Chemistry and Physics of Surfaces and Interfaces
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Lecture - 38
Atomic Force Microscopy (AFM) -3

Hello everyone. Welcome back to lecture number 38. And this lecture we will continue with the atomic force microscopy.

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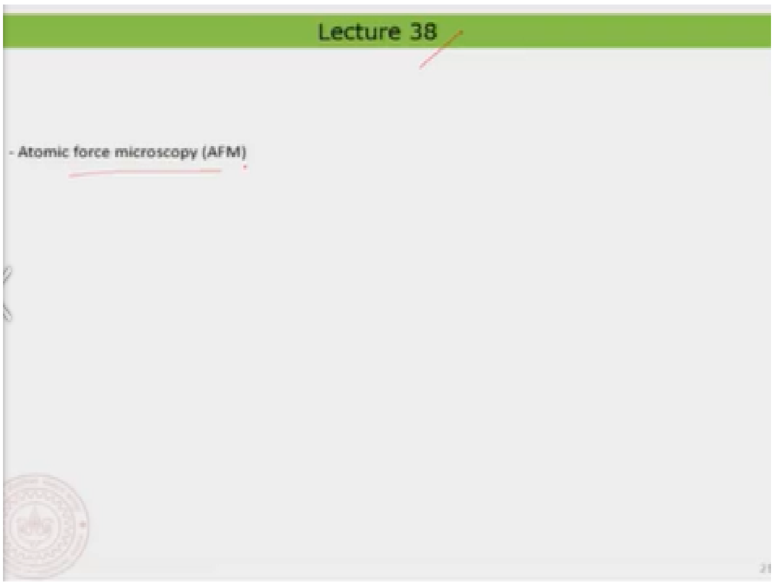

I will try to see a few more applications of atomic force microscopy. So, you have already seen in the previous lecture that using atomic force microscopy we can reach atomic resolution but the condition was basically to use ultra-high vacuum, so to do everything in ultra-high volume and then also to use an extremely sensitive a tip and an extremely sensitive cantilever. So, with that condition actually we can use or we can use this atomic force microscopy in resolving atoms on the surface. Or on the interface whichever you want to do it, so that possible. Now let me show you something more. So, where we stopped when we looked at the scanning tunnelling microscopy you recollect this molecule.

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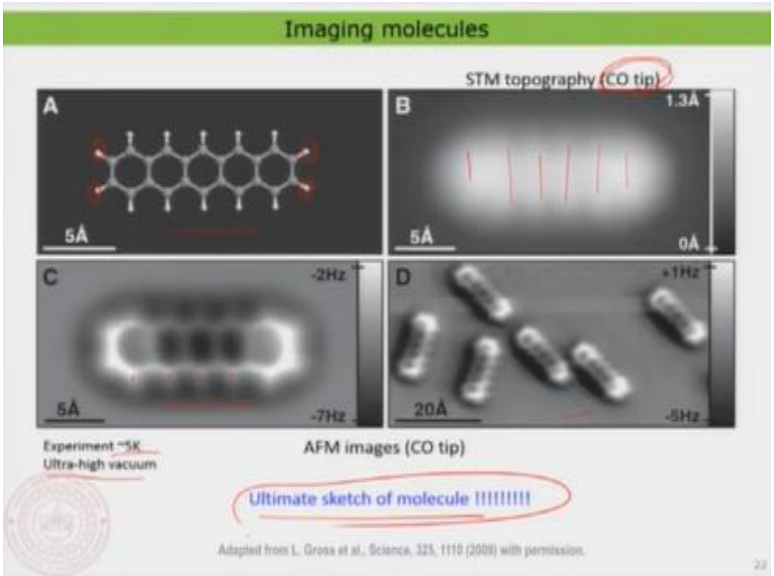

This was pentacene molecule and we said using a kind of carbon monoxide tip we can reach a very beautiful image and that is representing the molecular orbital. So, you also recollect that we have actually just compared it with the theoretical calculation and you have seen this kind of a contrast or the variation in the contrast is actually coming from originating from the electron density.

That is corresponding to a given molecular orbital depending on the bias and so on. Well, but you were always wondering in this case that why can we just see the molecularities. So, that was a question that we actually posed but we said just in the scanning tunnelling microscopy it is not possible because what we are measuring is nothing but the electron density of the surface or electron density of the molecule or whatever you are actually looking at. But now let me show you an image that should be the most important breath-taking image is actually an ultimate sketch of a molecule. So, now you see here this is anatomic force microscopy performed inside ultra-high vacuum condition at low temperature using carbon monoxide tip, that means the sharpest tip that you can imagine and then using the Q pulse sensor type of cantilever. So, good we can now resolve everything that you have a molecule and now you see clearly the five hexagons that are corresponding to the pentacene molecule and you can also see like in a large overview. There are a couple of molecules hanging around so you can nicely see the sketch of a molecule. So, this is really the sketch of the molecule and this is the ultimate resolution that so far actually achieved using this kind of microscope. There is nothing more we can do and I do not think there is much more we need to do in many cases because with this you should be able to understand the molecule clearly. Of course, something interesting I also want to draw your attention in this molecule is that typically what you know is that the electron cloud or the pi electron cloud is actually just moving across this hexagon and that is what we have studied in our fundamental quantum mechanics classes. And that is something you can clearly see here. But you also see that the electron density is basically also protruding a little away from the hexagon and that is actually because you have that carbon hydrogen bond. So, now you see a little bit more than what you have studied it is not just the electron density localizing around the hexagon it is also a little bit leaking out through the hydrogen. So, that something you would expect because hydrogen carbon there is actually kind of an interaction. So, what you are seeing now is kind of a sketch of the of the electron distribution around the molecule. So, that is the interesting thing about it and you also notice that in this case the hexagons in the middle that means the 3 hexagons in the middle is looking a little less brighter than the other ones.

There is also an interesting reason. because you know that there is this high extra hydrogen atoms for this last phenyl rings when you adsorb them on the surface. they are not actually absorbing flat on the surface instead the edge of the molecule is a little bit bending upward because these hydrogen atoms are kind of repelled away from the surface. Because of that you basically see that kind of a slightly boat shaped molecule in this case. This is very spectacular because now you are actually just seeing how the molecule itself and also even the shape of the molecule to a good extent you know that therefore very nice and that is why I am calling it as the ultimate sketch of a molecule and the ultimate sketch of a molecule sticking on a surface. So, that is very good.

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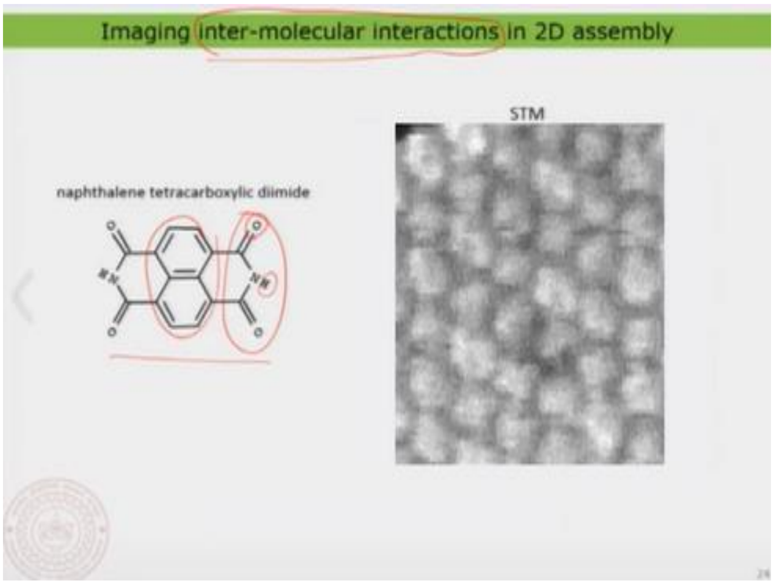

So, now what I want to show you here is actually the self-assembly of a molecule and can we also just somehow see the intermolecular interactions. So, this is something that we have so far not seen even in scanning tunnelling microscopy. What we have always seen is actually the assembly of the molecule and here I have a molecule as an example, so this is like naphthalene tetracarboxylic diimide, so that is the naphthalene part and you have the diimide part. And this molecule if you self-assemble them on the surface because you have this hydrogen bonding acceptor and a hydrogen bonding donor group. So, they are known to actually just make nice self-assembly. So, that is something that you see here, you can see basically that there are different orientation for the molecule so once the molecule in one row it is oriented like this and the other row it is oriented like this there is a slight difference in their orientation. So, that is basically to maximize this hydrogen bonding. You can see here the hydrogen bonding is maximized when they arrange like that and then they actually form a nice self-assembled pattern. So, this is very well known, so this was already known for quite some time and people do study. But the interesting question that people were asking, can we really see or can we really understand this intermolecular interaction through microscopy.

But when the atomic force microscopy performed at ultra-high vacuum conditions using the couple sensor, what people could resolve is actually something like this.

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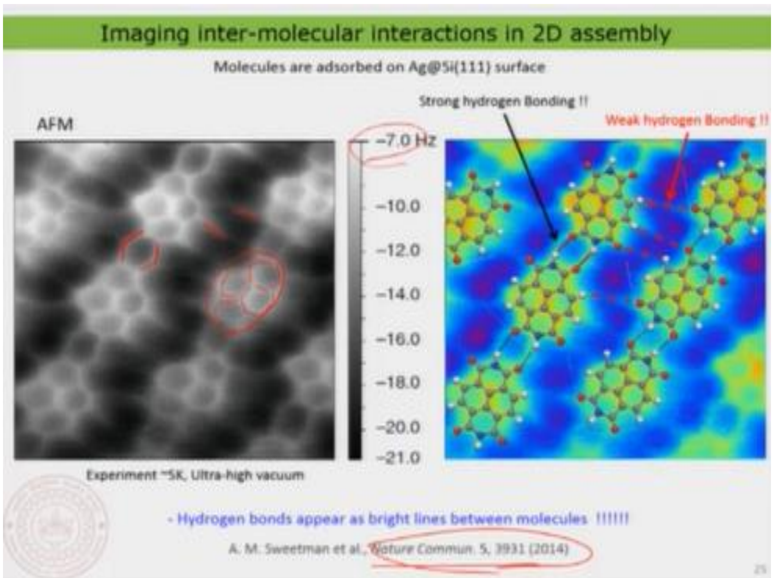

Where you clearly see the skeleton of the molecule. So, this is basically the molecule and where you have the inner hexagon, the two hexagon basically and you also have the diimide group here. You can clearly see the sketch of the molecule. So, I have here a comparison where I have actually taken the molecule and also put the molecular geometry on top so therefore you can clearly understand what is going on. So, you clearly see that the molecules are actually arranging like what you have expected because there is a hydrogen bonding they would basically just go like this. But now something interesting you would also notice you are not just only seeing the molecules you can also see something in between the molecule. Do you see this? You can also see something in between the molecule, what is that? Well, that is nothing but the hydrogen bonding.

So, now for the first time ever people could see basically the hydrogen bonding. We know that hydrogen bonding is also a very strong bonding. where there is a true charge delocalization between the atoms that participate within the hydrogen bonding and now you clearly see that there is a certain density of electron that is actually observed between the molecule that indicate there is a hydrogen molecule transfer between the molecules when you actually undergo hydrogen bonding. This is something you can now spatially resolve using atomic force microscopy. So, this is very, very beautiful. Now not just only that you have something more if you look a bit more carefully you see there are also other lines around it which is not just sticking at the molecule. It is extending a little longer. So, you can see these two lines they are extending a little longer and they are quite directional towards the other molecule.

What is that? Look at this is nothing but the oxygen hydrogen connection; there are also carbonyl group on the molecule. And that group is basically just kind of interacting with the phenyl CH bond also kind of a very weak hydrogen bonding, but even that is kind of visible within the atomic force micrograph image. So, this is quite beautiful. So, now I can basically by just looking at the contrast or the intensity. So, this is something that you can call it the brightness or the darkness. So, the brightness is basically imaging that you have a strong electron density which is moving around at that location and that you can basically just clearly identify using atomic force microscopy. That means we are not only just looking at the structure of the molecule. we are also looking at the intermolecular interaction in real space, this was never done before. So, therefore it was quite a celebrated paper and people were discussing about. So, this is one of the other possibility of atomic force microscopy.

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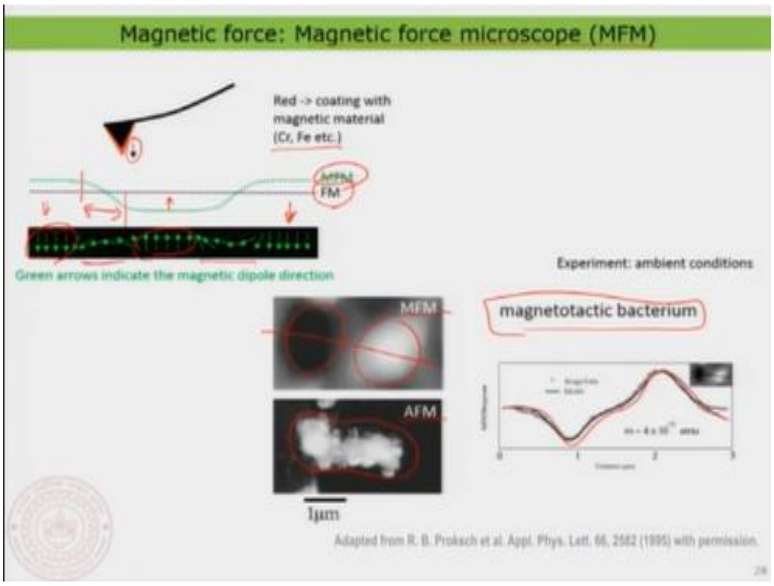

Now what I want to do is that, I want to just switch the topic slightly and then show you the magnetic force microscopy. So, in the magnetic force microscopy what we want to resolve is the magnetic contrast. So, the difference that you are going to see in this case is everything is going to be the same as before but the only difference is that the cantilever will be kind of modified with magnetic material. So, this is also possible to be done using e-beam epitaxy so that something I have also told you in the case of scanning tunnelling microscopy. There you have seen basically that we can basically just deposit the magnetic material on top of the tip and then you can make actually the tip magnetic. So, this is quite important ah because the magnetic contrast only result when you have a magnetic tip. So, now what I have here is a schematic of a surface, so this is a surface which is having a flat topography. So, there is actually nothing special on it. So, if you using force microscope if you scan the surface what happens is that you are going to get a flat topography so nothing special. But now imagine that I am going to deposit chromium or iron or cobalt or some kind of magnetic material on top of the cantilever. So, I also told you that this is now commercially available, so you can buy this kind of a cantilever tip combination and I have now deposited one of this material so it is up to you. And now depending on the tip magnetization so you are also going to get an orientation of the spin or the magnetization of the tip itself so that is very important because otherwise the image is going to be reversed.

Now I assume that I have actually a magnetic sample where I have different magnetic orientation like this. So, I have a down orientation, up orientation down and so on and in between I have kind of grants boundary between the two magnetization directions. So, it is not normally possible to have a spin up and then immediately spin down so it has to have some kind of a grain boundary. So, I can have this and this is something that you can actually create even on different materials and now the interesting thing is if I now move the atomic force microscope tip which is actually a magnetic over the surface. Now you see it is going to respond to the magnetization of the surface. You clearly see that these two it is actually similar poles because they are repelling you see the topography is slightly higher.

When it come to this one now you can see the orientation of the surface is actually opposite to what of the tip and therefore, they are actually attracting the tip and the surface is attracting therefore the topography goes down and then again when it comes here it is basically the opposite direction. So, now you see that depending on the magnetic domain the magnetization and therefore the magnetic domain you have a topography that is actually resolved in the magnetic force microscopy.

You clearly can now identify what are the different magnetic domains and also this distance is actually just giving me the typical grain boundary, what is the grain boundary? So, that is also very important, so that I can basically identify here. So, now using a magnetic tip I can now identify the magnetization of my surface. Now let me just show you two examples in this case. I have here a very interesting example I thought about is actually a magnetotactic bacterium. So, this is a special kind of bacteria that uses x magnetization to get oriented, so this is quite interesting creature. But now if you do an MFM the magnetic force microscopy and the AFM of the same bacteria simultaneously, those is something you can do simultaneously what you see is that in the AFM it looks just like a bright feature no difference. But in the MFM you see that there is a dark region and a bright region.

So, if you take a cross section of that so that means you take a cross section then you clearly see that I have a down and an up orientation. That is nothing but one of the edges of the bacterium is actually having a down magnetization and the other having enough magnets is actually nothing but a magnetic dipole this is quite interesting. Using this magnetic dipole is what this bacterium actually just aligns with the x magnetization. So, this is also a particular example I thought about showing.

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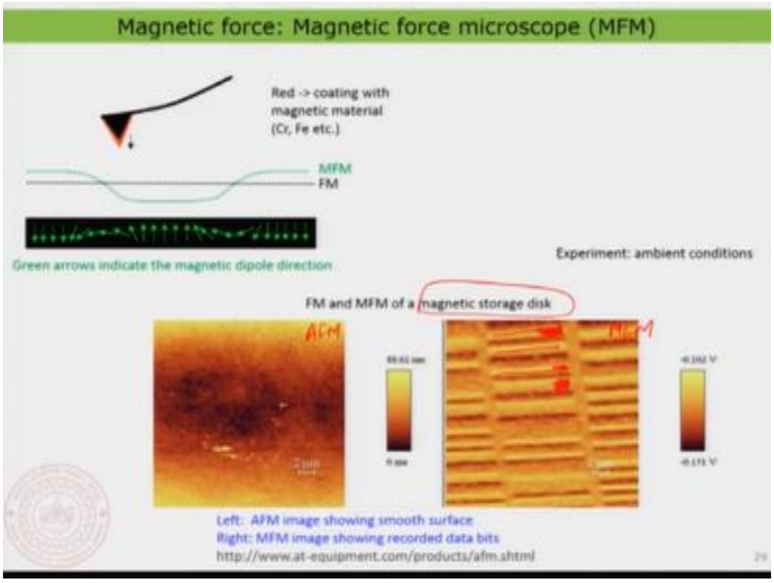

Now I want to show you another example which is actually a magnetic storage disk that we all use in our daily life. Now if you do the atomic force microscopy of that magnetic storage disk what you find is a smooth flat surface. But this is actually the MFM the magnetic force microscopy and there you see that these little features are showing the different domains that you create in order to basically generate the in order to basically store the data. So, this you can also see the width is actually varying so this is kind of moderately wide and here you can see it is really wide; there are some which are moderately wide and so on. So, this is basically nothing but you have actually written the magnetic information on the surface and that is nothing but the different orientation of the magnetization that is exactly what you can now image using your magnetic force microscope. So, this is very, very good.

But of course, just keep it in mind magnetic force microscopy is not able to resolve at the atomic resolution. So, this is one of the big problems but nonetheless it actually can resolve domain, so this is very beautiful. So, that is already something I have talked about.

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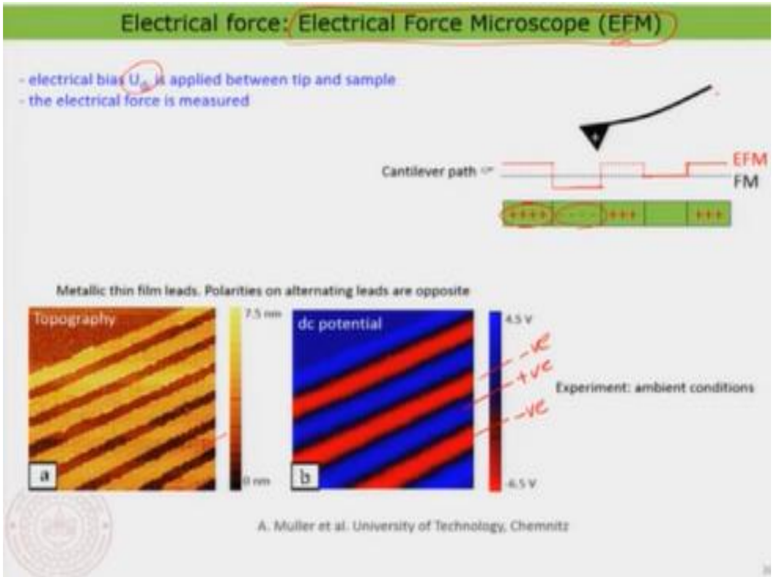

And then I can also something like measure the electrical force, so I am not going into greater detail about magnetic force microscopes but I have already given you the idea. But now we can also just do something like an electrical force between the tip and the sample. So, that is actually known as electrical force microscope. So, what you have to do is again a surface like this if the surface topography is flat the cantilever would normally flow like this. And then you have a constant topography, so there is no surprise. But now imagine that you apply an electrical field between the tip and the sample and assume that for some reason you have positive charge, negative charge, positive charge or neutral and so on, on the surface. So, some kind of a potential difference is actually created on the surface then you can basically identify that if you have a kind of positively charged or negatively charged tip. So, this is the interesting thing. So, now you see clearly that when the positively charged tip comes closer to this part so you have the like charges repelling. So, you have basically a high topography and then when the opposite charge coming you have a low topography because the cantilever and the tip is basically attracting, so therefore a low topography. Then somewhere here I have a neutral position that where the tip goes same as the force microscope and then again, a repulsive region and so on. So, that means basically if I have different charge localized on the surface, I can basically detect the charge using a kind of electrically conducting tip. Well, I have an interesting example here, so this is basically kind of electrical lead so this is kind of metallic wires which are very, very small wires of course put on a surface and now what is done in this experiment is that the alternate lead. So, this one is actually just applied so let me just understand so this is basically, this part is basically applying so I think I can understand here. So, this is negatively charged and then this is again negatively charged and this is positively charged and so on. So, what is done in the experiment is that alternate electrodes are basically just put on different bias. Then you basically have a kind of a positive negative positive negative and so on. Positive negative positive negative positive negative positive and so on so. You are basically just identifying the electrical potential of the surface nicely so with that you can basically just understand even the electrical charge that is on the surface. So, we using electrical force microscope you can actually also just get the electrical force distribution or electrical potential on the surface. So, that is the two new variation of atomic force microscope where you can also just get a magnetic contrast and also like kind of a potential or a charge distribution on the surface. So, that is something that you can also do but the only thing is that the EFM and the MFM is not able to generate atomic resolution but nonetheless they can actually just give you this kind of extra information which is otherwise not possible in a normal atomic force microscopy.

Well, with this I would like to conclude the lecture and I also have convinced you that atomic force microscopy is a beautiful technique and it has a wide variety of applicability in many different streams and we would be basically using this in understanding our surfaces interfaces and their microscopic structure. With this I would like to thank you very much for your attention and then see you in the next class. Thank you.