Soft Nano Technology

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Lecture - 37
Pattern Directed Dewetting – 2

Welcome back, we were discussing about pattern directed dewetting or how to align the spontaneous instability structures arising out of dewetting of a polymer thin film and towards that end, we have all ready discussed that one of the root is to dewet the film on a chemically pattern substrate, where you essentially want to trigger your rupture of the film over the areas where the film is non wettable where the substrate is non wettable.

Second thing we moved on is the possibility of aligning this on topographically pattern substrates and we just hinted, I just hinted to the fact that if you directly spin coat a film on topographically patterns substrate, you are not going to gate film with uniform thickness.

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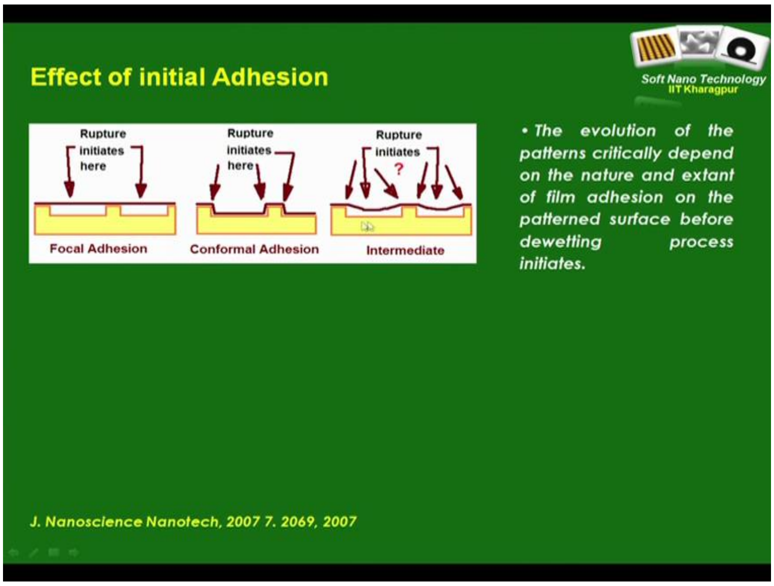

Effect of initial Adhesion

- The evolution of the patterns critically depend on the nature and extant of film adhesion on the patterned surface before dewetting process initiates.

J. Nanoscience Nanotech, 2007 7. 2069, 2007

Therefore, initially experiments that were aimed at aligning dewetting structures on a topographically pattern substrate, the samples were prepared very carefully by transferring them and even them we just discussed that depending on how you pick up your sample during the transfer process, you might have a focal adhesion, where the film in fact, touches only the race protrusions of the substrate and hangs feely you over the other areas or a conformal adhesion.

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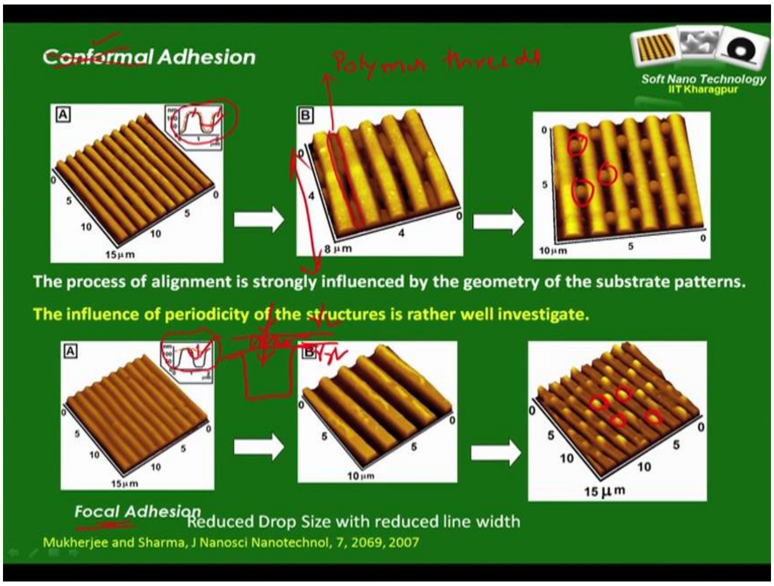

Conformal Adhesion

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The process of alignment is strongly influenced by the geometry of the substrate patterns.

The influence of periodicity of the structures is rather well investigate.

Focal Adhesion

Reduced Drop Size with reduced line width

Mukherjee and Sharma, J Nanosci Nanotechnol, 7, 2069, 2007

And this slide in fact shows a film of roughly the same thickness, I think it was tougher of forty nanometer was picked up on a grating substrate and this particular set of AFM cross sectional image. See here that advantages of the cross sectional image using AFM because you now know that you can take cross sectional image.

So, here you see by looking at the cross sectional image, you now know that in this particular case this is right here the heading is missing in fact, it is here sorry everything is right I am sorry. So, here you can see that the initial configuration of the film is it is in conformal adhesion. In contrast here the configuration of the film is it is in focal adhesion. And it turns out that if you allow this film to dewet these films rupture over the top of the substrates types and the entire amount of polymer goes and accumulates within these threads. Now what you get is you get these threads or you get these grooves filled up with polymer threads. And does it remind you of something? These are long right because this grating sought of ramp for several millimeters.

So, we talked about a form of instability that is manifested only in threads and yes it is reliance stability and therefore, these threads eventually disintegrate and you get droplets which are now aligned along the grooves, along the direction of the substrate is fine, but they are now resting inside the grooves. You can clearly see it in the AFM image. In contrast, if you have a focal adhesion what happens is over these areas where the film is hanging the surface energy penalty is maximum, because this is gamma L, this is gamma L. In contrast two areas where this is gamma L, but this is gamma SL of this side right. So, these areas correspond to the higher surface energy penalty and therefore the film ruptures here. Preferentially it is (Refer Time: 03:55) that I will show you nice video in the next slide.

So, what happens is the entire polymer accumulates over the top of the stripes. There again very long threads of polymer which eventually disintegrate due to Rayleigh stability, but here you see same thickness of film dewetting on the same template or the droplets are resting on the top of the stripes. So, what is the take home message? You can not only align on a topographically patterns substrate, not only align by dewetting on a topographically patterns substrate. But you can also by simply varying the initial conformation of the film which respects to the substrate patterns; you can control the positioning of the droplets. So, that gives you more flexibility in terms of controlling your morphology.

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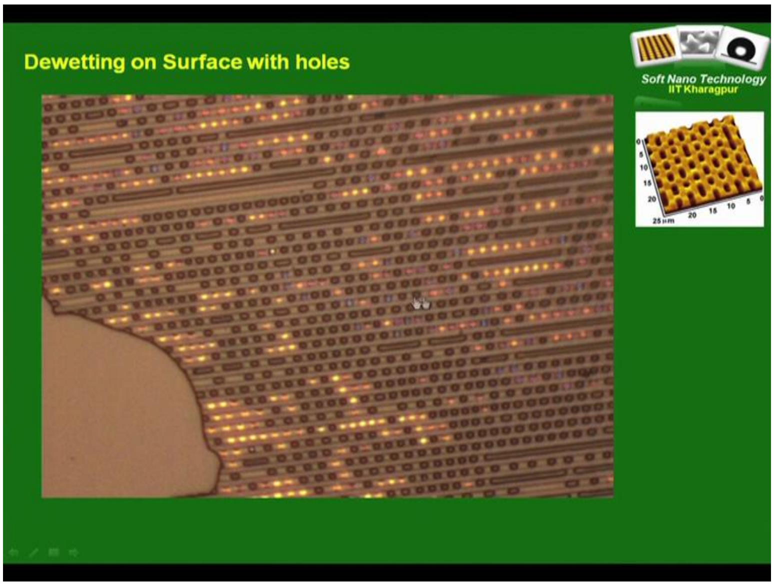
Dewetting on Surface with holes

Here is a slide, before here is a movie before I tell what it is; I will just give you a prelude. You have a template like this comprising area of holes and how to make it? By soft lithography of course, it is very simple. You take a stamp that comprises array of pillars, you emboss it and you get a hole like this. But we will see that in fact, this template or the substrate has been made using a grating patterns substrate and that is what we are going to learn when in one of the subsequent lectures remaining when we talk about elastic instability. But anyway a film was floated a polymer film was floated and top of this and it was exhibiting focal adhesion.

So, here you see, it is some sought of what I am showing is a snap short some intermediate stage. You see this part there was no pattern right. I am sorry it as again started to move. Anyway you see some of the holes are appearing to be brown. Over these holes the film is already ruptured, but some holes are appearing to be very bright yellow. In fact, those are the holes over which the film is still hanging. And all that has been done is in fact, this film has been exposed to the temperature of the film has been raised beyond this glass transition temperature.

And now see what happens? You see at certain locations some flash bulbs are going off right. You can see some of them are going off right here. And see some places they are going off and those are the areas over which the film that was hanging over these holes are rupturing and rupturing rather explosively. The rupturing there because a surface energy penalty is maximum there. I will repeat the movie again. You see, you can clearly see the some of the brighter holes that changing color and in fact, what it represents is this; whenever the hole was bright the film was hanging initially and then when you (Refer Time: 06:45) sort of rather explosively rupture of these areas.

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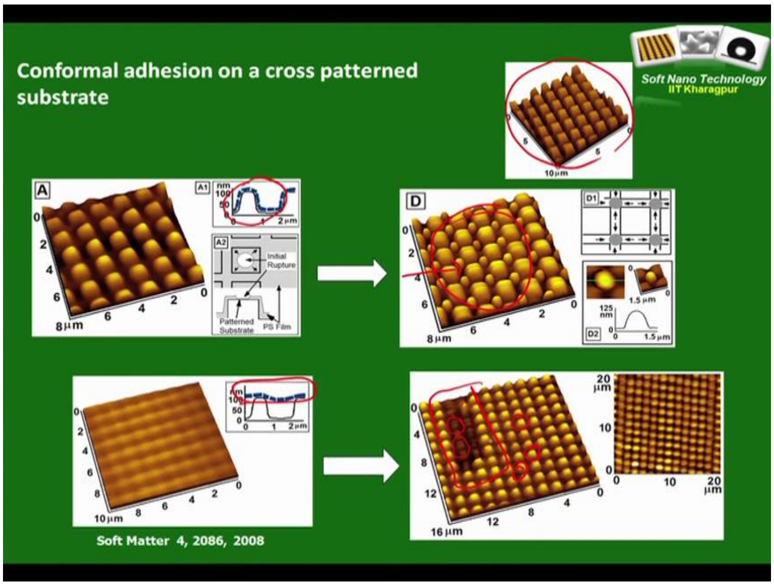

Conformal adhesion on a cross patterned substrate

Soft Matter 4, 2086, 2008

One can take a more complicated pattern like array of pillars and one can show that you can create more ordered structures in both the directions. So, with the 1D pattern substrate you can confine the structures, but the revolution in the other direction is start of not correlated to each other. So, you get order that is of these droplets, but see they are periodic within the stripes, but their orientation or ordering across the stripes is not periodic. You cannot control that. Same is a situation here, but if you take a 2D pattern substrate, it is obvious that you sought of predetermine the location where your drops are going to sit both in x and y and you can get a neatly ordered array of this beautifully ordered array of these drops.

Of course, here also the conformation is important because if the conformation is conformal then it goes and makes arrays is like this. In contrast if you have a focal adhesion you see that in fact, this is an image which is partly defective because you see, over some of the pillars due to whatever reason probably the film ruptured during transfer or something there was a no drop. And therefore, in the same frame the substrate is also visible otherwise it is very difficult to convince somebody that see the droplets are actually sitting on the substrates. But now if you look into the AFM image carefully, you can see the substrates which have divide of the droplets and some of them appear to be very bright because a drop a dewetted polymer drop is on top of them.

So this is in fact, a very very fascinating way of not only ordering your instability structure of the dewetted structures, but also a position them. But everything comes at a price such a wonderful technique is associated with a nightmarish sample preparation technique with this transfer.

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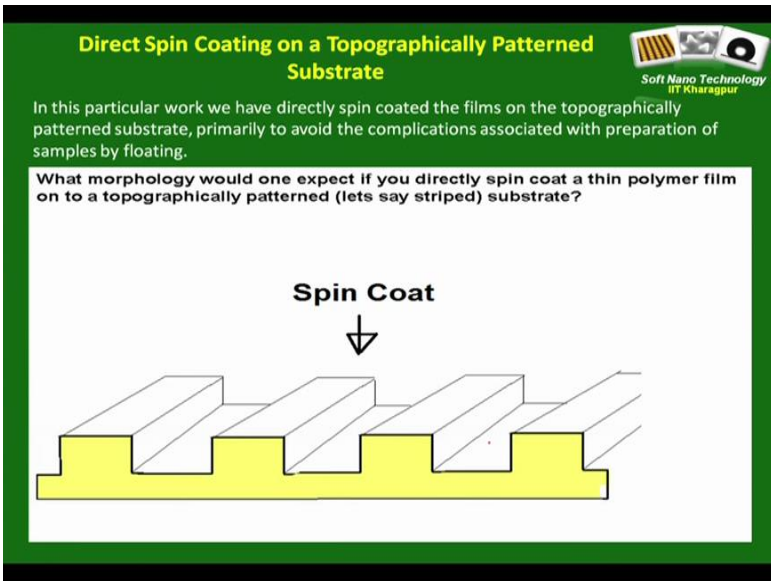

Direct Spin Coating on a Topographically Patterned Substrate

In this particular work we have directly spin coated the films on the topographically patterned substrate, primarily to avoid the complications associated with preparation of samples by floating.

What morphology would one expect if you directly spin coat a thin polymer film on to a topographically patterned (lets say striped) substrate?

And therefore, it was decided to do away with that and people decided to look into the reality of what happens if you spin coat a thin film or a topographically pattern substrate.

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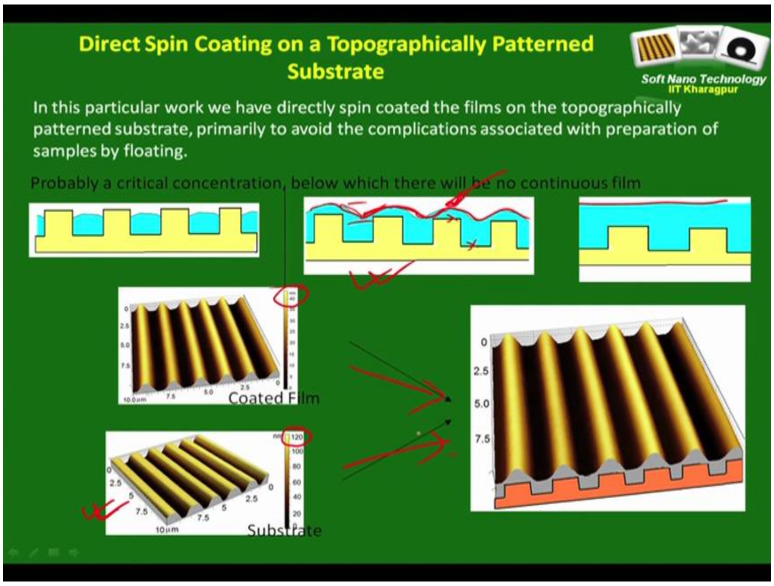

Direct Spin Coating on a Topographically Patterned Substrate

In this particular work we have directly spin coated the films on the topographically patterned substrate, primarily to avoid the complications associated with preparation of samples by floating.

Probably a critical concentration, below which there will be no continuous film

What most likely a happens is, what you would expect to happen is that the first thought that will come to your mind is, well probably you may not get a continuous film at all; if you are trying to coat something that is too thin. Too thin; what is too thin again? Too thin is a vig term, but the thought that might be coming to your mind is, well if my film thickness is too thin compared to too low compared to the height of the patterns, we will probably not get a continuous film. We will get film in which the polymer will the solute will be deposited only within the substrate groups.

Therefore, the subsequent thought that comes is well, if you have adequate material to covered the entire substrate and what is why you need more material as compared to a flat surface because you have more interfacial area because topographic structures. So, immediate thought that comes is that if you have adequate material to cover the substrate probably you are going to get a continuous film that covers the substrate.

But yes, because of the presence of the substitute topographies you would not most likely get a continuous film. You will get a film with an undulating top surface and how does it undulate? Probably the undulations are most likely going to be something like this. And now if you have, you are trying to quote a film which is very very thick particularly the film thickness is orders higher as compared to the thickness or height of the substrate patterns, you will asymptotically get nearly flat film.

Here is again a problem even if you would like to verify this morphology how do that? Because an AFM, please remember will allow you to scan only the top surface. AFM will not give you any idea about the interface. In fact, while I was talking about dewetting of a bilayer in one of the previous lectures, this is one of the problem there I really highlighted that there are very few experimental studies. I will show you some very recent ones. There are very few experimental studies on devoting of a bilayer and one of the reason is tracking the interface is itself a very very big challenge.

Anywhere so, if you want to verify well, how is the morphology looking? What did you do? If you are a good experimentalist what you will do? You will scan the substrate before coating and this is how very careful experimentation in this type of areas are in fact done. So, you scan you would like to scan or you would like to get an idea about the sample at every step. So, you would like to scan the substrate before the film is coated and you look into the morphology after coating. You see couple of interesting things.

Well the periodicity of the patterns as expected they are same. And what you expected? You expected something like this. You expected some undulations, but the undulations were likely to be sort of lower in amplitude as compared to the height of the features right. AFM gives you the heights absolutely no problem. You look very carefully that here the height is 120 nanometers; here the height is 40 nanometers.

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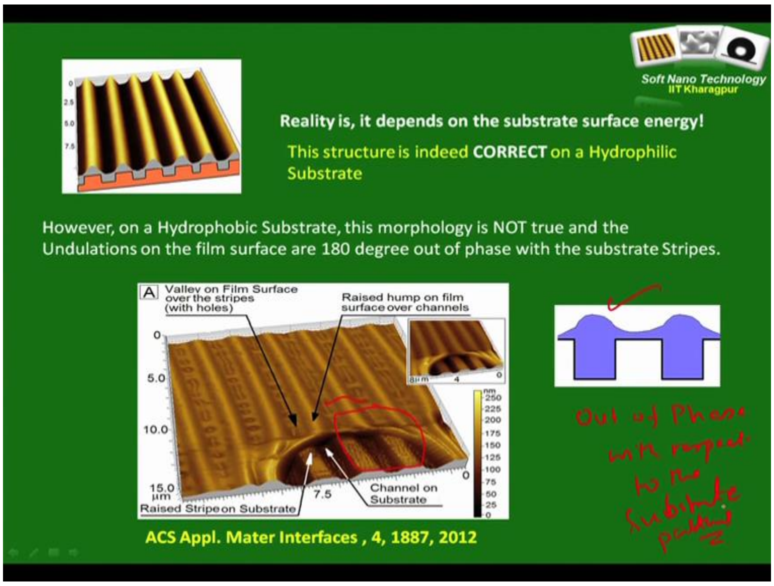

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Reality is, it depends on the substrate surface energy!

This structure is indeed **CORRECT** on a Hydrophilic Substrate

However, on a Hydrophobic Substrate, this morphology is NOT true and the Undulations on the film surface are 180 degree out of phase with the substrate Stripes.

ACS Appl. Mater Interfaces , 4, 1887, 2012

Out of Phase with respect to the substrate pattern

So, everyone is now convinced that this is the morphology. Turns out this is what spin coating was developed around mid-fifties that turns out that this is what everybody believed. (Refer Time: 12:24) exception either till this particular image received the attention. And what do you see here is that you have a continuous film coated on a topographically pattern substrate which has undulations on its top surface and it turns out or you find that the undulation peaks are actually resting on the substrate valleys. You look very carefully I will take a minute to highlight it again to all of you. This is the very very important observation I do not want to spoil the AFM image with the markings.

So, what you note is look into have all your attention over this particular area. What you see that as per your expectation, you have an undulation. You have an undulation on the top surface of the film, but this is the very carefully prepared sample where a part of the film was stripped off so that in one AFM frame morphology of the film as well as that of the substrate can be captured and that reveal something very very fascinating. What it reveals is this undulation on the top of the film surface in fact, rest over the substrate valleys.

So, this is the correct morphology not what we had discussed here. This is in fact, wrong and so, what you understand this is the morphology is out of phase with respect to what, with respect to substrate patterns.

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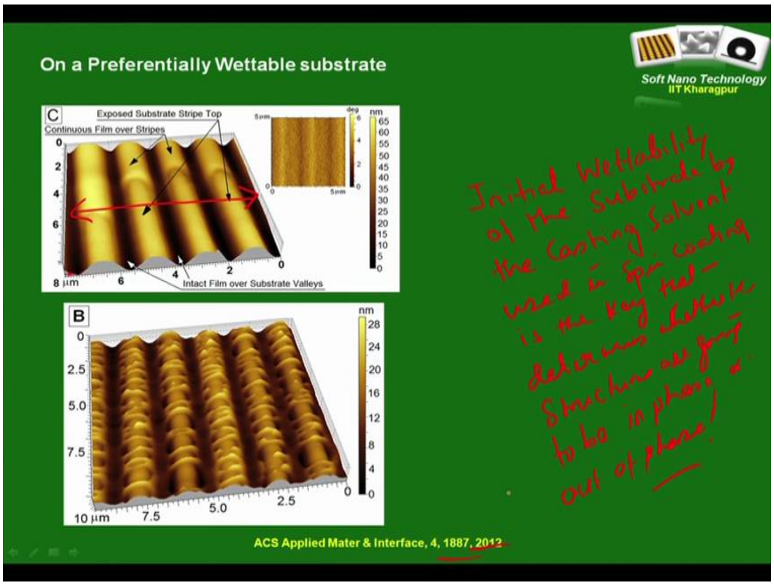

On a Preferentially Wettable substrate

Initial Wettability
of the Substrate by
the Casting Solvent
used in Spin coating
is the key that
determines whether
Structures are going
to be in phase or
out of phase!

ACS Applied Mater & Interface, 4, 1887, 2012

So is it always the case and more examination in fact, reveal that is not the case you in fact, get perfectly in phase structures as per you expectation. But what is in fact, the critical thing then? The critical thing is a very interesting thing. In fact, please do not also term the substrate to be hydrophobic or hydrophilic because you do not have water in the system.

It turns out the initial wettability of the substrate by the casting solvent used in spin coating is the key that determines whether the structures are going to be in phase or out of phase; in fact, such an important topic only realized in 2012.

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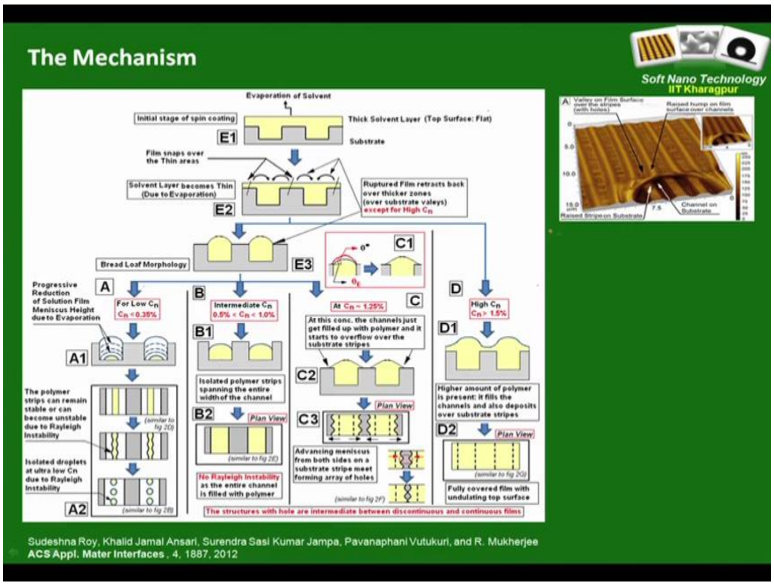

The Mechanism

Sudeshna Roy, Khalid Jamal Ansari, Surendra Sasi Kumar Jampa, Pavanaphani Vutukuri, and R. Mukherjee
ACS Appl. Mater Interfaces, 4, 1887, 2012

So, once you understand that and the mechanism in fact, when you look into the mechanism in fact, it becomes very very clear that something people have missed out because the samples were not properly investigated. Well if the contact angle and it is what is the critical value of this so called weighting and not weighting is not even in ninety degree.

So, it turns out that if the contact angle of the solvent casting solvent is of the order 30, 35 degree then you essentially head for a out of phase structure.

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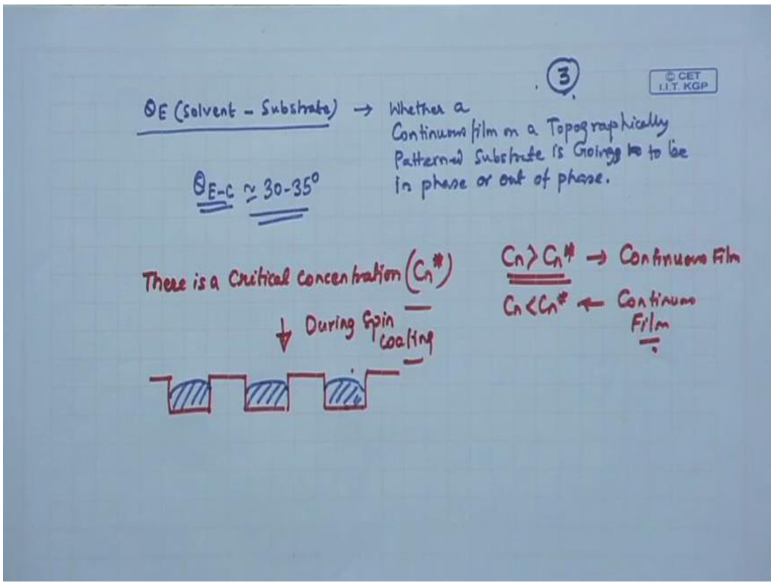

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θ_E (Solvent - Substrate) → Whether a Continuum film on a Topographically Patterned Substrate is Going to be in phase or out of phase.

$\theta_{E-C} \simeq 30\text{-}35^\circ$

There is a Critical concentration (C_n^*)

↓ During Spin coating

$C_n > C_n^*$ → Continuous Film

$C_n < C_n^*$ ← Continuum Film

So, equilibrium contact angle between the solvent use during spin coating and the substrate. This is the critical thing that determines whether a continuous film on a topographically patterned substrate is going to be in phase or out of phase. And this critical value is of order of 30 to 35 degree; nothing to do with 90 degree.

So, what happens is if the contact angle is of the order of 30 degree or something like that you see that the meniscus that your liquid makes with the substrate is something like this and once you agree to that in fact, it is very clear that you are going to get a structure that is out of phase. I will not going to the details of the mechanism that is the big too demanding, but it is there in the PPT. So, you can have a look into it carefully.

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Initial Film Morphology on a Non Wettable Grating as a function of Concentration

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On a wettable Grating

The undulations are in phase

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What turns out that of course, you get a continuous film, you analyze that and before a critical thicknesses at below it. So, I will put it like this. There are topographically patterns substrates. So, this is one of the issues, what is the configuration of the film on the topographically patterns substrate? But the other issue is when you actually start getting a continuous film that is essentially the first concerned that was raised. This was not exactly a concern, this was sought of it came out as an off shoot that there can be radiation in the configuration of the film, but this is in fact, the first concern.

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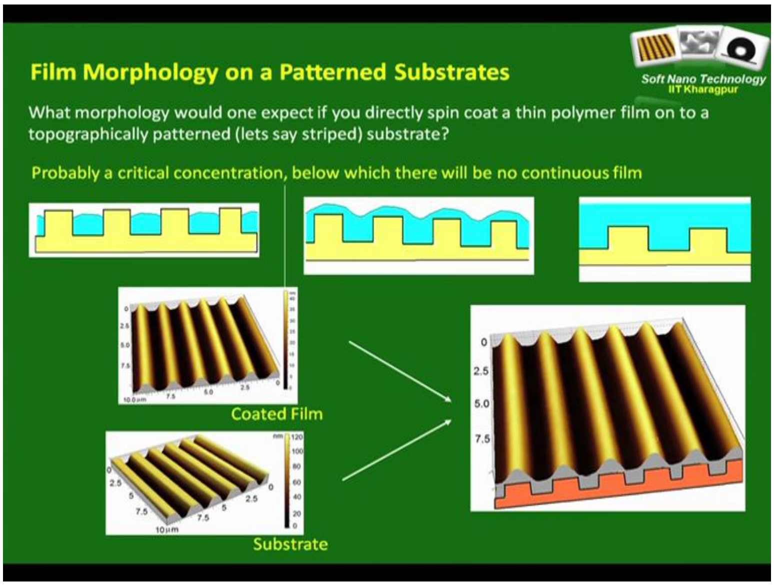

Film Morphology on a Patterned Substrates

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What morphology would one expect if you directly spin coat a thin polymer film on to a topographically patterned (lets say striped) substrate?

Probably a critical concentration, below which there will be no continuous film

Coated Film

Substrate

So, when does this transition take place and careful experiments in fact reveal that there is a critical concentration, let us mark it as C n star. So, if concentration of your casting solvent is greater than C n star to get a continuous film. However, if your C n is less than C n star, you do not get a continuous film fair enough that is something we were all expecting whether there is a move to the story. So, what did we expect? What we expected is, if the film is not continuous you will have the material somewhere into the substrate.

And how did look like? Probably we all expected that it will be something like this. It traits good enough but turns out that if you go on reducing the concentration of the solution, you do not get trades you in fact, start getting droplets straight away. And then if you look carefully, it turns out that it is logical because if you have these trades which are very low in polymer concentration, they in fact break down due to Rayleigh instability and result in these droplets. But when does this?

Even for example so, if you want to look carefully that during spin coating itself, this type of morphology is obtained. So, you can look into this particular AFM image for example, which very clearly shows there must be some numbers corresponding to the figures don not worry about it. You get isolated stripes of the polymer within the substrate groups. How does it happen? You need to; this is in fact apparently very simple observation science is nontrivial.

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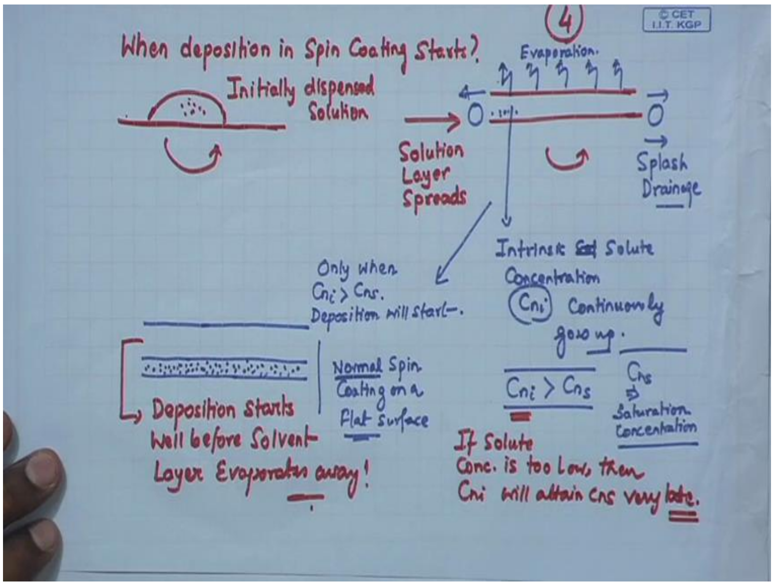

When deposition in Spin Coating Starts?

Intrinsic ~~Sol~~ Solute Concentration (C_{ni}) Continuously goes up.

Only when $C_{ni} > C_{ns}$. Deposition will start.

$C_{ni} > C_{ns}$

Deposition starts well before Solvent Layer Evaporates away!

If Solute Conc. is too Low, then C_{ni} will attain C_{ns} very late.

One needs to go back to the basics of spin coating which we discussed and one needs to understand when deposition in spin coating starts. And this is something that I mentioned or in one of the earlier lectures while I was discussing photolithography. It turns out that you dispensed the solution initially which is dilute a solution and then you rotate it. And then respective of how to whatever is equilibrium contact angle between these solutions and the substrate it is touch to rotate and the solution layer spreads.

So, remember this is on an over a rotating platform. And simultaneously what happens is the solvent of course, there is splashing loss splash drainage. But once the splash drainage is over, what refers the remaining amount of solution which can be in fact, five to ten percent of the amount of initial solution you dispense. That is why people typically term spin coating as a very wasteful technique because significant amount of the solution goes away by splash drainage.

But then once splash drainage is over, what happens is there is continuous evaporation of the solvent and as a result the intrinsic solution concentration continuously goes up right. Do you think such deposition will immediately start? No because this is a good solvent right. So, it has significantly high value of solubility and deposition will only start when C n i exceeds the saturation concentration. C n i exceed the saturation concentration and only then deposition will actually start.

Under normal spin coating on a flat surface when you want to get a continuous film, this deposition in fact, starts. What is normal regular one like you would like to get a continuous film, you do not want to do to any experiments and get discontinue as films like that and get fired by your boss. You want to have normal spin coating, what you choose your solution concentration in such a way that this deposition starts well before the solvent layer evaporates have a fully that is solvent layer is adequately thick.

Why do you want that? (Refer Time: 26:10) let me also ask the question what happens if the solute concentration is too less? If the solute concentration is too less C n i will attain C n s very late. What would this very late mean? It means by that time the thickness of the solution layer becomes also very low and by any chance if the thickness of the solution layer becomes in the range of 100 nanometers. Do I tell you something more?

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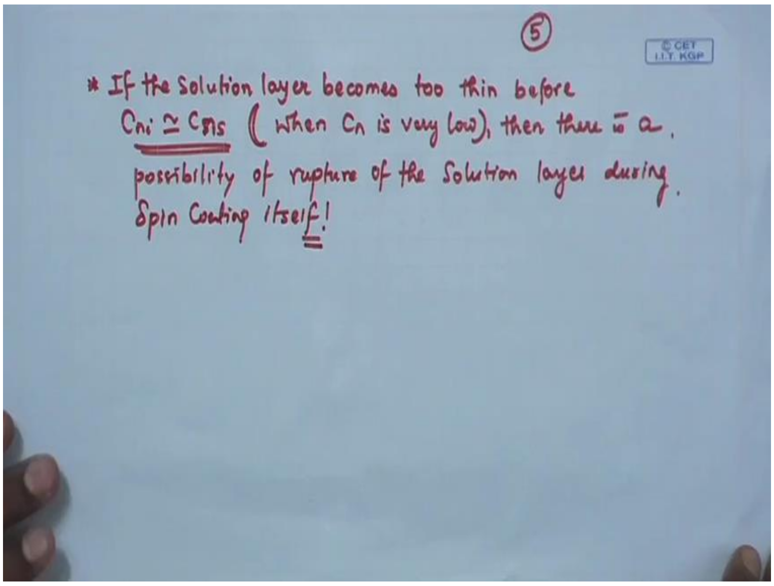

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* If the Solution layer becomes too thin before $\underline{\underline{C_{ni} \simeq C_{ns}}}$ (when C_n is very low), then there is a possibility of rupture of the Solution layer during Spin Coating itself!

Well, then all the physics of Van der Waals interaction disjoining pressure etcetera becomes active for this particular layer. And there is a possibility that this layer itself might ruptured. And I will pick up the discussion is the next class from here, but the take home message is if the solution layer becomes too thin before C n i equals C n s and this happens when C n is very low then there is a possibility of rupture of the solution layer during spinning or spin coating itself.

Hope you understand it. I will pick up the next class from here.

Thank you.