

Instability and Patterning of Thin Polymer Films

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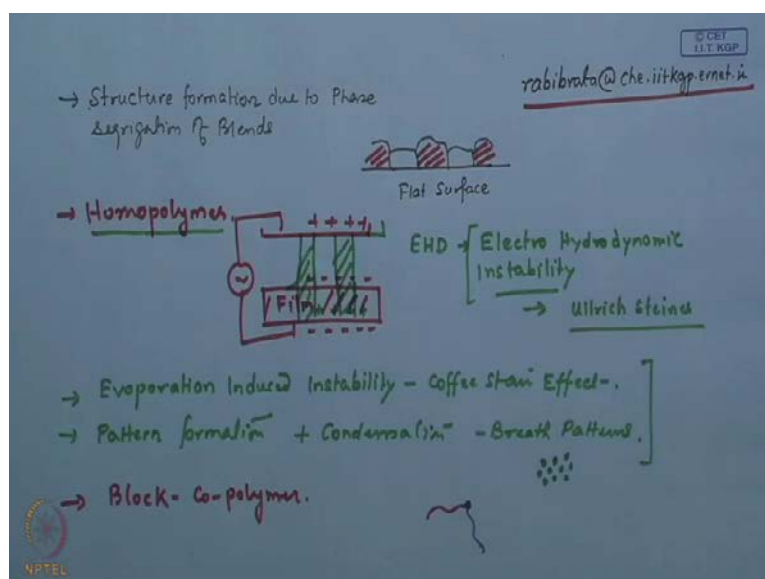
Indian Institute of IIT, Kharagpur

Lecture No. # 40

Gradient Surfaces

Welcome back to the last lecture of this course. I am very sure that you are pretty happy to reach the last lecture, and as I have told repeatedly before also, please send me feedbacks constructive, destructive, positive, negative, whatever at my mail id.

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So typically, when I take a classroom class in the last lecture, I do not teach anything new, but I do recapitulation of what I have covered. And also take questions from the students, unfortunately in a video course that is not possible, but we will tried to do reasonable good recapitulation of what we have covered in and the last of 40 lectures.

And the thing I will try to impress upon you , where exactly the two aspects of the course instability and patterning much. And how by understanding the physics of instability, you can sort of create patterns which as the potential for or how instability mediated patterning may be in conjugation with templating strategies may be in conjugation with top down approaches has the potential to be used as **(C)** patterning techniques. Now, we

have covered some aspects in the course on instability in mediated patterning, but please do not understand field that these are the only settings in which instability mediated patterns on instabilities are manifested. Instabilities and associated pattern formation is a possible in various other settings, which due to shortage of time and to keep the course content within reasonable limits I did not discuss.

For example, you can always look at the in the self organize structure formation in a polymer blend, comprising miscible blends or immiscible blends. So here, blend is a simple system where you have two polymers may be in the same solvent and you just spin coat. What happens is that, during the spin coating process itself there can be phase segregation, and you do not get a flat morphology like even if you go to on a flat surface and therefore, it is sort of results in a in phase segregated structures. So, you can have structures forming with blends. (No audio from 2:58 to 3:21) You can have look at some of the aspects; so you have two polymers in the system let us say the proportion is a is to b.

And, if you spin coat on a flat surface, you see some morphology; so what happens is the relative proportion of the two polymers and the extent of surface coverage by the each of the phases do not match. So, one of the phases which probably let us say 60, 40; the phase which has a 40 percent volume fraction covers or more or less than 40 percent of the surface. So therefore, the other phase if this 40 percent thing is occupying more than 40 percent then, what happens is the other phase which is 60 percent that as to now it is no more cramped. So, that is sort of takes the higher topography. In contrast, if this 40 percent phase is occupying less than 40 percent then that is the other remaining 60 percent phase's sort of more relax. So, that is sort of the takes topography which is or the height which is lower.

So, you can see variety of instability in this type of settings. Then, even with the homo polymer something which I did not talk, but is very common is an external field mediated instability. So, you have a film and you apply an electric field; let us say across this film. So this electric field the sort of within near gap sort of; configuration is pretty similar, to elastic contact instability, but the only difference is that in a elastic contact instability the destabilizing field that arises, because of interface Van Der Waal interaction. Here, you apply an additional field which can be electric field which can be a thermal gradient, which can be a magnetic field or whatever. And this application of this

field eventually results in polarization of this dielectric film, which is a polymer film in capacity geometry.

And therefore, if it is in liquid state, it sort of aligns in the direction of the field forming columns. So, this is what is known as EHD instability or electro hydrodynamic instability. And the advantage is that, the second axis due to the up externally applied field; that advantage is that you haven't, you are applying an additional field from outside. So, you have the ability now to control the strength of the field and therefore, you can destabilize film which is much thicker in the context that these type of films would these type of thickness is will never show an instability a spontaneous instability like deviating.

So, this is a very nice technique which has resulted in electro hydrodynamic lithography and advantage is so you get columns or other types of morphology depending on the whole lot of things like film thickness the field strength or the gap or the relative ratio between the film thickness, and the gap between the two electrodes something like that. So, you can search in the internet Ullrich Steiner at Cambridge university Cavendish lab, he is one of the pioneers in this field and now others entering in India Ashutosh Sharma's group work on this areas.

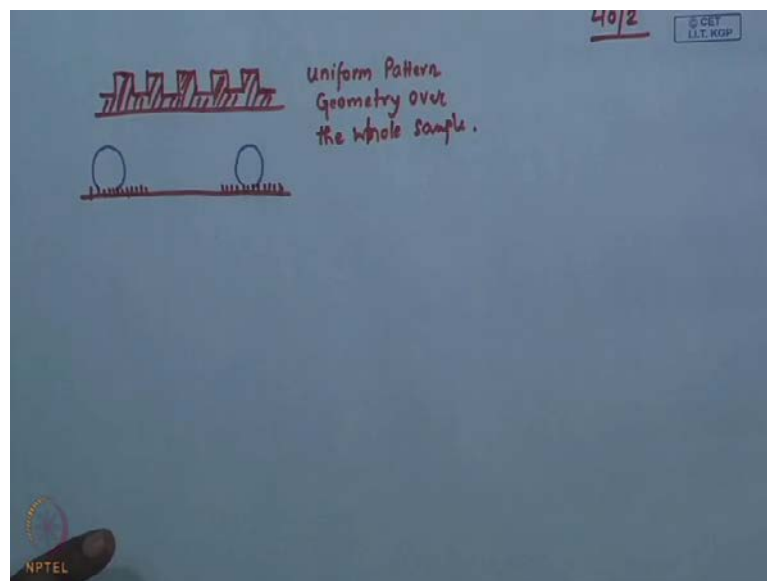
So, this type of instability is manifested in a **in a** viscous film, purely viscous film or it can also be seen in a **in a** soft elastic film. So, since the field strength is strong it can overcome of sort of the stiffness or the **or the** additional restoring force, in elastic film imparted by the physical cross links which are present. So, these are many one can look into the whole lot of instabilities, with evaporation induced instability the we briefly talked in the initial classes. Look at the coffee stain effect; one can look into the pattern formation associated pattern formation due to evaporation, as well as condensation which are known as the breath patterns alright. You just take out a cooled a surface cool surface and keep it in a humid environment, you see timing a droplets of water forming on the surface a beautiful examiner closed factory.

So, whole lots of things are there and it is an advance involving area. So, it is not possible to be recover everything in a **in a** frame work of a course, text books are coming up review papers are already available some of which I have sided and you can sort of consult. Of course, other thing we did not talk is the instability or the surface segregation

of what is known as block copolymers. So, block copolymer unlike a blend where you mixed two different polymers, block copolymer molecules are special so they sort of each of the molecule contains two blocks each representing a different species. So, they also exhibit their own internal assemblies of block copolymer molecules to a large extent behave like surfactants. So, there is internal self organization where self assemble depending on the system, depending on the composition, they have their own phase diagrams. And so, these are some of the things which we did not talk in this course and I am giving you the clues. So, you can search some of them in the internet to get some idea about what they are, but even then what we have talked is nontrivial and speech pretty significant to sort of get started, and any one of you adding towards research in this particular area I am sure will find course to be pretty interesting.

So, in the last lecture, I thought that I will give you a very little overview on another interesting topic, which is the fabrication of surfaces with gradient properties. And we have been doing some bit of work on this particular area lately. So, it is like this so far

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all the patterns that we have talked about the generation of all the patterns by soft lithography. What we have talked about. The pattern dimension or the geometry or the morphology of the structures we have considered is uniform across the whole sample. So therefore, if you are looking let say about the structure hydrophobicity of a pattern


surface. You would expect that where you dispense the drop, you will get the same contact angle the gradient surface is a slightly different.

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What are Gradient Surfaces:

Surface gradients are surfaces with chemical or physical properties that gradually change over a given distance. A gradual change in a physical property, such as the wettability, can be induced by a change in surface chemistry, for example a gradually changing surface composition.

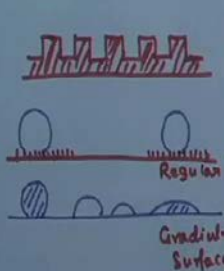
In general, surface-chemical gradients can be created in two ways. Either the outermost surface layer of a substrate is gradually modified, for example by irradiation with an energetic beam, or by chemical etching or a surface coating, such as a self-assembled monolayer or a thin polymer film, is attached to the surface in a gradual manner.



Where surface gradients or surfaces with chemical or physical properties **with chemical or physical properties** that change over a given distance. So, from one side to the other let say if the pattern topography or the morphology; or even the chemical composition sort of varies that is what a brilliant surface.

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Uniform Pattern
Geometry over
the whole sample.

Regular Pattern

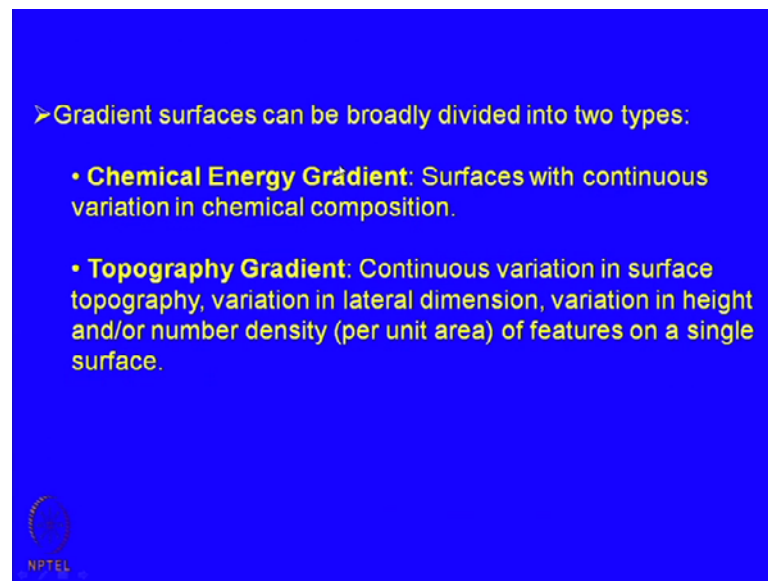
Gradient
Surface

Continuous variation of Chemical or Physical
properties along the length of the surface




So, there is a continuous radiation of chemical or physical properties along the length of the surface. So, in that case one might expect that on one end of the surface you have. So, this is regularly pattern **regularly pattern** I would say here it is a gradient surface. If you have fabricated you can expect may be at one side, it is exhibiting a hydrophobic a waiting regime on the other side it may be hydrophilic, and in between there would be continuous variation in the contact angles this is what is a gradient property.

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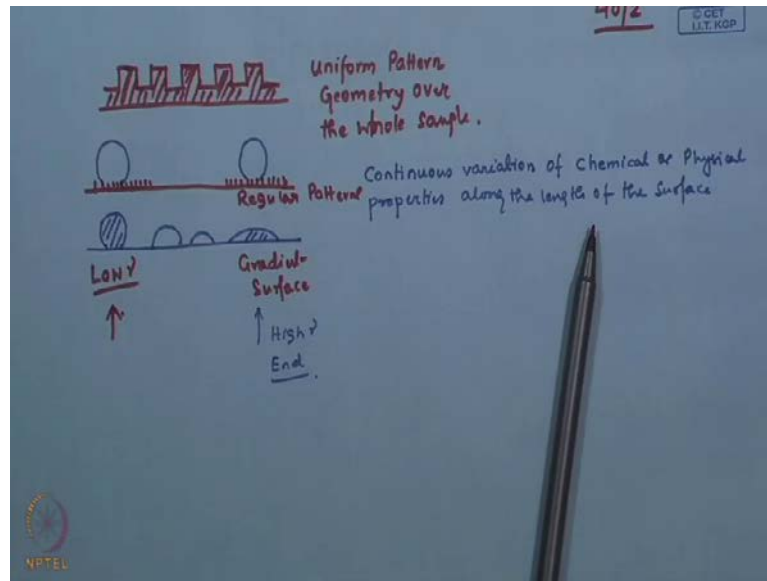
➤ Gradient surfaces can be broadly divided into two types:

- **Chemical Energy Gradient:** Surfaces with continuous variation in chemical composition.
- **Topography Gradient:** Continuous variation in surface topography, variation in lateral dimension, variation in height and/or number density (per unit area) of features on a single surface.

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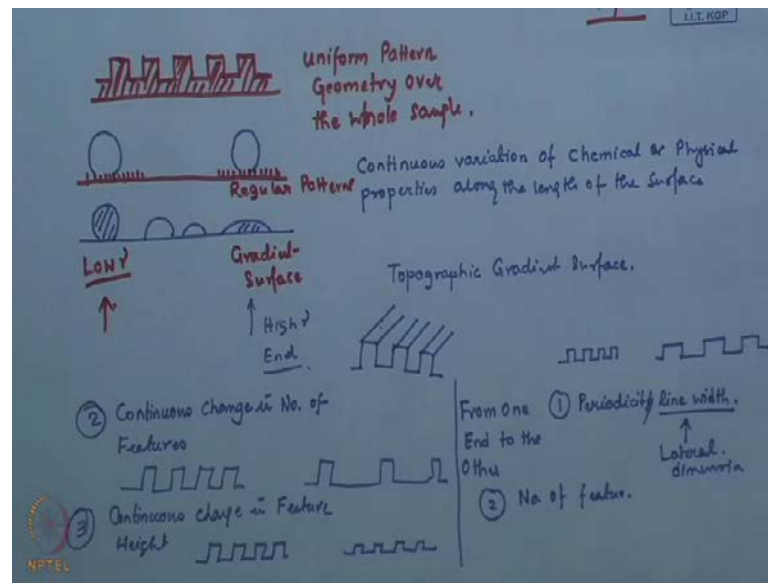
Gradients can be broadly divided into two types of categories of course, the first one is a chemical energy gradient which eventually results that is the continuous variation it boils down to the fact that they might be a continuous variation of the surface energy from one end to the other end of the film. So, on one end it can be completely low surface energy on the other end it can be very high surface energy. So, in that case you it will immediately translate to something like this.

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So, at the low gamma end you will have a high wet ability, and at the high gamma end you will have low wet ability. The other a possibility and let me also tell you that from the stand point of fabrication chemical energy gradients are more common, they are easier to fabricate and they are quite a few methods are already available. What we will do will briefly tell you I will briefly tell you some of the exciting methods of fabricating this gradients surface, and then specifically take up one interesting case study by which one can fabricate the topography gradient which is based on a soft lithography approach. So, that we make things are easier to understand for you. The other one of course, is a topography gradient so you have continuous variation in surface topography, which can be regular topography or also dissolved I mean, partial ordered structures.

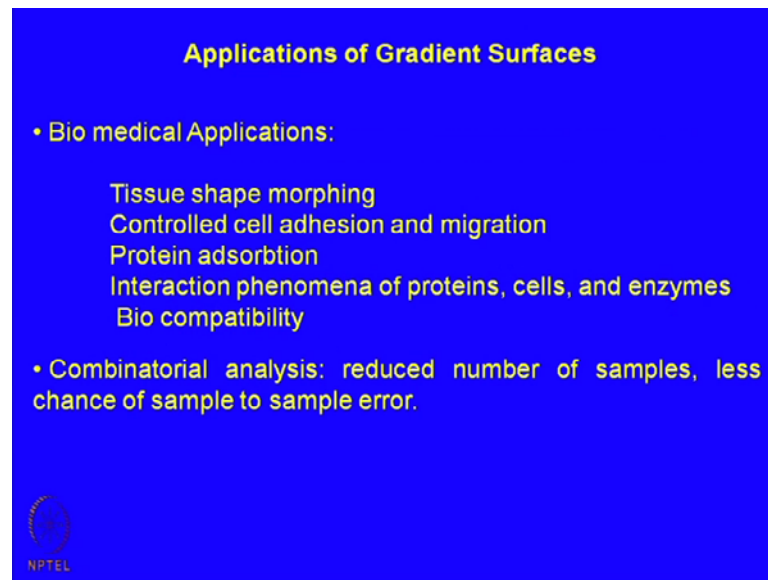
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So, it can be if one is talking about topography gradient surface, with regular structure let say if the structure we have talked most often is the grating. So, one can talk about topography gradient. So, that from one end to the other may be the periodicity and line width of the grating can change. That is you can have a continuous change in the periodicity, you can have a continuous change in the later dimension, you can have a continuous change in the number of features. Something like that you can have a continuous change in the feature height. So, these are all examples, of a topography gradient with a regular structure.


So, if you are talking in terms of let us say a simple grating, you can have a continuous variation of periodicity continuous variation of line width lateral dimension, continuous variation of the number of features, continuous variation of feature height or a combination of this from one side to the other. You can also have topography gradient with let say particles or other type of structures which may not be so regular. And so, let see some of that look at some of the methods by which you can make this gradients.

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Applications of Gradient Surfaces

- Bio medical Applications:
 - Tissue shape morphing
 - Controlled cell adhesion and migration
 - Protein adsorption
 - Interaction phenomena of proteins, cells, and enzymes
 - Bio compatibility
- Combinatorial analysis: reduced number of samples, less chance of sample to sample error.

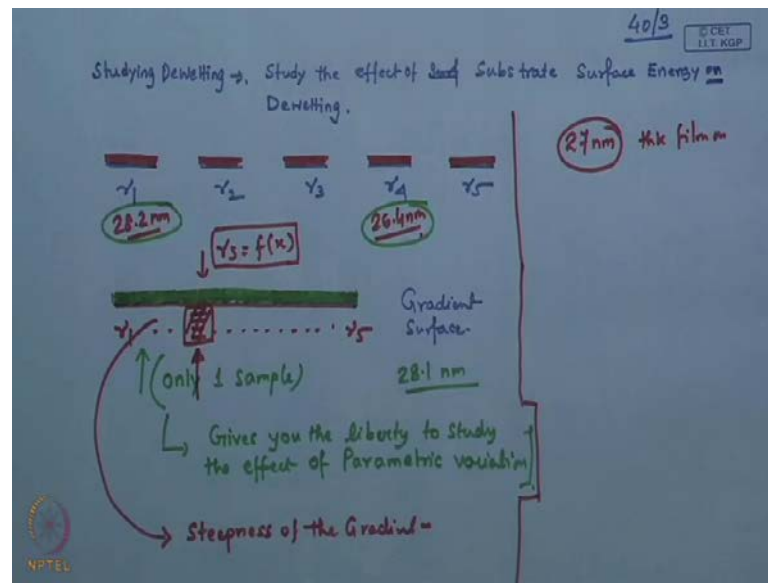
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But, before that let's have a quick look as to what are the applications of gradient surfaces. There are a whole lot of applications of gradient surfaces involved, because of the fact that within **within** a living body there are all sorts of gradients. So, for example, the transfer of oxygen or dissolved oxygen from blood to the individual cells is through the gradient in concentration.

So, any transport across a membrane whether it is a biological membrane or an artificial membrane there is a gradient. So, gradients exist everywhere, but gradient surfaces can sort of find a whole lot of applications in tissue, control cell, adhesion, protein adsorption, interfacial phenomena, involve in protein cell enzymes, bio compatibility issues etcetera, **etcetera** but most importantly even in our engineering and physical experiments they can be extremely useful, for what is known as combinatorial analysis. So, this reduces the number of samples to a large extent and also reduces the chances of sample specific errors.

So, I will give you the example which we will make you understand, given an example from what we have already studied, which will give you an idea or make you understand what can be the utility of a gradient surface.

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Suppose you are studying deviating and you would like to study the effect of substrate surface energy on deviating. We all know that substrate surface energy the wet ability sort of significantly influences the deviating path way and instability. So, how would you critical study this you would probably take 5 different samples, with 5 different surface energies, and then do spin coating under actually they do identical conditions and then will individually study the deviating on the each of the sample. So, this is your most likely approach if you are designing experiment. So, firstly you need 5 sets of samples, secondly the most critical thing you need any experiment, we all know from our school days there will be some associated experimental error.

And that experimental error can be in the form of variation of thickness. So, though you do a sort of your spin coating under identical conditions for each of these samples, there might be some timing variations in the thickness. So therefore, what you might be study in the deviating of a 28.2 nanometer thick will mole gamma one surface, and in contrast you might be actually looking at a 26.4 nanometer thick film on a gamma surface to the surface energy of gamma 4.

So, but this term this you will assume that you may be you will look at all the samples and you will so that we have studied the effect of deviating of a 27 nanometer thick film on the effect of surface on a 27 nanometer thick film. Reality is that across individual samples the way you have process the thickness will vary from one sample to other

sample. So, it is perfectly fine lots of experiments are done in this fashion, but this all accumulates to the experimental error, that you see error seen observation in experiments. In contrast there also the conventional way of being an experiment firstly you need 5 gram 5 samples, which can be expensive number 1, and number 2 is that you sort of there might be uncontrolled error or accounted for unnoticed error in each of the samples, which can be which varies from sample to sample.

Instead of that if you now can create let say surface, where the surface energy varies from γ_1 on one side to γ_5 on other sides. It is a gradient surface and now you do a coating. So, the coating as been done at the same condition So, whether its 28.2 or 26.4 or 27.1 it is uniform across the entire sample. It is uniform across the entire sample. So, the error that was coming up, because of the sample to sample variation of the error that is associated with sample to sample variation is completely nullified. So you have whatever is your film thickness, you **you** might have it is highly also do that you might have tried to coat at 27 nanometer thick film and you have resulted, you have got a 28.1 nanometer thick film that is highly possible, but that 28.1 nanometer thick film is uniformed over the entire sample.

Only the other thing is that instead of using 5 different samples now you require only one sample. So, this only one sample gives you the liberty to study the effect of parametric variation. Only thing is that unlike a these cases where may be by coating of saline or some surface active molecules you could create different surface energy here, you have to create a gradient first gradient surface energy or whatever you want and the second important thing is you need to identify your distinguish or quantify the stiffness of the gradient.


So that you know the precise surface tension as a function of surface property can be γ a **sorry** it can be any other surface property it is topography. So, you can see some of the idea so for example, if you are looking at a deviating over this location you must have an idea at as to what type of surface energy configuration or what is the surface energy at this particular location. So, these are the only two things that are necessary this type of analysis is known as the combinative analysis, and as you can see it significantly reduces the number of samples and less chance of sample to sample error.

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What are Gradient Surfaces:

Surface gradients are surfaces with chemical or physical properties that gradually change over a given distance. A gradual change in a physical property, such as the wettability, can be induced by a change in surface chemistry, for example a gradually changing surface composition.

In general, surface-chemical gradients can be created in two ways. Either the outermost surface layer of a substrate is gradually modified, for example by irradiation with an energetic beam, or by chemical etching or a surface coating, such as a self-assembled monolayer or a thin polymer film, is attached to the surface in a gradual manner.

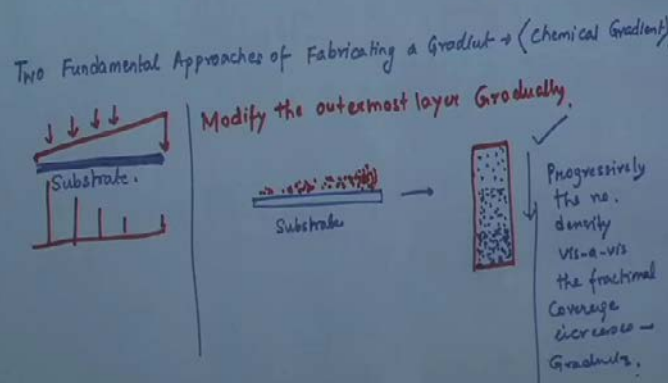


Now so, this is where one of the major advantages of gradient surfaces sort of coming in experimental studies related to nano scale or mezzo mechanical systems. So, important thing that from the stand point of fabrication that we need to understand is some techniques by which this gradients can be created. And as I have told that there can be two types of gradients the chemical gradients or the topography gradients. So, in generally the way a gradient is created is either the outer most surface layer of a substrate is gradually modified for example, by irradiation or the beam or chemical etching or whatever or the layer is attached to the surface in gradually manner.

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Two Fundamental Approaches of Fabricating a Gradient → (Chemical Gradient)




Modify the outermost layer Gradually.

Substrate

Substrate

Progressively the no. density vis-a-vis the fractional Coverage increases - Gradually.



So, there are essentially two approaches fabricating a gradient mostly a chemical gradient, but it can also be the approaches can be valid for a topographic gradient; one is the first is that. So, let us say this is the substrate so this is the outer most layer of the substrate and what you do, you modify this outer most layer gradually. So, let say you have a surface layer or same coated layer and you understand that let us say by u v exposure you can tell her it is a surface energy. So, you have some coated self as some do monolayer coated layer let us say which is giving you a contact angle of 110 degree. You know that if you expose it for 5 minutes the contact angle will be reduced to 90 degree, if you expose it for 10 minutes it will reduce to 70 degree, 20 minutes it will come down to 50 degree.

So, if you can do something like a moving u v lamp source, which sort of exposes at this location let say for 5 minutes, but remain stationary here for 10 minutes here, for 20 minutes here, for 30 minutes something like this. Then what are doing? You are essentially tailoring the extent of modification of the surface. And in this way you can create a gradient, the other way of doing it is if you are sort of if you have a substrate let say and you add some surface or some species to the surface in progressively varying numbers. So, suppose if you are adding some sample self assemble did monolayer molecules to the surface, and you add let say this many numbers over here, you add more number of molecules here, you had even more number of molecules here, you attach even more number of molecules here.

So, that way also it becomes possible to create a gradient so let us talk about this concept again a little bit. So, here let say this is over this zone this is the extent of coverage with the Sam molecules here, it is covered more and here its completely covered so let say the Sam molecules are hydro phobic in nature we understand. So, refer to our lectures on micro contact printing where we talked about the nature of this (()) or saline of the thiol molecules. So, if you do something by which you progressively vary the number density of this molecules on the surface.

So, progressively let say the number density vis a vis the fractional coverage increases. So, this results in also in a gradient. So, these are the two broad approaches by which a people are working on generating gradients, this is one of the simpler, approaches and majority of the chemical energy gradient that are fabricated even today are based on this

approach, but this is also possible and the case studying we will give on a soft lithography approach for generating topography gradient is based on this.

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Wettability gradient

The most commonly used technique for silanes was developed in 1992 by Chaudhury and Whitesides, who dissolved decyltrichlorosilane in paraffin oil and let it evaporate next to a silicon surface, kept vertical.

The silane diffuses along the surface, partially adsorbs and generates a gradual change in coverage.

This in turn results in a wettability gradient.

On such a surface, if a drop is placed it can move uphill due to the imbalance in forces due to surface tension acting on the liquid – solid contact line.



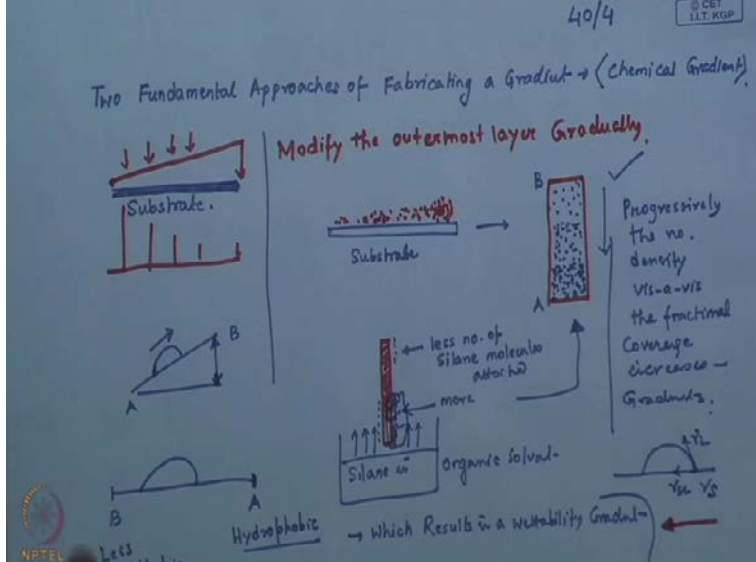
So, wet ability gradient the most commonly used technique is for silence was developed in 1992 by chaudhury and white sides all the did was the dissolved (())

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Two Fundamental Approaches of Fabricating a Gradient → (Chemical Gradient)

Modify the outermost layer Gradually.



Substrate

Substrate

Substrate

Organic solvent

Silane in

less no. of silane molecules attached


move

Progressively the no. density vis-a-vis the fractional coverage increases - Gradually.

Hydrophobic

Less hydrophobic

→ which Results in a wettability Gradient



I am **sorry** cannot pronounce the **the** name of the silant properly in paraffin oil and let it evaporate. So, all the did was this was the bath which contain the **the** silant in a organic solvent. And the surface which was to be silenced was simply kept like this. So, as the

molecules evaporated so, naturally the number of molecules that attached on to this substrate was more over this locations as compare to the far away corners.

So, this resulted in a morph in a system like this. So, if the silent let say the silence where hydrophobic so here, the coverage was nearly complete it so more than a single layer and here progressively the coverage reduced. So, if you now look at this sample or this glass slide, let see it is a simple glass slide from the a end to the b end here, its much the hydrophobic in nature as compare to lesser degree of hydrophobicity at this end. And there is a progressive variation, because as it is takes particle. So, the diffusion path of the molecules is higher.

So, here more number of molecules will attach and then progressively less number of molecules will attach as you go further away from the source of the molecules. So, this **this** results essentially in a surface with a chemical energy gradient which results in a wet ability gradient. If you now place there was a famous experiment they perform, that you place a drop of water like the drop of water on this type of a surface and it was kept on a in line in plane from the hydrophobic.

So, a end was here and b end was here. So, ideally gravity will always pull the drop downward, but here they could show the chaudhury and white sides very famous paper which appeared in 1992 science, that the droplet actually move upward. And this upward movement was due to the in balance in forces due to surface tension acting on the liquid contact line. So, what happens is if you draw a drop for the young's configuration with always regard this is γ_s , γ_l , and γ_{sl} , however here the gamma is continuously varied. So, the there was an in balance in the along the contact line which resulted in a passive driving force for the drop to move, and of the drop size was small the inertial effects was not very high, and this allow the drop to move up in against the gravity.

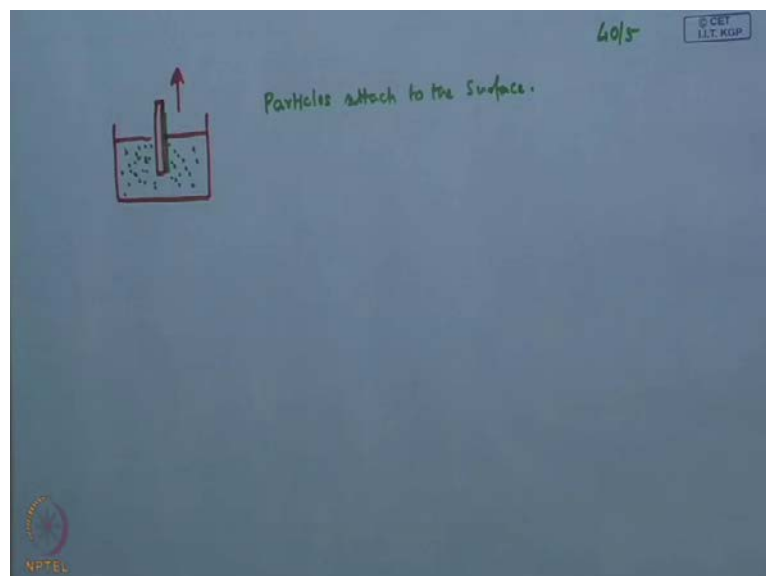
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- **Electrochemical gradient:** Surface electrochemical potential gradient produces a spatial variation in coverage of SAMs which results in a surface composition gradient.
- **Optical Intensity Gradient:** Gradient colloidal crystals with a thickness gradient prepared by dip coating technique leads to a gradient of optical intensity at the dip in transmission light.
- **Gradient chemical micropatterns:** Micro contact printing with varying contact time produces micropatterns that gradually and systematically change in their chemical contrast.
- **Microfluidic technique:** Controlled diffusive mixing of species in solutions flowing laminarily inside microchannels.

Plummer, S. T.; Bohn, P. W. *Langmuir* **2002**, *18*, 4142-4149
Li, J.; Han, Y. *Langmuir* **2006**, *22*, 1885 – 1890
Juthongpipit, D.; Faselka, M. J.; Zhang, W.; Nguyen, T.; Amis, E. J. *Nano Letts* **2005**, *5*, 1535 – 1540

So, this is the pioneering experiment and this as showed by many others subsequently. The attentive various other types of radiant like electrochemical gradient, where the surface electrochemical potential gradient produces a spatial variation in the coverage of Sam, which results in a surface composition gradient. You can create an optical intensity gradient. So, you take some colloidal crystals with a thickness gradient prepared by dip coating.

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So, this is a simple so you take bath of colloidal crystals and you are with drawing this is in fact one of the very common ways of a fabricating topography gradient. So, what you do you can dip it in a bath of nano particle or colloidal crystal and you can do two things. So, as you with draw some particles will attach to the surface. Now this rate of attachment can be controlled in two ways either, you vary progressively with draws speed or what you can do you can take a chemically pattern surface which offers different chemical properties on the surface which results in **in** a wet ability contrast or the variation in the extent of addition. And that will lead to different numbers umber density molecules attachment different equations. So, this is one of the most popular ways of fabricating topography gradient surfaces, and by inferring the density of the particles that are attachment.


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Fabrication of Topographic Gradient

The most widely used method is to attach nano particles or colloidal particles to a surface in progressively varying numbers.

A simple, robust technique is based on adsorbing gold nano particles on a polymer surface with chemical gradient.

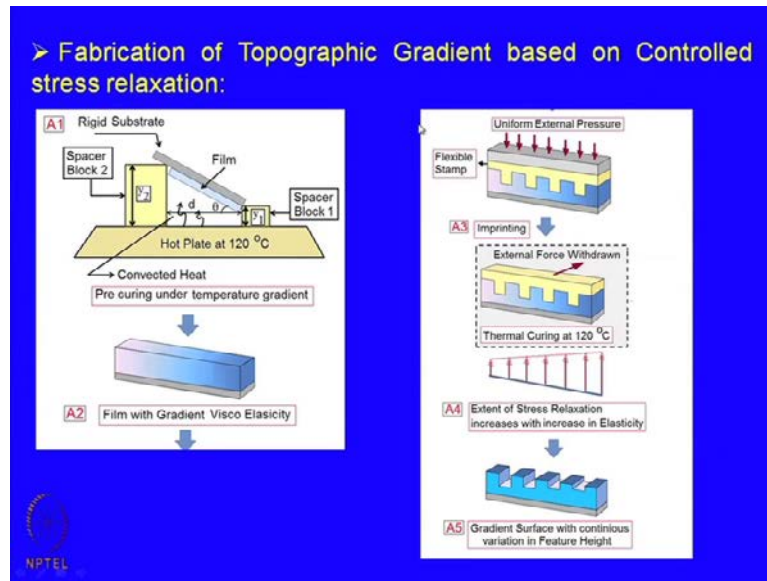
Approaches based on making a closely packed polymer colloidal array to a temperature gradient, which resulted in differential melting and coalescence of the beads along the length of the film, leading to a progressive morphological and roughness variation.



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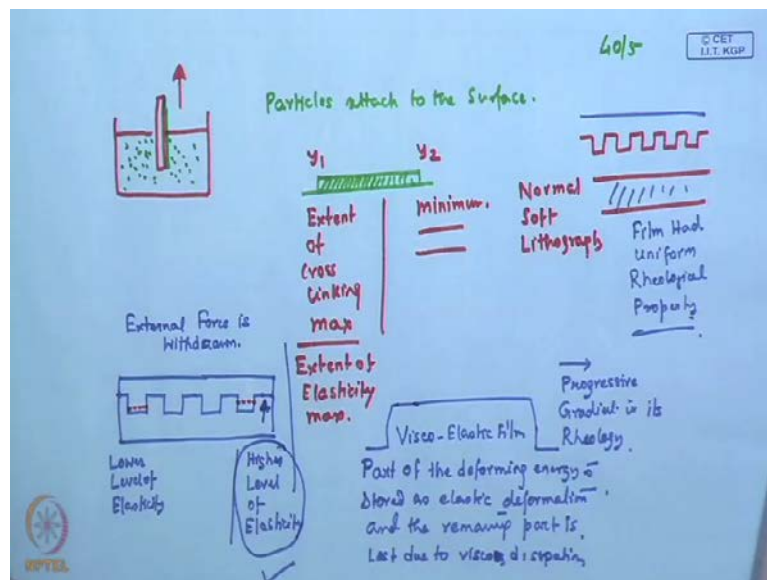
And there can there has been various other approaches of making these types of surfaces.

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We present here a very simple approach or so all that was taken we all understand about the sylgard film.

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Now so, we took a same sylgard film was taken and it was subjected to a temperature gradient like this. So, it was just a normal hot plate and it was kept a with two place blocks like this. So, different parts of the film surface where at different distance from the hot plate. So, if the film was cured for a infinite or preclude for a infinite duration different locations of the film d c different extent of heat. And we all understand the

thermal cross link will link of a **a** sylgard film. So, what happened is different locations the extent of cross linking was different. So, let say at the y 1 n which was closes to the hot plate, and the white went y at which was further from the hot plate here, the extent of cross linking was maximum in contrast here, and the extent of cross linking was minimum. So, eventually the extent of elasticity was maximum at this end as compare to the elasticity extent of elasticity was minimum at other end.

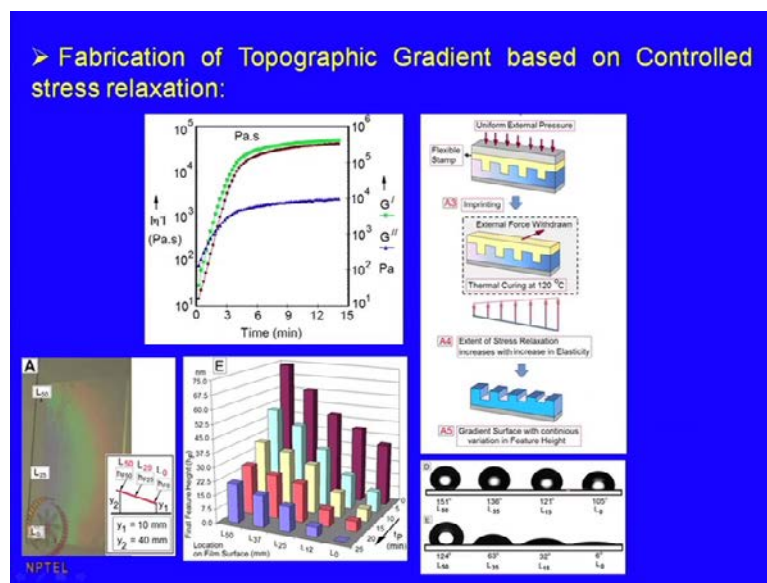
So, a preclude film for a definite duration the preclude in time can also valid at a progressive of gradient in the extent of visco elasticity. And what was done that this film with a visco elasticity gradient. So, in a normal soft lithography root or even in elastic contact lithography you where in printing a film which as uniform rheological properties. So, the fill had uniformed rheological properties in contrast here we are now talking about a film which as a progressive gradient units rheology. So, the level of visco elasticity varies from one end to the other of the film. Now this type of film is a is embarrassed or imprinted with a stamp under uniform external pressure, you can still probably get a prefect negative replica on the entire stamp surface, but think of the scenario that you apply on a external pressure you imprinted and then you with draw a the external force.

So, now you have withdrawn the external force by imprinting a partial cured visco elasticity film. So, what happens as we have talked in terms of elasticity instability in the previous class, ideally once the external force is withdrawn, this film will try to relax back to its original flag morphology, but and that is; because part of the energy that you have applied during this deformation which is causing the surface deformation at the length scale of each of the features is stored within the elastic matrix. This is visco elasticity film so it is not a fully crossing film. So, part of the energy is lost as viscose desperation in the form of visco desperation and part of the energy is stored within the elastic matrix which tries to relax back in the form of stress relaxation. Now what happens is as the extent of visco velocity varies from one into the other, and let say this is the y 1 and or let say this is the y 1 end, where the extent of the elasticity is maximum.

So, the extent of recovery will be higher in **in** this side of the film as compare to this side. And what will be the manifestation of the recovery of the stress relaxation that will be since the stamp is already placed on the surface. So, you have here you have film you had applied had applied on external force and external force now withdrawn and here

you have higher level of velocity here you have lower level of velocity. So, since the start of the energy since it is a visco elasticity film, and remaining part is withdrawn is lost due to viscose desperation. So, here the extent of energy that is stored within the as elastic deformation is higher and therefore, the stress will relaxation will b higher here, which will be in the form of pushing the stamp upwards? So, this location at this location the stress relaxation will be more and the film will push the stamp upward by an higher extent as compare to this location, and this eventually results in the film where you have a gradient in the feature height.

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So, it is because of this **this** typical rheological response you can see for a sylgard. So, with time it is a progressive cross linking. So, which translates in our case to the fact that the thought of the film which have receive more heat sort of is higher cross links states for a elasticity is higher therefore, the stress relaxation will be higher there.

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Course Conclusion

Utility is limited by lack of long range order.

Advantage:
*When feature size needs to be altered:
Any Existing Lithography Method
Requires New Stamp or Master.
In Methods Based on Self Organization of Thin Films:
Just Change the initial Film thickness!*

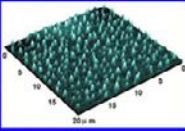
Aligned self organized structures.

Feature size generally scales with properties like initial film thickness, surface and interfacial tensions etc.


For example: Dewetting of a 40 nm thick PS film gives ~ 13 μm droplet size.

Is it possible to achieve droplet size of ~ 2 μm , starting with the same film?

Pattern Miniaturization



Dewetting



Mean Island Height

NPTEL 12

And eventually once you allow the film to relax it will result in structures with different gradients with gradient. Interesting thing is that here you can if you look at the experimental configuration we had use two spacer blocks. So, important thing to note two space of blocks where used, important thing to note is the stiffness of the gradient we can be controlled by two ways firstly by varying height of the two space of blocks. So, that is the first approach film can have two different spacer blocks which will essentially result in variation of the stiffness of the gradient in visco elasticity and which will eventually transform into the stiffness of the gradient of the final structure.

The other interesting or important thing is that there is a second tuning parameter and that tuning parameter is the pre curing time. So, you are doing a pre curing so if you are pre curing time is less, and then the film will remain in a predominately viscous state, in contrast if you pre curing time is more, then the film remains are progressively goes to a predominately elastic state. So, by varying the pre curing time you can vary whether you **you** would like to have your film during in printing in viscous state or in a gradually elastic state. So, if you pre curing time is less the film will be predominately in viscous state.

So, the extent of viscous dissipation will be lower will be higher, the amount of energy that will be stored in the form of elastic deformation will be lower and then therefore, you will get a gradient surface, but with deeper or higher feature height. In contrast if you

sort of which is very clear from this particular graph. So, this is the pre curing time and you can see that with increase in the pre curing time you can for all the procuring times you indeed get a gradient, but as you pre curing time sort of becomes higher progressive with over all depth of the features sort of reduces.

You can also take a different configurations of the spicier heights and can further control the stiffness of the gradient, with appropriate stamps with high aspect ratio it becomes possible by this way to create a this topography gradient can get transferred to wett ability gradient. As well and it is possible to achieve wett ability gradients within the hydrophobic resume for example, what you see here or I gradient which ranges all the way from the hydrophilic to reasonable hydrophobic extent.

So, this is just one example, what I decided to give you of a actually implemented or fabricated topography gradient surface, but there are very many ways to fabricated there but this is one rare example I must say where were a simple soft lithography approach has been used to fabricated topography gradient. And a more importantly that this gradient is created in one step method, because majority of the topography gradients the patterns you topography gradient surface is one wants to generate it is typically a 2 step process firstly you fabricate a chemical wett ability gradient, and then you attach particles to in progressively varying numbers. Or of course, one can prepare custom tailored stamp or masters with progressive varying feature size ad can creative.

But, then while discussing soft lithography we have repeatedly talk that, surfaces with our stamps with special stamps anyway have to be fabricated by some high end photolithography or other type of lithography techniques. And therefore, they are expensive to implement is this is a very simple way that one single stamp can be used and one can generate a photography structure. I would strongly encourage you to looking to other aspects of fabricated great gradients are other methods of a gradients which can be made or what are the other techniques, you can search in the internet. So, the whole lot of literature that is available again fabricating grandniece is a very advanced area of lot of researches still going on.

And as I have already told there is lots of application. So, me of the methods are required which are reported with where sophisticated instruments, like controlled exposure explosion there is a very popular method called flow coating. So, where it is **it is** you can

have look at what is flow coating. It is a flow coated which a allows you it is sort of comes with silicone and a doctor blade which sort of allows you to fabricated films with different thickness at different location very worst style method very simple, but it sort of allows you to make **make** gradients. So, if you are lets talking about a blame film or a block copolymer film with a flow coated you vary the film thickness from one into the other you immediately get variation in the morphology which can be a transferred or to topography gradient.

So, gradients are very interesting and sort of there they have quite bit of a application and a fabrication techniques are setting and they are involving. So, with that I think I will come formally to the end of this course, on instability and patterning of thin films. Just a quick sum up we talked about first about applications of mezzo patterned surfaces, and then talk a little bit about surfaces and then talk a little bit about surface will at phenomena, because we are talking about surface patterning at mezzo skill the mentions. So, after the course I expect that you understand what exactly is a thing film, and how they are different from layer of a bulk liquid bulk film or so essentially we classified it in terms of a where the inertial introductions are active and then first we focused a little bit significantly on different pattern in techniques and we argued that photolithography is one of the main stress in the micro electronics industry.

And though it is not particularly useful for patterning polymers, but having a good knowledge of its extremely its essential and therefore, we discussed a photolithography in somewhat more detail other important aspect of photolithography while it is sort of still finds utility in patterning of a in a course which talks about patterning of polymers, is at hot photo lithographically you can generates structures, which are sort of which can which actually can pattern only of photo resist layer which is again a polymer.

So, subsequently after photolithography we moved on and moved on to talking about different soft lithography, group of methods, which are the sort of a great polymers specific techniques, and we introduced you to **to** different pipes of patterns, like topography patterns, chemical patterns, and we showed a based on the soft lithography group of methods it becomes possible to create verity of structures. So, by micro contact printing for example, it is possible to create chemical patterns by methods like nano impedance, lithography capillary force lithography, micro modeling in capillary it is becomes possible to create topography structures.

A flexible method like micro modeling in capillary allows you to make structures not only in polymers, but also in collides which is extremely exceeding. And things like that we also talked about a very novel concept of micro contact printing, nu t n sorry we talked about micro transfer modeling. This allows you to extend the soft lithographic methods for fabricating three dimensional structures. So, that is a very important aspect where you can a create two 3 d structures based on a soft lithography approach at the mezzo skill. So, after we discussed on direct patterning or the top down lithography techniques we eventually move on to the instabilities.

So, we understood the surface interaction, we understood the Van der waal forces the intermolecular force, is there origin how they scaling sort of changes between introduction of two particles to introduction of two surfaces. And in the mean time you also had a detail understanding a reasonable understanding of one of the major characterizations tools that is used for in these type of studies, that atomic force microscope, because we argue that be making this structure at the mezzo and nano scales,

but it extremely important to a examine the structures and atomic force there is no better way to do it than an atomic force microscope if not for any samples it is for the fact that two three dimension, true resolution in the zee or you get the true height of the features. So, we did that and atomic force microscope again realize mostly on intra atomic interaction which is Van der waal forces. So, we understood the nature of Van der waal forces and then we examine, how these Van der waal forces sort of a amplifier in ultra thin film depending on a situation to situation, a leads to spontaneous disintegration or deviating of a ultra thin liquid polymer films. And will look into the experimental aspects as a theoretical aspects based on the governing equation and the linear civility analysis. We understood how the sign of the effective homer can constant sort of determines or the the partial divertive of phi with each that say del phi del h, that is the variation of the effect interface potential with h sort of a plays a decisive role theoretically on the stability and dynamics of a system.

We understood the roles of individual parameters, we understood how surface tension opposes an any sorts of instabilities surface and evolutions. We understood that how viscosity for example, controls as an important role it is sort of controls the dynamics of the system, but it never induce instability we also looked at how the or what are the

sequential events under which a film can eventually become unstable. And saw that how surface tension sort of undergoes a role reversal from an opposing role before the film ruptures to a role where it actually favors. So, happening up of a whole then we looked at the various aspects of a deviating stages and look at the different morphology.

So, formation of whole growth of holes the formation of reams pleasure of reams formation of ribbons, and break in breakage of the ribbons into isolated droplets. We also talked about the role of visco velocity and slip edge on dividing. And how the morphology sort of differs in cases where you have significant slippage or the viscose or how the effect of visco velocity becomes prominent as compared to deviating of a film which is in a fuel viscose resume. And subsequently we argued that in the last few classes, that instability in the way we also did mentioned about some special cases, one of them is boiler instability, how depending on which of the inter phase become substrate first how the overall morphology of the system can be significantly or strongly influenced by that.

We also talked about briefly about strategies two works out a strategy to **to** suppress deviating. This type of instability can be very excited from the stand point of basic physics as well as for some mezzo scale pattern formation, but from the stand point of a coating where a thin film finds maximum application this is completely undesirable. So, we talked about suppression of deviating and a 1 of the approaches we talked about a is by addition of nano particles, where we are good that the addition of this nano particles sort of locally alters the rheological properties. And finally, we talked about one of the limitations. So, we argued that in a instability mediator process you have additional handles or tuning parameters like film thickness etcetera **etcetera** by which you can controlled the pattern geometry pattern order things like that. So, the let say the periodicity of the structures can be influenced by issues like film thickness, surface tension things like that also the to the extent allow the instability process to run you can quench the process at any intermediate stage.

You can take advantage of the fact that most of the non-linear techniques non-linear methods and multiple steady states. So, you can sort of gift your technique in one of the directions, and you can sort of often to any metal stable minima to stop process stop the evaluation of that stage, but most of the instability mediation techniques sort of lack long range order and for that we have talked about in the last couple of lectures, about how

these instability mediator structures can be alien by suitable tempera ting strategies which include use of topographically pattern stamp or substrate which as a combination of self organization, and then top down lithography techniques eventually resulting in aliened instability structures. And in the last lectures as a special topic I will just introduced to you concept of a gradient surfaces. Hope you enjoyed the course **thank you** very much for attending.