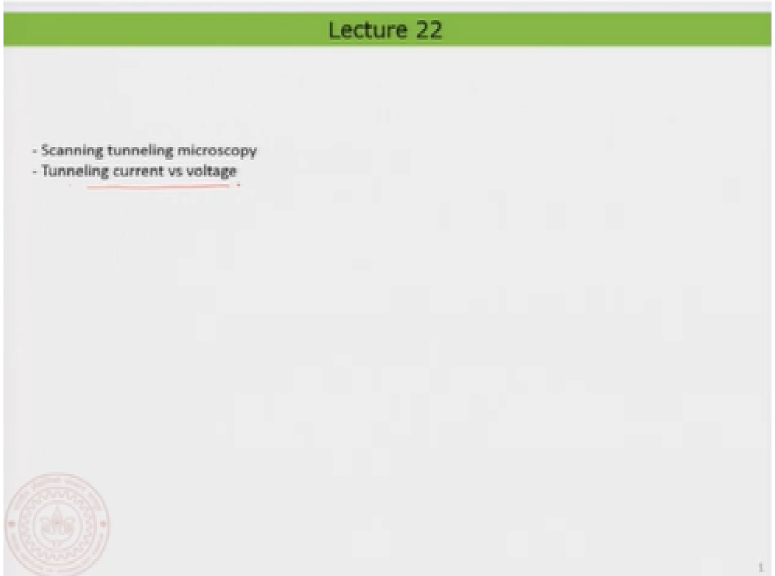
Chemistry and Physics of Surfaces and Interfaces
Prof. Thiruvancheril G Gopakumar
Department of Chemistry
Indian Institute of Science, Kanpur

Lecture - 22
Scanning Tunneling Spectroscopy-1

Hello everyone, welcome back to lecture 22. In this lecture we will continue in the scanning tunnelling microscopy part.

(Refer Slide Time: 00:24)

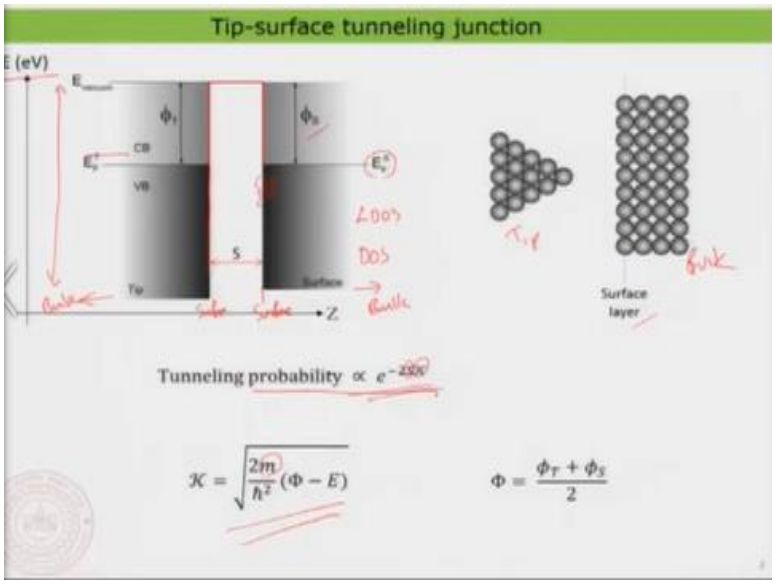


Lecture 22

- Scanning tunneling microscopy
- Tunneling current vs voltage

And today mainly we will focus about and in this lecture mainly we will focus about the tunnelling current versus voltage characteristics. Because you will understand that it is quite important for us to also understand how the tunnelling current actually varies with the function of voltage, because you are also going to finally use this kind of current voltage characteristic in understanding the electronic structure of the material that we are looking at. So, ideally in scanning tunnelling microscopy you can do the same time kind of imaging and as well as you can do some kind of a spectroscopy which is known as scanning tunnelling spectroscopy. And scanning tunnelling spectroscopy is nothing but the current voltage characteristics. So, we look in detail in the upcoming slides and that is what we are going to basically do today in this lecture.

(Refer Slide Time: 01:18)



Tip-surface tunneling junction

Tunneling probability $\propto e^{-2\mathcal{K}s}$

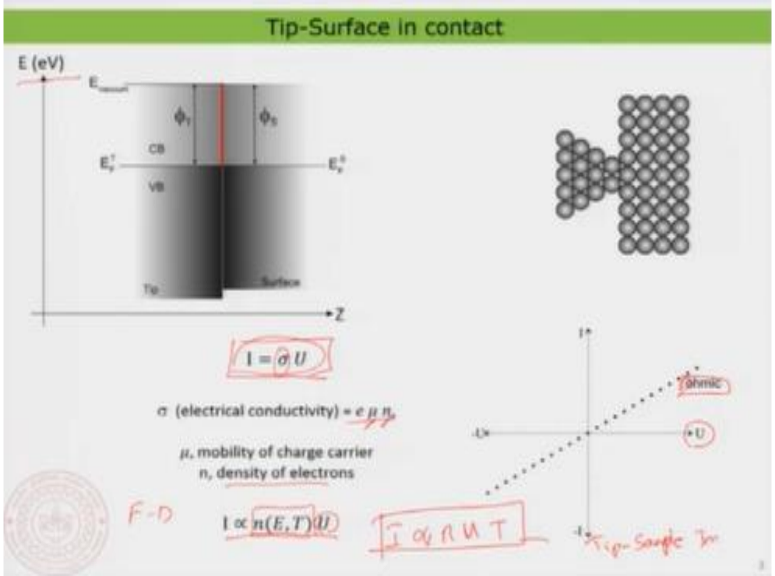
$$\mathcal{K} = \sqrt{\frac{2m}{\hbar^2}(\Phi - E)} \qquad \Phi = \frac{\phi_T + \phi_S}{2}$$

Well, you have already seen the tip sample tunnelling junction, so we have our surface layer the bulk of the material and we have actually our tip here. Now then we discussed yesterday in the previous class that the tip and the surface or the tip and the sample when you bring them closer, they would form the so called tunnelling barrier. So, the origin of the tunnelling barrier is something we have already discussed in the previous lecture and the most important characteristic that you have to recollect again is the work function. And also, the alignment of the fermi level that is something very very important when no bias is applied, the fermi level of both the surface and the sample is going to be aligned. That is the most important thing. And then I have also introduced something called the density of state. So, that is quite important. The density of state is nothing but the number of states that are available within a given energy unit. Of course, in solid it is looking rather a kind of band that is actually you cannot distinguish really any discrete energy levels the electronic levels itself. But due to the fact that you have enormous number of levels packed in a small energy. So, you mostly see it like as a band. But when I draw something like a flat line here, this is indicating that when you go along as a function of energy, the electron energy, you would say that around the surface so this is basically the surface of the tip and this is the surface of your sample basically. So, that is what it basically means and this is actually to the bulk of the tip and this is actually the bulk of the sample itself that you are working with. So, now you have the tip and the surface interface basically. Now when you when I draw a line in the energy diagram it is actually depicting that the number of states per unit energy is actually a constant throughout the image that I have depicted.

So, of course we have only looked at the region near the fermi energy. So, you can see that typically like the energy of this band diagram is represented in electron volt and as you see directly that this is not so much of energy. So, for typically for materials like gold for example the typical work function is in the order of about 4.5 to 4.6 electron volt. So, you already see that the scale that we are talking about is a maximum of 10 electron volt which is above and below the fermi level. So, in that region we are depicting basically that the density of state of the tip and the surface near their surface is basically a constant. So, that is what it meant by the line or when I draw it basically just like a line. So, you will see that this is a kind of an idealized situation or this is not applicable to all cases when we look into the example. But right now, for just understanding purpose this is good to start with. So, just keep that in mind that we are using something like a constant density of state for the sample and also for the tip and near the surface because we are actually just looking the density near the surface. So, this is going to be something known as a local density of state. So, this is generally known as local density of state. So, that also something to do with the location at which we are looking at that that is basically near the surface. Now then we have also familiarized yesterday something very important which is actually the tunnelling probability which is about the probability that an electron can basically tunnel from the tip to the sample or from sample to the tip which is strongly dependent on the decay constant that is basically the decay constant and the decay constant contain directly the work function, the average work function and also, the distance between the tip and the sample and that is the reason why for electrons you can also see in the equation the mass is basically coming to play. So, for electron the typical tunnelling barrier distance to measure something substantial is typically in the order of a few nanometre maximum. Of course, tunnelling occurs even at a very very large distance but you cannot measure it. So, that is the point you need to keep it in mind. But therefore, mass is also quite important and that is the reason why I was telling you or introducing you the other day, that this is quiet in a phenomenon that you would be observing or you would be feeling for quantum objects. Objects that are extremely tiny and also extremely low varying and also fast-moving objects like electrons, protons, molecules, atoms and so on. When the mass goes very high you would directly see that the tunnelling will just stop. So, that is the reason why we as classical objects having very very high mass, we will have no chance to tunnel for example. But electrons or like quantum objects like electrons have a very

very high probability for tunnelling and that can be understood just using this one a kind of approximate calculation you can do using this. Now let us start to do the so, called tunnelling current versus voltage characteristics that is quite important. But before we start doing the real tunnelling current versus voltage, I would just have a look at the so called typical contact current.

(Refer Slide Time: 07: 08)



Tip-Surface in contact

$I = \sigma U$

σ (electrical conductivity) = $e\,\mu\,n$

μ, mobility of charge carrier
n, density of electrons

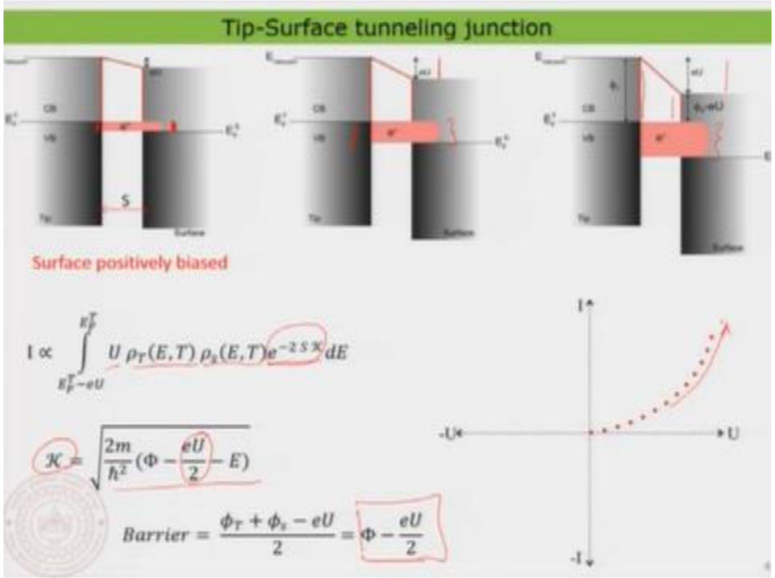
F-D

$I \propto n(E,T)\,U$

$I \propto n\,U\,T$

So, for that what I am going to do is I am going to take the tip put it into the sample. And now I have actually just made a typical resistive junction and when you have a resistive junction, well if you look into the energy diagram, so there is no much change so everything looks the same. But the density the materials are basically just coming in contact. So, that means you do not have any tunnelling barrier there. So, we do not need to bother anything about the so called tunnelling probability or we do not need to worry about basically the barrier or distances or anything like that. So, that contribution due to the tunnelling probability is just vanished. So, that means now the entire current is going to be directly dependent on the number of electrons that is available at the tip and in the surface basically. So, that is going to be basically all that is going to depend and that is why you know that the current in general is directly proportional to the voltage and that is actually having a constant here which is known as the electrical conductivity. And the electrical conductivity is basically written using the charge of the charge carrier that is basically we are considering here in this case it is electron, then something known as mobility, then n which is nothing but the density of electron. So, that is something to do with the material of course. But the density of electron, the mobility and then the electrical charge and then you can basically calculate the current. As you see directly that the current is just proportional to the voltage. So, now in this so, called contact junction if you would have basically varied the voltage from minus voltage to plus voltage you would have seen a linear dependence of voltage and current and that is something you generally call it as an ohmic type of contact or ohmic kind of junction so that is very simple. So, in general what I want to say is that the current is directly proportional to the number of electrons that is present near the junction. So, this is all what it depends so that is quite important and then the voltage. So, the voltage that at which you are basically measuring the current so these are the two factors. And now you also notice that here I have basically just marked this density as a function of energy, that energy is nothing but this electron energy or electronic energy. And t is actually also included because you remember that we have actually discussed the other day that when you define the distribution of electrons inside a material, one need to consider something known as a fermi Dirac statistic which actually tells you the absolute distribution of electrons within the material at a given temperature. So, normally if you do not consider the temperature at all, the density of state of the material remains the same but the distribution of electron within the band is going to be different, if you do not consider the temperature dependent. So, that is also the reason why I have the temperature dependence, so please have a look at the fermi Dirac statistic. So, that is something we have already discussed in the previous day, not in greater detail but just one can actually have a look at it. So, now this is what a typical ohmic resistance looks like or ohmic relation between the current and the voltage looks like. But now what we want to do is we want to basically just have the so called tunnelling junction where we build up the barrier and then we will basically see how the tunnelling current is going to be dependent on. So, now you obviously see that the tunnelling current is definitely going to depend on the density of state or the density of electrons itself and the voltage. And then when you have the tunnelling barrier there will be an additional factor. So, that means the current is proportional to the density to the voltage and also to the so called transmission or tunnelling probability. As you have seen because once you basically just opens up a small gap between the tip and the sample. Then you are definitely going to have the so, called tunnelling coming into play. Then the current is going to be definitely influenced by the tunnelling probability itself. So, now you will find that the current is going to be weighted by the tunnelling probability. So, that is the interesting part about it. So, this is actually valid for the tip sample junction.

(Refer Slide Time: 12:00)



Tip-Surface tunneling junction

Surface positively biased

$$I \propto \int_{E_F^T - eU}^{E_F^T} U\, \rho_T(E,T)\, \rho_s(E,T)\, e^{-2S\mathcal{K}}\, dE$$

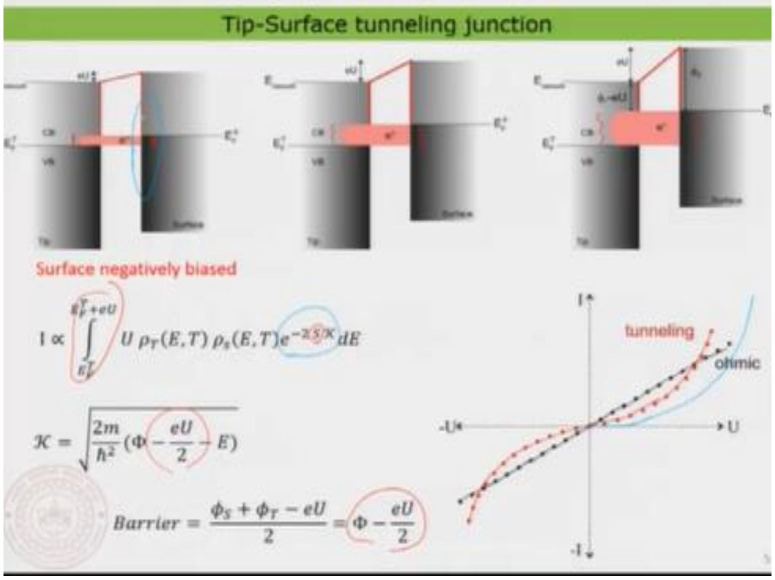
$$\mathcal{K} = \sqrt{\frac{2m}{\hbar^2}\left(\Phi - \frac{eU}{2} - E\right)}$$

$$Barrier = \frac{\phi_T + \phi_s - eU}{2} = \boxed{\Phi - \frac{eU}{2}}$$

So, now let us start to do the measurement so called current versus voltage characteristics. So, now you see that what I have done in this diagram it is basically the same as you have seen before. But what I have done is now I have basically just applied a positive bias onto the surface side. Then what happens is that the fermi level of the surface will actually be lowered with respect to that of the tip and that is exactly what you see there. Now the interesting thing is actually if you recollect what we discussed is when you apply no bias there is kind of an equilibrium between the electrons that are tunnelling from the tip to the surface and tip to the sample and sample to the tip. So, you would not measure any net current so, that is the point. But as soon as you lower or you apply a bias onto the surface so then the fermi level actually goes down. That actually means now there is this much amount of electrons can actually tunnel into the unfilled state this much unfilled state of the surface. So, that means now there will be a tunnelling of electrons from the tip to the sample and this much amount of density of state will actually be used because now when an electron tunnel from the tip to the surface there has to be an empty state to which the electron can tunnel in. Therefore, now you see that as soon as you actually apply a bias voltage there will be a flow of electron from the left to the right. Now that is interesting so we can basically plot that the same diagram as you have seen before for the ohmic contact. But now you see that the current is basically just increasing as you just increase the voltage, so the current has slowly increased. And that increase is directly dependent on how much empty states is available on the surface material or for the sample, let us call it. Now what I am going to do I am going to apply a larger applied bias so, that is what is basically indicated by this. So, I am actually applying a larger applied bias so that means I am going in the voltage axis more to the positive side and then you obviously see that I have more electrons. So, that is very clear because now more electrons from the left of this much electrons can basically tunnel into the unfilled states of the sample. So, that is interesting so then obviously what you would expect that the current increases again further. Now you can really really increase the voltage at a very large extent, so that is what is basically indicated by this the voltage is increased. Then you clearly see that I have started tunnelling a lot of electrons from the tip to the surface. So, obviously that is quite interesting and now you see that the tunnelling current is basically rapidly increasing as the voltage increases. But strikingly there is something quite different in this case compared to your ohmic contact. It is not anymore looking like linear as in the case of formic contact it is looking more like kind of a curvy nature for a constant density of state. So, that is quite important we will come to that that is also the reason why I have actually taken a constant density of state. And you see nicely that the current increases as the voltage increases. So, well you would somewhat guess because I have to consider also the so called tunnelling probability, that exponential function is also now weighted inside the current in the ohmic contact. If you recollect what we have done in the previous slide. Now that is quite interesting so we can basically therefore write down the current expression as again voltage, the density of state of the tip, the density of state of the sample and then you have this component that is basically the exponential factor which is actually taking into account of the tunnelling probability. So, now you clearly see that why we have this kind of shape for the tunnelling current itself. And now the only difference you have to keep it in mind in this particular case the so called decay constant has a slightly different shape where you also have to include the eU by 2 part which is actually the applied bias by 2. So, that is actually calculated like this because you have now to consider that the barrier on the left and the right are different. So, you clearly see it in this diagram the barrier on the left is exactly psi T so this is all the same. But here on the right side on the surface side you see that the barrier is basically lowered. So, now you need to basically take into account of the average of the large barrier on the left side and the large barrier on the on the right side. So, you take the average and that is basically done here. So, you would see that the barrier is also weighted with respect to the amount of voltage that you have applied while you are doing. So, that will also be included in this. So, that also is interesting that this exponential function is now also a function of the applied bias. That simply means when the applied bias is actually much

much much larger you would expect that the current shoots up very very high. And that is also the reason why as you increase the voltage the current actually shoots to a very very large amount compared to the lower voltage. And that is also the reason why you have this nice curvy shape for the current versus voltage characteristic. Now you keep it in mind that I have applied surface the positive bias onto the sample side. This is quite important and the tip is basically just kept it ground, so this is quite quite important. Otherwise, we are going to change the convention, so I will just come back to that in a minute. So, now that is the reason why I have basically now this positive current that is representing that the tip is basically the electrons are basically flowing from the tip side to the sample side.

(Refer Slide Time: 18:27)



Tip-Surface tunneling junction

Surface negatively biased

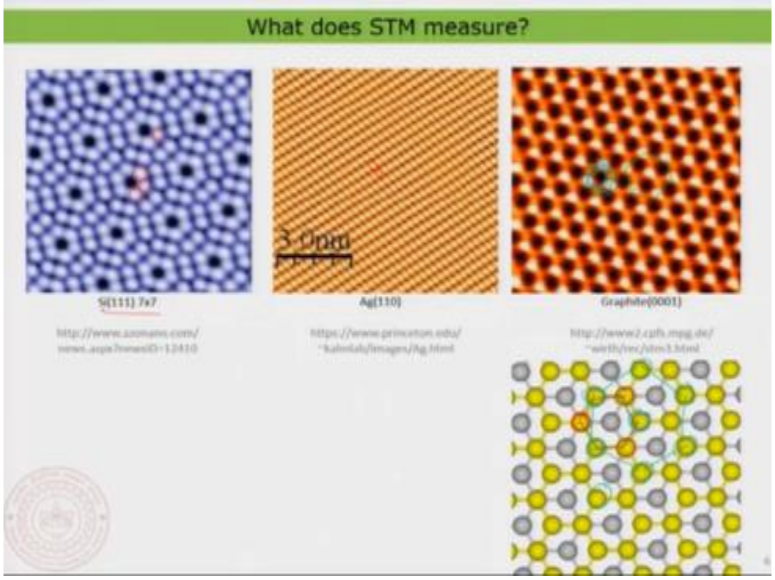
$$I \propto \int_{E_F^T}^{E_F^T+eU} U\,\rho_T(E,T)\,\rho_s(E,T)\,e^{-2S\mathcal{K}}\,dE$$

$$\mathcal{K} = \sqrt{\frac{2m}{\hbar^2}\left(\Phi - \frac{eU}{2} - E\right)}$$

$$Barrier = \frac{\phi_S + \phi_T - eU}{2} = \Phi - \frac{eU}{2}$$

Well now what I can do is I can basically just apply the negative bias onto the surface. So, when you apply the negative bias onto the surface what happens is now the fermi level of the surface goes up with respect to the tip, the tip is always on ground. So, now you see that the direction of the current or the direction of the electron is changed. Now the electrons are actually moving from surface or the sample to the tip. So, this many electrons from the sample is now getting tunnel into the empty states of the tip. So, everything just the same only the direction of the electrons change. Therefore, the direction of the current is also changed. Now you can keep increasing so that is exactly what you see here I have increased the current. So, now I can basically just increase the bias on the sample side so that we are basically just making it going higher and higher. Then you clearly see that I am going to get more and more tunnelling current as I increase the bias on the sample side. Now well that is exactly what I have plotted here so that would mean that the current is basically increasing. Then I can apply much larger voltage then you see clearly, I have increased the current to a larger extent. So, this is quite nice and now again here you see that the barrier is basically just varying while you are actually just varying the voltage. And then you can basically see that as the voltage increases to a very large extent you would clearly see that the current increases. Overall, what is interesting, now here is actually even when you take the two metallic cone, two metal and try to do some kind of a tunnelling junction, try to create a tunnelling junction and then measure the voltage versus current characteristics you would get you end up in this kind of an interesting shape for the tunnelling current instead of the ohmic like nature which is actually linear. But let us also have a look at the tunnelling current. So, it is exactly the same as the one before but the only difference is actually the limits are changing. Because you are actually just now looking with respect to the surface side or sample side. Well, I think it is it is quite straightforward you have to just change the limit but you can clearly measure this in a more systematic way. Now also here you see there is a small change in the sign here occurring and that sign is basically just taking care also of the shape of the current as a function of the voltage. So, then now we can also make a comparison so, now you clearly see that the ohmic contact type is basically just going as a linear function with respect to the voltage as you see here and the tunnelling one is actually having an interesting shape like this. So, that is the interesting part about it. Now this is what a generally it is looking like when you take two metal having similar work function and also assuming that somewhat constant density of state near the fermi level. But now we can actually ask ourselves a few questions immediately to kind of understand the scenario a little bit more carefully. So, imagine that now you are actually just doing another variable which is actually the distance. Imagine that now you actually just maintain a larger distance between the tip and the sample. So, you have actually just increased what would happen to the tunnelling current you could just think about it immediately. The interesting thing that is going to happen is that the overall nature of the tunnelling current as a function of voltage will remain the same. But as soon as you increase the distance between the tip and the sample you would assume that there will be a much stronger contribution from the exponential function which is the tunnelling probability. The tunnelling probability is going to be much much much lower in that case because you have actually just increased the barrier distance. So, obviously what is going to happen is that the tunnelling current is going to be looking very small and then it is going to increase like this. So, that is the interesting part or you can basically just think about having a different material having a very higher work function for example. Then also you are going to get into the same scenario, the tunnelling current would basically just lower or work with a material having a very low work function then your tunnelling current is going to increase. So, if you maintain a constant density of state for the sample and the tip which you cannot unfortunately choose by yourself. You have to choose a certain material to have these circumstances. But if you happen to have a tunnelling spectroscopy or tunnelling current versus voltage recorded then you would find that most of the time you are going to get just this kind of a shape for the tunnelling current as a function of voltage which is quite different from the ohmic one. So, that is quite important and this kind of understanding is very important because you will find that in the next upcoming slides that we will be looking or using this tunnelling current versus voltage which I am just going to call it now onwards as tunnelling spectroscopy to understand the electronic structure of the surface itself. So, if you want to understand clearly what is the electronic structure near the fermi level? Is it a constant or there is some kind of density variation? This is going to be clearly understood using this kind of tunnelling spectroscopy. So, therefore the understanding of the tunnelling current as a function of voltage is quite quite important.

(Refer Slide Time: 24:31)



What does STM measure?

Si(111) 7x7

http://www.azonano.com/news.aspx?newsID=12410

Ag(110)

https://www.princeton.edu/~kahnlab/images/Ag.html

Graphite(0001)

http://www2.cpfs.mpg.de/~wirth/rec/stm3.html

Now let us have a look a few images just for our kind of understanding. We have already just seen that in tunnelling microscopy we would be mostly looking at something called as the electron density because you are measuring the tunnelling current. So, that if you are measuring the tunnelling current that is directly proportional to the electron density of the surface or is the electron density of the tip. That is what you have seen in the previous slide. So, if you have looked at a surface then everything bright on the surface this is actually the silicon 111, 7 by 7 reconstruction; you have already seen this image in a previous slide. Now you can understand clearly why the atoms are looking brighter, the atoms are looking brighter meaning that there is a strong electron density around that particular atom. So, that is obviously something that you would also expect and atoms are of course something that you can identify separately. Then you see like each of these bright protrusions are actually representing that I have a very high density of state or I have a very high electron density localized at that point. Well, you would not be surprised seeing that because wherever you have the atom and that is the point where you have the highest electron density. You will see some surprising result in a little later but in general that is what you would expect and that is the reason why atoms appear brighter in STM. So, you can also see here this is a silver dimer that you find on the silver 110 surface you also see that everything looks bright which is actually indicating the presence of an atom. But something interesting that I want to talk to you about the graphite 0001 surface where you know that the graphite the top layer you have basically six atoms as you see here. But interesting thing is that in the STM image you do not basically see all the atoms to be equally bright. This is quite interesting because you can see that there are two different type of atoms in this. So, this the one which I am marking with the red is basically some kind of an atom which is having a neighbour just in the second layer. But the atoms that I have actually just marked here in blue are those atoms which are actually having no neighbour at the second layer. Therefore, in STM what you find is that always there is some kind of a triangle and this triangle, the dots here are nothing but the atoms that are having in the lower layer. The one which is actually depicted as red here is the one that you actually just see in between. So, you can see here there are atoms that are in between so, we could use probably a different colour like green. So, you can see here there are atoms that are in between. So, all together if you look you can basically just mark a nice hexagon as you would do here in the in the model. So, that basically means not all atoms are basically visible equally in the STM contrast and that reason is very simple. The atoms that are having no neighbour in the second layer is much more it is having a stronger electron density compared to the other. Because the other atom which is having a neighbour in the second layer is having some kind of an interaction with the second layer and therefore there is a depletion of the electron density. So, therefore, you would always find that these atoms to be brighter in the STM images. So, these are the atoms that are brighter in the STM image so like this. And that is the reason why you also see this big hexagon that is giving rise to the big hexagonal contrast that is in STM which is looking like this. So, therefore it is quite important that the electron density of the surface or the image of the surface itself is not just a simple sketch of the atomic lattice but this is basically the sketch of the electron density that is distributed around the surface atoms. This is quite interesting. So, we look into more details in the in the upcoming lectures on this. This is an important topic to be interested and that we are going to see it in the next lectures. Thank you very much for your attention.