Chemistry and Physics of Surfaces and Interfaces
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Lecture - 20
Scanning Tunneling Microscopy

Hello everyone, welcome back to lecture 20. So, far we have looked at the different type of adsorbates on surface like atomic adsorbates, small molecular adsorbates and even larger molecular adsorbates we have already checked. And also, while we were looking at the adsorbates on surface, we have also tried to look at using a scanning tunnelling microscopy. So, mainly using microscopy we were basically kind of understanding the microscopic structure or the arrangement of atoms and molecules and so on, on the surfaces. Of course, we have not looked carefully into the details of that microscopy itself because you have already seen that at every point of our discussion, we were using a scanning tunnelling micro graph, scanning tunnelling microscopy images to understand really the microscopic and molecular level structure of the adsorbates surface. So, it is clear that you are convinced that we need to actually understand this microscopic technique in greater detail.

So, that is what we are going to do in the next four to five lectures we will try to understand basically, what is scanning tunnelling microscopy and what are its additional applications than what we have already seen in the previous lectures. So, scanning tunnelling microscope is basically the topic that I am going to cover in couple of next lectures.

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And the scanning tunnelling microscope comes under a broad class of microscopy known as scanning probe microscopy. So, I will come to that in a minute and today's lecture we will be looking a little bit more into the details of scanning tunnelling microscopy.

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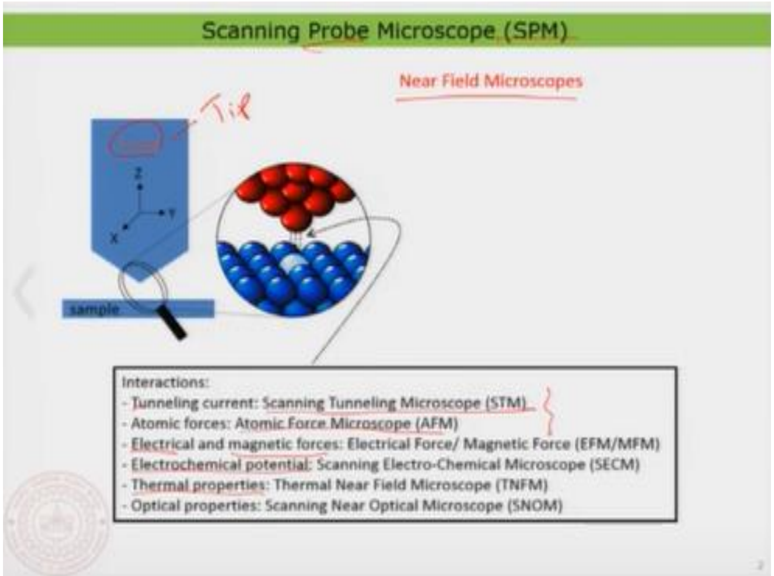

So, what is scanning probe microscopy? So, that something what we will first look. So, Probe is generally something that you can use to investigate something. So, that what a probe means. You might also have noticed that people who are having like you know vision problems; they usually carry a stick that is known as a Probe. And they normally what they do is they carry that Probe or the stick to identify the obstacles. So, they move across and as soon as they find obstacle, they would just basically move the probe over that. So, that is kind of identifying or probing the surface along which they are working. So, the same idea is also what we use here in in generally surface or scanning Probe microscopy that is the general classification SPM. It is known as what we do is instead of using a big Probe; we are basically using something known as an atomically sharp tip.

So, Probe this is also an atomically sharp tip so the tip can of course be made up of different type of material depending on what you want to prop. So, that the most important thing that you keep it in mind. So, what you have is always a Probe, but the prop is actually capable of scan along the x y and also along the z direction. That is the key point. So, you can basically just access all the three different axes while we are using this Probe.

And now you take a surface bring the Probe or the tip on top of the surface and scan across the surface and Probe what is on the surface. So, that exactly what a scanning probe microscope does. But the interesting thing is that unlike other microscope like optical microscope or electron microscope there you are basically investigating things from a further distance, but in this case your probe is at a very very close proximity of the surface. That means in the order of a few nanometre away from the surface is where you basically have the tip investigating the topography or the nature of the surface itself. and that is why it is generally known as a near field microscope so because you are actually just looking things in a in a close proximity and of course, the image that you obtain is not a direct image.

It is basically some kind of an information that you extract from the surface and then this is basically then converted to an image. So, that is what basically you do. Now let us look at the possible interaction that you can lead to an image on the surface. So, these are something what makes the different type of Probe microscopes as you see here scanning tunnelling microscope generally known as STM.

In that you measure something like tunnelling current between the surface and the tip. So, to measure of course current you need to definitely apply a bias between the tip and the sample. Sample tip you apply a bias between them and in the very very cross proximity if you move the tip then you can actually measure something called a tunnelling current. So, we look into that in greater detail because it is quite important for us to understand the tunnelling current. So, if you measure tunnelling current then it is generally known as scanning tunnelling microscope. So, you are ideally measuring the tunnelling current across the surface and then you are probing the surface as a function of tunnelling current and the x y plane. So, that is what you do. Now if you are measuring something like atomic forces that is acting between the surface and the tip.

Then you have something known as atomic force microscope, then you can measure many different other forces like electrical force, magnetic force, then you have actually electrical force microscopy or magnetic force microscopy generally known as EFM. MFM and so on which is another type of atomic force microscopy but where you are actually just looking at the electrical force that is acting between the tip and the sample. In atomic force microscopy the only difference is the tip is not just floating like that it is basically just kept on something known as a cantilever will definitely have several classes on atomic force microscopy towards the end of the lecture. So, we will look into that in detail, but just to be aware at this point of time that in the case of atomic force microscope the tip is always placed on a cantilever. So, that is the slight difference between them. Then one can also measure electrochemical potential that is actually just acting between the tip and the surface or you can measure thermal properties or temperature difference between the tip and the sample. You can also measure optical properties are many many things that you can actually measure from the surface using a tip but the design of the tip is definitely going to be different depending on what you are going to measure. Therefore, each of them is in itself is an interesting topic to understand and to study for example. But in in our context we are only going to deal with the scanning tunnelling microscope and atomic force microscope because these are microscope that can reach a resolution of atoms you can basically see atoms you have already seen in some of the images in the previous classes, we can really see atoms and surfaces. So, therefore we would be looking only at this microscope in our context. And therefore, I will be basically just discussing with you the tunnelling microscopy and the atomic force microscopy in greater detail. So, let me then start with the tunnelling microscope first and then to after we have a look at several examples and the use of scanning tunnelling microscopy then we will basically look at the atomic force microscope in greater detail.

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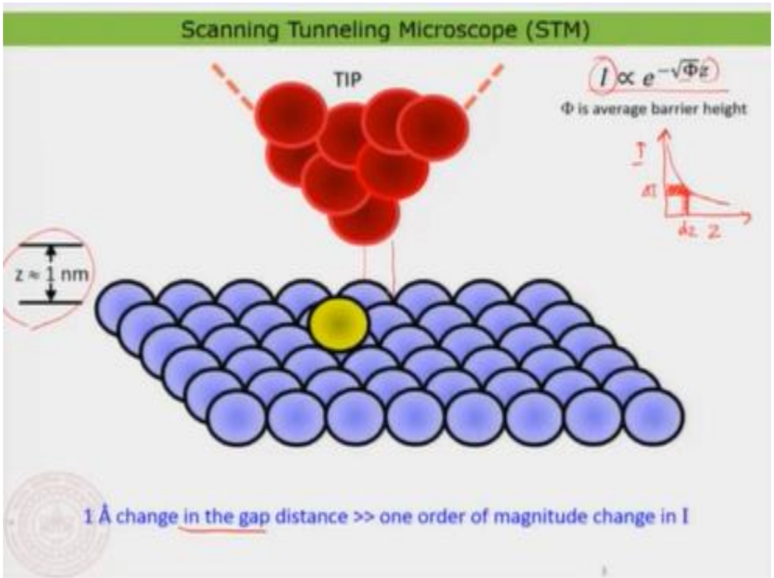

Good, so what do we have in scanning tunnelling microscope? So, I would basically like to investigate a surface of this type where I have a surface lattice, so you can see the blue atoms are nothing but my surface lattice and then I have added an adatom on top of the surface. So, you by now you know what is an adatom, it is actually the atom or the adsorbate atom that you have deposited and I have an atom which is sticking on top of the surface.

Now I want to investigate this surface basically. So, this is of course a schematic picture, and I want to basically investigate and get the atomic resolution of the atom on the surface so that you can basically understand where the atom is exactly sitting on the surface. So, this is what our task is. So, how do we do that in scanning tunnelling microscope? Well, the most important requirement in scanning tunnelling microscopy is to have a tip. But not just any type of tip you need to have a tip which is atomically sharp. So, that is the most important requirement. So, you might be wondering at this stage how can, we make an atomically sharp tip. So, I will just give you the tips later during the lecture. But of course, believe me that you can make atomically sharp tip and that is the most important requirement to achieve atomic resolution on surface. You will actually be convinced when we look into the working principle of scanning tunnelling microscope. Now the interesting thing is that you need to bring the tip in a in a very close proximity to surface in the order of a nanometre or two nanometre something like that. And now you need to also apply a bias between the tip and the sample. That also means the tip and the sample should be conducting in nature. Semiconductor metal or of course you would also find thin films on metal can also be investigated. And that actually the the one of the biggest drawback in scanning tunnelling microscope as you will see that we are limited to use semiconducting or conducting sample or ultra-thin films of insulator. So, this is all what we can basically do with scanning tunnelling microscope.

But do not worry it is quite exciting nonetheless you can investigate quite a lot of interesting aspects using scanning tunnelling microscopy. So, that the most important thing. So, now I apply a bias between the tip and the sample. Now once you apply the bias between the sample and the tip there will be a current that is passing between the tip and the sample which is strongly dependent on the distance between the tip and the sample. But not just in a very simple manner it is actually dependent in exponential manner with respect to the distance and then you also have a dependency of something known as average barrier height or the barrier height. You will see in the next slides what is this barrier? Meaning, it is actually some kind of a potential barrier that limits the electrons to go through. Because as you see directly in the; image there is some kind of a vacuum that is between the tip and the sample.

They are not connected. So, that the interesting thing they are not connected but there is some kind of a gap in between and I am assuming that all this thing is actually happening in kind of a vacuum space which is meaning that there is no medium which is actually in meaning that there is some kind of a barrier there is a potential barrier that limits the electrons to pass from the tip to the surface. Well, that is what the tunnelling itself means. It is actually a quantum mechanical phenomenon we will see in the next slide. But what is important at this point of time to notice is that this tunnelling current is strongly dependent on the distance. So, that means if you would have plotted basically the current versus distance, current versus distance then it would have looked like this kind of an exponential function. So, you directly see that if I would make a small change in z. So, if I would make a small change in z so that means z then you can see that there is a much stronger change in the current; that what is interesting about the exponential function itself. So, the delta I corresponding so that is what I have actually just written here. So, the change in current as a function of distance is much much much stronger. Now let see the interesting aspect. So, now the tip is basically just placed on top of an atom.

So, assume that you are actually just having your tip exactly placed on top of an atom, then the average distance between the tip and the surface is basically smaller compared to you move the tip to a position which is in between the atoms. So, you naturally see that here the z is larger. So, in a way I want to say is basically that z prime is greater than z. So, the position z prime is basically representing that the tip is in fact in between two atoms where the distance between the tip and the sample is higher. So, what is a consequence? The consequence is that there will be a drop in current of about one order of magnitude. So, if one angstrom distance changes; then there is an order of magnitude change in the current happens. So, therefore what you would expect is that when you move the tip. For example, across the atomic lattice so now you scan the tip across the atomic lattice you would find that you can measure basically a high current here, a low current here. So, ideally this small difference that delta I is nothing but representing some kind of a change in tunnelling current as a function of distance. This is nice what do you see in the line profile the current line profile is that you basically see that there is a kind of nice profile that you have created which is exactly replicating v atomic lattice. That means you have resolved the atoms. This is exactly the principle at which the STM works.

Now you can do the scanning. So, you have actually now moved the tip along one line. So, now you can basically move the tip to a next line scan move to another line scan and you can basically just make many many many lines scan and as soon as your tip basically reach on top of the adatom you would directly find that there will be a strong change in the distance because the tip will actually just be mating the atom in a very very close proximity. There is a strong change in the current and that would mean the position where the adatom is sitting will look much brighter in the image. So, therefore you can identify the atom itself on the surface. So, now let us look at an image. So, what you are going to basically see is the sum of many many many line scans and you do across the x y plane.

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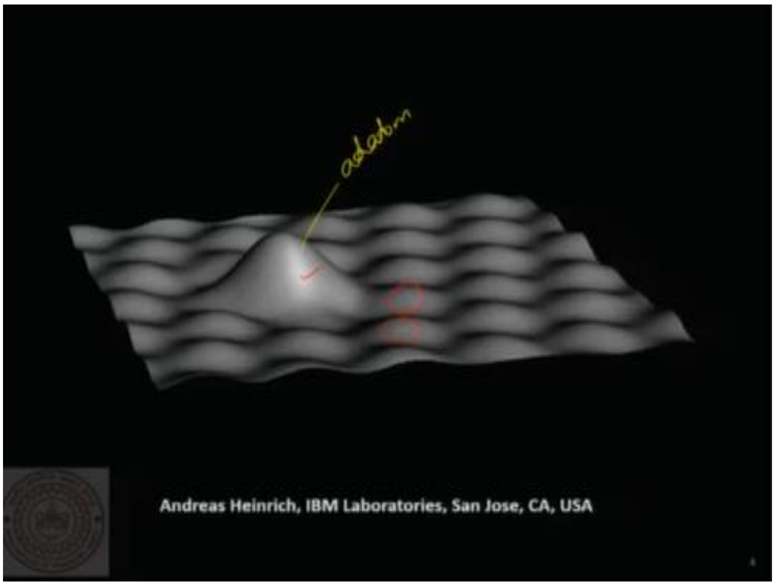

And when you do that, you basically get something like this, where each of these bright regions are corresponding to the surface atoms and this is basically the adatom. That you have deposited on the surface. So, now nicely you can resolve the atoms in a beautiful way and you can get the atomic resolution on surface. So, this is quite interesting. So, it is unimportant at the context what is the type of material that you are using. Because also later you would find that it is hard to get something like a material related contrast in STM but nonetheless what you would be looking at is something called an electron density of the surface. But with that you can kind of recognize what is the different positions of atoms of the surface or what if you put actually adatoms on the surface and so on. So, we look at several examples now onwards and then you would; basically just can understand this a little bit more, better.

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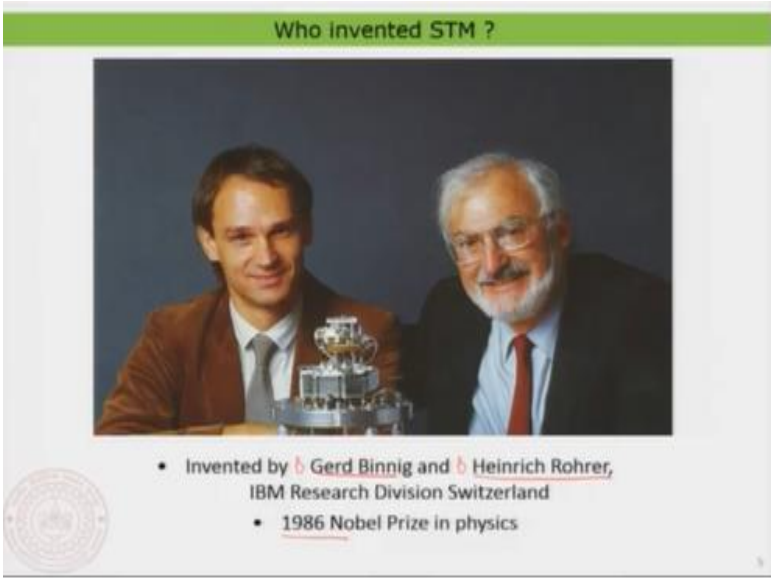

Good, who invented scanning tunnelling microscopy? So, that is the most important part. So, actually was invented by Gerd Binning and Heinrich Rohrer. So, they are basically just colleagues working in the IBM Research Division and they have invented the microscope itself about 1980 so 1979 to 1980 so they have actually invented. And you can see they have got the Nobel prize awarded within just five years. This is actually one of the discovery for which the Nobel prize was awarded almost immediately after the discovery. So, you will actually just see that how powerful this technique or how powerful this technique became that people recognize within five years that this is going to be one of the most important tool in nanotechnology itself. You will see that in my upcoming lectures that we will use scanning tunnelling microscopy to do. And understand a lot of interesting things that you will also find at some point this is not just some told to image but this is also a tool for doing things on surface. So, that is the interesting aspect about it. But I just want to also recollect a story at this point that in 1986 when they got the Nobel prize in physics for the discovery of microscopy. There was also another person who actually just got the Nobel prize in physics.

Which was also for microscopy in fact that was for electron microscopy and that was actually given to Ernst Ruska. But the interesting thing what I want to tell here or recollect here he actually invented the electron microscope in 1933. But he got the Nobel prize after 53 years. Normally you know that Nobel prizes are actually coming after quite a lot of waiting but the discovery itself was kind of recognized immediately after five years. Because this is actually one of the most important discovery where people could first time ever realize see atoms in real space. And also, some of the most unsettled questions were answered immediately because seeing is believing. So, if you have a photograph, you believe that. This is the point.

So, here you have images of the surface so you will believe it. So, that the most important exciting part about it.

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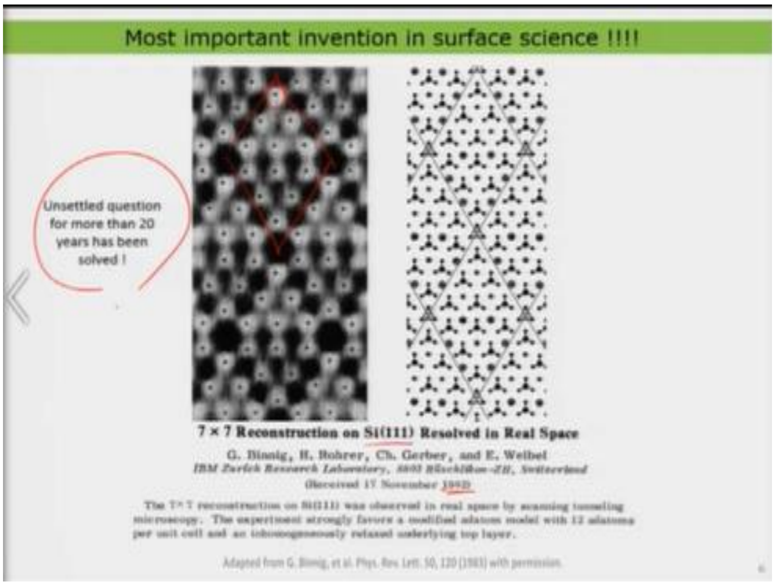

So, now I will show you one of the most important discoveries that actually just triggered during this time. You can see the publication is about 1982. Immediately after they have invented this microscope one of the surface that they have looked at was actually the silicon 111 surface and not just the normal silicon 111 surface because by now you know that silicon 111 surface is actually getting something called a very stable reconstruction known as the 7 by 7 reconstruction So, the 7 by 7 reconstruction was for the first time ever resolved in space. So, you remember this image that we have already looked at it and these are basically the adatoms that we have already looked at it and that was actually just giving rise to this kind of nice 7 by 7 supercell. Of course, the image at 1982 is not as flashy as the one we have seen in our previous lecture but you can see this is the first image.

And then what was actually just interesting is that this was actually an unsettled question for about 20 years in surface science but just with the help of scanning tunnelling microscopy you can see the name of the paper itself was like resolved the silicon super silicon 111 reconstruction in real space. So, then immediately after this there were several images were taken on different surfaces reconstruction of surfaces which was unsold.

All those things were immediately done and then people realized that this is actually one of the greatest discovery of that time and then was given the Nobel prize in physics. Well, the same people were also involved in the discovery of atomic force microscopy by the way. So, that is also the the important aspect of of these people. So, you can see these are the people who finally invented together with the few other people like Gerber and Werbel and so on.

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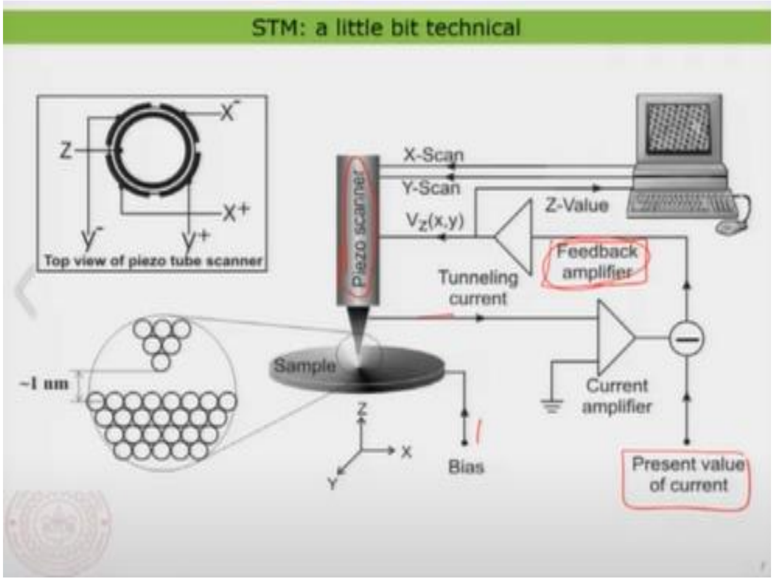

Well, just an important thing that I also want to show here is actually a little bit of the technical aspect. So, now um you need to actually also just consider now the point is like one of the most important technicalities that I need to also move the tip very systematically on the surface but the movement of the tip should also be at the atomic scale. But normally no mechanical device could achieve this. But then one can actually use something called a Piezo scanner where a Piezo ceramic material is used as the scanner material and Piezo material is something you might be; knowing that is actually a material which can actually respond if you apply a bias. So, that you can basically deform them by applying a bias, and changes the deformation that happens to this kind of material is in the order of angstroms or nanometre.

And therefore, by carefully applying the voltage you can basically do the so called scanning of the small dimension because you have seen in the images what we are looking at is only a few nanometre by few nanometre dimension. So, this is quite a small dimension. Now that is the most important thing a Piezo ceramic scanner and the tip is always placed at the Piezo ceramic scanner and then you have the sample. So, you apply of course a bias between the sample and the tip and that what you see here. So, you apply a bias between them. And now the most important thing is when you measure so you apply a bias so you basically place your tip on top of the surface and then you apply a bias you measure the tunnelling current. When you measure the tunnelling current you always maintain something called a feedback.

The reason is simple because if the surface is actually more corrugated, let say having some kind of topography and if you move the tip across the surface the tip, need to respond also to the surface. So, that means immediately when the tip see that there is a small protrusion on the surface it will measure a very high current then the tip should also get slowly retracted backward. Otherwise, the tip will just get bumped into those protrusions.

Therefore, a feedback mechanism should always work between the scanner and the tunnelling current measurement and that is why you would always find that there is something called a feedback loop system is actually working. And that is maintained by something called a set current. So, you measure or you set a certain value for the current and that value of current will always be maintained while you do the scanning.That is quite important otherwise you would basically be ending up kind of crashing the tip into the sample. So, that is why the z scan is always so the z value is basically always been used back in the in the scanner. But x and y are independent the x can so the x voltage that you apply on the piezo and the y voltage that you apply on the piezo are independent but the z is always been connected to the so called feedback system. So, that you can basically retract or move the tip up and down. That is quite important. So, that a little bit of the technical factors for that.

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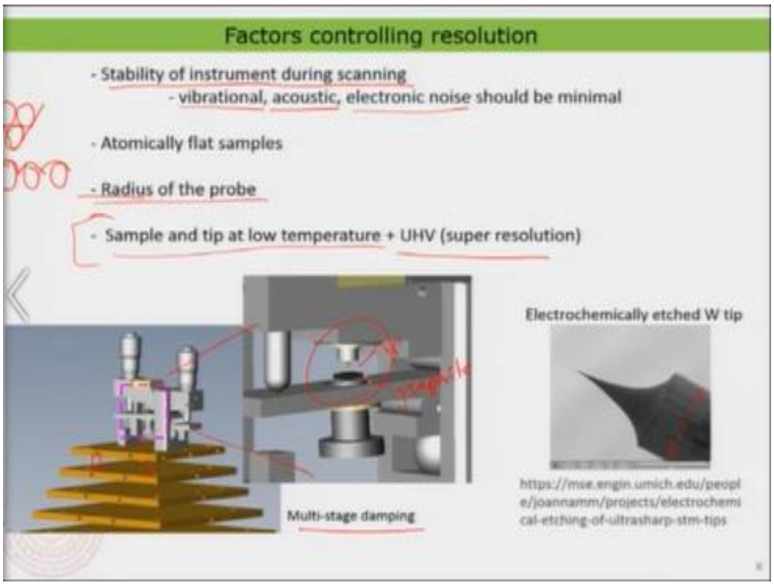

And then there are also some most important factors that are actually controlling the the resolution of the imaging. That is most important is the stability of the instrument during the scanning. You might obviously think about it because you know that you are actually just looking at atoms and imagine that your tip is actually oscillating at a frequency which is in the order of a millimetre or something you will never ever see an atom. So, therefore it is important that you need to have a tip which is very well stabilized. So, that the imaging is very stable. So, how do you do that? You need to basically cut all the vibrations because if the microscope is actually sitting somewhere. The vibrations that happen around for example you cannot walk around the microscope. This is something very interesting because if you walk around the vibrations, you would basically excite the floor. And that excitation can actually couple to the microscope and then the microscope would also start to vibrate that means eventually the tip will vibrate. If the tip, vibrate you cannot resolve the atom. So, therefore it is quite important that you cut the vibrations of the surface. And therefore, normally these microscopes are kept on some kind of a vibration damping tables or vibration isolation tables.

Then all the acoustics that means you cannot also talk in front of the microscope because your voice would also basically couple to the tip and the tip can actually just get excited depending on on what you speak for example. So, therefore it is extremely important that you need to have a quiet vibration free ambience. Then also, like electronic noise should also be minimized therefore normally these kinds of microscopes are kept in the ground floor or in cellars. Where you have to have a vibration damping table and also the acoustics of the room should also be maintained. So, that the microscope itself is very stable in terms of the vibrational acoustic kind of noise that can couple to the microscope. Well, that is also something you can see here this is actually like kind of a multi-stage damping that also something very routinely people use that this is actually, the microscope itself you can see where the tip. So, this is the tip and this is the sample so here it is actually a graphite sample. So, you have a sample and a tip and the whole assembly, this is the whole assemblies as you see here. The whole assembly is basically kept on something like a multiple stage damping. So, that each of these feet would basically be connected by some kind of a rubber pieces so that when there is a vibration at the lower floor it will just get damped while it actually come closer to the STM. So, that is quite important. Then you need to have most of the time atomically flat surfaces so you cannot imagine like using STM on an extremely rough surface having some kind of nanometre or 10 more than 10 nanometre roughness. So, this is quite difficult to work with scanning tunnelling microscopy. Therefore, like most of the time you will find that the STM images are always taken on flat surfaces. So, this is quite a requirement. Then the most important thing is actually the radius of the probe. Imagine that you want to resolve atoms that are spaced like that. If I would use a tip which is much much

much bigger than that of the spacing between the atoms you cannot resolve it very obvious. Therefore, the sharpness of the tip should also be typically in the order of the radius in the order of the spacing between the atoms on the surface. So, therefore it is quite important that you need to make an atomically sharp tip or nearly atomically sharp tip. Well, that surprising how you do that well this is actually something called an electrochemically etched tip so this is using an electrochemistry you can basically etch materials out of a small wire. So, the wires are typically just in the order of a quarter of a millimetre wide. But you can still remove the materials and then you can get extremely sharp tip or you can even take a wire and then by just using a mechanical cutting you can also make atomically sharp tip so that surprising but you can basically do that. Then the sample and the tip at low temperature is like not an absolute requirement but if you can have the sample and tip at low temperature inside an ultra high vacuum chamber.

Then you can basically get super resolution that means you can see sometime not just that a molecule is sitting on the surface you can see what is inside the molecule. That means even the atoms inside the molecules and so on you can see. We will look at a few images to understand this in greater detail but this is actually kind of an additional requirement, not the most important requirement. But as you see these are quite the most important requirement the stability the atomically flat surfaces radius of the probe and these are extremely important and but with the lower temperature facility you can go to a better resolution because low temperature already cools down the entire system and therefore, like all the thermal noise can also be avoided in the low temperature system.

So, that is the interesting aspect about it and with this you can basic basically start working and making images of atomically resolved in atomic resolution. So, in the next class what we are going to do is we are going to basically just understand what really STM measures and what is the origin of this contrast that you see and then we will start to apply that to different type of materials. Thank you very much for your attention.