over the substrate protrusions, but as it forms the threads now solution threads, here you see the preexisting primary droplets acts a second heterogeneous nucleation sight over which again the solution layer undergoes a ruptured resulting inner area of alternating droplets. Of course, when it is PS and PMMA unit to ensure that there is no

preferential attraction of PS towards PMMA because they exhibit very low interfacial tension. So, in this particular case probably a sailorization step to screen the preferred interfacial interaction was necessary forget about that detail.

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But here you see, you get array and then comes another problem. These are area very similar polymers, but people claim them to be different they are of the same size and your array from shows an image based on which you cannot see anything. You just see a beautiful array. So, how does one identify? In fact, in this picture you can see some of the drops are identified a marked with green and some are marked with red. Turns out that the green ones are PMMA drops, but how do you identify?

In fact, you had one has to do a very careful experiment; one has to take this sample to an UVO chamber because UVO destroys PMMA. So, one can take the advantage of that to preferentially remove PMMA and then rescan again, but then one problem is that one has to ensure that you are scanning the same area. For that one needs to use the marker or something like that under the AFM and so, this is an alternate droplet area.

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Recently very recently some experimental studies on pattern directed dewetting of a bilayer have also come. So, for example, people have looked into the dewetting of a bilayer on a dewetting pattern substrate. And now based on the concept of spin coating on a topographically pattern substrate you understand that the initial morphology can be different types. So, you can have both bottom and top layer to be discontinuous due to spin coating or spin dewetting. You can have the bottom layer to be discontinuous and the top layer can be continuous above that or you can have both the layers to be continuous.

So, there can be various different configurations. See we all ready talked even when we were discussing about bilayer of a flat film there are so many complexity associated with the bilayer of a flat film. And now you understand on a topographically pattern substrate because of the phenomena of spin dewetting, you can have extremely complicated situations and therefore, that in fact highlights why bilayer ordering of an unstable bilayer on a topographically pattern substrate has not been studied so intensively.

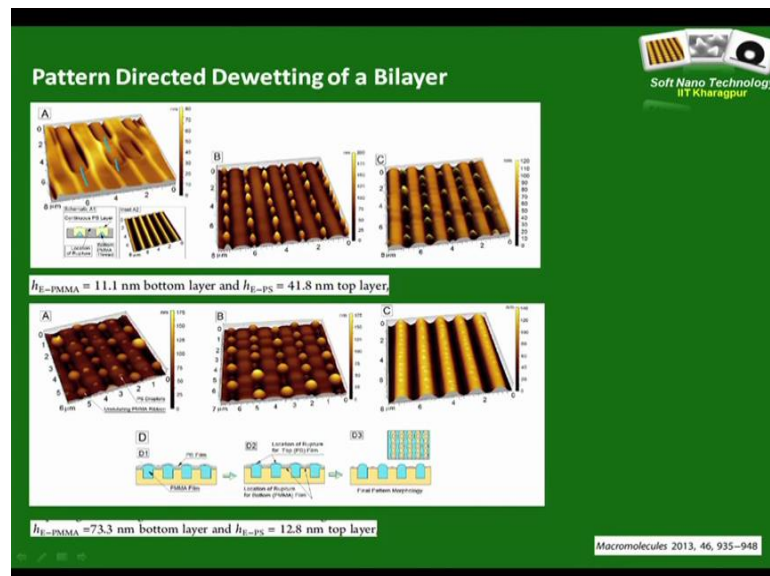
So, again a write your structures in fact, form depending on the initial film thickness. I must also highlight one particular thing. How do you define thickness of a film? A continuous film or a discontinuous film on a topographically pattern substrate because typically we are used to identify this as the film thickness right, but even if your film is continuous on a topographically pattern substrate you have undulations like this where in

fact, film thicknesses is a different. So, a convention is followed is to represent an effective film thickness. What it means is the coating condition or the coating the casting solution concentration that is used under identical condition, whatever would have been the thickness of a film of this particular polymer or solute on a flat substrate of the same material that is typically termed as effective film thickness.

So, this is a very convenient way because irrespective of whether you have a continuous film on a topographically pattern substrate or a discontinuous film on a topographically pattern substrate, you can always used effective film thickness. So, this alternate droplet array you just saw how it works. This bilayer dewetting pattern directed bilayer dewetting is not included in your course I will try not to include it because it is very complicated.

But you can just appreciate the science for the next couple of minutes is that here you can see that you essentially talk about this initial configuration where both the layers are discontinuous there confined within the grooves. And as you annulet you straight away lead to an array of core shell droplets the bottom layer do get first and then in fact, the Rayleigh instability sets in both the layers leading to the formation of core shell droplets.

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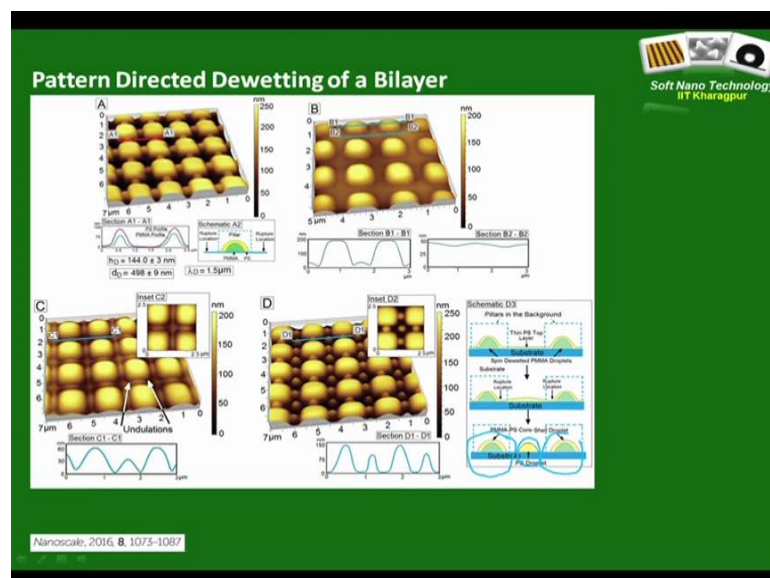
One can show some different levels of ordering, if one looks into a system like this. This is a type two system where the bottom layer is discontinuous and it ruptures into; so, bottom layer is discontinuous and the top layer is continuous, but it is thinness over the

substrate protrusions. And therefore, you can see it is rupturing over the substrate protrusions and gets confined over the substrate grooves and here again Rayleigh instability sets in. But you still get an undulating thread and you can in fact, carefully by removing one of the layers can examine that in fact, the bottom layer ruptured and resulted into area of droplets and over which the top layer was showing continuous, but undulating threads; very fascinating physics and very rich physics in fact.

Here is a very special example where both the layers in fact continuous and it is extremely interesting to note that in fact, when you are coating the second layer it is in fact, in phase with the undulations of the first continuous layer because of the fact that both are polymer and the solvent fully wets the preexisting bottom layer. And you can see that this particular case. So, it is a very fascinating example of how complicated things can become in a bilayer.

So, what I mentioned is that you have a continuous bottom layer like this and then one has a continuous top layer also and which is in phase. And in this particular case the both the films ruptured. So, the bottom layer ruptures over the substrate protrusion. The top layer ruptures over the thinnest areas of the preexisting bottom layers. And this in fact, results in a very beautiful structure where these large droplets are PMMA ribbon and the droplets resting on the substrate protrusions at p s droplets.

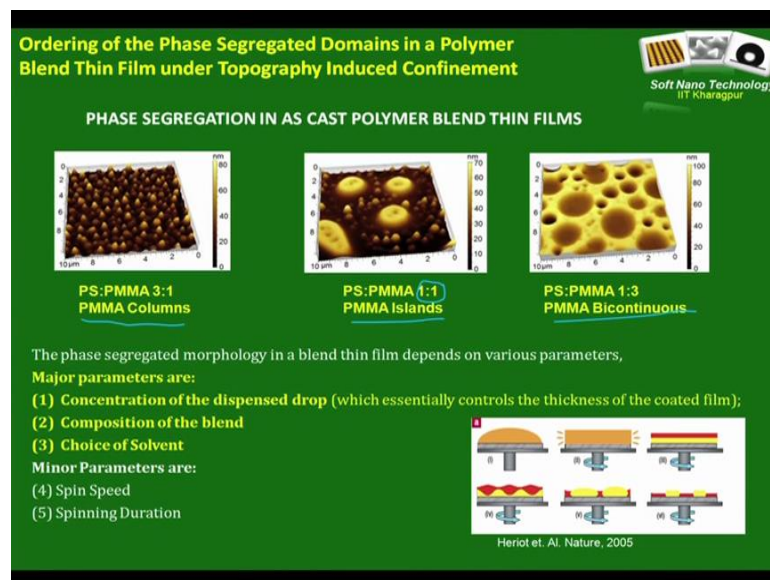
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So, you see you can create multifunctional surfaces. One can also use pattern directed dewetting on a cross pattern substrate to create great looking structures. For example, this is again in fact, a type of an alternating droplet array resulting from a combination of spin dewetting and dewetting of the top layer.

But here the issue is that one of the drops is a core shell drop and the second drop is a bear polystyrene drop subsequent one is again a core shell drop. So, these parts are just for your appreciation. So, that you enjoy how creative science can be at the highest level, but for your exam you do not have to worry about the dynamics.

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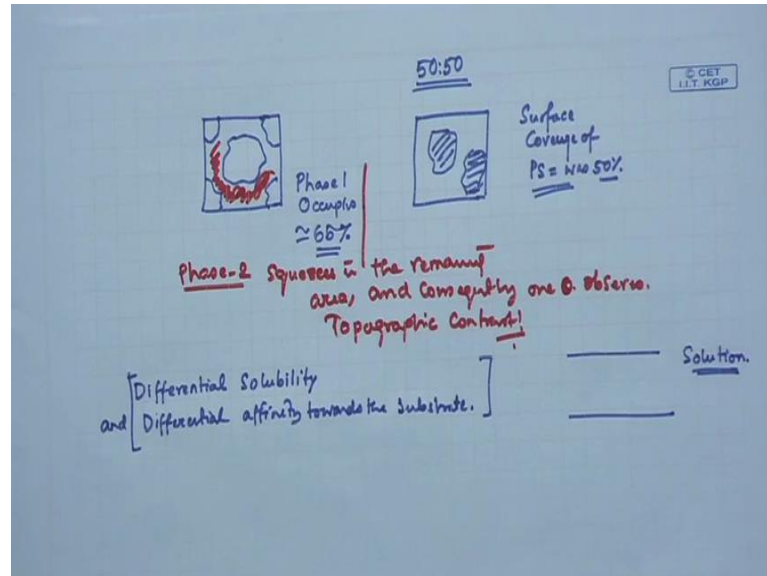


I will just quickly move on to another very interesting area not a bilayer, but it is called a blend. All you do is that you have a common solvent in which let us a two polymers which they are immiscible, you sort of mix them and spin coat them right. So, one classic example can be you take some toluene in which both PMMA and polystyrene dissolves and you simply mix them and spin coat on a flat surface. And what you see that unlike a homo polymer in fact, you do not get films which are flat instead you actually get some a topographically structure films straight away.

So, how does it happen and why does it happen? Simplest way to explain it is to consider or realize that the two polymers that are you have taken though they have solubility in the same solvent have different properties. So, very simple way of putting it, so for

example, if you look at this particular image it is a one is to one blend. So, 50 percent PS by weight 50 percent PMMA by weight.

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Now had the two polymers so, its 50:50 had the surface coverage of let us PS one was 50 percent. Suppose 50 percent of the surface was covered by phase one is the polystyrene would have covered 50 percent of the surface. Then the remaining 50 percent of the surface would have been conveniently covered by the other phase and you would have still seen in fact a flat surface.

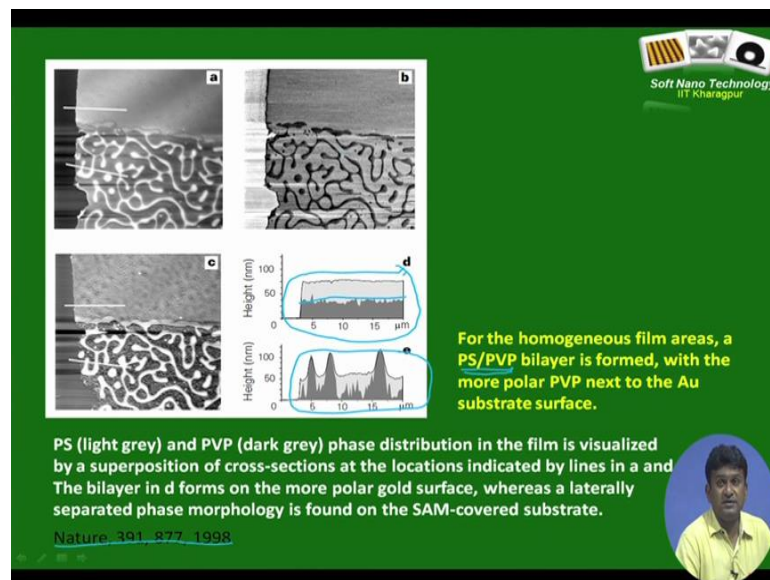
In fact, it would have been very fascinating to in fact, create chemically in homogeneous flat surfaces. But unfortunately that does not happen. Why does not happen? Simple way of understanding it is not the mechanism. Simple way of understanding is one of the 50 percent phase, let us say occupies let us a phase one occupies is that numbers I am taking to make it understandable 65 percent.

So, what it means that phase one is sort of preferentially waiting over the substrate. So, what does phase two do, the other phase because mass has to be conserved it cannot evaporate away. It is a polymer. So, the vapor pressure is low. So, its squeezes in the remaining 35 percent of area and naturally what will immediately happen. So, the phase two consequently one observes topographic contrast. There are lots of arguments to how these phase segregation happens because initially you are taking a solution where both the phases are completely miscible.

However, what is important to understand the though phases are completely miscible, these two polymers will have differential solubility even towards the same solvent and often they might have differential affinity towards the substrate. These are important parameters. So, there can be differential solubility there has to be and so now, it is easy for you to understand that if in the same solution you in fact, know that a the intrinsic concentration has to attain the saturation concentration then only the deposition will start. And therefore, it is obvious that the polymer phase which has lower solubility will in fact, start to phase segregate ahead of the other polymer. And therefore, that deposits when the substrate is flat.

The second polymer which has in fact, higher solubility will take some time to get start depositing and therefore, by the time the surface might have been filled up by the first polymer to a large extend. Therefore, the second polymer sort of makes taller domains. So, this is one of the possibilities. There is also possibility that out of the two polymers one polymer preferentially spreads over the surface. So, that might in fact, attract this is particularly valid if you have polar polymers as an example I am going to show very soon.

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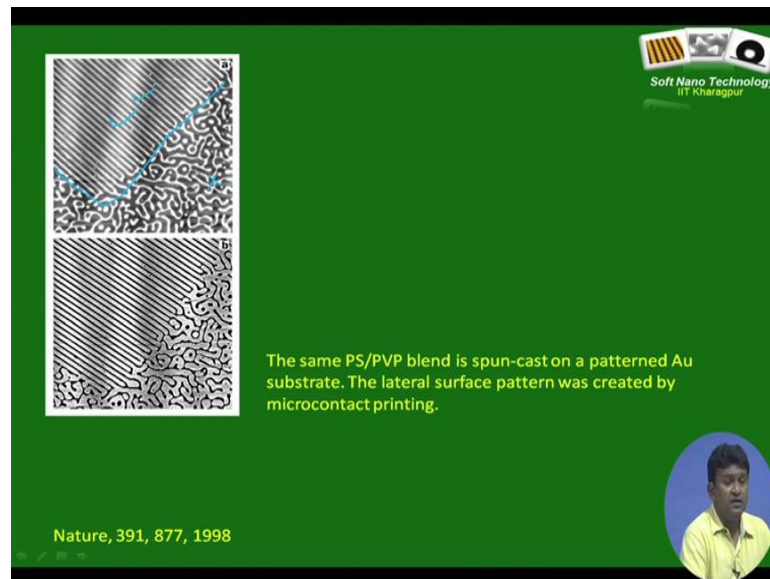


This will particularly attract one of the phases ahead of the other and in fact, there are examples where for example, this is a beautiful example with polystyrene PVP. PVP polyvinyl is an extremely polar around a gold coated surface. You in fact, do not get a

phase aggregation at all. You in fact, get almost a bilayer because of the fact that PVP has preferred orientation towards gold.

In contrast, if you take a SAM coated self organize monolayer coated substrate which is neutral to both the polymers. You see phase aggregation. This is in fact, a pioneering work about twenty years back that was done and published in nature by Woolwich Tyner where they in fact, investigated all these issues. And this in fact, also gave people the clue to align this random phase segregated domains even in a polymer blend by taking a chemically pattern substrate.

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For this particular example again gold stripes were created on a flat surface by micro contact printing. So, it was gold substrates which were micro contact printed with SAM and one can clearly see, these areas there were no pattern. Therefore, you see phase segregation. However, these areas there were the neatly aligned gold stripes where the PVP interacted at here is to the gold surface and other phases polystyrene goes over to the SAM.

So, these are again chemical patterns being very cleverly used for aligning polymer blends. Blends are a huge topic and I just wanted to give you a flavor because we are talking about thin film instability. Unfortunately in this particular course I will not talk about blending in great detail, but there are lots of other courses and material on polymer blend thin films. Even blend thin films dewet if you anneal them. But there can be a

situation why the film does not dewette, but the domains may further reorganized depending on their viscosity molecular weight affinity towards a surface relatively spreading coefficient etcetera. So, it is a whole very very demanding area of polymer thin film were lot of research activities going on.

So, with that we sort of come to the end of a dewetting and while talking about dewetting me also talked about spin dewetting and pattern dewetting. Only one topic I want to cover remains is another form of instability which is known as contact instability in a soft elastic film. That is exactly what we will cover in the next two lectures and one can also in fact, use contact instability to create some ordered structures. Again to create structures which is not a mere negative replica of the patterns; and if time permits, in the last lecture I will do some sort of a quick raping up.

Thank you very much.