Chemistry and Physics of Surfaces and Interfaces

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Lecture - 23
Scanning Tunnelling Spectroscopy-2

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Lecture 23

- Scanning tunneling microscopy
- Application of tunneling spectroscopy

Hello everyone, welcome back to lecture number 23. In this we will continue the scanning tunnelling microscopy and particularly we will start to look at the applications of tunnelling spectroscopy.

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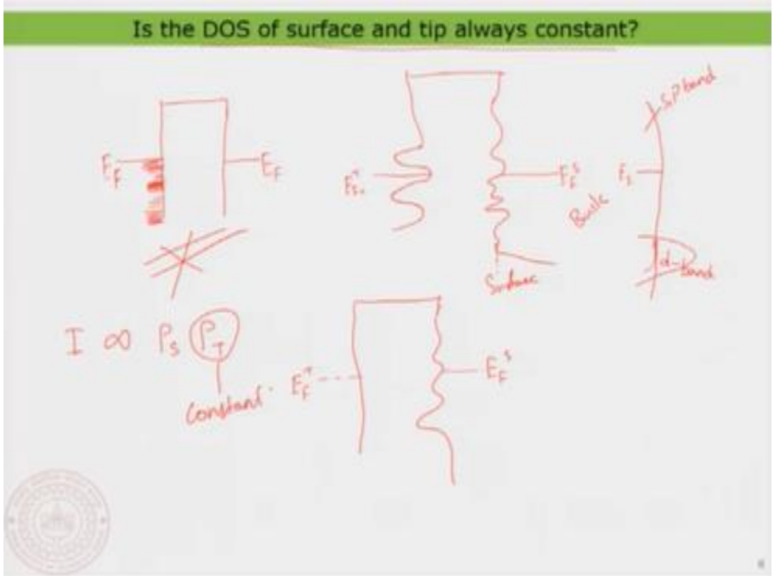

Is the DOS of surface and tip always constant?

So, but before that we will continue a little bit on the discussion that we had in the previous class about the question that we asked whether all the time the density of the state of the tip and sample being constant. So, that is something I have already told you that the situation that we have always looked out is some kind of an ideal situation. So, it is not necessary that all the time that I have this kind of constant density of state at the surface of my tip and the sample. So, well then, the question is actually how does the density of state looks like. Well, why should be the density of state within the band energy diagram be constant throughout the energy space? It is not necessary. You can have a variation. For example, I can have a very very large number of density here then I can have like only a few states in this region. And I can then have again a very very large density here and then I can have for example again, small density here, large density here and so on. So, this is actually something possible. But in material generally you would not be still able to see discrete levels, this is quite clear. But just this is again some kind of an exaggerated image. So, please keep them in mind that this is not scaled. But what I want to basically now show that if you would be like plotting something like the density as a function of energy. Then you would find immediately that there is actually a variation. So, there are some area where you have a high density, a low density, a high density, low density, high density like this you can have a variation. So, then if I would just complete a kind of function that would look like this for the surface where somewhere you can call that I have somewhere here the Fermi level of my material. So, this is just the tip so this is something like that I can have or when I take actually my sample so I can also have some kind of a varying density of state that could look somewhat like this. So, again somewhere here is the Fermi level of my sample so, there is something like that. And somewhere up here, I have my barrier. So, now you see the picture is not anymore looking like as you have seen in the previous case. So, let us also mark that this is actually the bulk part of the material and this is actually indicating something like the surface. And you already see that it is not looking very nice as you would actually expect or you generally have seen in the previous diagram like this. So, this is not very correct, so this is kind of an idealized picture. So, if there is a variation in the density of state for the material near the surface then you can actually have kind of variation in the density of state of the material. And then everything is going to look basically like this. So, that is all right but that that is something we are going to basically determine because we want to clearly understand the electronic structure of the material using the tunnelling spectrum. Well, of course you see that in the previous expression that we have written that current is definitely proportional to the density of state of the surface or the sample and the density of state of the tip. Well, this is not very good because if I would take basically the product of these two varying density of state then I am going to get basically a very very complex picture. So, therefore it is quite important that you choose a material which is typically having a density that is kind of constant. The question is there a material that is existing like that. Well, if you would take for example materials like noble metal like gold, silver, copper, platinum is not correct, gold, silver, copper. So, these kind of material normally have an interesting density of state near the Fermi level. So, we can try to depict that they are typically looking like this. So, you have basically a broad s band near the surface. So, this is kind of a broad s band and somewhere here is my Fermi level. This is the E Fermi and deep inside or lower in energy so you would find basically the so called d state. So, these are actually the d band and here is basically the s and p band. So, why I am calling it as a s and p band it is actually because the density itself or the electronic levels itself is originating basically from the s and p type of atomic orbitals from where the material itself is formed. And the d states are basically looking at these states are mostly at the lower part of the energy. So, now you see near the Fermi energy, you typically see that the density of state is kind of constant, this is good. So, that means if I would be basically using gold as my tip or copper as my tip then you can basically say that well I can also have something like a material which is having a constant density of state. In that case I can kind of get a tip which is actually somewhat looking like this, not again I am not drawing it straight because there is small variation. And then I can basically just look at my sample that is actually having some kind of a varying density of state. Somewhere here is actually the Fermi level of my surface and somewhere here is actually the Fermi level of my tip, then you can see this is actually my new barrier and there the density of state of the tip itself that means this part is actually a constant. So, that is a constant and then I can basically use this kind of thing to understand now the density of state of the sample itself. Because now anything that you will be measuring will actually be strongly influenced by the density of state of the surface or the sample itself because that is kind of you are going to take a multiple of basically the density of state of the sample and the tip and the tip is basically acting as a constant. Of course, it contributes to the current but not to the variation in the current. So, that is something you are going to see in the next slide we will do it again systematically. But just wanted to have a quick summary here that do not all the time assume that you have a constant density that you are working with. You have to choose the right material. So, that means tip you can normally construct or prepare using gold or copper or silver then you can usually come up with this. But people also use other trick to do that I will just talk about that in the next slide. And then you can have a constant density for the tip and then you can clearly understand the variation of the density of state of the sample because one is actually constant. Now what I want to do is actually to also introduce to you something called a surface state. That is something which is also ubiquitous on surface that is something which we cannot avoid. So, that is the reason why we are going to talk about that. Here again I am going to now show you how exactly the tunnelling spectroscopy is measured and how you use some of the variation in the density of state and how do you basically detect that clearly in this spectroscopy. So, that is what I am going to do. So, here again now assume that you are using kind of a tip that is having a constant density of state near the Fermi energy. So, that something which is now clear to you. And also assume that the surface is again having a constant density of state it could be basically because I am using a gold as a surface for example. If that is the case then I can also assume that the typical density of state near the Fermi level of the sample is also going to be a constant. But there is something interesting that you have to consider called the surface state that is unavoidable. Why is it unavoidable? Because we are actually just looking at the surface. What is a surface state in fact? When you look at this depiction here.

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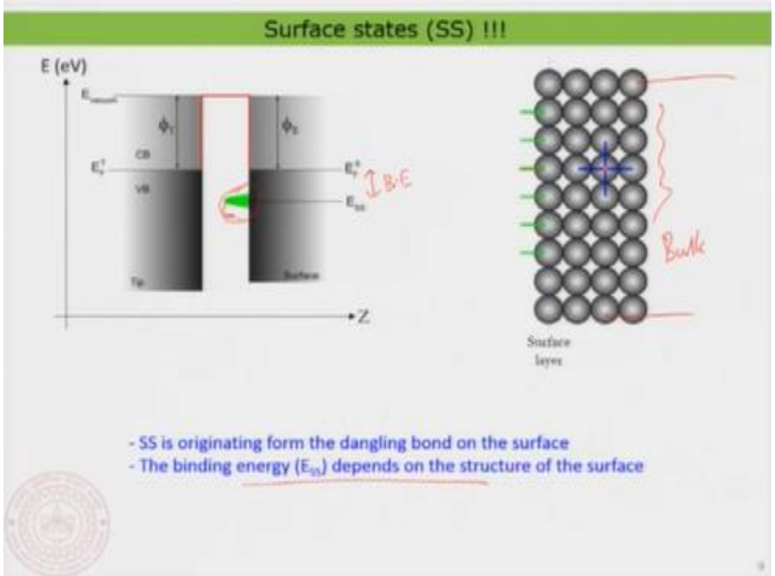

Surface states (SS) !!!

- SS is originating form the dangling bond on the surface
- The binding energy (E_{SS}) depends on the structure of the surface

So, this is again bulk. The material continues basically in this way and here you are actually looking at the surface layer. And now you clearly see that the number of coordination of a bulk atom in this simple depiction, it is of course a single layer of the material, I am not looking at the entire bulk material. But you see here in the bulk, the coordination of the material is four in this case and here you can see that there are actually something like a dangling bond which is present or so-called unsaturated coordination for each of the surface atom. Now the point is if you would basically just make a coordination of an element and then try to build up a solid, all the atoms need to be basically connected to its neighbour. What if it is not connected to its neighbour? Then of course you are going to actually just have some kind of excess electron which is something you can call it as a surface state. Some additional electron density would actually just appear near the surface because you have a kind of a non coordinated site on the surface. And those kind of things are actually known as surface state and surface state could basically be appear like this in the density of state. If you have a material, having a constant density near the surface then typically you would find that the surface state is the kind of extra density that is present on the surface. So, that is what I have depicted here with this green Gaussian function. That is depicting that somewhere close to the Fermi level you have actually an additional increase in the density of state and that is actually coming from the surface state. Now the energy difference between the Fermi level and the surface state that means this part here is something known as the binding energy of that surface state. This is basically the binding energy of the surface state. And what would be characteristic? You would find that I will show you a couple of examples that you would find that depending on the structure of the surface whether it is a 111 surface 100 surface or 110 surface or more complex surface or depending on the material that you use for example silver, copper, platinum; whatever material you choose the surface state is going to basically just move up and down and that is actually the called as the binding energy. And depending on the material, the binding energy of the surface state is going to be varying. So, that is something you should also keep it in mind. Now this is quite important so that is exactly what I said the structure is quite decisive in the binding energy of the material, binding energy of the surface state and this is something you cannot avoid in the when you work with a surface. So, that is something you have to keep it in mind.

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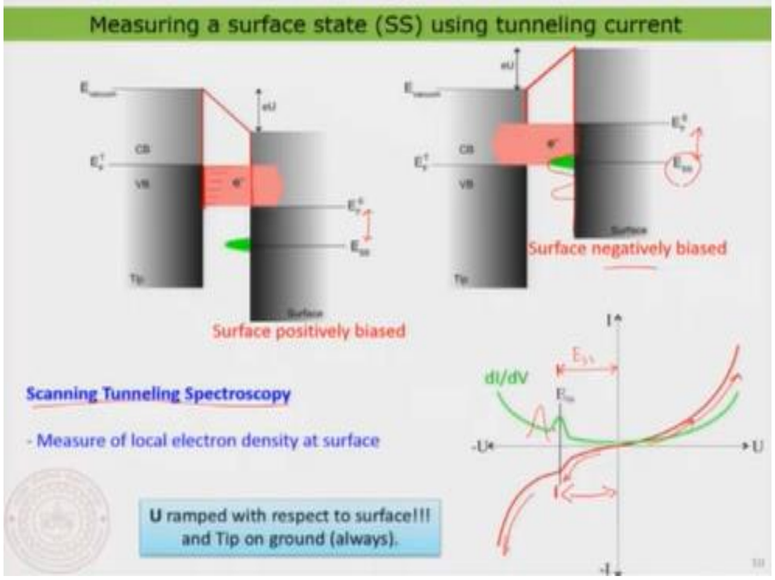

Measuring a surface state (SS) using tunneling current

Scanning Tunneling Spectroscopy

- Measure of local electron density at surface

U ramped with respect to surface!!!
and Tip on ground (always).

Now using this surface state what I am going to do? I am going to do basically a tunnelling spectroscopy. Now let us take this particular case where I have the tip and then I have the surface or the sample and having a particular surface state and the surface state has a given binding energy. So, that is actually this magnitude here as we have seen. Now what I do is measuring a current voltage characteristic. I have already told you the current voltage characteristics is nothing but the spectroscopy eventually. So, now since the density of state is constant for the unfilled bands as you have already seen so here the density is basically constant for the unfilled bands of the surface and the density of state of the tip is basically constant near the Fermi level. When you apply a positive bias onto the surface what happens is that the electrons as we have seen in the previous slide would simply go like in this increasing fashion as you have seen in the previous case. Because you can see that both the density that is actually just coming inside the window where you apply the voltage is just constant and therefore, as we have seen in the previous case you simply see that the current increases very strongly as the voltage increases. So, nothing interesting at that side but now something quite interesting would happen when you actually just reverse the bias that means if you reverse the bias to negative bias. So, that means now the sample is actually having a negative bias. So, that means a Fermi level of the surface or the sample is basically higher. Now the electrons are actually tunnelling in this direction. Now you see something quite interesting that the density of state of the surface is kind of constant up to this. But suddenly somewhere around the energy corresponding to E_{ss}, there is a strong increase in the density of state of the surface. Therefore, what you would expect is that you would also expect a kind of quick increase in the current when you actually just apply the negative bias. Then afterwards again the density is constant. So, you can see that the current just increases like on the other side. But something very spectacular happen around this particular point and that inflation or the change in then current is actually happening somewhere at this particular energy. That means this difference in energy is nothing but this difference in energy and at that point you clearly see that there is a quick increase in the current that is quite interesting. Can we do something interesting with this? Yes, we can. We now take the first derivative of current as a function of voltage that is nothing but the differential conductivity or the conductivity itself. So, now if you do the first derivative, why we do that? It is actually because the step can actually be just seen as a peak function. And now you see that the step is actually just changed to a peak function and the peak position that is what I said peak position from the 0 voltage is actually corresponding to the magnitude of E_{ss} or nothing but the binding energy of the surface state. That is very interesting, that is very striking. That means using the tunnelling current as a function of voltage measurement. The current voltage measurement you are now able to determine basically the position of the surface state of the sample. This is quite striking and that is the reason why we are now going to call this technique or this method as tunnelling spectroscopy. Spectroscopy is generally a measure of energy of any material. So, you have of course seen that different kind of optical spectroscopy that you do and there what you typically measure is actually the energy. But here also what you are doing using this particular type of measurement you are also getting into the energy diagram of the material and that is why we call this as a spectroscopy. So, when you name the scanning tunnelling spectroscopy it generally means the current voltage characteristics and the current voltage characteristic performed at the tunnelling junction. Well, you keep it in mind that we have of course taken a very simple and ideal situation here; where the only variation in the density of state on the sample side is the surface state. Everything else we said is not really having any change we said everything else is a constant. That is a kind of ideal situation but you will see that later that you can create this kind of ideal situation. There are materials which are actually having this kind of characteristic and we can use those kinds of material in just understanding it. But later we can make things more complex. So, one more thing if there would be like a difference so now assume that the surface state would be somewhere here then you would find that the peak position would also shift to another energy. So, then the peak position would be fined here. So, that is what I said. So, now depending on the material on which material you do this spectroscopy so you can basically identify the different type of surface states and their energies and even the density of state the number of state because the height of the peak should also represent basically the number of states near the surface state. So, that is the interesting aspect. Now you would ask a question here at this point. Well, your tip can also have surface states is not it? Yes, it can have a surface state. That is what I have depicted again. So, taking again a material which is having a constant density. But as I have already told you that surface state is something that you cannot avoid because this is a characteristic of a surface. So, if I would take a tip then I have of course a lot of surface also for the tip. Therefore, surface state of tip is also something unavoidable. So, I have actually just again made a very simple schematic diagram here.

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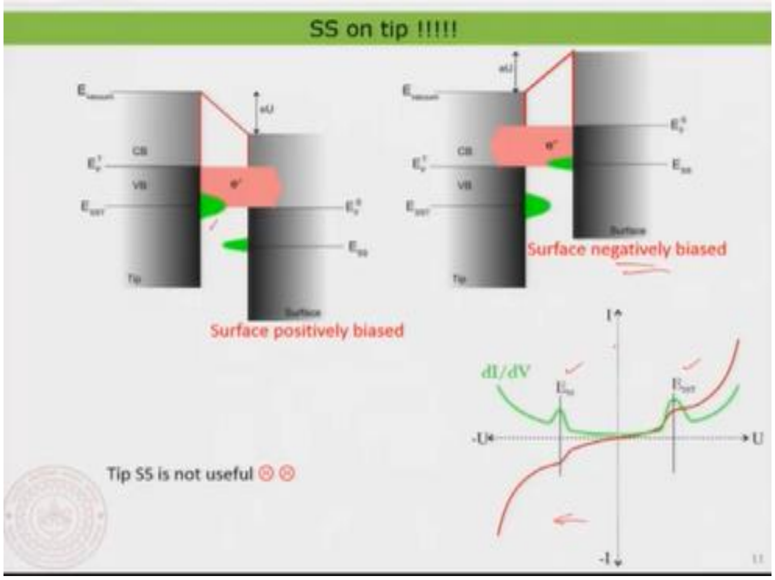

SS on tip !!!!!

Surface positively biased

Surface negatively biased

Tip SS is not useful ☹ ☹

The same as on the right side, the surface is having a surface state and now I also have a surface state for the tip. That is actually depicted on the other side with this broader green Gaussian function. So, that is basically looking like the surface state of the tip. Now you can simply imagine that depending on the bias that I apply, I am going to basically detect both the density of state due to the surface state of tip and the surface state of the sample. Now how does your I-V characteristic looks like or the tunnelling spectrum look like. You clearly see on the negative side we are going to basically see the surface state of the sample so this one and on the positive side, we are basically going to see the surface state of the tip, because you can see clearly that when the electrons basically turn on from the tip to the surface is where I have the influence of the surface state of the tip. Now that means your tunnelling spectrum is going to look like this. And then if you take actually the first derivative of this then you see that I am going to get basically two peaks. The two peaks nicely in this case I can assign because this is the tip and this is actually the surface. Of course, it is all right, because everything looks more ideal here, I can have an identity. So, there is no problem it looks like. But imagine that you are working with an unknown tip or you are working with an unknown sample then how would you basically identify which one is the surface state of the tip or which one is actually the surface state of the sample. That is quite important question. Therefore, the tip surface state is not very useful. So, therefore what we want to do is basically we want to actually kind of get rid of the surface state of the tip itself.

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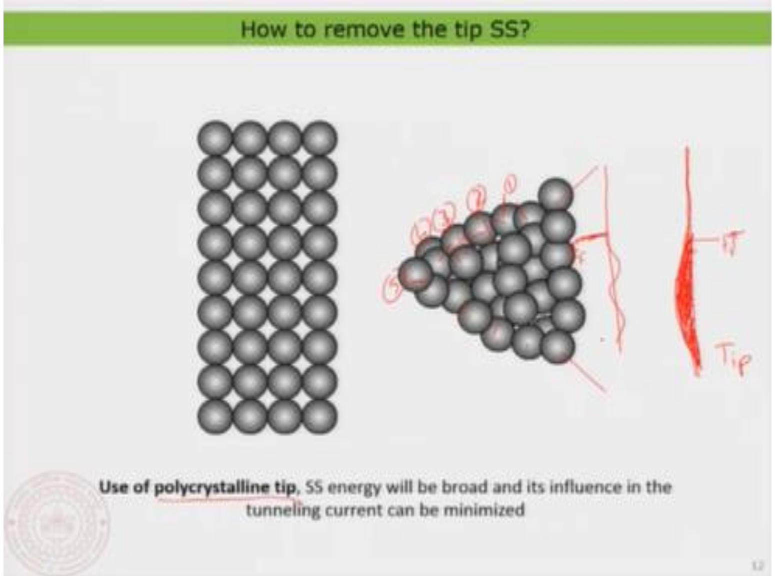

How to remove the tip SS?

Use of polycrystalline tip, SS energy will be broad and its influence in the tunneling current can be minimized

How can we do that? That is something we can have a look. This is how the surface state this is how the sample is looking and this is basically how the tip is looking and then you would equally say that well looking like that I cannot basically unavoid the surface state of the tip, it has to be present. But the reason is because all the atoms here are having kind of similar appearance. So, this is basically the bulk of the tip. So, this tip of course the tip apex atom looks slightly different coordination. But all other atoms are somewhat looking similar in terms of the coordination. So, therefore I would basically say all the surface states that is originating from all that surface atoms of the tip should be somewhat identical. But imagine a situation that I use something like a polycrystalline material. Well, now the interesting thing is that every atom is having different type of coordination. Every atom is basically looking quite different. So, that means every atom is going to have different coordination which also means the surface state. So, now let us draw a line here and having your Fermi level of the tip and then I am just saying that the surface state of let us say this particular atom like 1, 2, 3, 4. I am calling different atoms like with numbers then you would find the surface state originating from that type of the atoms like the one is actually somewhere here, then the atom which is two of course different because their neighbourhood is slightly different, then they are going to be here, the third one is maybe here, the fourth one is maybe here, the fifth one is maybe here. Then eventually what you see is that there is a broadening due to different type of surface states that are present on the tip which is good message for us. Because eventually instead of having a simple peak like function you have eventually made some kind of a broad surface state function for the tip. Therefore, what people do is that people use also polycrystalline material if you cannot identify a material which is having a surface state which is more defined like I told you like the gold for example is a case where one could think. But normally people always use a polycrystalline material be it gold or tungsten, tungsten is something that generally people use for making tip. Because tungsten is quite stable and also very strong in terms of its shape and things like that. So, therefore people prefer making a tip with a tungsten, but any metal you can use. But the only thing that you have to keep it in mind use polycrystalline tip then the problem is solved that is a good message. So, if you have now a broad tip so this is how the tip is going to look like and then I am not really worried about the density of state of the tip, because it is having a broad function. So, that is not going to be clearly affecting my measurement. And then I can now have the surface so this is basically my tip in this case, I have just changed the direction. So, if this is the Fermi level of the sample now, I can see like if I have some kind of variation in the density of state of the surface. Then now, I can basically measure that much more nicely. Because the density of state of the surface is somewhat defined. So, that is the interesting part about it.

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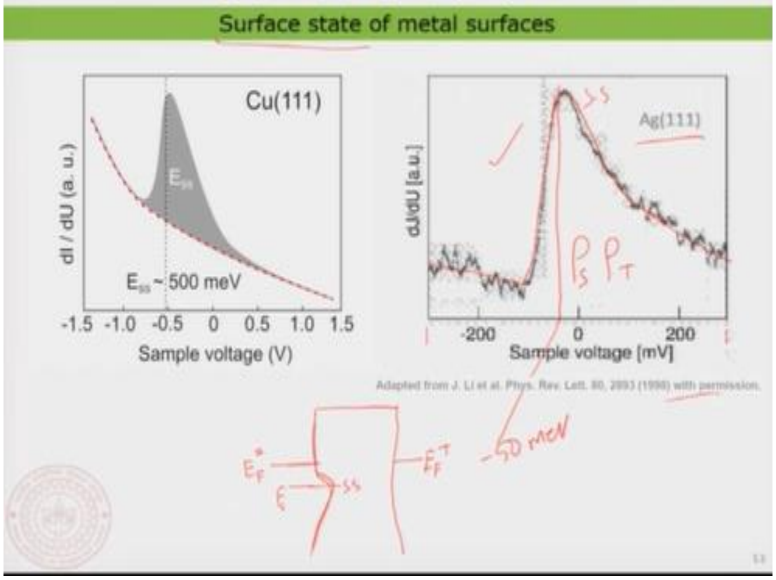

Surface state of metal surfaces

Adapted from J. Li et al. Phys. Rev. Lett. 80, 2893 (1998) with permission.

Now I want to show you the examples. So, this is true measurements. So, welcome to the true measurements. So, this is to really excite you and to show you that we can do it and we can understand things. So, of course old measurements as soon as STM was invented people were basically just got excited as I have told you. Because this measurement or this technique has given a lot of opportunity to understand things in a greater detail. So, people started measuring things and this what you are seeing on the left is actually a copper 111 surface. And you have used a tungsten polycrystalline tungsten tip to measure the density of state of the surface. Now you see the variation. So, this is from minus 1.5 volt to 1.5 volt and what you only see is that the density of state in general is just looking like this. But you have a nice step like function here and that is nothing but the surface state of the copper; and if you look at the energy here that is around somewhere around approximately 500 milli electron volt negative with respect to the Fermi level, so that is the reason. So, that is why it is going down. So, that is typically for the copper it looks like. And now for the silver is also measured here, Ag 111 surface. There again the window of voltage is a little bit smaller in this case. And you see generally it looks more or less flat. But the only thing that you see in this case again is the surface state of the silver 111 surface. So, that is quite important. And if you look at the energy of this so you can see it is somewhere around 50 milli electron volt negative, so that is the entire thing. So, that means if you look at now the density of state of your copper 111 surface or silver 111 surface and so on, it would generally look like that, you can draw the density of state like this. Somewhat looking like this, peak down and then going like this and somewhere here is the Fermi level of your surface and then here I have my tip probably with a broad density of state due to the surface state. So, this is basically my E_f tip and now I have my tunnelling barrier. So, this is exactly what is in this particular case because you can re-extract. Because you know that what you are seeing is a product of the density of state of the sample and the density of state of the tip. So, now I can somewhat re-extract everything back and then I know that somewhat also since the reason why I am using a polycrystalline tip. I also know that clearly that this is actually kind of a constant nearly constant and then everything is basically coming from the surface and that is actually just this one and this is the surface state itself. So, this is the energy of the surface state and that is something you can clearly measure. So, I only have shown you two particular examples but you can clearly do this kind of experiments on any surface and then you can measure the density of state. And typically, what I want to show you and I will also show you a little later a lot of measurements that is done making adlayers on top of copper 111 or silver surface where we would be basically just assuming that the density of state of the copper is kind of flat near the Fermi level. And then we can basically use this kind of spectrum in understanding the adlayer structure itself. So, that is why in our case I am going to select actually these kinds of examples in understanding the thing. Well, of course, you are not limited as I have already told you. You can take any material combination in understanding then you are going to end up in more complex tunnelling spectroscopy or tunnelling spectrum ideally.

Thank you very much for your attention. So, we will see more examples in the next class. Thank you very much.