

Instability & Patterning of Thin Polymer Films
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Lecture No#26
Atomic Force Microscope – V

(Refer Slide Time: 00:34)

Instability and Patterning of Thin Polymer Films
Atomic Force Microscope - 5

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Lecture 26

Welcome back, this is probably the last lecture on atomic force microscopy. We have already spent four hours discussing different aspect of atomic force microscope. So, I understand, now you are a little well conversant with the instrument, you understand what are the critical hardware components or elements of the instrument and you also understand, sort of discussed in some more detail about the two primary modes by which an atomic force microscope, sort of, scans or generates the information about a surface. And they are, if you remember the contact mode, which is the most simple and the conventional mode of imaging and the intermittent contact or tapping mode. We have also talked about the non-contact mode in somewhat detail.

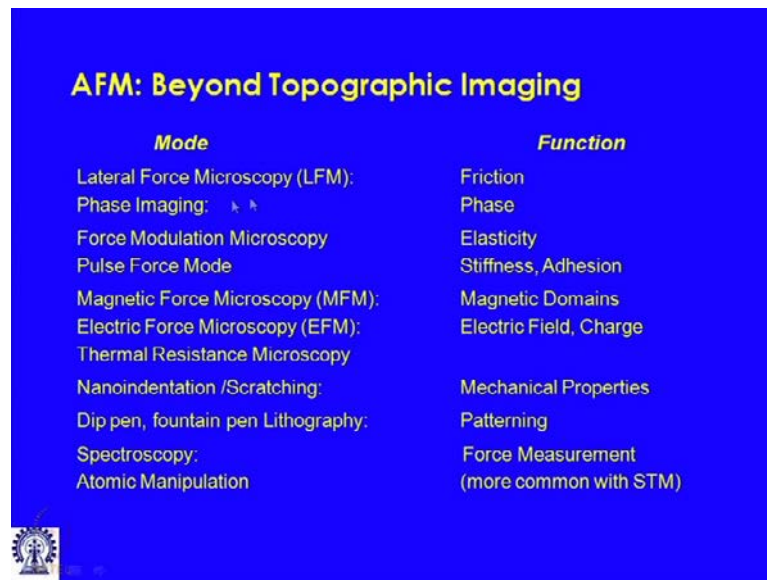
Now, as you have realized or we have repeatedly been mentioning or discussing, that unlike other microscopes where an image of the sample to be scanned under a great deal of higher magnification is taken in an atomic force microscope, a probe actually goes to

the surface and fix up the point-by-point information about the topography and reconstructs it based on data rendering to generate your image. So, as the probe actually, physically visits or physically comes in contact in most of the cases or even in non-contact mode, is in proximal contact with the, is in proximity to the surface.

So, in addition to the topography or how the surface looks, a whole lot of other information can also be, sort of, acquired from these measurements or even performing the atomic force microscopy or some of them can be, sort of, just comes as an auxiliary out of the normal or the stranded modes, like contact mode, imaging or tapping or intermittent contact mode imaging. Some of the modes can be, sort of, some of this additional information can be extracted under some specific conditions, for example, examples of which include magnetic force microscopy or electrical force microscopy. These are type of very specific microscopy tools, which can be, sort of, used to identify different domains with different magnetic orientations or electrical charge or electrical property.

For example, if you look at computer hardware or an erstwhile old floppy disk, these are magnetic storage media, but topographically they are absolutely flat, there is no topography contrast. So, if you see it under any stranded microscopy, including scanning, electron microscope or if you do a normal routine contact mode imaging scan with an atomic force microscope, what you will see, that it is most likely completely flat substrate. But under MFM, for example, magnetic force microscopy, which is not a direct output of any one of the modes, like contact mode or intermittent contact mode, but sudden specific arrangements specialized (()) etcetera needs to be used, it becomes possible to identify these magnetic domains. So, this is what is called as a secondary imaging mode.

(Refer Slide Time: 04:32)



<i>Mode</i>	<i>Function</i>
Lateral Force Microscopy (LFM):	Friction
Phase Imaging: > >	Phase
Force Modulation Microscopy	Elasticity
Pulse Force Mode	Stiffness, Adhesion
Magnetic Force Microscopy (MFM):	Magnetic Domains
Electric Force Microscopy (EFM):	Electric Field, Charge
Thermal Resistance Microscopy	
Nanoindentation /Scratching:	Mechanical Properties
Dip pen, fountain pen Lithography:	Patterning
Spectroscopy:	Force Measurement
Atomic Manipulation	(more common with STM)

There are a whole lot of things, that can be done and also, before I forget I must mention, that in addition to imaging, the rastering action can also be, to some extent, used in patterning technique as one of the direct write patterning technique and in most cases, this is what is known as or referred to as the DPN or the dip-pen nano lithography operation. So, we will talk about some of this and some of the secondary imaging modes of an atomic force microscope.

So, we have already... So, here some of the information about or some of the mode, that the atomic force, the secondary atomic force microscope imaging modes, so they are lateral force microscopy. And we also have a small list of the functionalities, we have phase imaging, we have force modulation microscopy pulse force mode, etcetera. Then, we have magnetic force microscope and electrical force microscope, particularly, we will pickup lateral force microscopy, phase imaging. These two are interesting because they are direct offshoot of the contact mode and the intermittent contact mode imaging. No additional mechanism or nothing needs to be done, this information just comes out and any sort of standard or conventional or commercially available instrument.

If you are doing contact mode imaging we will get the lateral force of the friction force image straightaway. If you are doing an intermittent contact or tapping mode imaging, you will get the information about phase imaging. We will discuss in little bit of detail what they are, then we will talk about, little bit about the force modulation microscopy,

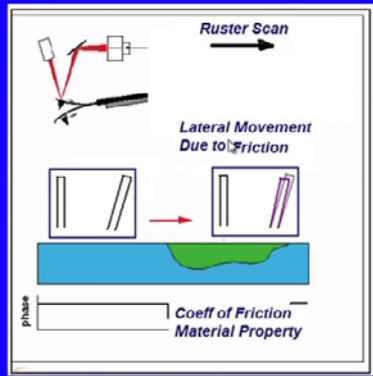
which (()) has an additional pulsation and oscillation during contact mode. So, this is distinct from tapping mode or non-contact mode, which sort of gives about the local elastic property of a surface. We will not talk about pulse force mode; this is some sort of an extension about force modulation microscopy.

So, anyone who is interested can, sort of, figure out what this is, then we will try. I will try to give you some glimpse about the magnetic force microscope and electrical force microscopy, both of them, sort of, has very similar operating principals. They, they, sort of, involve a contact mode scan, as well as, the non-contact mode scan and then, one has to be do some bit of clever subtraction of the scans, you get to indentify the different domains. They rely on the fact, that the different forces in proximity to the surface of the different scaling property and therefore, they are different. So, we will see how it looks like. Then, there can be other types of microscopy, like thermal resistance microscopy and nano-indentation and scratching and then, we will discuss this bit, little bit in detail, dip-pen nano lithography for, for patterning of surfaces.

One can, we mentioned, that one can also measure the force between a surface and, and between two surfaces using an AFM, so I will try to give you an example where these forces can be measured. And we will see that the colloidal probes, we talked a couple of classes before, plays an important role in measurement of these forces.

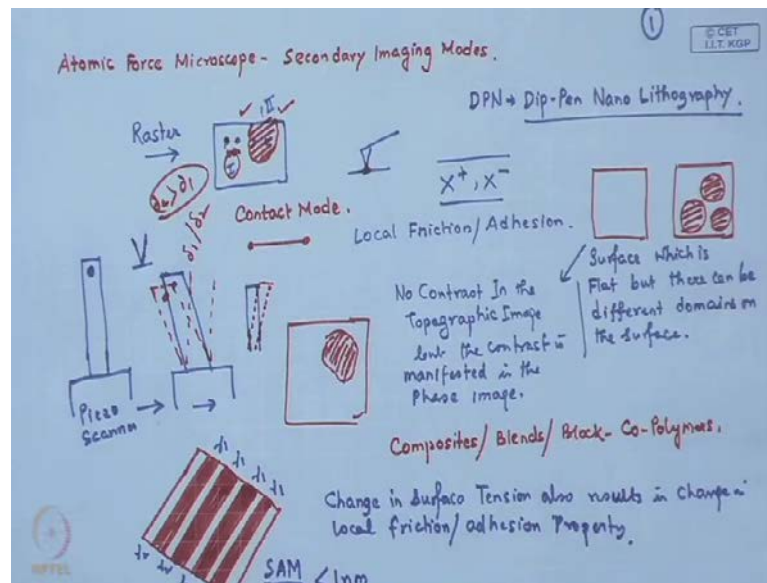
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Lateral Force Microscopy (LFM)



- Powerful extension of Contact Mode AFM.
- Goes beyond Topographical imaging to detect:
 - Friction
 - Adhesion
 - Mapping of different components of composites, block co-polymers etc.
 - Mapping of different surface energy domains.
- It measures the torsional deformation of the probe, rather than its vertical deflection.

(Refer Slide Time: 7:08)



So, what is lateral force microscopy? It is, very simply put, it is as follows. As we are dragging as during the raster action, as we are dragging your cantilever tip along, along a particular surface, so what happens is, at any every instance of time, as the sort of tip visits any specific point depending on the adhesiveness of the material, there is a force of adhesion between the tip and the surface. Now, this nature of adhesion, or of, and it has to drag, so the, from one point to the other it travels along the surface. We have already talked about contact mode, so this travel from one point to the other, it is the surface, the tip is dragging along the surface. There is static, there is a dynamic friction between the tip and the surface.

Now, you understand, you, if we have a different domain, a domain of a different material or let us say, different phase on the surface, then what we will happen? The frictional property over hear, let us say, the phase one and the phase two will be different. Therefore, when you are, when the (()) sort of applies the same voltage for the motion in the x direction by manipulating the x plus and x minus components of the Piezo. We already have talked about all these things.

What happens is, under the same force, the extent of local adhesion or the local friction between the tip and the surface becomes different or becomes a function of the phase of the domain, or in other words, if this is your cantilever from the top because of localized friction and let us say, it is sort of, there is a lateral distortion or lateral moment of the tip

in along this. Because what is happening, when you are dragging the tip here, the tip is in contact, the, the sort of Piezo moves from this direction where it is mounted, so this follows or drags like this. So, to what extent there is going to be lateral torsion or twisting is a function of the friction properties.

So, if over this zone and this zone the frictional properties of the level of additional different, then what is going to happen? The extent of twisting over the zone one and extent of the twisting over zone two we will be different. So, it is something like this, what is shown here. So, if this is the sort of the lateral displacement or deflection over this particular zone, let us say zone one, since the surface property also affects the friction property, as well as, the adhesion, the extent of lateral distortion or lateral deflection is different on, on the phase two. Therefore, in addition to the stranded topographic contrast, you also get an additional contrast in terms of it due to this lateral distortion and which correlates, essentially, localized friction and adhesion properties.

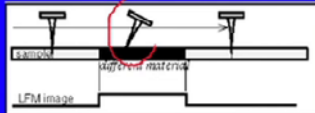
So, in this way you can map different components of composites or different domains or different domains are block-co-polymer are biased on a surface even when their might be no topography. So, you can have situations where there is the topography looks perfectly flat, but you can find out, that there are different domains, which appear in the friction image of the lateral force contrast. So, this gives you an idea, that this is a surface, which is flat, but there can be different domains on the surface and this contrast generates does not get reflected in the topographic image. So, this contrast, no contrast in the topographic image, but the contrast is manifested in the phase image.

So, this is what is lateral force microscopy. This gives you some sort of an idea about the extent of twisting, you can say, depending on one location to the other. I would say, that every location because of this motion.

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Lateral Force Microscopy (LFM)

- During scanning in contact mode the cantilever bends not only along normally to the surface but also the cantilever torsional deformation occurs. (Twisting)
- LFM measures the torsional deformation of the cantilever during scanning in contact mode.
- The lateral deformation depends on frictional force acting on tip.
- LFM studies are useful for imaging variations in surface friction that can arise from in homogeneity in surface.



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Atomic Force Microscope - Secondary Imaging Modes.

DPN → Dip-Pen Nano Lithography.

Raster → $\frac{dI}{dx}$

Contact Mode.

Local Friction/Adhesion.

No Contrast In the Topographic Image but the contrast is manifested in the Phase image.

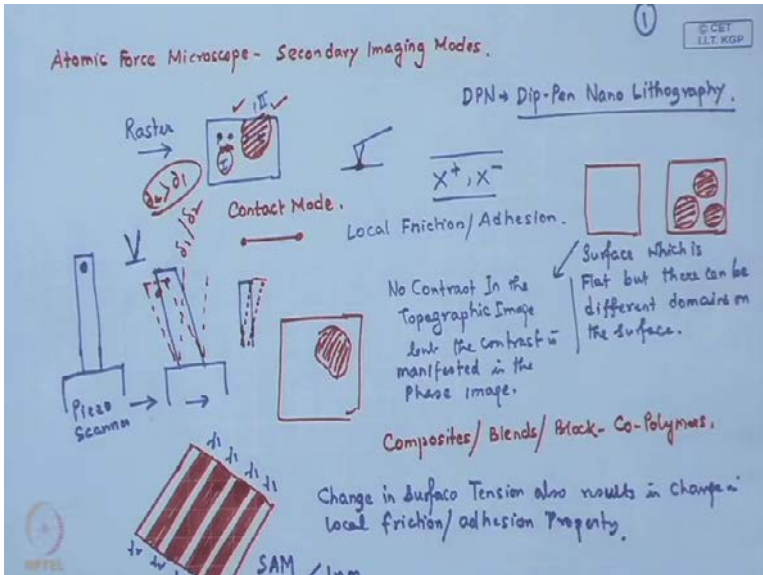
Surface which is flat but there can be different domains on the surface.

Composites/ Blends/ Block-Co-Polymers.

Change in surface Tension also results in change in local friction/adhesion property.

Piezo Scanner

SAM < 1nm

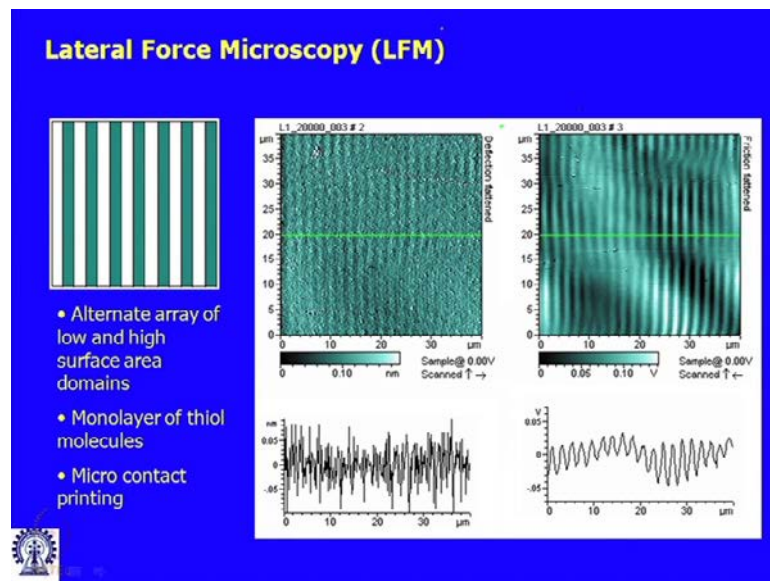


So, you have, I will repeat the figure you have. This is the cantilever, you are looking from the top, your TP is below this one, so you cannot see it from here. TP is below this one and touching the surface and this side it is mounted to the Piezo scanner. So, as a part of rastering the voltage is given herein to manipulate the x plus and x minus. So, this tries to move you and location where the tip is in contact with the surface. Because of the friction, static friction, this tries to hold back. So, this moment has an intermediate configuration like this, there is a time delay you can say.

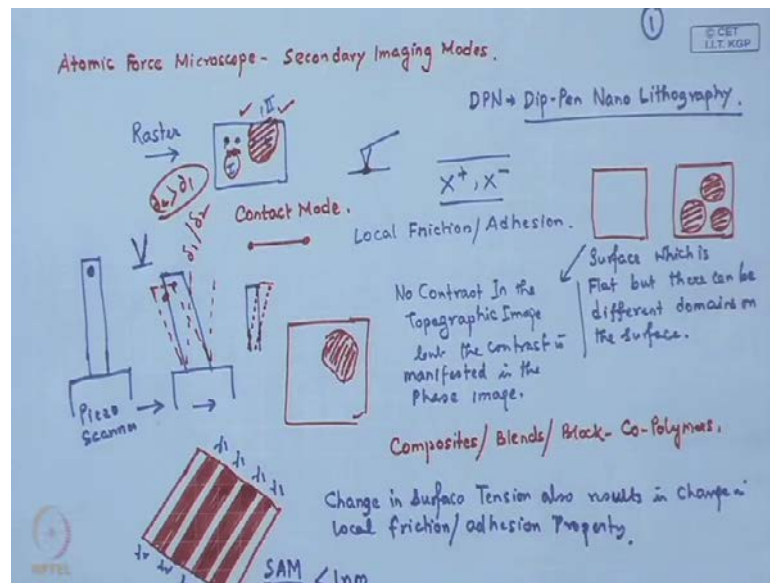
Now, this extent of, whatever is the delay or this deformation of deflection in the lateral direction, whatever that is, that becomes now a function of the local friction or adhesion on the surface. So, if a surface has higher level of friction, of the frictional opposition to movement of the tip along the surface or there is a domain, which is, which has higher friction, offers higher friction or is more adhesive than the extent of the lateral displacement, lateral distortion will be higher.

So, in that case, Δz will be higher than the Δx and is, there are distinct domains on the surface, which have different friction or adhesion properties, of course, this will show up as an additional contrast in the phase image. So, this is all about lateral force microscopy, very powerful tool to identify different domains, particularly useful in analyzing composites and blends and block-co-polymers.

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When exactly the, so other, an important aspect I, when we were talking about micro contact printing I showed this image, if you remember, five, six classes before and we showed, that I will discuss this in detail. So, micro contact printing, if you remember we talked about making of a surface, which is chemically patterned. So, there is no topography. So, there is virtually a flat surface, but you have isolated domains here, which have, let us say, higher or lower surface energy.

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But topographically this is flat, but so, but we know, that since we have micro contact printed, it is, these are surfaces, so these are areas where the surface tension is gamma one, these areas where the surface tension is gamma two. So, change in surface tension is also, also results in change in local friction or adhesion property. So, now, when you do a good contact mode scan, these are, if you remember these are self-assembled mono layer, so these are one molecular layer thick, which is sub-nano meter, so topographically nearly flat. But you have these domains, which have different surface properties, the friction properties, surface tension, adhesion, they are different.

So, what would you expect? You would expect, that your topographic image will be perfectly flat, but this, now you understand, that this contrast will be visible in your phase image and look at this image set now, it is exactly the same thing. So, this is the topography image or essentially, the diffraction image where it is nearly flat, but you see

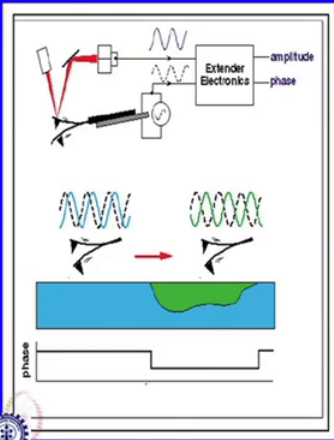
it is the frictional image and you very clearly see the presence of the strips, which are the different wettability regimes.

What you need to understand, that this friction image, of course, you know how the image has been generated, so it has been rendered brighter and darker zones. What you cannot say looking at this image is, whether the brighter zones or the darker zones corresponds to the gamma one areas or gamma two areas. This is something we cannot say looking at the image. What you must understand, that this gives you an idea, that there are some domains, which has difference in surface properties. It can be friction, it can be adhesion, it can be surface tension, whatever. But whether the darker one or the brighter one looks correspondence to the higher surface energy, low surface energy, you cannot directly correlate.

What you can correlate? You can look at the amount of voltage that is necessary and based on that you can identify, that domain, which offers more resistance, the black one offers more resistance to, for the tip to move on or it has got higher level of friction, that you can tell, but you must have some physical idea about what happens after you quote the surface with (()) layer from and how the friction gets altered. So, this is some application of lateral force microscopy.

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Phase Imaging

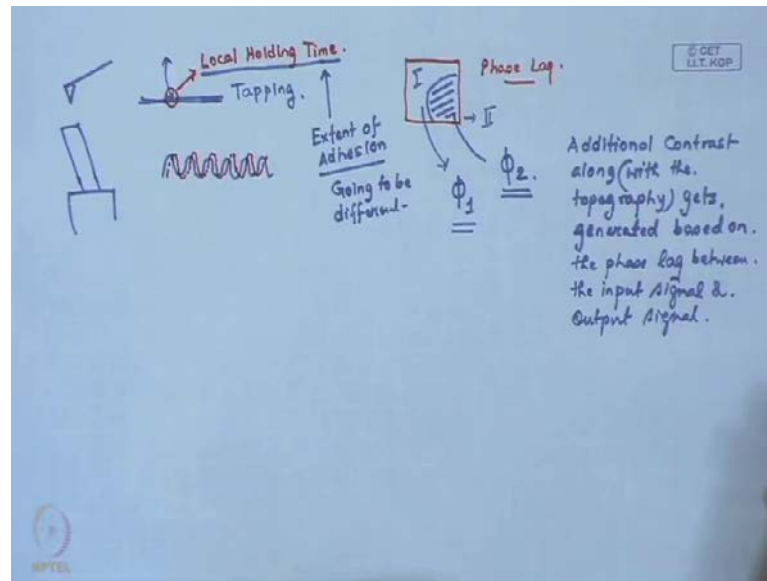


Phase imaging monitors the phase lag between the signal that drives the cantilever to oscillate and the cantilever oscillation output signal.

Phase detection images can be produced while an instrument is operating in any vibrating cantilever mode, such as tapping mode AFM, MFM, EFM.

- The phase lag is monitored while the topographic image is being taken so that images of topography and material properties can be collected simultaneously

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An exactly equivalent of lateral force microscopy in intermittent contact and tapping mode is the phase imaging, which essentially is, phase imaging monitors the phase lag between the signals that drives the cantilever. So, we understand that non-contact mode, as well as, an intermittent contact mode, there is an additional drive that sort of oscillates the cantilever like this, what you know here. So, what happens here? Due to the localized friction there was a lateral deflection or twisting of the cantilever. What happens here? Here, it is continuous oscillating and intermittent contact, it sort of tapping the surface now, depending on the adhesiveness here. So, so this is, let us say the input cycle, input pulse that is going on, sort of, that is oscillating the cantilever.

Now, depending on the nature of the, extent of the nature of, extent of local adhesion, there might be a delay, time delay or a phase lag between the input signal and output signal. So, this is like for a nano or pico second, as, as the surface sort of taps, it seems local contact. So, it sort of, you can argue, that this is some sort of local holding time. It is like due to the extent of the, due to the effect of adhesion, it sort of locally held for a friction of second or mini second, pico second.

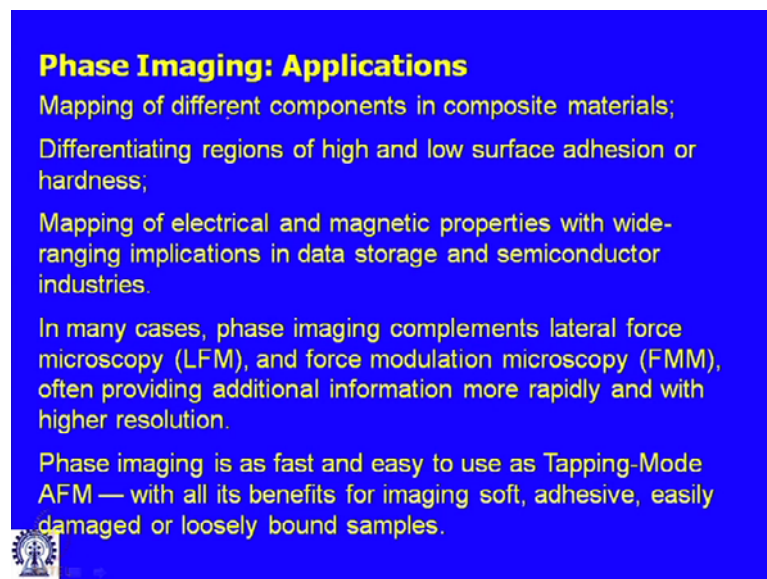
If the whole surface is made up of the same material, then what will happen? Of course, this, whatever is the time delay it is going to be same all over the surface and therefore, the phase lag or, or the phase lag in the sense, that phase lag of the, between the input signal and the output signal, the phase lag between the input signal and the output signal

is going to be uniform all over the surface. However, now again the same thing, if you have different domains on the surface.

So, this is let us say domain two and this is domain one. So, what will happen? Because of the surface properties of the different, they are this local holding time of the, extent of the, which is sort of a measure of the extent of the adhesion is going to be different. So, over here if that delay, that lag is by, let us say, is by an amount ϕ_1 degrees over here, the lag might be ϕ_2 degrees. So, there will be an additional contrast along with the topography gets generated based on the phase lag between the input signal and output signal. So, it is like this.

So, you see, let us say this green line is the input signal and the dotted line is the output signal, so you can see there is a phase lag. Now, the cantilever sort of encounters a different zone, let us say zone two, which let us say, has higher level of adhesion. So, therefore, the phase lag increases.

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Phase Imaging: Applications

Mapping of different components in composite materials;
Differentiating regions of high and low surface adhesion or hardness;

Mapping of electrical and magnetic properties with wide-ranging implications in data storage and semiconductor industries.

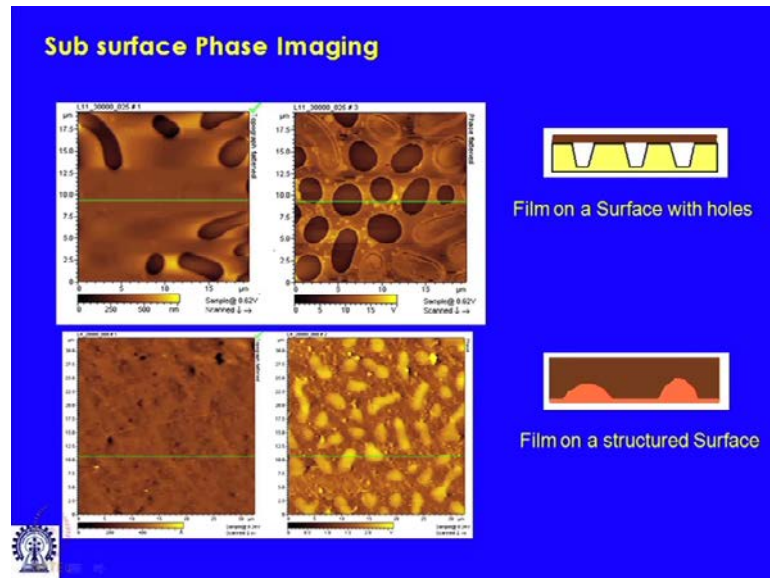
In many cases, phase imaging complements lateral force microscopy (LFM), and force modulation microscopy (FMM), often providing additional information more rapidly and with higher resolution.

Phase imaging is as fast and easy to use as Tapping-Mode AFM — with all its benefits for imaging soft, adhesive, easily damaged or loosely bound samples.

So, it can be sort of used for mapping of different composites or different components in composite materials; different regions of high and low surface adhesion or hardness. In, in many cases phase imaging complements lateral force microscope and force modulation microscope, something which as we are going to talk in a little detail. Phase imaging is fast and easy to use as tapping mode with AFM and with all the benefits for imaging (()) adhesive and loosely bound samples. So, this is a very nice extension. So,

you do not have to do anything, really no additional fixture or nothing is required, but all you need to do or this phase image is sort of consensus and auxiliary output to the standard intermittent contact or tapping mode.

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This is couple of example. So, this is how sub surface structures can be sort of imaged using, based on the phase imaging. So, this is a special example we had a sort of a holey surface and surface at some holes and which we have covered with a thin polymer film like this.

So, how the sample was prepared and all that, we are skipping the details. So, what we had was these whole square covered with the polymer film, which was have about 40 nano meter thick in this particular case. This is an example from our work in our own group, so very nice example for domain strength of phase imaging.

So, if you look at the topography, of course these areas are flat. These are some of the areas where the film has already ruptured over the hole and therefore, you can see the hole. So, there is nothing great, but over this area you have feeling, that the, that the surface is complete flat and which is also the case. But since there is a difference between, let us say, this area and this area because over this area when the cantilever taps, it is actually tapping on the surface on a, on a film, which is coated on the substrings. In contrast, when it taps over this particular area, it is, because it is tapping over here at this surface, it is tapping at a film, which is, which is self standing, which is sitting on

hollow cylindrical (()) or something like that. So, therefore, there the phase lag between the input and output signal over this area and over this area will be significantly different and precisely that we can see now in the phase contrast image.

So, this part of the film, which topography show, there is perfectly flat, there is nothing in the phase contrast image. You see, that it beautifully shows the sub surface holes. So, this is one of the strengths of phase contrast imaging. Similarly, you can have a film, a thick film, which is coated on a surface, which contains these types of random structures, on that a polymer film has been coated, which is perfectly flat. So, we, in one of our earlier lectures have talked about coating of a polymer film on a structured surface and we also argued, that if the film thickness is adequately thick in comparison to the height of the features, then film can be flat. So, this is a perfect example of that.

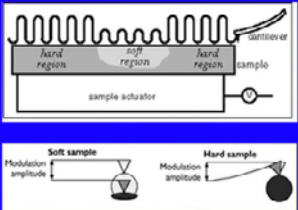
Topography shows, that the film is very, very flat. However, when you look at the phase, the phase can pick up these sub surface structures. The idea is very clear, here it is tapping over a film, which has local thickness of, let us say, H_1 . In contrast here, because of the surface features it is tapping over a film, which has film thickness of h_2 . So, there is a difference between the level of stiffness of the film over the two zones and which is aptly manifested in the phase contrast image. So, these are some examples of phase imaging.

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**Force Modulation Microscopy:
Secondary imaging Technique**

In FMM mode, the tip is scanned in contact with the sample, and the **z feedback loop maintains a constant cantilever deflection (as for contact mode AFM)**.

- Further, a periodic vertical oscillation signal is applied to either the tip or the sample. The amplitude of cantilever modulation that results from this applied signal varies according to the elastic properties of the sample.
- From the changes in the amplitude of cantilever modulation, the system generates a force modulation image --- a map of the sample's elastic properties.



The diagram illustrates the Force Modulation Microscopy (FMM) setup and its response. The top part shows a cross-section of the AFM system with a cantilever tip in contact with a sample. The sample is divided into three regions: 'hard region', 'soft region', and 'hard region'. A 'sample actuator' is shown below the sample. The cantilever tip is shown oscillating vertically. The bottom part shows two graphs of 'Modulation amplitude' versus 'Modulation amplitude'. The left graph shows a 'Soft sample' with a large modulation amplitude, and the right graph shows a 'Hard sample' with a small modulation amplitude.

The third mode, that we are going to talk to, there is another secondary imaging mode, but this one has to sort of work out additionally with some additional fixtures or additional inputs. It does not really come out free, like lateral force microscopy or phase contrast image is the force modulation microscopy. What is done in force modulation mode? The tip, it, it essentially, is a continuation of a contact mode in force modulation mode. The tip is scanned in contact with the sample and the feedback loop maintains a constant cantilever deflection. So, this is what is done in, in a contact mode AFM.

Further, a periodic vertical oscillation, oscillated signal is applied to either the tip or the sample. Now, the amplitude of the cantilever modulation that results from this applied signal varies according to the elastic properties of the sample. What it means? It means something like this. So, you are doing a contact mode imaging and now, you are giving an additional oscillation. Now, depending on how flexible or how elastic, soft your surface domains are. So, if you encounter a soft zone, softer zone, what will happen? This modulation or frequency, that this additional oscillation you have given, this will allow the peak to, sort of, penetrate or deform this softer region. In contrast, if it now encounters a hard or stiff region it will not be able to, sort of, deform it and therefore, there will be a difference in the output signal of this additional oscillation, that you have given over the, over a hard and soft region.

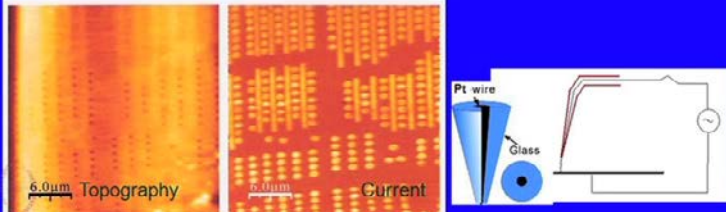
So, in hard region the amplitude of the output oscillation will be almost same as that of the input oscillation. However, over a soft region a part of this oscillation will get (()) or the dissipated over the softer zones and output signal will be much shorter amplitude. So, this can be sort of transferred into an additional contrast to generate. What is the main roll of FMM, force modulation microscopy? So, from the change in the amplitude of cantilever modulation, the system generates, generates a force modulation image, which essentially is nothing, but a map of the sample's elastic properties.

So, we can map the elastic properties, the local elastic properties of a, of a specific surface with nano meter scale lateral resolution with force modulation microscopy.

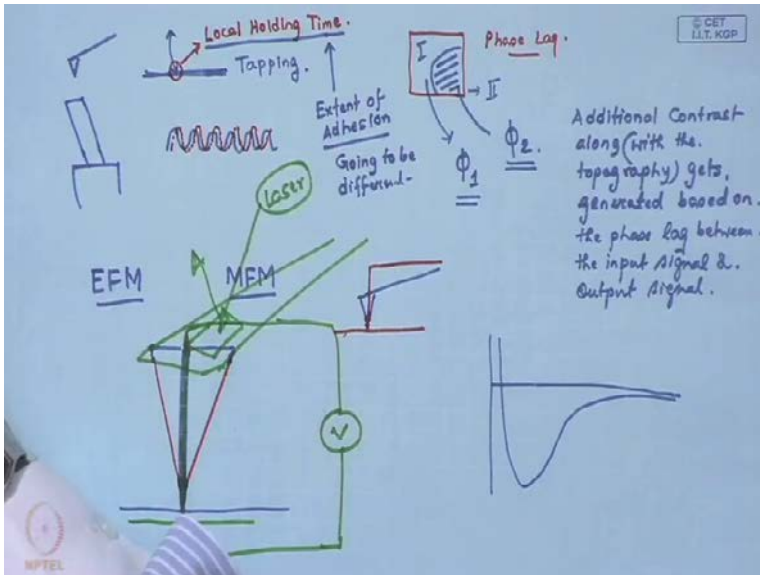
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Electrical Force Microscopy (EFM)

- A conductive AFM tip interacts with the sample through long-range Coulomb forces.
- These interactions change the oscillation amplitude and phase of the AFM cantilever, which are detected to create EFM or SP (surface potential) image.
- Mapping of different electrical property domains .. Screen printed circuits, or semiconductor chips etc.



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So, next week (()) to the other class of techniques, these are particularly EFM and MFM I should focus, I should mention, that is, the electrical force microscope and magnetic force microscope. These are very unique techniques, which sort of, allow you to identify either distinct electrical domains based on long range Coulomb forces, by taking advantage of the Coulomb forces or magnetic domain, by taking advantage of magnetic interaction.

So, please do not forget, that we are talking about an instrument, which goes by the name atomic force microscope and no way it is sort of limited to Van der Waal's force only, the Van der Waal's interaction only, that is impotent to realize. In most cases or in most generically, irrespective of the material Van der Waal's interaction will be present and therefore, the normal modes, like contact mode, tapping mode, they primarily work with the Van der Waal's forces. But the moment you have a setting where other types of interaction forces are also present, for example columbic forces or the magnetic forces, they can also be utilitised to identify different domains.

So, let us say, so in order to, however, in order to operate these two techniques, specifically EFM and MFM, we need a secondary circuit. So, what needs to be done? In addition to the cantilever assembly we need to have an electrical contact with the surface. So, through which a bias has to be given. So, typically, a platinum wire is sort of drilled through a glass probe like this with an annular opening through which the platinum wire is sent, so it, I will draw it in greater detail, so this is the probe. Now, it is a little bigger than the standard silicon probe, does not really matter, so what, what it result is a little bit of loss of lateral resolution. So, this is how the probe looks like now.

You typically insert a platinum wire or any wire, conducting wire through this and this is the surface. So, as it approaches, the wire physically comes in contact with the surface there is. So, the surface has to be conducting surface and you complete a circuit by applying a voltage (()) from outside. So, in addition to this beam bounce probe, etcetera, etcetera where the laser is operational like a stranded AFM. You additionally have an electrical source, electrical circuit, which supplies the (()). Now, what we do here is that you have to understand, that this is an interaction curve based on pure Van der Waal's interaction. So, if there are other types of interaction, then what will happen?

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Electrical Force Microscopy (EFM)

EFM is based on the fact that van der Waals forces and electrostatic forces have different decay characteristics ($1/r^6$ and $1/r^2$).

As the tip is moved away from the sample, the van der Waals forces rapidly decrease and the electrostatic forces become dominant.

This nature of the curve might change, but what you need to understand, that this coulombic forces for example, so this coulombic force, electrostatic forces have a much reduced decay characteristics as compared to Van der Waal's forces. So, let us say, between particles Van der walls forces 1 by R to the power 6 and we know that and coulomb forces 1 by R square.

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EFM

Contact Mode Scan: -
'+ve'ly biased Tip

Contact Mode Scan.

1 Scan of EFM

(1) A contact Mode Scan.
(2) Non contact/scan with an applied voltage.
(+ve)ly biased.TIP

So, even with understanding all this if you do a scan with this probe, as well as, the circuit through which the bias is given along the contours of the surface, so let us say,

this is the contours of the surface and here you have some positively charged domains, here you have some negatively charged domains, something like this and you give, let us say, positive bias. So, your tip is now positive, but if you still do a contact mode scan over here we will still get nothing, but the topography.

If you, so this is the contact mode scan and from this no way you can define, that what are the different domains are charged domains and please understand these are differently charged domains, so they might not have direct significant on a different additional friction properties. So, the phase image might also be very, very blank, it might not be able to pickup.

So, what is typically done is, along with biased turned on or the voltage turned on, you typically would do a non contact scan also. So, if you do a non contact scan what will happen? It sort of follows the contours, but when it comes close to this area, since you have a positively biased tip and you have a positive electric domain over here, so there will be a local repulsion. So, instead of following the contour it will, sort of, drift like this and then again it is back So, this part is neutral, so there is absolutely no problem, it will follow.

And what will happen over here? So, let us say this is the topography. You can get to this topography by doing a contact mode scan or by doing a non contact mode scan, also by turning the voltage bias off. When you now do an additional scan with turning the voltage biased on, what will happen? Now, the tip is positive, this is negative, so there will be an additional attraction. So, this area, there will be drift. So, this area there will be a drift, this area there will be repulsion and this area there will be an attraction. So, now, when you super impose these two scans. So, the regular contact scan, as well as, the non contact scan, what you have performed with a positively biased tip, so this is information you can get, so one EFM scan.

So, I will repeat what you are doing. We have a, instead of a regular tip all you have a glass tip with a, which is follows. So, this makes, it is little larger, nothing, no other harm. So, it is like, you just, sort of, take a tip with, which is little wider. So, that might lead to a little bit of loss in your lateral dimension, nothing more than that. This is mounted as usual on your cantilever and all other properties remain the same, only

additional thing is you insert an electrical wire, platinum wire, maybe, through it and you apply a voltage, bias the sample.

And then, what you do as part of one scan of EFM? You first do a contact mode scan, then you do, withdraw the, withdraw the tip little bit and do a non contact mode scan with an applied voltage and you know, that you have either positively or negatively biased the tip. We can bias tip during a contact mode scan as well, but since at local proximity (()) contact it is in the repulsive regime, the repulsive Van der Waals, the repulsive component of the forces will dominate and you will miss out any additional electrical signal.

So, you are, if you remember, that when you are doing a contact mode imaging, you are over this zone. So, irrespective of whether you have a biased tip or not, these repulsion forces will, the local tip-tip surface interaction forces will dominate and therefore, and we will be missed out.

So, when you do this to and let us say you know, that you have a positively biased tip and then, what you can find out from here is that a map of the domains for the electrical conductivity domains. So, you know that you have a positively biased electrode. So, this part must be positive because what has happened, that over this area the non contact scan shows a higher separation distance. So, this is possible only if there is a repulsive force between additional repulsive force, between the surface and the tip in this area.

And what can be the cause of this additional repulsive force? You know, that you have positively biased tip. So, only when, only if surface at that particular location can have or surface has a positively charged domain, then that can explain this additional repulsion in contrast here over this particular area. You see, that there is some sort of an additional attraction between the surface and the tip and this attraction can originate now, that since you have, you have a positively biased tip. So, therefore, it is only possible if you have a negative domain or negatively charged domain on the surface.

So, that way you can sort of generate a local variation in the, in the electrical property of a surface. So, this is what is done. So, this is often one single EFM scan involves two scan and this is, you can understand the utility of non contact imaging also. So, often you have to operate in the subtractive mode.

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Magnetic Force Microscopy

Magnetic force microscopy (MFM) images the spatial variation of magnetic forces on a sample surface.

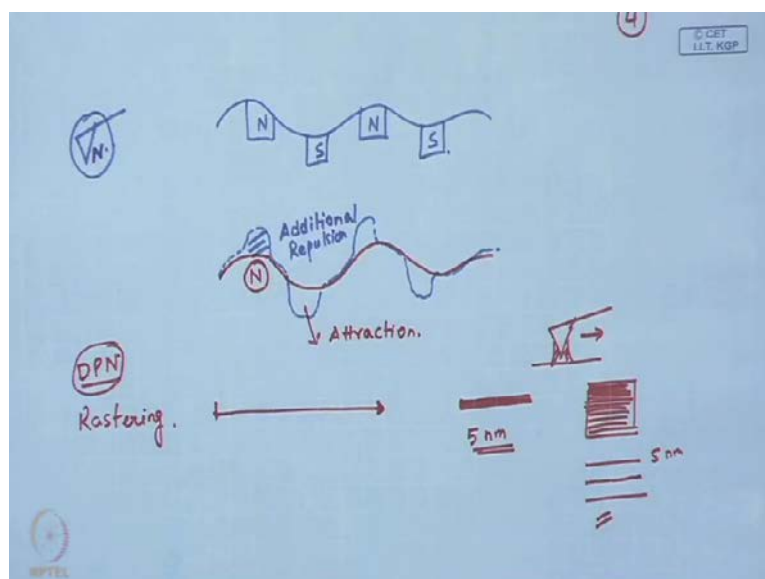
For MFM, the tip is coated with a ferromagnetic thin film.

An image taken with a magnetic tip contains information about both the topography and the magnetic properties of a surface. Which effect dominates depends upon the distance of the tip from the surface, because the interatomic magnetic force persists for greater tip-to-sample separations than the van der Waals force.

If the tip is close to the surface, in the region where standard noncontact AFM is operated, the image will be predominantly topographic. As the separation distance between the tip and the sample is increased, magnetic effects become dominant.

Similar thing can be also possible for with a magnetically, magnetic tip, with the application of a magnetic field, what is known as the magnetic force microscopy. It sort of images the special variation of magnetic forces or magnetic domains in a surface MFM tips, electrical EFM tip. So, one has to use an electrical ware, so we make the circuit and makes it conducting and MFM tip. Of course, it has to be coated with a ferromagnetic thin film and image taken in the magnetic tip, contains information about both topography and magnetic properties of the surface.

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So, exactly in the same way one can, one needs to know what type of tip one is using, whether it is N or S and we might be having surface topography with this type of different domains. So, you do a contact mode scan and then, you do a non contact scan to find, that there are certain zones where it is deviating.

So, understanding that whatever was the magnetic property of the tip there is an additional repulsion and this is only possible if there is local and domain over this surface area. Similarly, here you find that there is some attraction and this is possible only when you have domains of different magnetism. So, this is how MFM works.

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Magnetic Force Microscopy

- Used for measuring magnetic properties of the material.
- Special tips with a coating of magnetic material used.
- Magnetic force imaging work by first determining the topography along a scan line, and then lifting a pre-determined distance above the surface to re-trace the line following the contour of the surface.
- In this way, the tip-sample distance should be unaffected by topography, and an image can be built up by recording changes which occur due to longer range force interactions, such as magnetic forces.

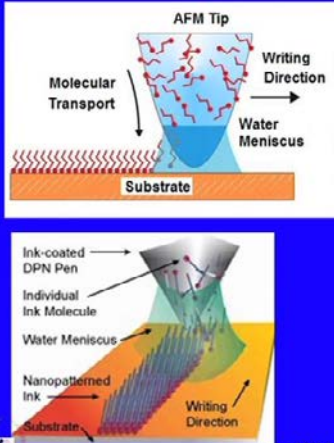
Topography

MFM Image

This is an interesting image of a hard disk, computer hard disk, floppy disk. As I told you, that if you do a simple topography scan, you find this is perfectly flat. So, there are low features, but if you now do MFM scan, you can identify, that there are magnetically active domains. So, this is in a nutshell the basics of magnetic force microscopy.

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Dip Pen Lithography



- Program your own Pattern!
- Direct and single step process.
- No requirement of Mask, Resist Layer.
- Tool: conventional atomic force microscope (AFM)
- Ultra-high resolution features with line widths as small as 10-15 nm with ~ 5 nm spatial resolution.
- Selective functionalization of surfaces with patterns of two or more components is possible.

Chad Mirkin, <http://www.chem.northwestern.edu/~mkngpr/dpn.htm>

The next thing is, of course, we move on to the last part of our discussion on AFM, which is the patterning application. What you need to understand, that again during the rastering action, you are actually, you are physically dragging the cantilever, the tip along the surface. And we have also talked somewhere during our discussion, that during contact mode imaging there might be possible meniscus formation due to (()) of water, which is present in the surrounding.

So, what happens is, that as you raster or drag the tip along the surface, this water meniscus also travels along with that. So, one can use this water meniscus, which forms or one can form it artificially by controlling the humidity that is also possible. Now, it is certain molecules, let us say, sub sam molecules, we already know about the sam molecules, if they are sort of mounted on, on the tip, so the tip, what you do is you just dip it before scanning in a layer of sam. So, if you do that and then try doing rastering scan following a contact mode, following contact mode, so along every line as the, as the cantilever sort of, as the tip sort of moves, it is going to this, water meniscus is going to act as or going to deposit the sam molecules on to the surface.

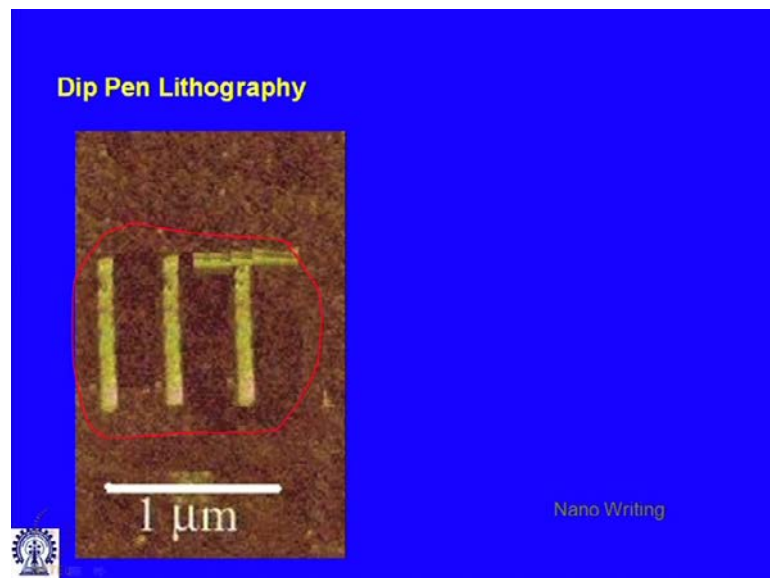
And you know, we have discussed while talking about the micro contact printing this sam molecules, depending on the legend x and y, sort of, orient and bind to the surface. So, in a way every scan will result in very tiny, but very uniform domains of sam molecules and the zones over which the cantilever has, has not scanned, there will be no

deposition. So, this way you can, sort of, create very, very narrow lines of different wettability regions, which is known as the dip and nano lithography and up to 5 nano meter structure, down to around 5 nano meter lateral resolution can be created by this.

So, this is what you have to do is you have to just, instead of a regular scan, because if, if you do a regular (()) it is going to sort of cover the whole area, we have to just program the movement of your tip. And then, so you allow your tip to move here, then sort of, it skips 20 nano meters and then comes back here then again 20 nano meters (()). So, you can in this process create 5 nano meter lines of a more or less wettable species. Species, depending on nature of the sam molecules, you are using at a periodicity of 20 or 30 or 40 nano meters, whatever you want. So, you just need to program the movement of the scanner and rest of the things is perfectly fine.

What typically ensure, that when you are writing, it, it is in the writing do not, you are not interested about the exact topography and you want your surface, your tip to drag along the surface. So, generally during writing the feedback, loop is generally turned off, a specific force is set and cantilever is or the tip is sort of ensured, that tip drags over the surface.

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So, this is what in a nutshell is dip pen nano lithography. So, here you can see, we wrote something using silent molecules, of course this is a little wider, roughly about 80 nano meter width. So, there are multiple movements, so that to make it visible.

So, these are using SAM molecules, but more interestingly, what is important, that you must realize, that this image is not a topographic, but a surface contrast image because again, if you write with SAM molecules, these are virtually feature, height less single molecules, so that topography contrast will be virtually very, very less. So, we cannot pick it up in the topography, but this becomes visible in, in the phase contrast image, which you already understand. So, you see that AFM can also be used for writing, sort of, something like nano writing.

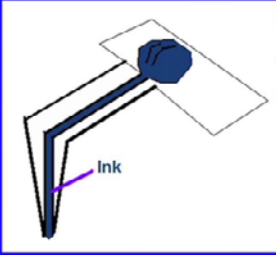
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Fountain Pen Lithography: Applications

- Uses a hollow AFM probe, as used in case of N-SOM or S-NOM.
- The probe is connected to an "ink" reservoir.
- The problem of "refilling" the probe is solved elegantly.

Disadvantage:

- Not compatible to all brands of AFM
- Poor Resolution, thicker lines as tip diameter becomes large



The diagram shows a hollow AFM probe with a blue ink reservoir at the top and a sharp tip at the bottom. A purple line labeled 'Ink' indicates the flow of ink from the reservoir to the tip. The probe is shown in a cross-section view, highlighting its hollow structure.

So, these are some of the applications. So, it can be used for nano writing for example. Well, one of the classical approaches is to dip this AFM tip in a liquid SAM layer and then from this meniscus and drag. One limitation is that it writes as long as the molecules are available. So, once it writes a while or travels a while, all the molecules get exhausted and then it may drag, but no molecules get transferred. So, in order to overcome that limitation, something called the fountain pen lithography came up, which uses the concept of this hollow probe, which we talked about while talking about this electrical force microscopy.

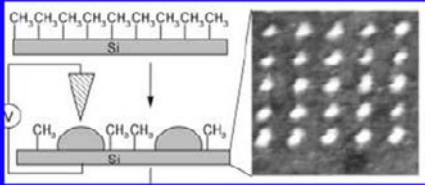
So, exactly using those hollow probes, that you just add a reservoir over which you dispense the ink. So, the ink due to capillary action follows through this hollow probe and this is now dragged, rastered along the surface. So, all along it goes on, it is depositing. So, we do not really run out of the problem of, running out of the SAM

molecules. So, it sort of uses an in situ ink reservoir and one can, sort of, do a refilling also by dispensing a drop, which is a microscopic entity over this zone. Disadvantage is that this is not compatible with all brands of AFM and since you have to make them hollow, so the radius of curvature of the tip is higher. So, the resolution is poorer.

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Tip Induced Oxidation

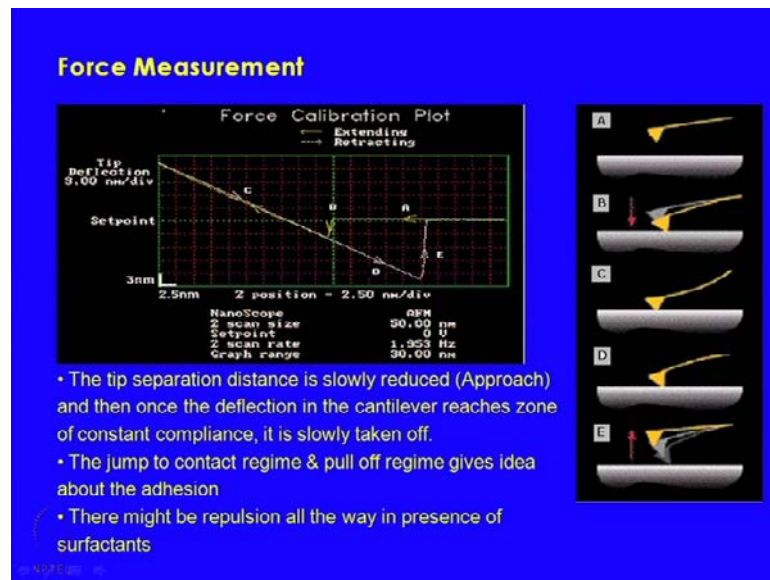
- Field effect induced oxidation has been applied to substrates like Si, Ti, Ta, Cr etc.
- Electron induced oxidation has been applied to organic resists, SAM, LB films etc.



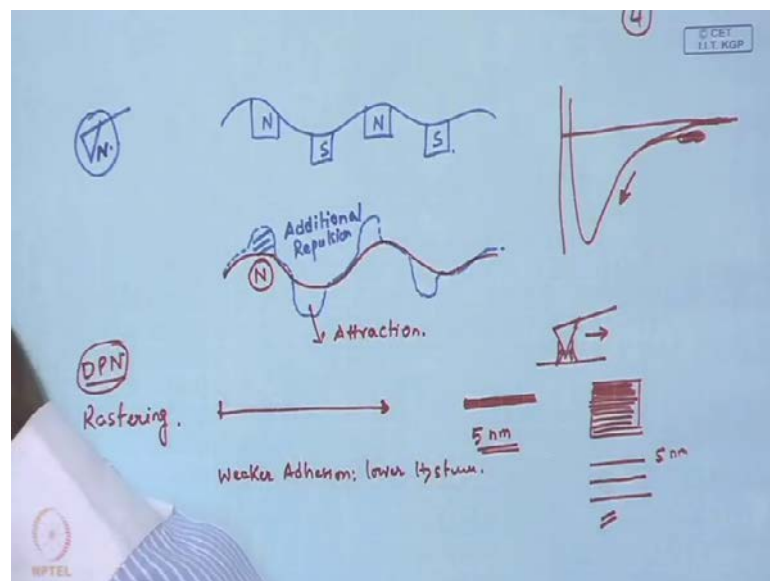
One can also use this concept for, let us say, something like a tip induced field effect, tip induced oxidation on surfaces like silicon, titanium, (()), chromium, etcetera. So, electron induced oxidation has also been applied to organic resists and something like that. So, it is a combination of electrical force measurement and writing.

So, you just go to the appropriate location of the surface and then turn on the bias depending on the, the material and the reactants available. You can have localized oxidation when you turn on the biased. Other location if you do not turn on the bias, there is no reaction we can make very nice arrays of oxides or materials, like silicon, (()), titanium, etcetera.

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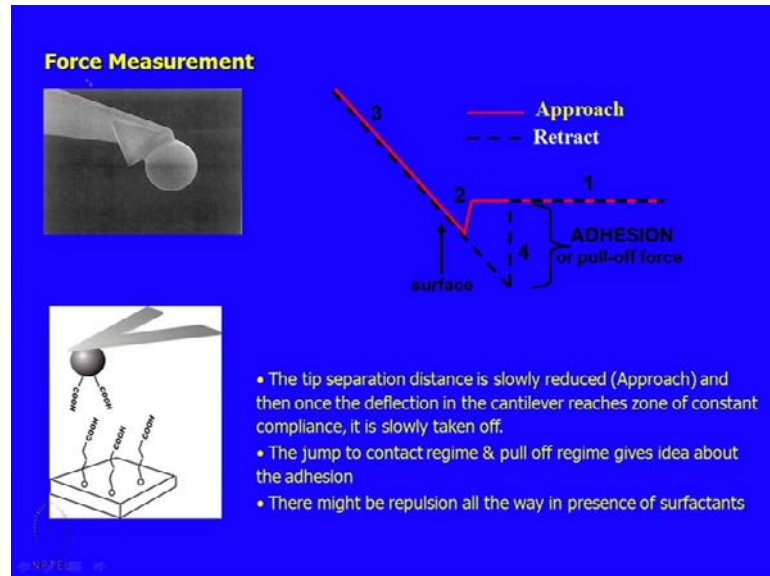
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Of course, the last thing, that, that is also possible with an atomic force microscope lines in the fact, that during the approach and the debonding stage and withdrawal stage. So, withdrawal is something we did not mention, but once the scan is over we will, of course, withdraw the tip from the surface, it actually follows the force curve. So, utilizing, that one can measure the force between two surfaces that the tip of the cantilever and the surface we want to scan. So, this we understand this is the cantilever probe at far away distance this is jump to contact then this repulsive regime and then you

try to withdraw what typically happens is that the withdrawal the bonding the attachment and the withdrawal stages are different.

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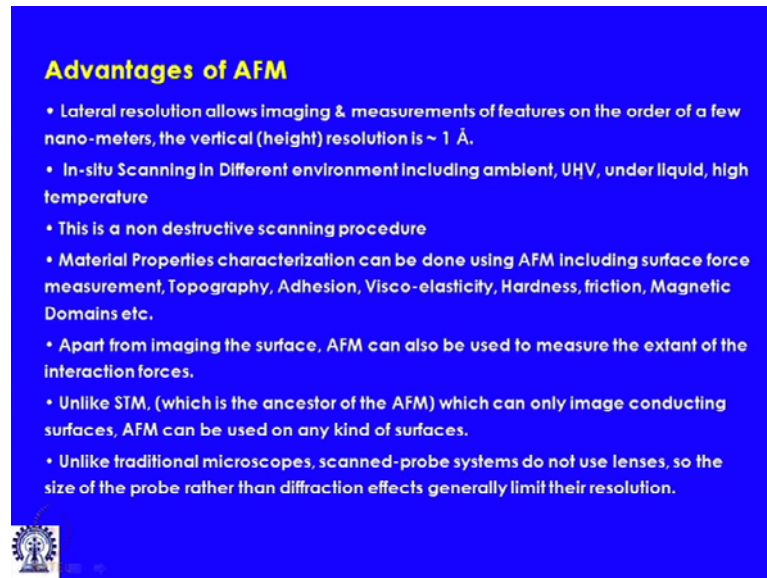
So, there little bit of hysteresis between these two, the, the separation distance at which it jumps to contact and the separation distance. This is the separation distance between the z piezo the height of the z piezo and the surface at which, sort of, it detaches. So, this hysteresis of the gap in these two is the measure of the extent of the addition of the surface. Weaker is the addition of the surface, lower will be the hysteresis, so weaker adhesion, lower will be the hysteresis.

One can do this type of experiment with a standard tip, but it is generally, customary to use the colloidal probes, here we talked about the colloidal probes. So, colloidal probes find maximum application in finding out the measure in the forces between two surfaces. So, it can have situation, for example, if both the probe and the surface are coated with the surfactant molecules, then same species. There can be situation where there can be long range repulsion. So, you do not see an attraction at all and all the way you see a repulsive interdiction.

So, this type of forces can be measured, this can be quantified and this find, sort of, give you an idea about the adhesion of the surface, as well as, the nature of introduction between other surface, between the two surfaces. So, firstly, look by, looking at the nature of the curve one can find out whether the nature of the interaction is attractive or

repulsive. And second thing is if it is attractive, one can find out the pull off distance, the extent of addition based on the hysteresis. So, whole lot of things can be done by using an atomic force microscopy.

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Advantages of AFM

- Lateral resolution allows imaging & measurements of features on the order of a few nano-meters, the vertical (height) resolution is ~ 1 Å.
- In-situ Scanning In Different environment including ambient, UHV, under liquid, high temperature
- This is a non destructive scanning procedure
- Material Properties characterization can be done using AFM including surface force measurement, Topography, Adhesion, Visco-elasticity, Hardness, friction, Magnetic Domains etc.
- Apart from imaging the surface, AFM can also be used to measure the extent of the interaction forces.
- Unlike STM, (which is the ancestor of the AFM) which can only image conducting surfaces, AFM can be used on any kind of surfaces.
- Unlike traditional microscopes, scanned-probe systems do not use lenses, so the size of the probe rather than diffraction effects generally limit their resolution.

So, that sort of brings to the last line and last couple of slides sort of this class of this topic, the advantages of AFM. So, one can achieve lateral resolution allowing imaging and measurement of features and order of few nano meters, and the vertical resolution can be as low as one Angstrom, one nano meter vertical height, of course, it is almost possible to achieve in any standard AFM.

So, in situ scanning in different environment including (()) that is the most important thing. If you are talking about any other high end microscope, like scanning electron microscope or a transmission electron microscope, they work only in ultra high vacuum. They need to have a significant vacuum, so that the electrons clouds do not deviate because of collision with the air molecules.

In AMF, nothing is needed, you can have excellent atomic force microscopy scans in (()) condition. You can also have scans under liquid at high temperature, at low temperature, almost anything and everything we want. So, that sort of opens up or has a whole lot of in situ imaging. This is a non-destructive scanning procedure, so you can look at your sample and then again reuse it for any subsequent experiment or subsequent processing.

Material properties - so in addition to visualizing the topographic properties or the exact features, surface features, other material properties can also be quantified or directly measured using an AFM, which we discussed in this particular class in terms of the secondary imaging mode. So, you can have ideas, like localized friction, adhesion, surface tension or contrast in that, as well as, electrical and magnetic property domains by specialized techniques, which we talk like electrical force microscopy or magnetic force microscopy. One can measure visco-elasticity by force modulation microscopy or the elasticity, the hardness, friction, magnetic domains, etcetera.

Apart from imaging the surface, of course, as we have already talked AFM can also be used to measure the extent of interaction forces or quantify the interaction forces between a surface and, and between two surfaces. So, one can look at the interaction forces between identical surfaces or by dissimilar surfaces by using colloidal probes, which are preferred tools for measuring the force, interaction force for an AFM or between two surfaces. And then, unlike STM, which we will talk very briefly, you remember, that STM requires a short conducting tip and conducting sample to work. The ASA, AFM does not have any such limitations and it works equally well for a conducting, as well as, non-conducting sample or, or any type of a sample.

So, polymer, ceramic, gel, liquids, everything can be, sort of, investigated with an atomic force microscopes and unlike traditional microscope, SPM system do not use lenses. So, the size of the probe limits the resolution of your feature rather than the diffraction effects that typically limits the resolution in optical microscopes, as well as, in scanning electron microscopes.

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Advantages of AFM

Optical and electron microscopes can easily generate two dimensional images of a sample surface, with a magnification as large as 1000X for an optical microscope, and a few hundreds thousands ~100,000X for an electron microscope.

However, these microscopes cannot measure the vertical dimension (z-direction) of the sample, the height (e.g. particles) or depth (e.g. holes, pits) of the surface features.

AFM, which uses a sharp tip to probe the surface features by raster scanning, can image the surface topography with extremely high magnifications, up to 1,000,000X, comparable or even better than electronic microscopes.

The measurement of an AFM is made in three dimensions, the horizontal X-Y plane and the vertical Z dimension. Resolution (magnification) at Z-direction is normally higher than X-Y.

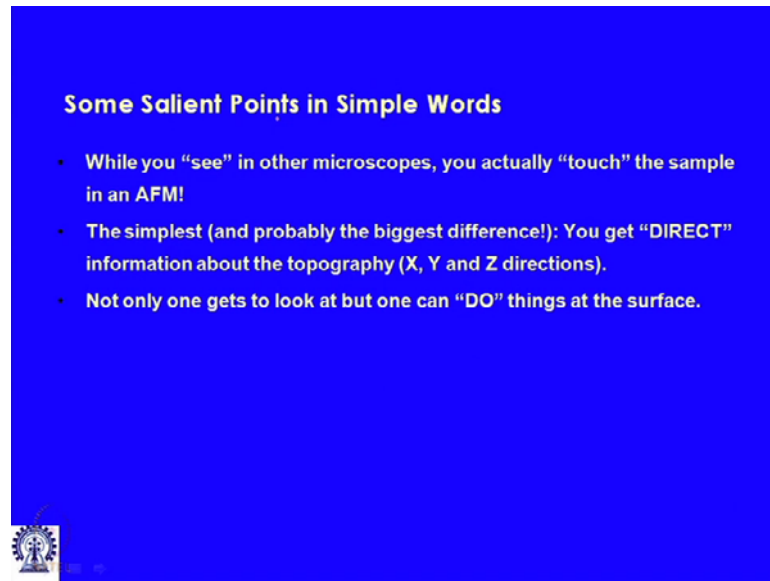


So, same things, it is sort of a comparison of AFM with other class of microscope or optical or electron microscopes. So, optical and electron microscopes can easily generate two-dimensional images of a sample surface with magnification as large as one million times for an electron microscope.

But what is important, that these microscopes cannot measure the vertical dimension. So, none of these microscopes, irrespective of very, very high resolution, can give you true vertical resolution or true three-d resolution. So, you can have a very clear idea about the feature size, lateral size of the features, but the feature height. Of course, in a scanning electron microscope many of you have seen tilted images and things like that, but that really fails to, still fails to quantify the exact feature height, which is not possible to be produced in, in an optical microscope and therefore, you cannot measure the exact depth of holes or height or pit or things like that.

AFM, which uses a sharp tip to probe the surface, which has by raster scanning can image the surface topography with extremely high magnification and up to ten million times and that is not very important, but what is important is that you can see features, which are laterally down to one nano meter or tens of nano meter, is very, very easy to see and vertically one can go down to one nano meter. And most important thing, most fundamental, apart from the operational aspect, AFM gives you a true three-d image. So, you have all the three dimensions x, y and z accurately measured using an AFM.

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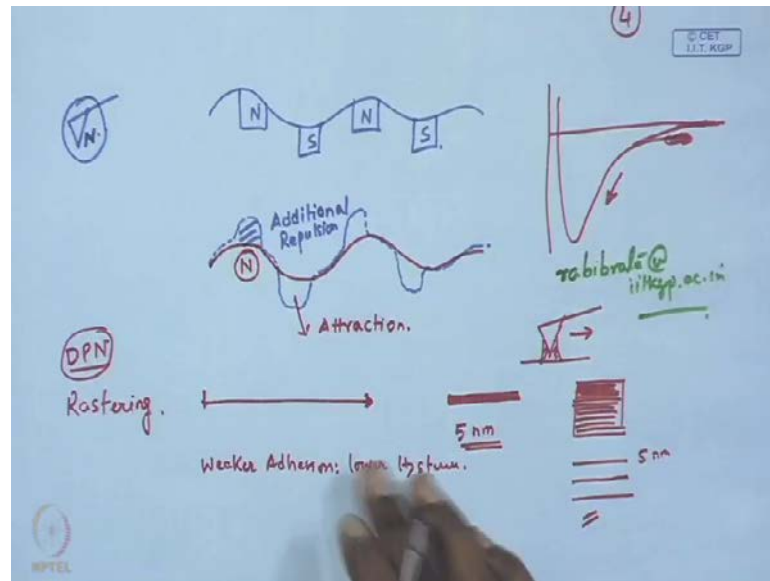
Some Salient Points in Simple Words

- While you “see” in other microscopes, you actually “touch” the sample in an AFM!
- The simplest (and probably the biggest difference!): You get “DIRECT” information about the topography (X, Y and Z directions).
- Not only one gets to look at but one can “DO” things at the surface.

So, last slide, some salient points in simple words. While you see in other microscopes you actually touch the sample, in AFM and the simplest and probably the biggest difference is, you get direct information about the topography in x, y and z directions. So, all the three direction in all other microscope irrespective of all their sophistication, they are limited to x and y only. And since you, you have the ability to touch the sample you can do things there, do thing on the sample, which include you can (()) it, you can dispense, you can invent it, you can dislodge molecules and do whatever you want to do.

So, that is all I would like to teach you in this particular course about the atomic force microscope. Please go through the lectures again and again and try to build your own concept, it is very simple. Apparently, it might be new, but that is the whole intention of an advance course, to expose you to newer developmental areas in which development is still taking place or which are really state-of-art.

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I would strongly encourage you to look into additional complementary literature. So, a search in the internet with keywords like atomic force microscope, contact mode, tapping mode, intermittent contact mode, etcetera, should give you whole lot of literature. And I have repeatedly been telling that in case if you have any doubt, do not hesitate to email me, I will be happy to answer to any questions.

Thank you very much.