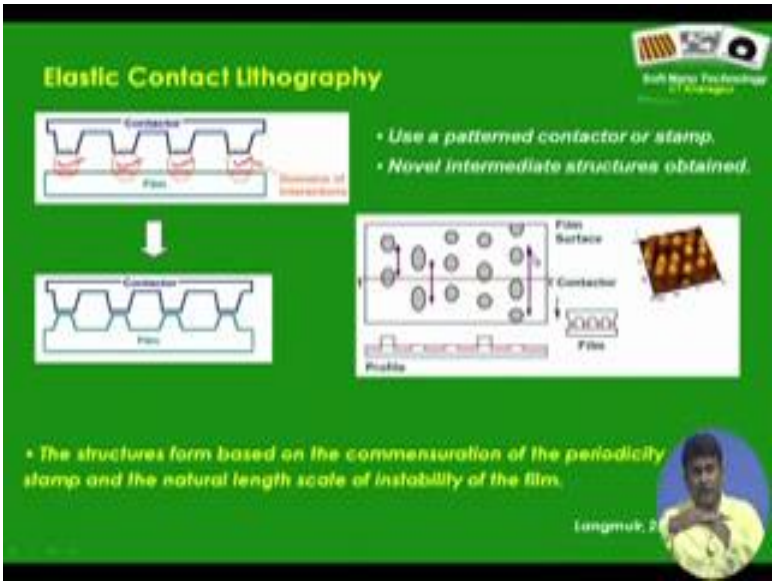
Soft Nano Technology
Prof. Rabibrata Mukherjee
Department of Chemical Engineering
Indian Institute of Technology, Kharagpur

Lecture – 40
Elastic Contact Instability – 2

Welcome back for the one last time, last lecture of the course which will be on Elastic Contact Instability. I will try to rapid up bit fast and then have a quick over view of the course. Let us see how time permits.

(Refer Slide Time: 00:32)

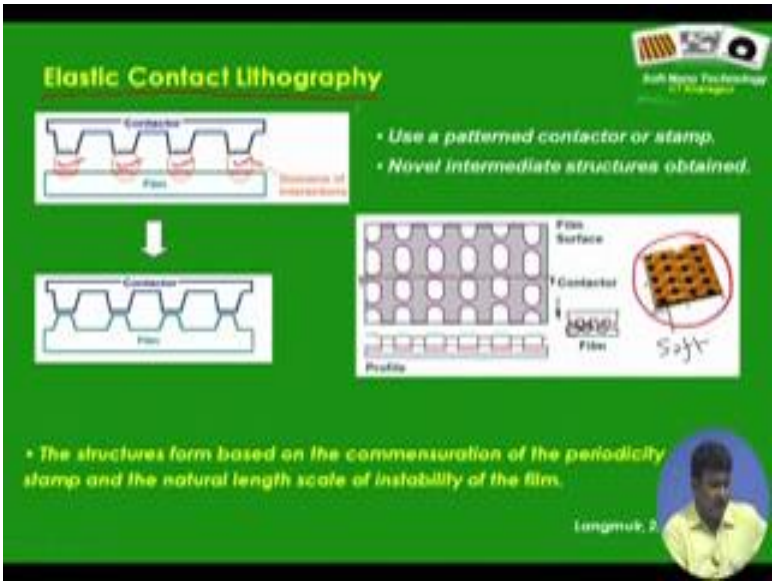


So, we were talking about contact instability, and the idea now we are discussing is can these elastic instability structures be aligned with the topographically pattern stamp. Our expectation is that if one takes a aggregating pattern stamp one would expect the inter facial interaction to be active over these areas and therefore, it is expected that probably a positive replica will happened.

Let see what actually happens. So, here is a sort of composite pictures that will give you a detailed idea about what is happening. Here are the two AFM images that is obtained in experiments. Here is the sort of the contactor which is initially far away from the film. And here is in fact a zone where in the form of schematics I will try to emphasis what exactly is happening.

So, initially the contactor is approaching the film it still far away, so therefore there is no interaction. And then you see the first signs of interaction as you have seen in the video I was showing in the previous class was in the formation of columns for a flat contactor of the columns were completely random, but here you see that the columns are not random, but they form they are sort of aligned and they form only below the stamp protrusion which is logical you approach. Further, in fact the strength of the attraction between film and these areas the protrusions of the contactors sort of increases. And as a result of more numbers of columns appeared, as well as some of the column which of already formed they sort of tend to get stretched along the direction of the contactor, protrusions.

(Refer Slide Time: 02:13)



And as a result you do get a positive replica of the stamp. How do you know that you have got a positive replica? One quick answer is that the height of the pictures here does not match the height of the stamp. And which is possible particularly if it is slightly higher is only possible if it a positive replica, negative replica it is not possible.

Then of course, one knows that if one goes on pressing one will eventually this will become an embossing process. So, one will eventually get a negative replica. So, what happens then if the film at the stage where a positive replica has formed on the film surface the contactor is still pressed; and if you press that please do not forget that these replicated stripes themselves are soft, these are very soft they are not permanent they are

still in the elastic stage; they are soft. And you press them from top so what happens is, now these stripes starts to exhibit lateral undulation which is also very logical.

But, what is very interesting is that these patterns have a periodicity of 1 micron to something like that two micron something so their pretty close each other. And now the belched out portion of the adjutant undulations they are very close to each other. And again what is a good number when their in the range of active Van der Waals interaction because they are after all interacting in near, so there is no chance of any repulsion. These undulations simply show enough.

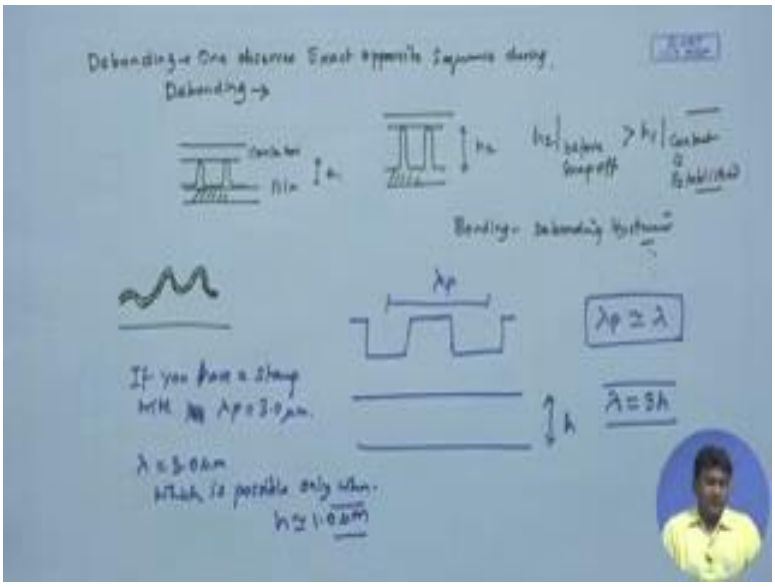
And therefore, what it forms is an array of holes. Which in fact you have seen in the context of dewetting there was a pattern directive dewetting video of few lecture back where we use this identical substrate was used, but what is the real novelty of this technique from the stand point of patterning. You start off with a grating pattern stamp and then you create an array of holes with to the order.

So, this is the real advantage or this is the real novelty of cleverly utilizing elastic contact instability with a patterned stamp. And this is this technique is known as elastic contact lithography, really rare capability of obtaining 2 D structures starting from a 1 D stamp. There are of course, beyond the stage if one continues the approach one eventually gets a perfect negative replica.

(Refer Slide Time: 05:02)

There are certain conditions under which this perfect replication takes place.

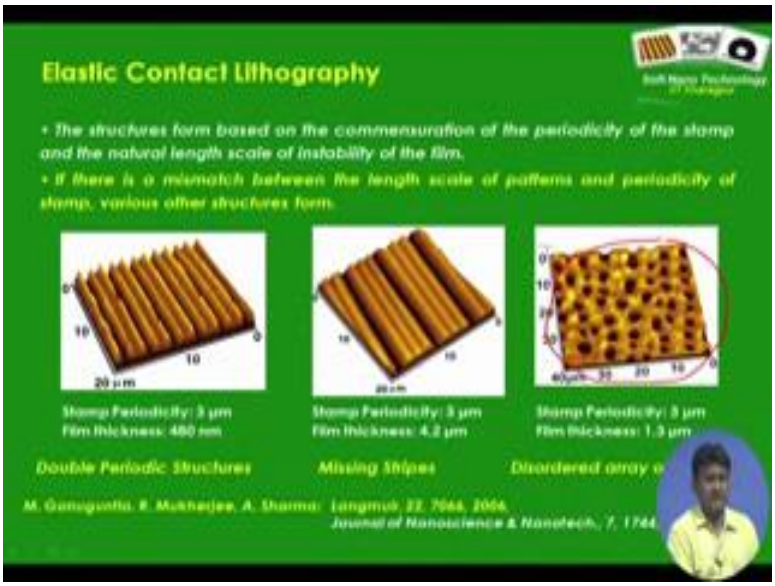
(Refer Slide Time: 05:13)



And one of the conditions is the periodicity of the patterned stamp that is lambda p and you have a flat film where the thickness is h. Therefore, its natural links scale of instability is 3 h. So, this type of pico liter bigger formation or array of holes occurs only when lambda p is come insulate with lambda.

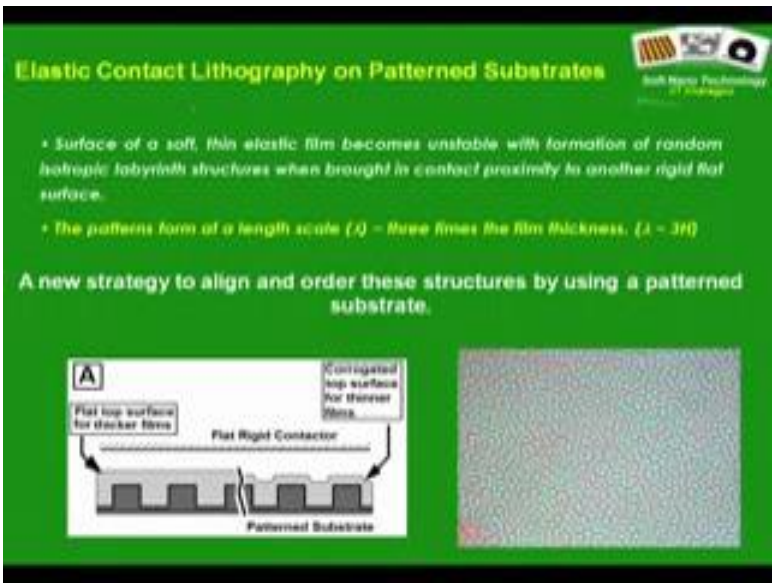
In other words, if you have a stamp with lambda p equal to 3 micron your film must have lambda equal to 3 micron and which is possible only when h is of the order of 1 micron. If there is mismatch in fact this type of secondary instability and their joining up is not observed.

(Refer Slide Time: 06:25)



In fact, these are some of the images where there is a mismatch. There is bit of science into but I will not going to all the detail. Here you see the extent of mismatch very less, and therefore the bigger formation of the whole formation has taken place, but they are distorted they are not that will ordered. These are cases where there is significance mismatch. And therefore I will stay away from commenting on that.

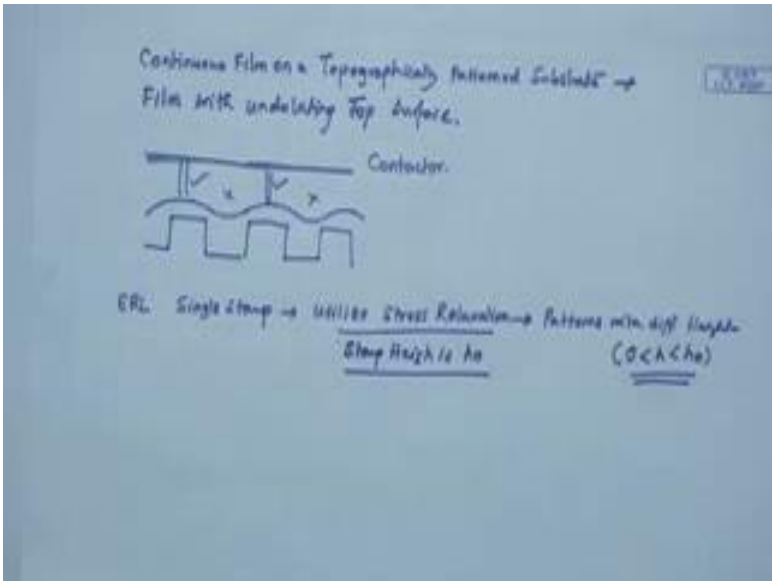
(Refer Slide Time: 06:48)



Of course, one can also use in a in a bit clever way a flat contactor on a patterns substrate, because only couple of lecture back in the contexts of spin coating on a

topographically patterned substrate we have discussed that on a topographically patterned substrate if you have a continuous film.

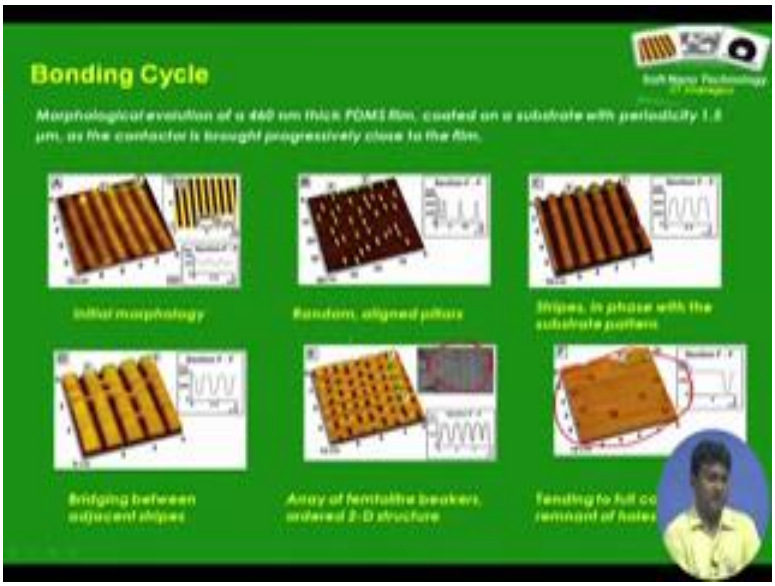
(Refer Slide Time: 07:14)



Continuous film on a topographically patterned substrate leads to a film with undulating top surface.

So what happens is this. So, you have a topographically patterned substrate and on that you have a film, and there are undulations. If you now bring in a contactor from the top, the interaction is favor in these areas as compared to other areas. And therefore, you get the special variation what is essential to impose ordered to this type of a completely isotropic structure. So, here the image sort of shows the variation to be too small, but these are the areas where you have a preferred attraction as compare to the other areas.

(Refer Slide Time: 08:45)



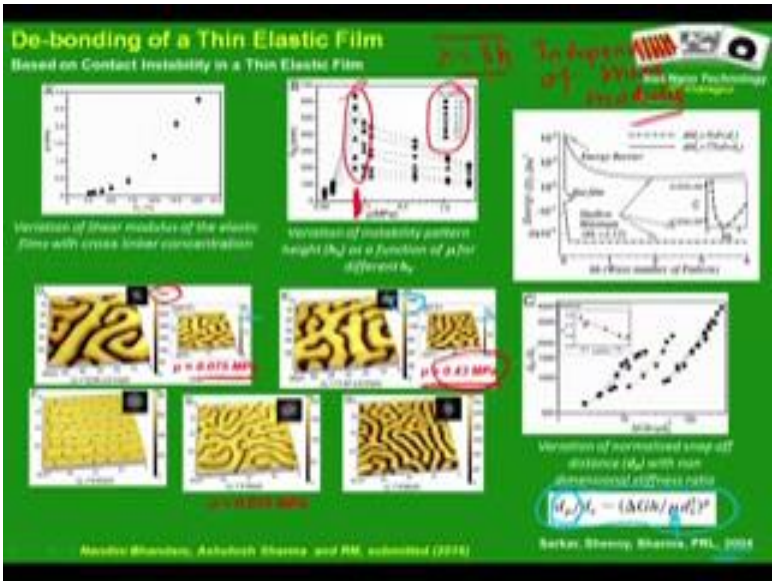
And as a result you can again see here of course, one needs understand the final conformal morphology will be a flat film because the contactor is flat. But intermediate stages one can again see this beautiful array of these 2 D holes a forming when there is a commensuration between the periodicity of the substrate patterns in this particular case with the film thickness. One will understand what film thickness one is talking about; it is essentially the effective film thickness.

Since you a looking at the topic force microscope images and this is the evaluation sequence you have an undue initial film with undue of surface, then initial manifestation of instability is with the formation of pillars, then positive replica and then something this and then complete conformal contact.

(Refer Slide Time: 09:35)

Again here also this perfect ordering happens only when there is a perfect commensuration between the two otherwise there is distortion; for example, here thicknesses much more. So, you again see those labyrinths, but because of the presence of substrate pattern you see, the labyrinths sort of tend to get bit digitized in their sort off bit aligned, but you know condition you can say that the structures are aligned or well order.

(Refer Slide Time: 10:00)



Sort of the last thing that one I would like to emphasis is that while I was talking about elastic contact instability. I mentioned one thing that there is a hysteresis, in fact as you try to debone the film it also undergoes morphological transition. The morphological transition sequence is exact opposite to that observed during approach. But more importantly as we discussed that during the debonding the film sort of there is hysteresis and the separation distance at which the film snaps of is in fact higher than separation distance at which the initial contact is established.

This can be attributed to be priming may be. As the film comes in contact with surface, it might be forming some pining strong pining with the surface. There might be other reasons one can argue where it the elastic steepness of the film there are lot of theoretical formulation for example. And Sharkar and Sharma have worked out a kinetic path way which shows why this hysteresis is exist.

Again I will not go into the theoretical aspect, but what it means is that this is similar to pulling something out then stretching it, and the idea is that if you can freeze the structures of this stretched structures just I head of detachment you can sort of come up with a very very novel concept of trading structures, which are taller than the original pattern. Now that is fascinating because in the context of this stress relaxation based elastic recovery lithography we have seen that using a single stamp it is possible to create patterns with different feature height.

In the context of elastic recovery lithography or ERL, single stamp utilize stress relaxation, to get patterns with different height. All this we have achieved. But the limitation is, the height of the patterns varies between 0 to h 0 were stamp height is h 0. And you now know adequate amount of soft lithography, nano imprint lithography, etcetera, and etcetera. So, you know that any of the properly executed lithography techniques, it is possible to create part of negative replica, where the height of the replicated structures will match a 0. But can you think of a technique that creates structures which are taller than h 0. And the answer is till that it is not doing able.

In any case you have see in that high aspect ratio structures or tall structures are very very important if not anywhere else in case of consisted of waiting. Because achieving consisted necessitates achieving high RF. And for at attaining high RF one needs in fact have height of the features. Even in classical photo lithography, if one would want to

make structures which are high, one would require ethical layer of photo resist and then you know that there are whole lot of problems that we crop up because as the photo resist layer becomes thicker.

There issues going to be like exposure and all that whether it will be uniform across the thickness etcetera and etcetera. But here I would again like to high light and this is at completely recent development in fact there is a possibility that, during the debonding stage the structure or whatever patterns form they get pulled up. And if one can frees then ahead of the detachment one can in principal create structures that are taller than the original stamp pattern.

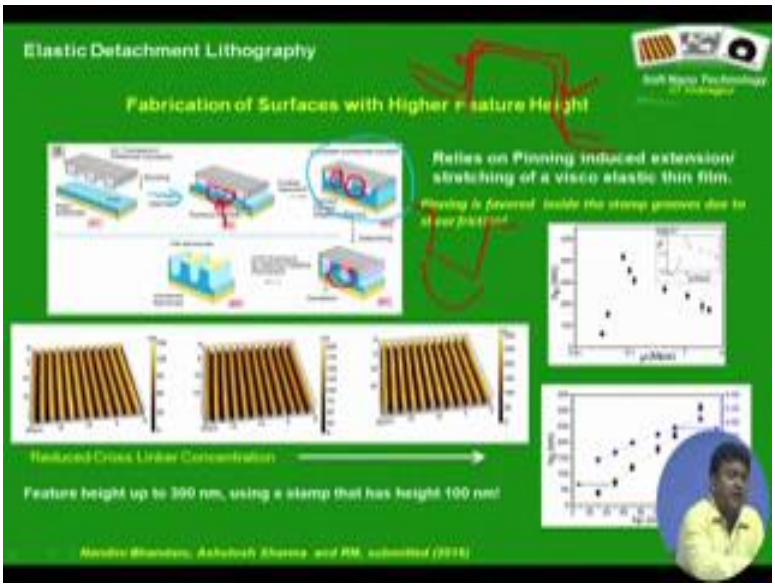
And so here are some images that give you an idea of something more interesting; is that though the instability links scale the wave ling is independent of the shear modulus. It turns out that is debonding the maximum height that can be achieved during the debonding that depends on the exact shear modulus of the film. In fact, it is in this range were for all the film thickness you see the debonding height is maximum. Of course, these experiments are performed with flat stamp therefore there is no ordering, but you can see from this images for example; that a film with this particular share modulus 0.075 mega paschal the debonding highs of the patterns is 350 nanometer.

In contrast if mu the share modulus is sorry, if the share modulus is 0.43 mega paschal then the height is above only 180 nanometers. And in both the cases you see that the very carefully performed experiments initial contact is an established when the separation distance is of the order of 60 to 70 nanometer see. So, this is in fact indirect or very direct validation that is Van der Waals forces between two surfaces sort of stretch up to about 100 nanometers may be slightly less than that. So, there are certain theoretical formulations by professor Sharma's group which suggest that as mu decreases the snap of distance increases. There is a physical revels paper in to 2004 which gives this. I will not again going to the details of this, but it is already there.

So, in principle now by taking elastic films of different share modulus and the utilizing the debonding or sort of freezing the patterns just ahead of detachment in principle it seems like it is possible to make structures, which have different feature height and which are tall. But with the flat contractor he does not make any sense because the structures are random and of course, there is a clue that yes during approach contact is

establish at 70 nanometer separation. So, the structure height is only 70 nanometers and during debonding is goes out. But the real strength can be achieved only when a pattern contract there is used.

(Refer Slide Time: 17:45)



And now everybody knows based on all the concepts of elastic contact instability that in order to achieve structures at the length scale of each pattern you need to have a perfectly commensurate structure. So, one chooses a film thickness according to the periodicity of the stamp available. So, this is the whole sequence so you can see that initially you see a positive replica when eventually complete conformal contact negative replica, and then you try to devolve then what to do expect? What to do expect is that one interesting thing or difference from that of the; what is different from that of the flat contractor is the film the replicated patterns are pint in a stronger manner inside the groups, because of the presence of the surface walls.

So, when you pull it up those areas sort of gets stretch like this, because I will just redraw. This is one group and here has the film found also from this side, so these areas of the film because of the presence of the side walls these side walls sort of act as a clamp and pull the film up. Therefore, the first cavitations take place below the stamp protrusion. So, if you have a stamp protrusion like this the first cavitations take place here. While it is important to note that during approach sequence the first patterns is formed below the stamp protrusions.

So, with the pattern contractor there is not only you can sort of in principle creator structural usage we have not discuss, but you can imagine that one can do that. But there is also some sort of a difference in the path way it means bonding and debonding. If you look into this figure again and carefully, then that becomes very clear that, during approach your first structures appeared below the stamp protrusion as expected here. But during debonding the first cavities also appear at these areas. And then this is simple result that you vary the share exact modulus of the film and you sort of reduce the cross linker concentration one can attain patterns which are 300 nanometer high using a stamp that is only 100 nanometer height.

So, this is no longer a negative replicative is not even a positive replica it some sort of a stretch replica of course, before detaching the stamp you need to fees them. There is of course, another concern this is after all a stretch elastomer, so are the structure permanent their going to sort of relax out very soon experiments over a pro long period of a time shows that the structures are permanent. So this in fact takes the way. So, this goes by the name elastic detachment lithography because you sort of exploit the physics of debonding in a very clever way this is sort of the first evidence were tall structures can be created using a shallow stamp.

(Refer Slide Time: 21:22)

One can. In fact, utilize something I did not mention in the context of elastic contact lithography, but May I will just start upon so that you can enjoy the excitement one can.

Of course, these particular cases were you see you have chosen a film thickness were lambda p is equal to lambda equal to 3 h so that patterns form below each stamp protrusion. Now if there is a miss match, if your lambda is higher than lambda p then what happens? Lambda is higher than lambda p means h is such that 3 times h is greater than lambda p, it sort of exceeds that.

What happens is even in this particulars case, the elastic instability structures sort of rather faithfully obey their natural length scale of stability. So, you actually get structures like this. So these are the bigger structures, and this obeys the lambda equal to 3 h. So, one single structures spans below several of the stamp protrusion and this periodicity matches lambda equal to 3 h, Which gives a route for creating a wider structures from a stamp with narrower feature that is fine.

But what is more interesting is now if you deboned the areas of the film which are in contact with stamp sort of detach in sort of steps over the stamp protrusion, it is sort of follow goes in to a gradual detachment more, and that allows you to create structures. As one sort of pulls the contractor up word the structures become progressively taller and additionally they become narrow.

So, we had talked about duty ratio, so here under this particular condition which apparently is not commensurate for creating structures because the there is no commensuration you can not only create tall structures, but using a single stamp by wearing the extent of detachment you can create structures, which have different duty ratio.

(Refer Slide Time: 23:47)

So, that is sort of all that I wanted to teach in this particular course. And let us see what have the stuff we have learned. So, we had a pretty longish introduction, so you should know; what is nano and what is unique about the nano, and particularly what should come out from this particular course is apart from the quantum size effect the length scale of 100 nanometer is important because between two surfaces that is the range were Van der Waals forces remains active. So, that leads to issues related to spontaneous in stability being films. Of course, we are talking about liquid films here. And we also talk about utility of nano pattern surfaces in creating super inevitable surfaces, hydro phobic surfaces, optical color and things like that. And that that is what we studied in introduction.

Then we moved on to the basic concepts were we understood surfaces tension and its components in a bit in more detail, and we realize that even Van der Waals force is responsible for major part of surface tension also. I mean surface tension in variably has a signature of Van der Waals forces. There can be other factors like polar interaction, aesthetic interaction, which may also contribute to surface tension

We talked about wetting rescinds like Cassie state and Wenzel State on a pattern surface and we talked about Young's equation. We now very well understand what is hydro phobic surface? What is a self cleaning surface and stuff like that? And then additional

new thing that you have really learnt is Laplace pressure that is across a curved be to it surface there is a pressure gradient.

(Refer Slide Time: 25:36)

Then we talked about patterning techniques. In fact, this has been split in to two modules; one of the modules is photolithography, the other module is soft lithography. We had really detailed discussion on these so not repeating. You understand photo lithography is a specific technique. In fact, whole progress in microelectronic industry realizes on that.

But in contrast soft lithography is a suit of polymer specific techniques and there various varieties and you can create a chemical pattern you can create a photographic pattern whatever.

(Refer Slide Time: 26:07)

Then of course, you have created the patterns, but you need to sort of visualize them and that is where the utility of your atomic force microscope comes in. So, we realized or understood how the AFM is evolves from the discovery of STM, AFM, in fact many ways changed the perception about vision because AFM never captures a picture it generates a date file.

And towards the end we talked about spontaneous instability and dewetting of a liquid film and then the issues related to that; theoretically under what condition a film becomes unstable, based on spreading coefficient as well as based on effective interface potential. We talked about the experimental evidences how the morphology is evolve, formation of ream and things like that. And then we also talked about dewetting of a by layer were there are extreme complexity because of the coupled deformation of 2 Deformable interfaces.

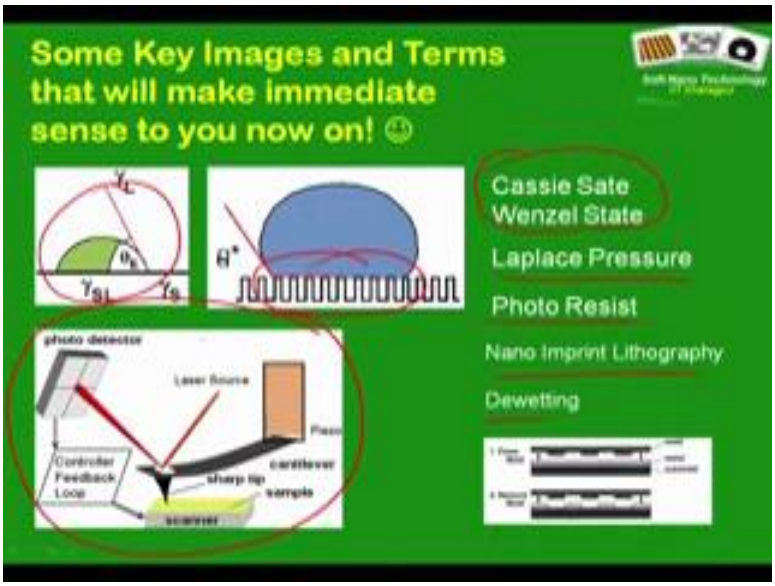
We talked about patterned directed dewetting and while talking that we in fact talk about spin dewetting as well, dewetting during spin coating and creating structures based on spin dewetting.

(Refer Slide Time: 27:14)

Then this is one area that I could not cover in greater detail, I wish I had some time to cover this phase segregation and de mixing in a polymer blend this a huge area, but I just gave you some glimpses of that. And finally, in the last phase we talked about the elastic contact instability, the short wave nature, lambda equal to 3 h, and how the patterns are made permanent and the techniques like elastic contact instead lithography and elastic detachment lithography.

And while we are discussing soft lithography we had talked about elastic recovery lithography, hydro gel base stinking and now elastic detach lithography in this particular lecture.

(Refer Slide Time: 28:00)



So, that sort of concludes my course. There are some of the key images and terms which should remain impregnated to your mind. Now that you have attended this course for example, this one always reminds you of the drop setting on a liquid surface and the Young's equation. This is the Cassie state, and from now onward Cassie and Wenzel these two terms should made perfect sense to you. You should now understand what is Laplace pressure, photo resist, nano imprint lithography, soft lithography, dewetting, in this picture should always remind you of an AFM.

So, with that I thank you all for attending this course from my team here along with my (Refer Time: 28:34) Nandini and Anuja. And I really hope that you enjoyed this course.

Thank you very much from IIT, Kharagpur.