Chemistry and Physics of Surfaces and Interfaces

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Lecture - 37
Atomic Force Microscopy (AFM) - 2

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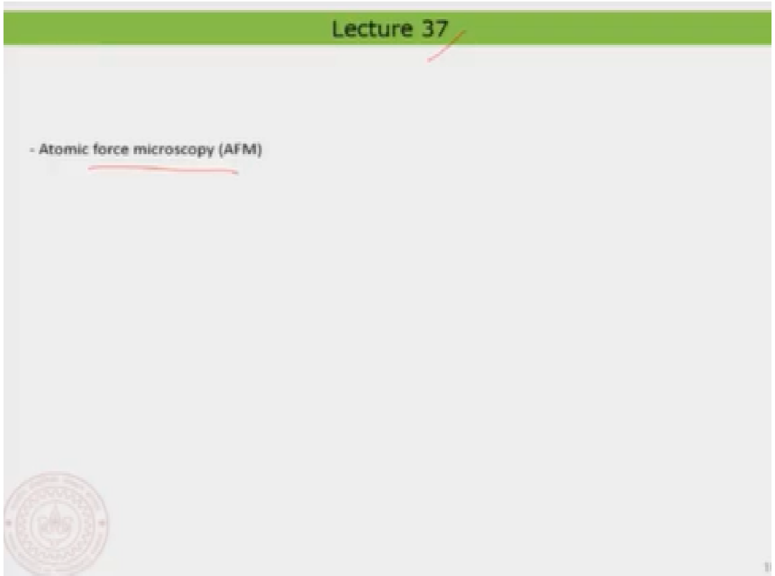

Hello everyone, welcome back to lecture 37. So, in this we will continue where we stopped in the last lecture, we look at the atomic force microscope and particularly the technical aspects before we go in to look at the examples.

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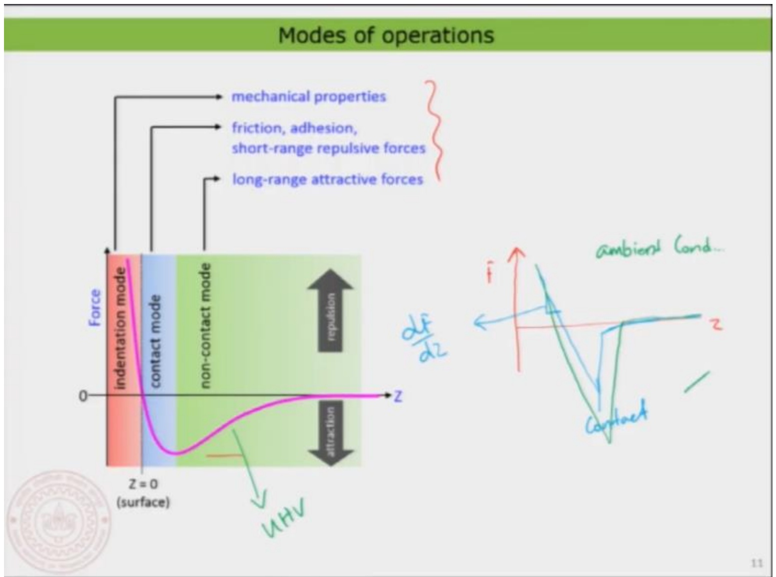

So, what we have done in the last class was looking at the force curve and then familiarizing the mode of operation. So, the mode means like at which force range you are basically just operating. So, here I told you like this are the very broad classification so like the non-contact and the contact mode and indentation mode. So, we also have seen that depending on the operation mode you can basically just kind of understand different things. Because we know that in the non-contact regime you have basically typically the attractive forces and in the contact regime you have the repulsive forces. and, in the indentation, mode is something where you really indent the cantilever-tip combination or the tip into the sample and we look at the hardness of the material or force that is required to deform the material. Now although this looks very interesting this kind of a force curve is not something you cannot find in the ambient condition.

So, this is a force of therefore truly applicable in high vacuum or an ultra-high vacuum definitely. Because in the ambient condition you are going to have additional influences due to the atmosphere. So, you have like wet atmosphere high humidity you can have hydrophilic forces hydrophobic forces many bulk forces are actually acting on the tip cantilever combination. So, you will never be able to see this kind of a typical Lennard jones type force curve in the ambient condition. So, therefore whatever you see here is a very idealized picture yeah or a very in principle picture and but this is actually something you can reproduce inside an ultra-high vacuum or in a high vacuum chamber. But you will also see that atomic force microscope has been widely used in ambient condition because you would actually sometime come across with biological samples or any type of material.

I told you that this is this mode or this method is much more versatile than scanning tunnelling microscopy. So, therefore you will also find it in normal conditions ambient condition. In that case the force curve has a slightly different shape so, that is what I want to basically just show you here. So, I again have this kind of separation between the force between the tip and the surface and the force. But here it is going to look slightly different is going to look like that you approach. So, -everything looks good. So, it initially it would just have a very small variation in the force or something like this you would observe then suddenly you would find tuck a jump to contact and so this is because the moment you basically just come close. So, there is a huge force that is acting on to the cantilever and the cantilever force constant is not basically just capable of withstanding that forces then it come directly to a contact to jump. So, then it will look basically like that so once you are in contact so that means somewhere in this regime. Here you are already in contact and then when you increase the or when you approach again further then you basically just get into the material. So, this is already the indentation mode so this is the slope again is interesting because the slope is directly df by dz which is actually the so, called deformation or the hardness of the material. And then when you go back it is not necessary that you will always go along the same path. Because you have a strong adhesive force it may actually just go with a slightly different path that it would even look like this and then finally it would just go like that. So, this so, called huge dip is actually corresponding to the adhesive force between the tip and the surface. So, in ambient conditions this is actually something which you would commonly observe. And this would be something applicable in ultra-high vacuum because the model that we have used is actually like 2 atoms coming closer and this is where you do not have any medium in between. So, that is the reason why this type of a force is actually something you observe in in high vacuum or an ultra-high vacuum. But typically, in ambient condition you would see a force curve that is of this type. So, that is the thing that you have to keep it in mind. But it is not an issue but it is actually having different applicability and therefore you can basically just apply that in different conditions.

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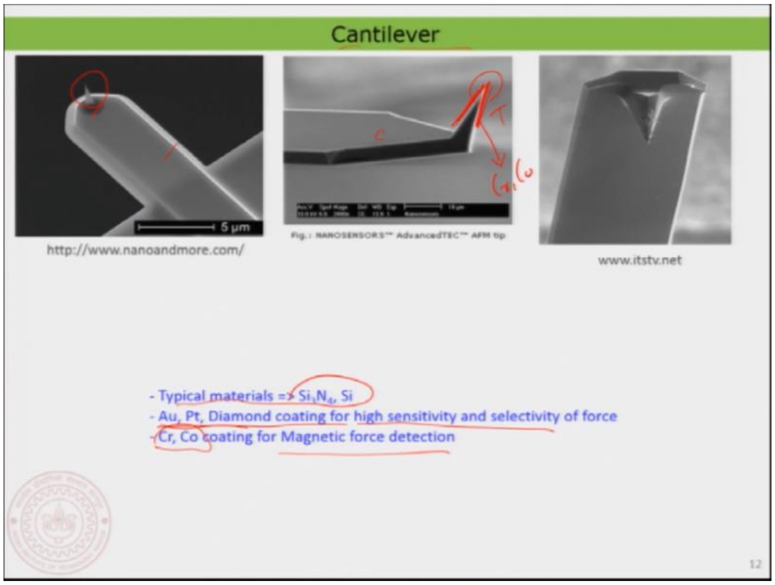

Now let me just show you the most important thing which is actually the cantilever tip combination. So, I have actually a few scanning electron micrographs so it is like electron microscopy images of a few different type of cantilever. So, you can of course now commercially buy them the STM tip you remember you could actually just make very easily. So, you have to take a very thin wire you have to use a mechanical cutter cut it and then you have a tip.But here it is not possible because you want to have a cantilever associated to a tip. Therefore, you have to basically just process these using different techniques and then you basically just buy it commercially. So, this is it so this is the cantilever part and this is the tip you can see and of course you can get different type of cantilever part and also like tip so they are looking slightly different and also depending on the application.

Mostly the material that you use for making the tip is actually kind of silicon nitride or silicon they are easily millable. So, this is all iron milled structures so they are actually easily millable they and also the hardness of the material is good enough. Therefore, they are actually just kind of a preferred material. But you can also get tips which are actually having gold, platinum you see diamond coated to increase the sensitivity of the measurement. Because you remember like whenever you have a cantilever you need to have a laser reflecting on the back side of it. So; to get basically the position sensitivity. Therefore, it is also important that the back side of the cantilever must be coated with gold and platinum and diamond coating is basically to increase the strength of the tip itself. So, there are different kind of things are available in the market and this will all increase the sensitivity and the selectivity of the force. This is very important, and you can also just buy this chromium or cobalt coated for particularly magnetic force detection. So, you will also see towards the end of this topic that we will also be looking at something called magnetic force microscope, there to get the magnetic contrast what you need is actually to cord this tip using a magnetic material. So, you need to basically code with chromium cobalt and so on.

So, this is something that we have also done you remember in the case of scanning tunnelling microscopy to make actually that magnetic sensitivity so you need to have like a magnetic materials coating. So, this is the main important thing or the heart of the atomic force microscope itself.

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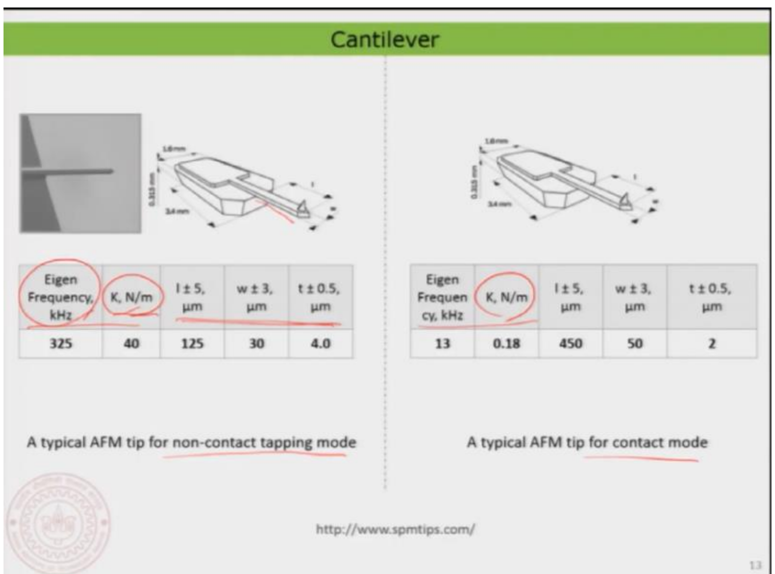

Now let me also show you a few more technical details about a cantilever. So, this is of course not the entire chart this is a very simple schematic that I am showing a cantilever so this is basically the cantilever and the tip. So, this is the most important thing and the cantilever has a very specific length width and thickness. So, this is something you can see here and that will define the Eigen frequency or the frequency of the cantilever. So, the cantilever can basically just even oscillate at a at an Eigen frequency if you excite. And that Eigen frequency is quite important because you will see that there are special modes for that it is quite important and also the force constant. So, you remember the force constant is important for us because if you want to actually calculate the force from the deflection you need actually the force constant. So, therefore the force constant and the Eigen frequency is basically defined by these geometrical parameters like length width and thickness of the cantilever and that will define these 2 parameters and they are very important. Because you can see that this kind of a tip with a high force constant is normally used in in a mode called non-contact tapping mode. You will see what is that and then this kind of a soft cantilever you see like here the force constant is basically a 0.18 newtons per meter. And this kind of a cantilever is something that you use for contact mode. So, but there is a big list of course I did not want to actually just bother you with that list but whenever you are actually getting into the application you can actually just understand that in a greater detail. But what I want to show you or what I want to basically tell you that depending on the application you need to basically choose different type of cantilever.

But there are also cantilevers without tip or with a with just a spherical dot at the at the at the apex if you want to only do kind of mechanical force measurement on different surfaces and so on. So, you can get a variety of tip cantilever combinations.

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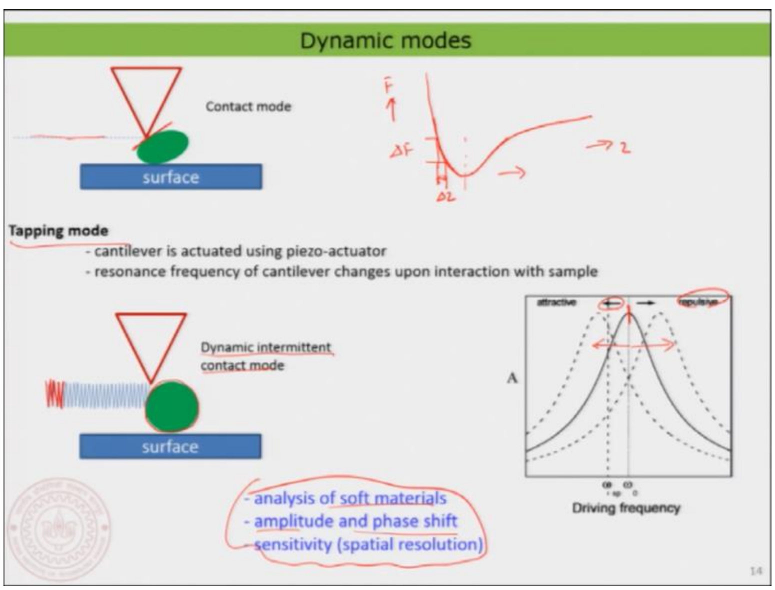

So, now all the modes that I have talked about is actually kind of non-dynamic mode. So, that means your cantilever is actually stagnant and you have a tip and you are basically just moving the tip across the sample so, that is what you do. But in the beginning of the discovery of scanning sorry the atomic force microscopy people were mostly; preferring to do contact mode. Because that contact mode was the one with which you can actually get a better resolution.

The reason is very simple if you recollect actually the force curve that we have just drawn the force was looking somewhat like this so this is the distance and this is the force. And typically, if you look at the non-contact region so that means in this region what you see that the variation in the force as a function of distance is rather small compared to the contact region. So, here you can see the contact region the change is actually much sharper that means for a small change in the distance. So, like here again the so, called delta z I have a large change in the force delta f, this is something which decides the resolution of a microscope. That means the so, called sensitivity of z deflection is much larger for actually the contact region so that actually is due to the nature of the force itself. So, because you have this very long-range attractive forces, so, the force is basically varying very slowly with respect to distance. Therefore, generally contact mode was preferred in the beginning.

So, but the problem with the contact mode is this you see like I have here a circular object which is now when I do the contact mode there is a very high chance that I would actually just deform it. Because the tip is actually going in a very close vicinity of the surface so there is a chance that I can basically deform things on the surface. So, if you for example want to understand something with molecules with biological molecules or with soft samples polymers and so on.

The moment you actually just scratch your tip over the surface or in a so, called contact mode there is a huge chance that you basically deform the surface. And whatever you are seeing is something like deformed surface and not the true surface. But of course, we still want to do the contact mode so that is clear because the change in the force is much more sensitive or much more detectable is in the contact regime so therefore, we want to do the contact mode. So, then people thought well why cannot we do something like a dynamic mode. What do you do? You basically take the cantilever and activate the cantilever and let it resonate at its resonant frequency. That means the cantilever is all the time vibrating at its resonant frequency and now the interesting thing is now you can look here, this is basically in the contact mode the path that the tip follows it is kind of a linear path.

But in the dynamic one you are going to basically just do this kind of a path because your cantilever is all the time going up and down. The advantage is you can almost go near to the surface but the point is the time of contact is very very very less because the tip is actually not coming all the time in contact with the surface. So, ideally the tip is coming in contact it is going back coming contact is going back again coming contact is going back. So, therefore in the dynamic mode you basically do not deform the sample of the objects that are actually just present on the surface. And therefore, you can see here I can basically see my object that was originally circular in shape is actually having no deformation because the contact time while you just pass your cantilever tip combination around that object is very very less compared to the contact mode. This is generally therefore known as dynamic intermittent contact mode. So, you are intermittently contacting the surface but not continuously like in a contact mode. So, this is a very sensitive mode and that mode therefore is able to analyse soft materials. And the interesting thing now is that since you are actually just moving at a resonant frequency what you are basically just going to measure is the change in amplitude phase and also, the frequency the resonant frequency.

It is actually what is shown here if this would be the resonant frequency of the cantilever. Now when the cantilever is coming in contact to the surface you can basically have the attractive or the repulsive force. So, depending on the type of the force your cantilever resonant frequency would go down or upward. That means I can basically measure continuously the change in resonant frequency. And also, I can measure the change in amplitude of the frequency or I can basically also change the phase shift. This is quite interesting I am not going to show a lot of details but phase shift also has something to do with the material contrast. It actually can resolve material contrast and you can basically just see this kind of changes you can basically measure in the dynamic mode or generally it is known as a tapping mode, but it is a dynamic intermittent contact mode.

So, that is very good so you can basically now do not worry about the deformation of your sample or the surface itself you can actually gently work on this mode and you can nicely analyse the surface even if it is having soft materials. So, that is the interesting stuff I will show you a few examples to convince you the fact of dynamic mode.

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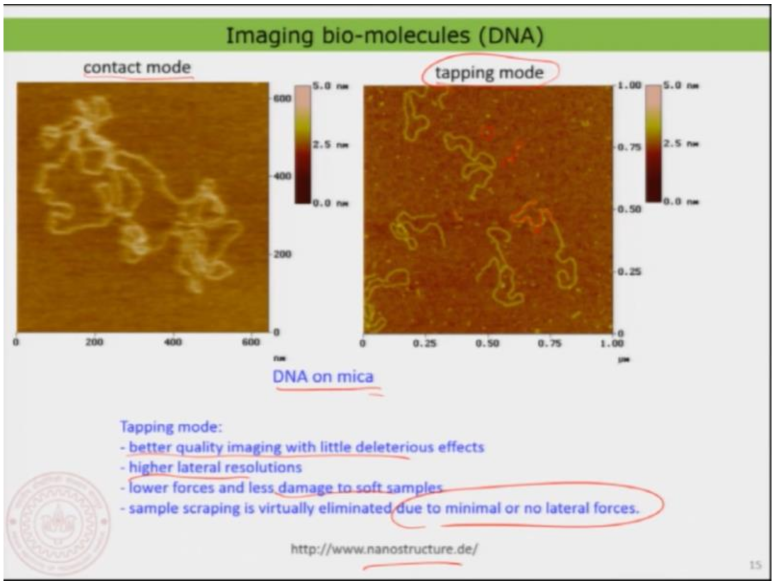

And dynamic mode is actually now the most popular in fact. So, now here I have basically an image of a biomolecule DNA molecule taken in contact mode and in tapping mode. So, this is not a simultaneous mode of course not you have done it in a in a separate way so, the DNA molecules are actually just sticking on mica surface. So; this again nice crystalline surface that you can use and there you see basically that when you do the contact mode.

You can basically see that of course you see kind of trendy structure but you cannot basically resolve the details because there is lot of deformation of flickering that is actually happening to the strand itself. But now you see when you do it in the tapping mode it is really beautiful you can clearly see the DNA strands separately. You can even see tiny bit of details and you can even see on the surface small features are actually nicely resolved compared to what you have actually seen in the contact mode. So, this is beautiful therefore you already see that the quality of the imaging is improved to a very high magnitude and also you have a high lateral resolution. So, that is the major issue otherwise every time you are deforming your object that you are looking is actually deforming. And it is basically even increasing the size of it. So, that means you are not really measuring the actual size of the material.

Then what you since you are actually just applying only coming and very gently and in intermittent mode. So, you actually just cause less damage to the surface and therefore there is no lateral force that is basically applied between the tip and the sample so, that is very useful. So, therefore what you would basically find that most of the time tapping mode is something that is very commonly used in ambient conditions. And also, in ultra-high vacuum and it has been also like been widely used for biological samples and so on. So, that is the reason why I also thought of showing you this particular example you can see a few more details in this online source but you can actually also find that in general literature.

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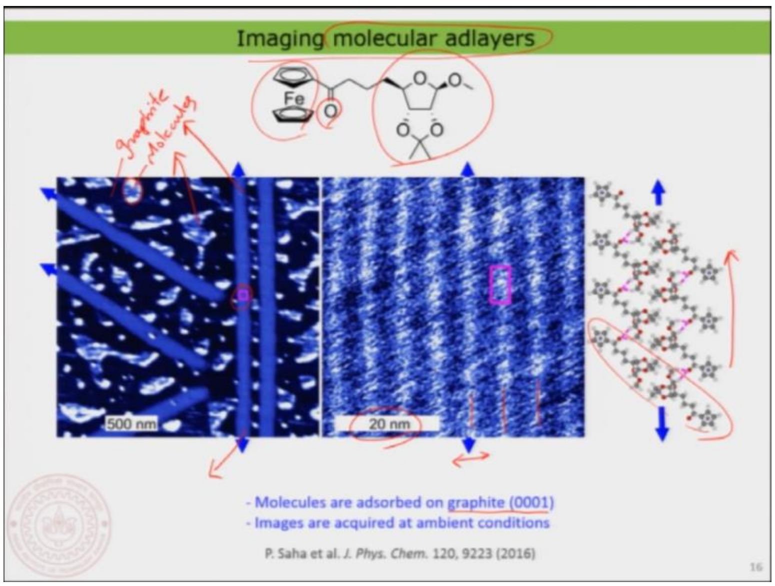

Well, I also have here a nice image of an adlayer of molecule on surface. So I have here a graphite surface and a molecule is basically absorbed. So, the molecule is kind of a ferrozine derivative so this is a sugar derivative of ferrozine. And what we do like in the previous example we have looked at we basically just kind of self assemble this molecule on the surface and have a look how they self assemble.

Now this dark region is nothing but your graphite and these bright regions are the molecules so these are the molecules. So, molecules and here you also have molecules. So, there are two different type of molecular arrangements so one is more like a non-crystalline amorphous phase. So, that is what you see here this is basically amorphous and then you have here this blue region which is corresponding to a very crystalline molecular arrangement.

So, that means the molecules are nicely making this self-assembled pattern there. So, there the molecules are actually just forming long long islands. And that is what you see now I can actually just zoom into a small region inside and then you see these kinds of lines. And these lines are actually corresponding to this kind of a dimer chain of a molecule. So, you have this molecule has a capability to form a kind of strong hydrogen bonding mediated through this carbonyl group. And then what they do is they form a dimer and they actually just make this kind of nice chains and those chains are something what you are basically just visualizing in this image. So, that means using the tapping mode you can basically just image nicely globally and also you can go down to a very high resolution. And also, you can see things at the molecular level that is the interesting thing about this particular mode of operation. And therefore, I told you this is the mode that we are going to be generally used if you are not interested in understanding the friction forces of the surface so that is the aspect.

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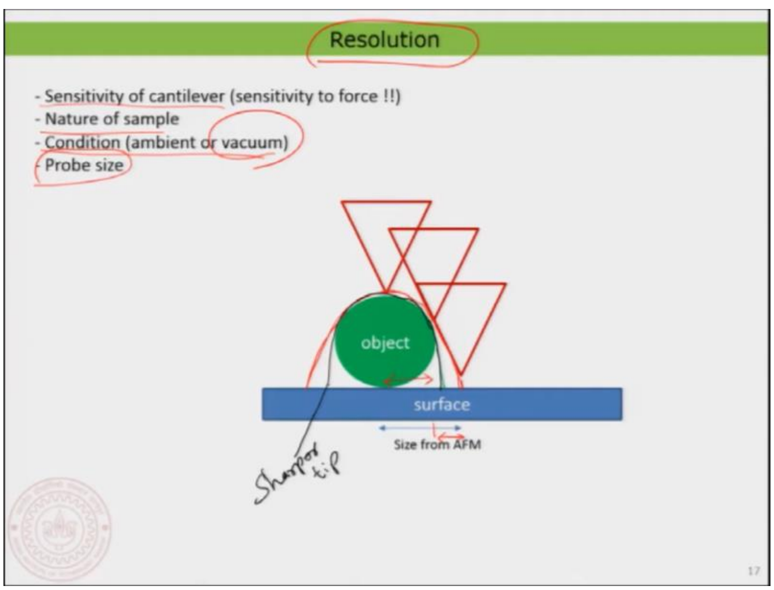

Now when it comes so far what you have seen is that all the time, I have been showing you like images which is not as resolved as in the case of STM. So, the question is it possible to really resolve at the atomic scale is it possible? Well, the answer is yes, but there are a lot of conditions in this case compared to scanning tunnelling microscopy that you need to take into account particularly you need to take into account about the sensitivity of the cantilever.

Because the problem is it is not just limited only by the tip you also have a cantilever associated with this. So, therefore the cantilever quality or its sensitivity in detecting the force is very very important. Then the nature of the sample if you are actually just taking a sample which is actually hydrophilic in nature so you would never going to get actually an atomic resolution at that because the surface is always going to be covered by water. And if you want to work with that you know going to basically just end up in quality images or if you have a surface which is extremely soft and then you are not going to basically see much. So, this is quite important. So, therefore the nature of the sample and also the flatness of the sample or the atomic flatness of the sample is very important. Then the condition as I have already told, you have seen in the previous slide that I have showed you like the typical force curve like you would expect or the theoretical expectation is only possible in vacuum.

In ambient condition you see there are strong forces like the adhesive forces hydrophilic hydrophobic whatever force that you name you have strong forces that is actually acting on the tip. Therefore, you do not have much of a chance in getting high resolution or the so, called atomic resolution in ambient condition. But none the less in the previous example I have showed you that you can go down to a certain level. And you can see features that are corresponding to the molecular details but not an atomic level. Therefore, it is quite important you will see that is what I am going to show you in the next slides. That vacuum is very important when you have vacuum you would basically just avoid or eliminate a lot of conditions that is necessary for doing the measurement and then you can get the actual measurement done in vacuum. And then you can actually get atomic resolution I will show you that and then of course the most important thing is the size of the probe. So, that is of course like you expect, I have here an interesting scheme to show you. So, if you imagine that this is the object that you are actually just trying to resolve on the surface and if this is from tip and then if you basically just move the tip across this object let us move the tip. But since the; diameter or the size of the tip is actually decisive. You can see because you have a larger size the tip would always follow a path like this and then it will basically end up at a position like this. So, that means what you are going to image is something like this and not the real size of the object. So, this is what the real size is so like the real size of the object is just this much but you see what you are measuring is this exaggerated size in AFM.

Therefore, it is quite important to have actually like, a sharper tip. And if you are making the tip sharper and sharper there is a chance that you would basically just end up somewhere here and then you can basically just get an image which would look like this. So, therefore it is quite important to use a sharper tip. So, this is actually for a sharper tip and the other one for a broader tip. So, that is quite important.

Now well therefore it is limiting to basically just do this. So, therefore people thought we can basically now think about making an extremely sensitive tip. And an extremely sharp tip like an atomically sharp tip. So, can we do that yes if we do and everything to be done inside a vacuum. So, by combining an extremely sensitive cantilever inside ultra-high vacuum using an atomically sharp tip people thought let us make actually a kind of special cantilever.

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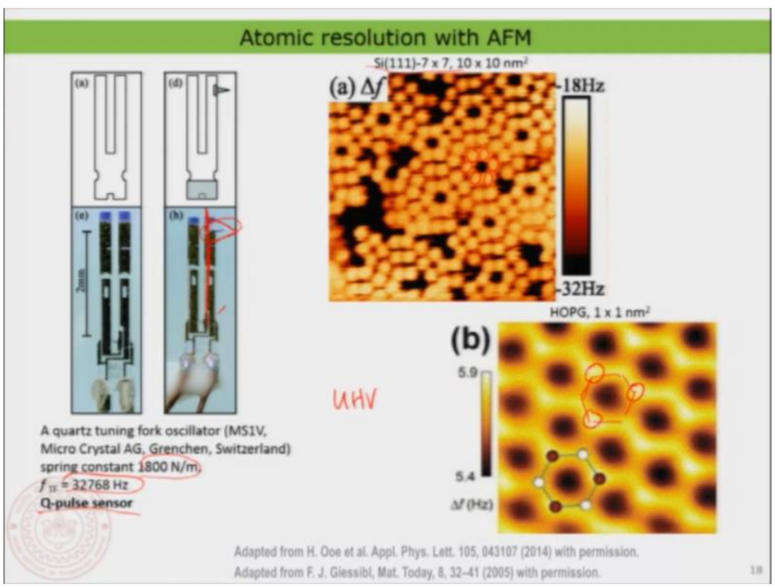

So, this cantilever is actually known as a Q pulse sensor this is nothing but a tuning fork it is not anymore, a cantilever it is a tuning fork. And this particular tuning fork is actually originally used in a Swiss watch that cantilever you can actually connect a very sharp tip so that is nothing but a metallic tip like you use in STM. And then this is actually now connected and this would be your cantilever and this is nothing but the tip.

So, now you have actually an extremely sensitive cantilever having a very high force constant and a very high frequency and then a sharp tip then what you can do is you can basically resolve atom. So, now you have the silicon 1 1 1 7 by 7 reconstruction you see basically the same thing that we have observed previously that each of these bright spots are nothing but atoms. That is the interesting thing or I can actually just go down and measure the graphite. And you see here I have clearly this nice hexagonal pattern with three atoms being brighter and the other atoms are actually just kind of a less bright. And therefore, I am basically able to resolve the atomic resolution using this. So, therefore this is done inside UHV. So, this is quite important ultra-high vacuum using a cantilever this which is extremely sensitive and then you can basically just measure the atomic resolution.

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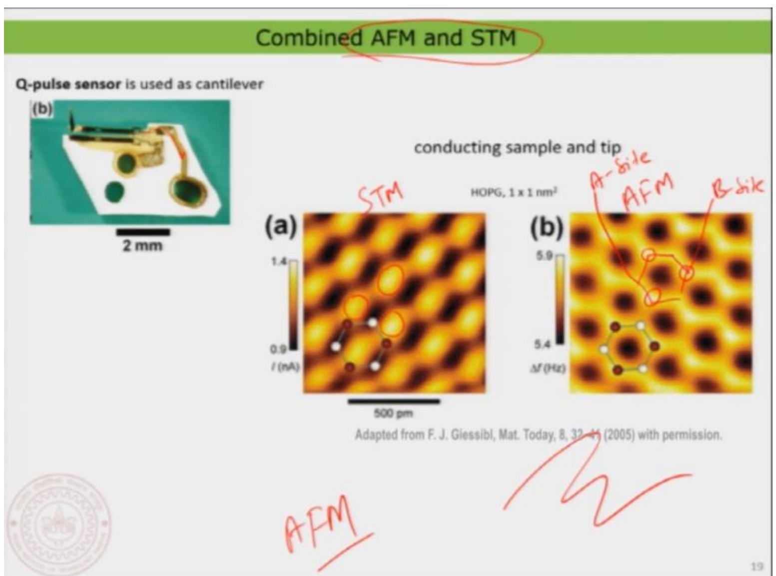

Well, I can also therefore combine it now you think about that this particular cantilever is also having an electrical connection and the cantilever itself is actually conductive then I can simultaneously measure the current and the force together. So, that is actually the combined atomic force microscopy and scanning tunnelling microscopy this is a beautiful technique which is a combination of two most important tools in surface science coming together. Then what you can do is you can basically just measure simultaneously the scanning tunnelling micrograph and actually the atomic force micrograph. So, you remember that in scanning tunnelling microscopy what you are basically just looking is the kind of electron density of the surface. And that is a reason why you are only able to resolve these alternating atoms of the hexagon of graphite but you can see that is not the case in AFM.

You can basically just see the entire hexagon with 3 atoms being slightly brighter than the other because this corresponds to the B side and this corresponding to the A side of the graphite. So, please refer to our previous lecture that we have already discussed it. And now you see that you have an absolute skeleton of the surface so the surface is absolutely imaged using AFM. So, this is very beautiful so now we have an AFM. We have a technique with which we can basically just go down to atomic resolution and resolve things at a greater detail. So, in the next class we will see a few more examples and a few more interesting applications of scanning tunnelling microscopy and AFM together. So, that is the interesting aspect and we can actually just come up with that. So, today right now this lecture is concluded. Thank you very much for your attention.