Soft Nano Technology
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Lecture - 31
Dewetting – 2

Welcome back. We have just started to talk about continuous instability and dewetting in an ultra thin film. Now this what ultra thin film should be clear to you in our context, ultra thing film is a film, forget about numbers where we are defining that there is active Ven der Waals interaction between this 2 interfaces. So, this is the most important term active Van der Waals interaction.

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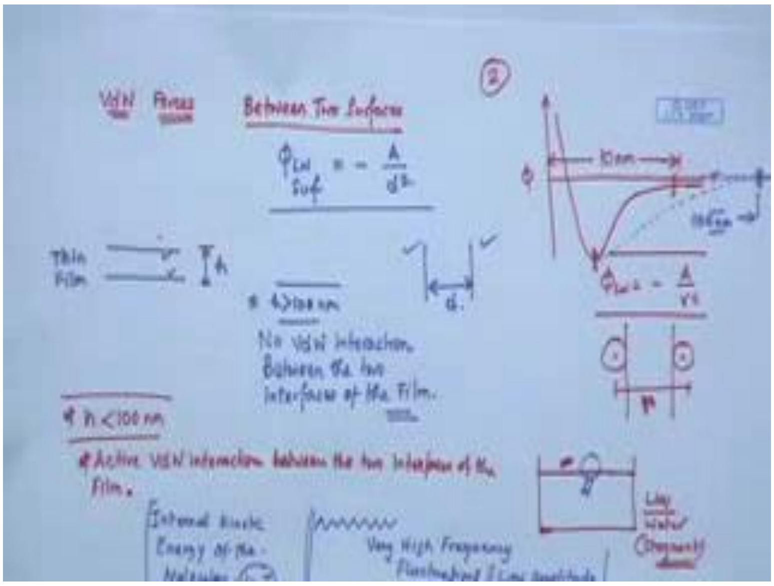

Terms out that between two surfaces Ven der Waals interaction stretches roughly about 100 nanometers, arguably some people say it is even lesser does not matter that is why we will stick. What is the thin film or ultra thin film, where there is active Ven der Waals interaction between these 2 interfaces and of course, what are the necessary conditions for the film to be command stable.

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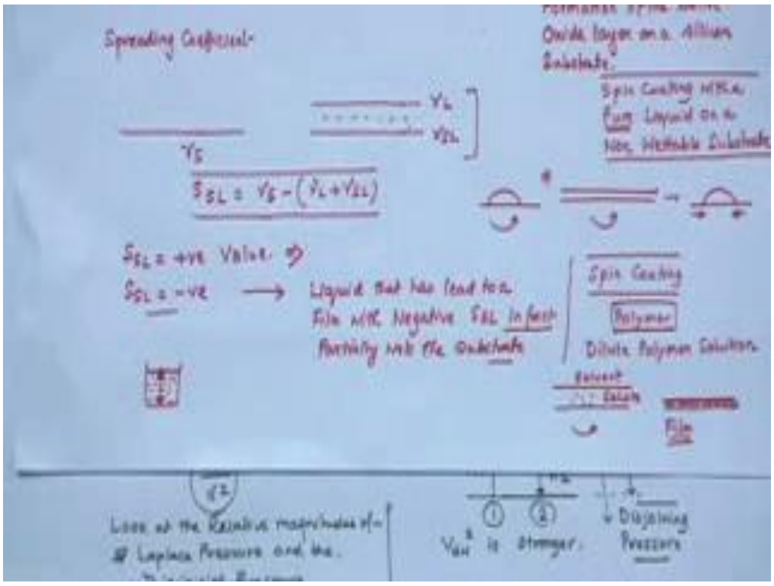

So, one of the thing we need to understand is very clearly is the spreading coefficient, the sign of the spreading coefficient plays an important role because please do not forget the native oxide layer on a SP on silicon surface is just an 1 and half nanometer, 1 and half to 1.8 nanometer and it is most difficult to discharge. It was been very good from the san point of microelectronic fabrication had this layer been unstable to develops on it is own does not happen.

So, the movement of film is very thin, it may not be unstable; it is unstable only on the certain conditions and one of the first criteria for instability is the sign of the spread coefficient. Of course, what the spreading coefficient does not taking account is the thickness of the film. So, even if you have a very thick layer, where based on the local surface energies at the spreading coefficient is not it which is negative, spread coefficient that layer is not going to rupture or no instability is going to be manifested because a thick layer is sought of stabilize by gravity and therefore, spreading coefficient is spite having an negative sign will not influence the film instability.

In fact, the situation becomes most complex and this so called continuous instability; is manifested only when the film thickness is very thin, thinner than this limit up to Ven der Waals interaction, the affect of Ven der Waals interaction stretches, why? In order to understand that, we now talked about another additional concept and that is the dynamics study state prevailing on the surface or any free liquid surface and what is responsible for this dynamic study state? The kinetic energy internal kinetic energy of the molecules are responsible they sought of lead to some fluctuations, but that does not cause any damage to the liquid surface right because these fluctuations are high frequency, very low in amplitude compared to the macro scale.

So, if you have a 10 centimeter deep water in a bicker, or one meter deep of water in a bucket, or few hundreds of meters depth in a reserved wire or a pond or may be few thousand few kilometer depth in an ocean it hardly matters, because this amplitude is a few nanometer. What happens because of the internal kinetic energy of the molecules the surface are fluctuates and the movement there is fluctuation it enhances the surface area as we have seen like this. So, that sought of triggers the Laplace pressure which flat and sought the film.

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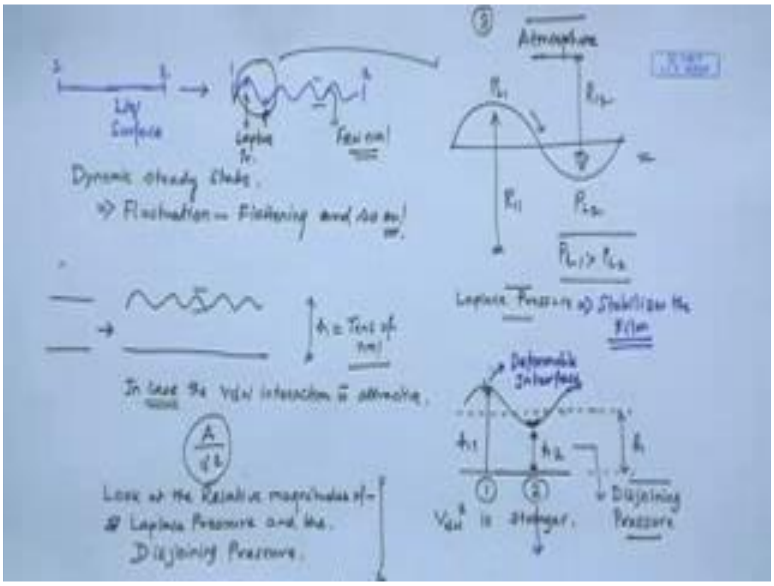

So, surface tension driven Laplace pressure slatence the film or stabilizes the film and there is in fact, no destabilizing field at all. The problem becomes more complex when the film thickness is below this range or in other words the amplitude of the oscillation becomes of the same order of that of film thickness and then if one looks or a examine snap shot of an oscillation that is specific times scale, than certain important thinks needs to be looked into that at any given instance of time the film is not flat, but there are in fact fluctuations and because of this fluctuations the strength of the Ven der Waals force at point 2 is stronger than that at point 1 and therefore this is a deformable interface not therefore, this is a deformable interface please understand that. And this is a experiencing a force, exhorted by the presence of the substrate, which favors the growth of the amplitude.

So now, you have for the first time a factor that in fact and favor the growth of the amplitude. So, Laplace pressure is still present, Laplace pressure is still trying to stabilize or hinder the growth of the amplitude, but the so called Ven der Waals force driven is joining pressure is in fact trying to enhance the amplitude, instead of let into flat an out.

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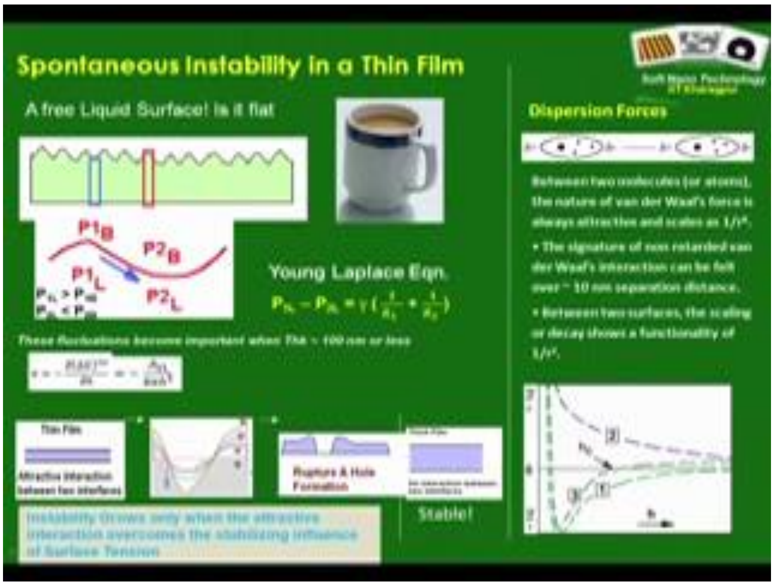

So, they are might be a situation, in case the strength of the Laplace pressure Ven der Waals force driven disjoining pressure is stronger than the restoring strength of surface tension, then the amplitude, the fluctuations instead of stabilizing down with time might in fact grow and grow up to what extent?

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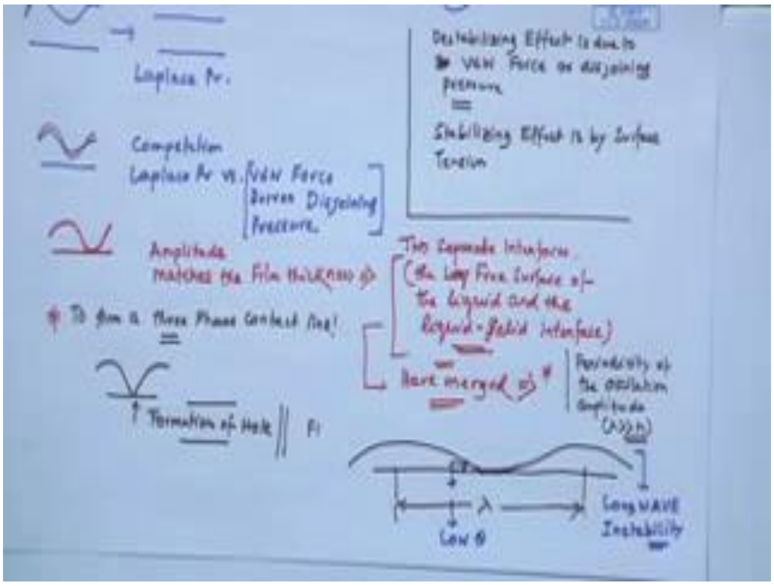

Well they will in fact grow. So, typically we are used to this another fluctuation and you know who is responsible for this flattening it is the Laplace pressure, but in a thin film if you have a fluctuation there is a now a competition between Laplace pressure verses Ven der Waals force driven disjoining pressure and as a consequence what happens is, in case the strength of this disjoining pressure is stronger than the Laplace pressure then amplitude will grow, but grow up top where?

It will grow till the bottom of this fluctuation touches the substrate or the amplitude matches the film thickness what would that mean? That would in fact mean that the 2 interfaces, the liquid the free surface of the liquid and the liquid solid interface. These two in fact have merged. Merged to form what? This to have merged to form a 3 phase contact line and that is associated. So, it is like this now that is associated with the formation of a hole.

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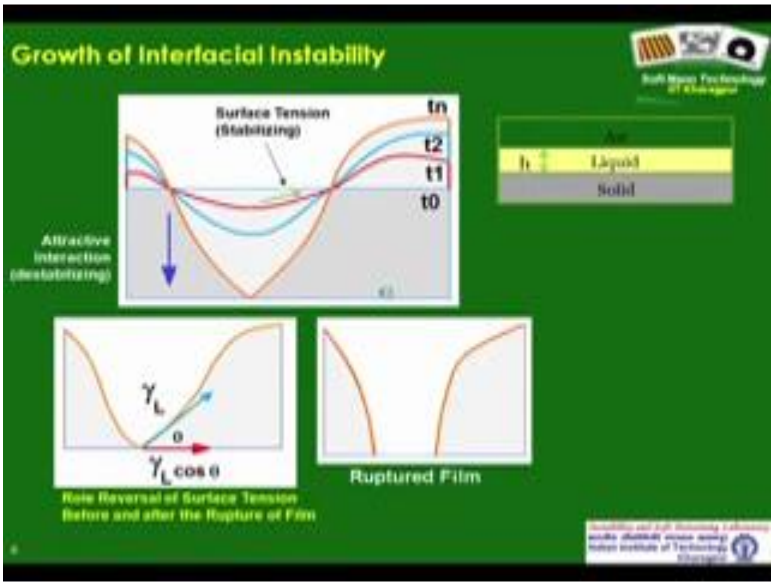

So, this is it. So with progress in time the amplitude in fact grows right and therefore, that is associated with a formation of a hole. So what as in fact happened the film has ruptured the formation of hole in fact is an indicator that the film has ruptured right. So, this is how it goes. So, formation of the hole in fact is associated with a rupture of the film. In fact, we are very close to I am very close to showing you a real video which will tell you what exactly happens, but before that I must highlight one very fascinating aspects and that is from the discussion so far you have had a feeling that the destabilizing effect is due to Ven der Waals force or disjoining pressure and the stabilizing effect is by surface tension, but the amazing thing happens the moment the film ruptures.

So, this is a hole and you see it has formed a three phase contact line. In fact, the ruptures take place like this it does not take place like this; there I will talk about the fact that these amplitudes have a lambda, the periodicity of that amplitude. I will not take up a full mathematical treatment, but the periodicity of this oscillation amplitude lambda is much much greater than film thickness. In fact, this form of in stability is that is the reason it is called long wave instability. So, what does it mean that the contact line forms like this at a very low value of theta, when the hole forms? Now does it remain you of anything, well now you have a different situation and what is the situation? You have a solid substrate and you have a layer of ruptured liquid.

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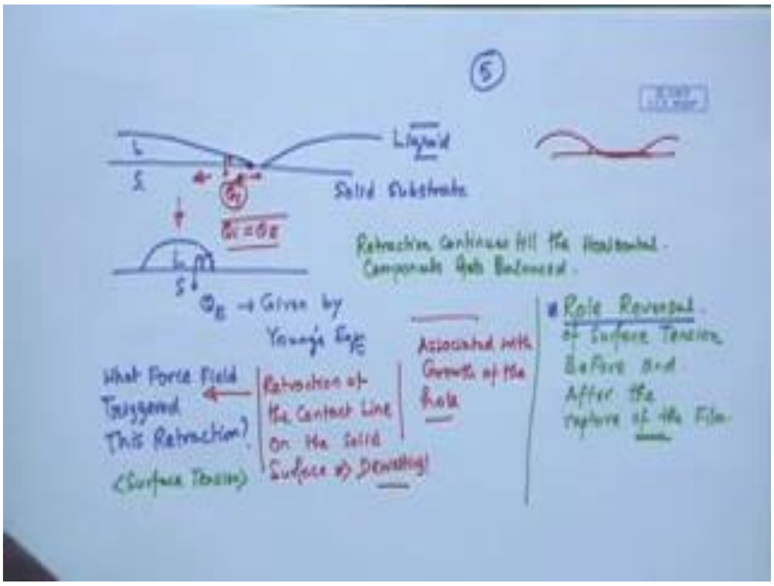

Now, is it clear why this. So, called liquid thing is important because of the fact that in case you do not have a liquid film right. If you have a solid film which is rigid you might have this type of Ven der Waals interaction active, but they interface this interface is no longer deformable. So, it is too stiff and therefore, it will not deform therefore, what happens is that even if you doing experiment with polymer at room temperature the films do not dewette.

For a polymer whose TG is at an elevated temperature let us say 100 degree centigrade or something like that. At room temperature the film does not dewette. Now you understand that in fact, at room temperature even this fluctuation spectrum is sought of significantly obscene because it is stiff interface it is a hard film, but when you take it to the liquid form you start seeing all these things right.

Therefore depending on the strength of the disjoining pressure and if it is stronger than the stabilizing effect of Laplace pressure, it is possible that the instabilities or the undurations group. Now once the amplitude has match that of the film thickness you now understand that the film has ruptured. So, you have a liquid over a solid, but what you additional know? You additionally know that for a liquid on a solid system it has a specific equilibrium contact angle, that is given by, you all know that now given by Young's equation and look how it has ruptured it has in most cases it has it has ruptured with a very low value of theta as a if you like tangent and it simply torches. So, since it is a long wave instability ruptured take place like this way in very low initial value

So, now what will happen? If you now try to balance the forces over here this is the intrinsic contact angle and you see that the horizontal components of forces are no longer balanced. In fact, it this many scars now wants to retract, retract up to when? Up to the point when theta I matches theta equilibrium. So, you see a retraction of the contact line, line on the solid surface, which is dewetting and it is associated with growth of the whole fair enough whole growth.

In fact, the reality is even more complicated we will soon see that when we talk about little more about the experimental details after we of course, have a fear deal of idea of the disjoining pressure that is my priority now, but what triggered, what force field triggered this retraction and for that let me just highlight this, but do you know destabilizing effect is due to Ven der Waals forces stabilizing effect is due to surface tension.

But now look here what force field triggering the restriction and hole growth? Well it is nothing, but surface tension right. Why? Because young equation is not valid in this configuration and retraction continues till the horizontal components get balanced. So, that is very interesting. In fact, what we just realized that there is. In fact, a role reversal of surface tension before and after the rupture of the film. What does it mean? That till the film has not ruptured the surface tension or Laplace pressure. In fact, trying to stabilize the film by suppresses the growth of the amplitude, but the moment that 3 phrase contact line has formed, the film has ruptured. In fact, surface tension now aids hole growth.

So, there is in fact very fascinating role reversal of surface tension before and after the ruptured of the film. Having said that let us sought of look in to some of the movies and it is sorry this movies not working from here I will just run it. So, here you can see what you are now seen is in fact a poly stride in film. In fact, is difficult to even get it to the original configuration it dynamics are so fast what you are seeing is a poly stride in film a spin coated 40 nanometer thick poly stride in film, simply hit it beyond rich class transition temperature. You have not done nothing else the film has been spin coated from a solvent in tall win and then you simply hit it up beyond rich class transition temperature you actually this has been imaged under an optical microscope, using a real time camera see what happens.

So here you already see the holes which now you should understand that these holes the film has ruptured and you see the film is growing, they the holes are growing and there are some dark spots here and this also have dorm. So, much that you suddenly see the film is completely disappeared and. In fact, I have a nice let us stage image let us stage microscope.

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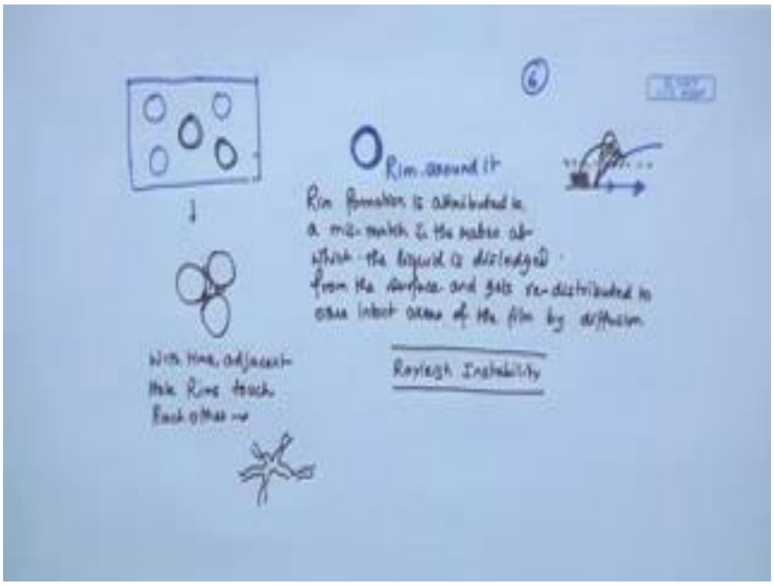

So you see this is what happens? I will see I will tell you what happens before I explain. So, what happens is here for simplistic discussion we have talked about the growth of a single hole, but reality is that there are multiple holes on a film actually under experimental condition, multiple holes formed right simultaneous due to the same physics. In fact, one of the things that you might have noted is a I am really sorry it is not working from the power point that every hole is sought of, suppose if you a tracking this particular hole it is sought of surrounded by a thicker out line and it terms out these are hard core experimental facts, that every hole that appears has a circular Rim around it.

So, it is configuration is not like these as we were talking just when explain the role reversal of surface tension etcetera it is more complicated. And it terms out the Rim formation is attributed to a mismatch in the rates at which the polymer or the material is dislodged from the surface, but see that is another advantage of using a polymer it does not evaporate away because if you use a highly volatile liquid, it will holes will form, but the material will simply evaporate away therefore, you do you have no idea where the material has gone, but here since it is a polymer it has very low weeper pressure it does not evaporate a way.

So, this material that was there in the area, over the area where a hole has formed has to get diffused to other intact areas of the film and so there is a mismatch at the rate at which the liquid is dislodged from the surface and gets redistributed to other intact areas of the film by diffused. There is a mismatch and that manifest with the formation of Rims. So now, this holes are growing each one of them has Rims and so what happens with when the diameters of the individual holes become larger the adjutant Rims touch each other.

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So, with time, resulting in some sought of the holes are now completely gone the morphology changes totally in some sought of a cellular structure as you saw in the second movie you say some cellular structures like this form. And what you can conclude is you had a hole over each of these areas which have sought of grown in size, their Rims have joined up with each other forming a cellular structure. Now these cellular structures in fact you need to consider the mass balance. So, the entire material of the film that was spread over the entire surface is now confined in this narrow thread.

So, they are sought of very tall and long tall Sharpe and sought of very long thread. So, they are very high aspect ratio threads and these types of threads with liquid threads, with time exhibit and instability that is known as Rayleigh instability. I am sorry I do not will not have the time to go in to the mathematical formulation of Rayleigh instability, but one can take the young Laplace equation in an access symmetric form in more generalize form and one can very easily explain Rayleigh instability observed in a in a long liquid thread, but any way what happens is this cellular structures eventually breakdown due to Rayleigh instability in to isolated droplet us you see for example, if you look at I will I will repeat this movie again.

So, if you look here carefully any one of this thread. So, you have a clear thread and with time these thread is disintegrating in to see here it a thread is about to break down just follow that mouse on the screen and it forms isolated droplet us. So, that is how the morphology of a dewetted film looks like. There are 2 aspects. So, now I guess this image sequence makes sense to you, there are other critical issues I mean what you actually see here is some sought of a secondary instability around the Rims. Let us avoid those complications for the time being.

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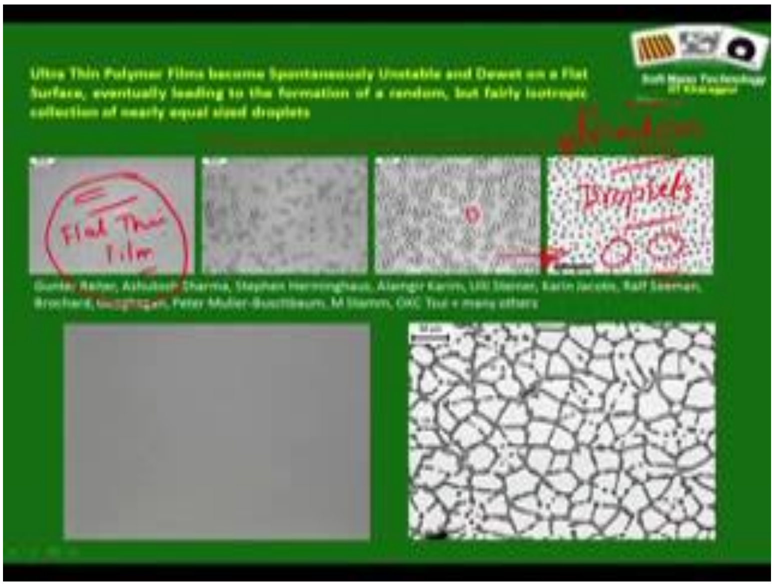

So, but what you observe is that you start off with a flat film and what have you done in fact you have done nothing apart from hitting it up and based on it is own thermodynamic consideration the film it itself has evolves. So, first the film has ruptured, then the ruptured holes are grown in size and then eventually this has led to the formation of droplet us. So, they are several issues one can argue whether. So, first thing is the signs are very fascinating.

They are have been people who have contributed significantly in to this areas, but if you look in to the hole evolution sequence there is something very fascinating that comes out we have been talking about. So, many complicated nano fabrication techniques there by you do soft meth graph you do this that, but here you see that you have done nothing you have take a flat film which is so easy to create by spring coating and the film has involved to form this droplet which are again few Mick transform even smaller than that in size. Only problem is that these are random.

So, you need to think of doing something. So, that one I mean one orientation of research is to sought of alien this structure and you will be very fascinated to note that often these structures are alien by dewetting a film on a soft lithographically pattern template. So, soft lithography technique is a top down technique, this is sought of a self organization technique or a bottom up technique in some ways. So, you essentially combined the basic concepts of top down and bottom up approaches to create some very beautifully order structures.

Research also has moved in to I mean I do not think I will covered that again that there are issues where people looking at how to enhance the stability of thin film even on non wet table surfaces because that becomes very very important because of this type of possible ruptured due to spontaneous in stability, people avoid ultra thing films and now you understand that films are very important at as resist layer and things like that and since the features sizes have really come down in microelectronic devices often it might be necessary to actually look in to for any thin film which as stable. You do not want your photo resist layer to rupture during your photo lithography process right.

So, these are the issues which people are looking at, but I will talk more about this dewetting and how to alien the dewetting structure etcetera, but before that in the next lecture I am going to take up the interaction between the Ven der Waals interaction between two surfaces, which will give us a mathematical foundation to understand disjoining pressure.

Thank you.