# Soft Nano Technology
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## Lecture – 36
## Pattern Directed Dewetting – 1

Welcome back, now to the 36 Lecture of the course. So, we are nearing the completion. I am not very sure how you have enjoyed while I really hope that you have enjoyed the course and you have been following the lectures and have submitted the assignments. And I would really like all of you to sit for the examination.

Get a certificate and I mean it is very simple, if you have just heard the course, the lectures and gone through whatever material that we have uploaded. I am sure you will do the very very well in the examination. I never ask the questions which I have not taught and therefore, I just check how your able to grab whatever I have taught. So, I really hope to see all of your names appearing in the answer scripts that we are going to evaluate in few weeks time from now.

Any way of course, you are. The other thing is that you can always send in the discussion forum or through the form of email any specific suggestion that you may want to have a specific improvement you would like to have. Of course, please do not forget that the frame work does not allow us to interact inside a class which is of course, the most sorts after and well desired way of teaching at least I feel it that way where at least you get a glimpse of what the subject is and what we do and stuff like that.

So, considering the limitation of this framework, I am sure you have enjoyed the course. Anyway coming back to topic, we have been talking about spontaneous instability and dewetting of ultrathin films. And we have looked into the issues from somewhat theoretical details and now we understand that it is essentially one can look into the magnitude and the sign of let us say a parameter like effective Hamaker, effective interface potential, all let us say the disjoining pressure and one can sort of have a qualitative idea about the stability of the film.

Of course, the entire theoretical framework that we have discussed so for is considering Van der Waals sources because Hamaker constant is the constant that is defined only for

Van der Waals interaction. So, you can always ask what is going to happen in real situations because we have even the neglected the polar interactions. Well it turns out that most of the polymers until and unless you actually take semi crystalline polymers something like that or conjugated polymer to be more precise, they lack the polar interactions. And therefore, their behavior it has been surprisingly found in fact, that is rather well captured based on a theory or formulation that only considers Van der Waals interaction.

Of course, the other important aspect since we are using a polymer so, what we gain is that polar interaction is mostly absent in the system that is true, but what is really lacking in the formulation that we have talked so far and that is where actually deviations in experiments do come in, I must admit that is we are also neglecting the strategic interactions. And now you should all understand that for a long chain polymer molecule the entanglement is indeed there, strategic interactions is there which are neglected in whatever we have talked so far. In fact, honestly speaking considering strategic interaction and issues like that is still at the research level. I mean there is lot of work going on, but it will probably take some more time before these topics make their way into text books.

The other issue is that I did not teach particularly because of the paucity of the time as well as due to I did not want to make the course really very heavy and complicated. I did not the hydrodynamics of thin film which is even in fact; rather simple approach one can just look into the navier stokes equation and do a linear stability analysis. And in fact, one of the resources that I have referred to that is my NPTEL lectures and the web material you can find it there. It is not included in this course, but any of you who are interested, who want to study it further you can always do that.

You will find there that viscosity, the polymer viscosity or the liquid viscosity has been consider similar to that of Newtonian fluid and that is also not correct because of the entanglement effects and this presence of the long chain molecules polymer mails in fact, exhibits significant amount of non-linear behavior or non-Newtonian behavior and those things needs to be incorporated in the development of more precise and accurate theory. But one thing is very convincing that whatever be the precise rheological model that in fact, does not affect the stability that sort of alters the dynamics evolution sequence and some recent experimental studies of course, suggest that they might also altered the morphology during evolutions.

For example, I briefly mentioned that we talked about this rim formation around a growing whole and depending on the level of viscoelasticity. So, if issue is that we are looking at a dewetting of a rather viscous film, the profile of the out of the periphery of the rim or the rim profile is rather symmetric.

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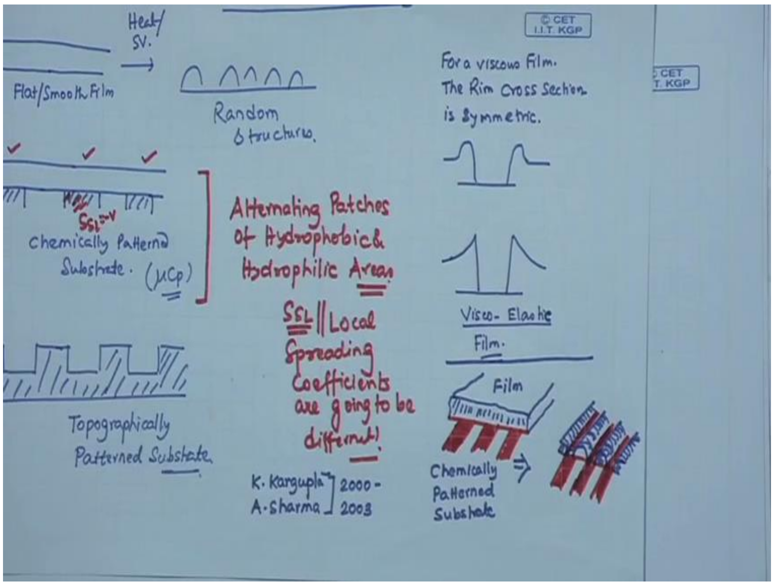

So, what it means is for a viscous film, the Rim cross section is symmetric, that is it is something like this. However, if you looking at dewetting of a strongly viscoelastic film you know, you can choose the molecular weight in such a way that the film exhibits significant level of viscoelasticity, the rim profile of an terms out to be something like this. I am not going into the detail but why it happens, but this has been experimentally observed and so this is how the viscoelasticity affects the evolution morphology in addition to the dynamics.

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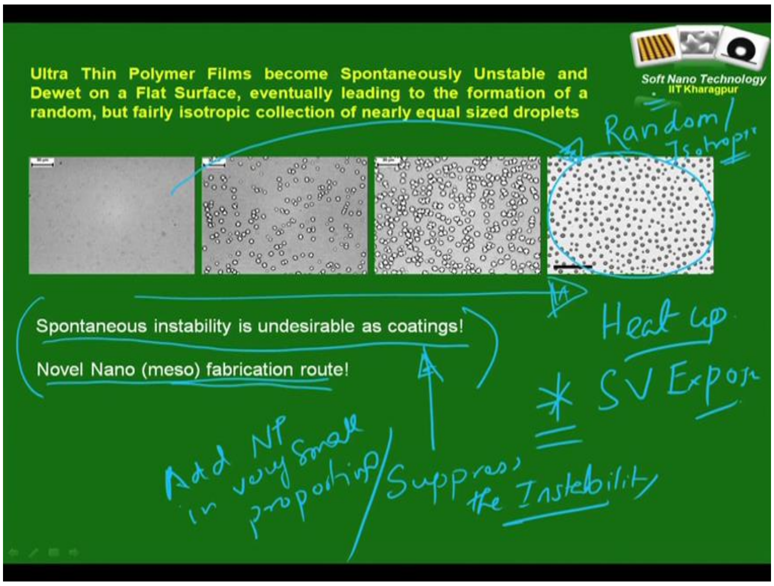

Ultra Thin Polymer Films become Spontaneously Unstable and Dewet on a Flat Surface, eventually leading to the formation of a random, but fairly isotropic collection of nearly equal sized droplets

Spontaneous instability is undesirable as coatings!

Novel Nano (meso) fabrication route!

But, what we will focus in this lecture is something different. See we have, we are now all familiar with this particular picture which is essentially the key evolution sequences of a polymer films. So, you have flat film and what I had hinted that one fascinating aspect is you only spin coat a flat film and do nothing. All you do is this film behave like solid a room temperature because there glass transition temperature is about room temperature, if it is a polyester rim or a PMMA film. In fact, there TG is a close to hundred degrees centigrade. So, at room temperature irrespective of the weight ability of the substrate sin of the effective interface potential you are not going to see any dynamics.

But all you have done in order to trigger this evolution sequence is to heat up the film or to expose it to its solvent vapor. There are certain differences I must admit between solvent vapor exposure and heating up of the film. I do not want to going into all of them, but one of the major things that you may want to consider is that though you consider despite you considering the fact that there is coefficient of thermal expansion, the expansion in a polymeric material is not very large.

Therefore, after heating when the film is about to dewett, its thickness is roughly of the same order as that of the initial thickness of the film. But when you do the second approach that is you do a solvent viper exposure, I have already mentioned that what happen are the solvent molecules entered into the film matrix and they swell. So, one immediate difference that you can observed is that in the latter case, at the point when the film is about to dewett it is actually thicker than its originally thickness.

Anyway for this course again, yesterday when one of the earlier lectures I mentioned that I would like to talk about many more detail aspects of the dewetting. If I take a dedicated course on dewetting; that means, see depending on the feedback and response of this particular course that I will decide. So, if I ever take that I will probably discuss all this in great a detail. However, what is important is irrespective of the precise route is this form of spontaneous instability is undesirable as a coating and I already mentioned that research work is already going on to suppress this instability. And one of the preferred routes is in fact, to add nanoparticles in very small proportion.

So, what happens is in fact, very exciting. Instead of a pure homo polymer film, now you actually have a Nano composite thin film. You have these Nano particles and these Nano particles exhibit dynamics with respect to the polymer chain. In fact, based on the entropic interactions it has been shown by several workers that these Nano particles huge to migrate to the liquid substrate interface. Because what happens is the polymer chains which are again the long chain molecules, their rotational entropy sort off gets truncated because of the fact that they are sticking, the once there are sticking to the substrate. So, if a polymer molecule is release from the substrate and is replaced by a Nano particle in fat that polymer chain gains conformational entropy and that is how the system is thermodynamically favored right.

But again that is a topic I will not touch upon, but what is more interesting is that what I was trying to highlight and got deviated is that you started off with a flat film and you are creating some Nano and meso scale structures. So in fact, instability spontaneous instability in a way is a route for Nano fabrication or novel meso scale fabrication with soft materials. Limitation is we have seen how beautiful the structures you can make while we were studying soft lithography and photolithography. And these structures are random and isotropic.

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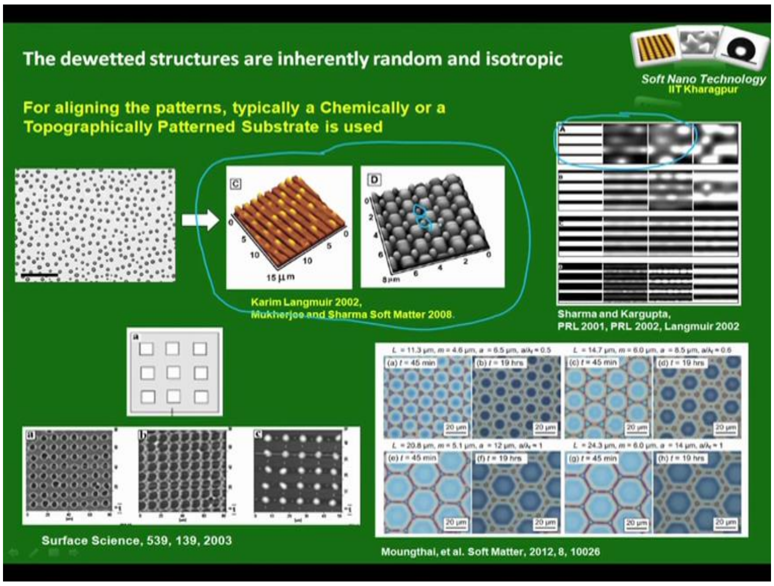

The dewetted structures are inherently random and isotropic

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For aligning the patterns, typically a Chemically or a Topographically Patterned Substrate is used

Karim Langmuir 2002,
Mukherjee and Sharma Soft Matter 2008.

Sharma and Kargupta,
PRL 2001, PRL 2002, Langmuir 2002

Surface Science, 539, 139, 2003

Moungthai, et al. Soft Matter, 2012, 8, 10026

So, such structures are often of no use. So, significant research is in fact, aimed at aligning these structures. You cannot really take a flat film on a flat substrate and align it. In fact, you need to do something and that something turn out to be, there are two very popular approaches and some not so popular research level approaches which people have tried out. In fact, those approaches are to use a patterned substrate and that patterned substrates in fact, includes you can either use a chemically patterned substrate or you can use a topographically patterned substrate to and so, what you do is in a nutshell flat smooth film is what we have talked so far. You either heat up or expose to solvent vapor and you get some random structures.

In contrast what you do is in order to align them; you would like to take either a chemically patterned substrate or a topographically patterned substrate. I am drawing the film on this topographically patterned substrate a big later. Let us consider a chemically patterned substrate. So, now you seamlessly know in fact, how to perform these experiments. How do you make this chemically patterns substrates? You simply make them by micro contact painting. And therefore, what are these chemical patterns? You typically have chemical patterns with alternating domains of hydrophilic or hydrophobic areas.

And now you also know what is hydrophobic and hydrophilic. In fact, with respect to water typically hydrophobic patches will have low surface energy hydrophilic patches will have high surface energy. So, that in fact translates most likely to the fact that the spreading coefficient on one of the patches is in fact, going to be negative; in fact, probably over the hydrophobic patches and the local spreading coefficient over the hydrophilic patch are going to be positive. So, variation to be different and do I really tell you more? The answer is no. So, suppose if these are the areas where the spreading coefficients are negative, let us say these are the hydrophobic patches. Thermodynamically the film is unstable over here whereas, here if the spreading coefficients are positive or they have much lower value in principle, the film is stable over these patches.

So, what are you essentially doing? You have a film which is periodically unstable over certain locations and essentially you would like the film. Now what you are doing is you are specifying heterogeneity in the form of the substrate; in fact, it is a chemically hydrogenous surface. You want the film to rupture over the hydrophobic areas and that is exactly what people have done? People have taken micro contact printing surfaces. So, these are in fact some excellence simulation results and you can create or you can achieve what is known as templating that is, whatever is the geometry of the chemical patterns that gets reflected in the topography of the dewetted film.

So, under perfect templating, this is what the original papers talk about. So, if this is, please understand these are chemically patterned patches. So, topographically they will be roughly smooth. So, you take this is the substrate, let us say rate corresponds to low surface area domains and you take the film on top of that. So, let us consider we are taking a cross sectional view we are talking about. So, this is the film. What you would like to expect under appropriate condition and what are the conditions? Let us not get into that.

You can look into tons of wonderful words by Kajari Kargupta and Ashitosh Sharma around 2000 to 2003, was the area they have lots of talk plus publications on this particular area. And you would expect in fact, if these are low surface area domains. So, you would expect that after dewetting, the film profile could be something like this. Why because I hope the picture is clear to you because over these red zones; so low surface area patches and therefore, it is lightly that the film will rupture over these areas.

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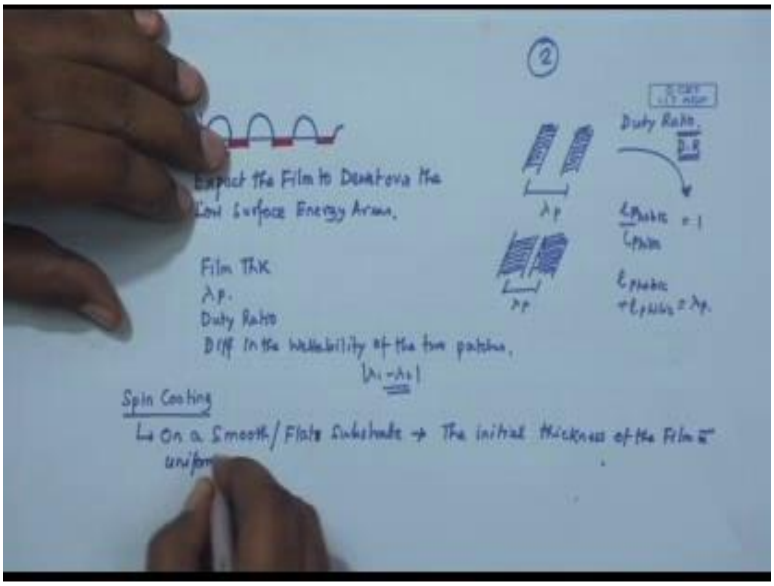

Expect the Film to Dewet over the Low Surface Energy Areas.

Film THK

λp.

Duty Ratio

Diff in the Wettability of the two patches.

$|A_1 - A_2|$

Spin Coating

↳ On a Smooth/Flat Substrate → The initial thickness of the Film is uniform

Duty Ratio. D.R

$\frac{l_{phobic}}{l_{philic}} = 1$

$l_{phobic} + l_{philic} = \lambda_p$.

So, you essentially probably the picture got a bit clumsy; you would expect the film to dewet over the low surface energy areas. However, simulation and subsequent experiments also shows that of course this, first let me discuss this that there is compete I mean there are whole lot of parameters that effect the ordering. Please do not understand that the movement you take a chemically patterned surface, you are going to get order that is not going to be possible because film thickness is a critical parameter. Film thickness also gives you with the natural length scale of instability, the periodicity of the patches, the duty ratio of the patches.

The duty ratio essentially is the term which is like you have let us say, this alternating patches that a periodicity of let us say lambda P. But you see, you can also have structures like this. Same periodicity, but here the ratio or here the width of the let us say hydrophobic patches is more as compared to that of the hydrophilic patch. So, duty ratio is something like a ratio of let us say L hydrophobic minus L hydrophilic. And for this type of a surface of course, you can immediately figure out that summation of this phobic plus philic is going to give lambda P and most of the structure the gratings we have we consider because as a easiest to fabricate often we have this ratio is equal to one for a surface like this. So, this ratio is often referred to as the duty ratio. You can just check out the net what is the classical definition?

So, film thickness, periodicity of the structures. So, let me just make a quick list film thickness periodicity of the structures, duty ratio, differences in the wettability of the two patches that is an important parameter. So, if you have lambda 1 and lambda 2 over here, the magnitude of lambda 1 and lambda 2. In fact, matter is there is a beautiful paper publish something around two thousand seven or eight which in fact, shows that there is a critical value of this lambda 1 minus lambda 2 below which the effect of ordering, it is completely destroyed.

Anyway so, this is the beautiful area, I must also mention a wonderful story and which highlights the strength of stimulation related or theoretical work. This entire work has I mentioned, these are the two pioneers in this field and both are from India IIT Kanpur. The entire development was first simulated and theoretical predicted and experiment subsequently followed. So, this is what good theory can in fact, do. This is how good theory can enrich science.

Moving on what is the other approach. So, the other approach; so, one is patterned direct a dewetting, but to use a chemically patterned substrate and in fact, this has receive to more attention. The second option is to use a topographically patterned substrate. Now and you see we already have some a FM images which actually shows that this dewetted droplets which where random can be beautifully ordered on a topographically pattered substrate. So, for example, if you take this particular figure on the right side, each one of these tiny droplets or dewetted droplets and the cross patterned is a lithographically, soft lithographically fabricated template.

But we talk about this topographically patterned substrate. In fact, I am going to spend some time on this. But does it rim any question on your mind as to why I have not drawn the film on top of the topographically patterned substrate? It is in fact, a very good question to ask and the answer is, the answer to this is not trivial because so far, we have only considered or always considered on a smooth flat substitute and therefore, in the context of dewetting even on in the context of chemical patterned directed dewetting, the initial thickness of the film is uniform.

But if you look at this condition, is it possible for you to get a uniform film thickness if you spin coat. And this is not a hypothetical problem because one thing I would look to remained you that in photolithography, the spin coding is not popular because you would like to do soft lithography or dewetting. Spin coding is popular because photolithography extensively requires spin coding. And in photolithography when we talked about this concepts of mescaline and things like that, you have seen that you might have to coat several layers or you might have to perform photolithography several times and over a preexisting patterned. So, essentially the question of spin coating on a patterned substitute is nontrivial and I am sorry to say fundamental understanding was rather poor which sort of got corrected very recently.

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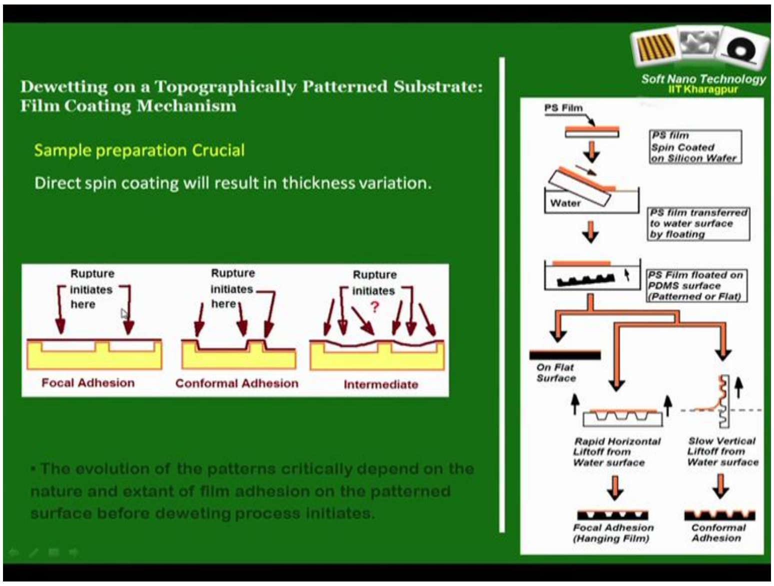

**Dewetting on a Topographically Patterned Substrate: Film Coating Mechanism**

Sample preparation Crucial

Direct spin coating will result in thickness variation.

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

However initial patterned directed dewetting experiments on topographic pattern surfaces, people where little scare to on honestly speaking nobody knew how exactly this variation takes place on a topographically patterned substrate the film thickness variation. So, what was done was very painstakingly the samples were prepared by coating it on a flat uniform silicon vapor or mica sheet and then floating it on water and then transferring it on to the topographically patterning substrate.

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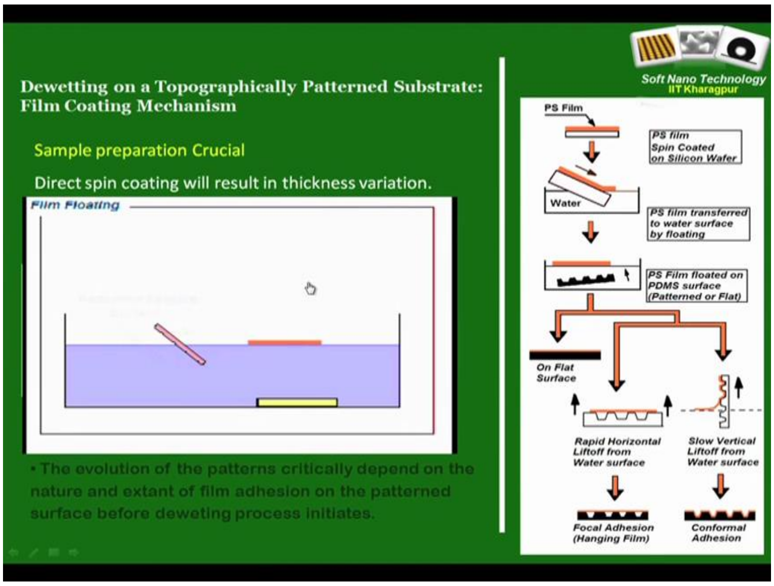

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So, this way you ensure that your film thickness at least remains constant or uniform. It was also shown that the way you transform that is the way you recapture. So, this is sort of a cartoon that gives you an idea what was done. This is a layer of water; you take the film you, need to have really very good hands. So, this this was coated on a flat surface then you float it on water is every possibility that there will lot of wrinkles those are going to spoil your samples and you capture it with a patterned surface. I will repeat it. So, you coat it spin coating on a smooth surface then you float it on water and then you recapture it with another topographically patterned substrate.

So, this was how initial samples for these where these experiments where created. And it was also shown that the depending on the angle at which you pick up your sample, you can have two different initial configurations. So, if you picked up your substrate vertically you actually get a completely conformal addition of the film which respect to the substrate. In contrast if you pick it up horizontally, you sort of get a film morphology which is hanging which is in contact with only the protrusions and hanging over the other areas.

So, depending on how you prepare your film you could either this lead to this and lead to this. Running out of time in this particular lecture so, I will start my discussion for the subsequent lecture which will also continue on patterned dewetting from here.

Thank you.