Chemistry and Physics of Surfaces and Interfaces

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Lecture - 24
Scanning Tunneling Spectroscopy: Applications-1

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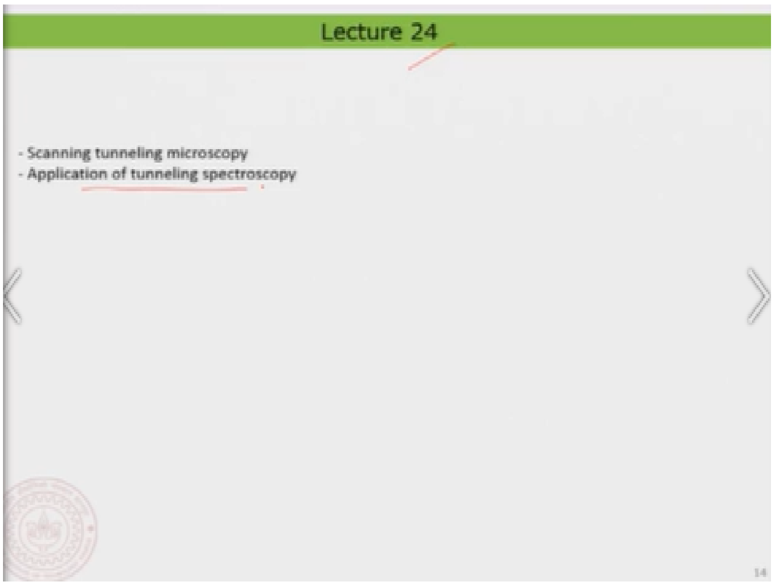

Lecture 24

- Scanning tunneling microscopy
- Application of tunneling spectroscopy

Hello everyone, welcomes back to lecture 24. In this we continue the tunnelling spectroscopy. We look at a few more important applications particularly today we will look at how to characterize the electronic structure of surface and also in how to characterize the electronic structure of more complex surfaces and things like that. And we will try to use tunnelling spectroscopy as a tool in understanding the electronic structure of the surface itself, surface and also adlayer.

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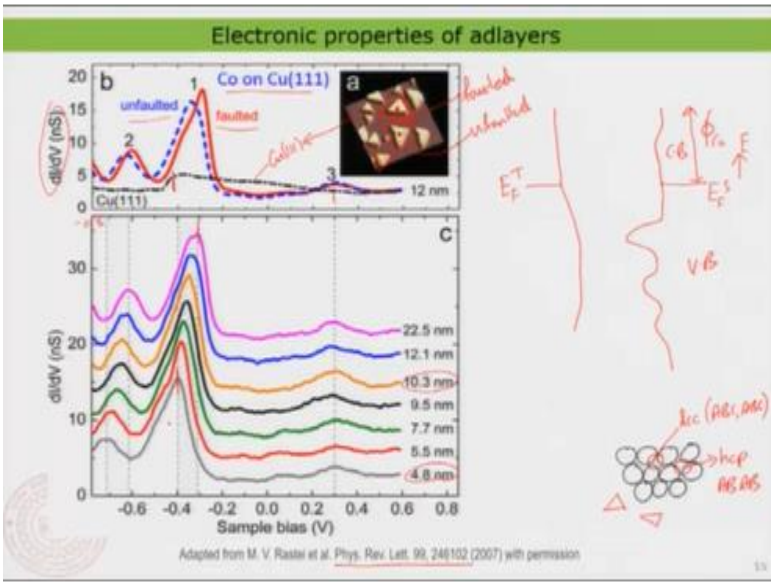

Electronic properties of adlayers

Adapted from M. V. Rastei et al. Phys. Rev. Lett. 99, 246102 (2007) with permission

Well, let us take an example yesterday or in the previous class what you have seen is that we have looked at the tunnelling spectrum of a normal copper 111 surface or a silver 111surface and you have just seen that it has a surface state only. Because you also have to keep it in mind that we are always measuring the tunnelling spectrum near the fermi level so around the fermi level. So, that means some electron volt below the fermi level and some electron volt above the fermi level. So, in that range since for copper or silver or gold typically the density of state is constant, you do not see much of features you would only see the surface states the characteristic for them. But now in in this lecture what I am going to show you is actually a cobalt island that is deposited or cobalt adlayer that is formed on copper 111 surface. So, this example we have particularly looked in the previous classes where we have actually understood this in greater detail and we also looked at the microscopic structure of these kind of adlayer on copper 111 surface if you recollect. So, I thought I will choose the same example so that you can also now look at the electronic structure of the same material. Now what you see here is actually a spectrum that is recorded in a window of about 0.8 volt to about 0.8 volt. So, it is not so large window that you are looking at, it is a small window that you are looking at. So, you can basically see the spectrum inside. Now here interesting thing is the black spectrum. Well just keep it in mind that here we are directly discussing with the dI by dV not anymore looking at the current voltage characteristic, we took already the first derivative because that is the most informative thing. So, therefore you would find most of the time on the y axis it would be either dI by dV in nano siemens. So, sometime you would find it without any unit or you would find tunnelling conductance things like that is what you are going to see on the y axis which means it is directly the first derivative. Because we have already seen that the first derivative is directly the measure of the density of state of the surface, if the tip is basically a constant. A tip is actually having a flat density of state and that problem also we have addressed because most of the time we are going to work with polycrystalline material. Now you see interesting here so the thing here is that this is actually directly measured on copper 111 surface and now you see the copper 111 surface as expected has no huge variation in their density of state, what is all you have is actually this surface state variation. The variations in the density of state due to the surface state so that is all you have from the surface. But now striking this is basically the copper, so this is basically the copper 111 surface that the image and now when I do the spectrum on these islands here. So, these bright islands are nothing but the cobalt islands on copper 111 surface. So, that is something we have already seen. So, when you now record the spectrum on these islands you see something spectacular you see something like a strong variation in the density of state, it is not anymore looking like a flat density of state it is much more much more different than what you have seen for the case of copper 111 surface. That is exactly what I told you that the density of state of different material is strongly depend on the material and also its structure and this is not going to be a constant at all. So, what is for us important is that to understand the electronic structure of the material and now you see that the density of state of the cobalt deposited on copper is looking like that. So, if I were to draw a kind of density of state of the material that we are studying so what I would be basically just doing so somewhere here I have my Fermi level of the surface and then I have here you can see like when I go to a negative voltage. That is basically representing the density of state from the filled region that actually means the conduction band and the positive bias is basically representing the density of state coming from the unfilled band of the material. So now you can see the unfilled region it is somewhat looking like this, I have a small variation around here and when I go down I have much much stronger variation in the density of state like this. So, this is how the variation looks like so it goes like this, this is how in the energy scale. So, this is basically the energy scale of the electronic levels and somewhere here you have the work function, somewhere here you have the work function of cobalt and then you can basically say this is how the density of state varies. Now obviously your tip also you can put it here so the tip may actually be just having a very broad density of state from the surface state of the tip. But that is something which we do not need to care anymore. So, this is basically the tip looking and now you can see this is the tunnelling junction itself it is not anymore like what we have been discussing in the very beginning. But no problem but if you would assume a tip which is having a kind of constant density of state then you see clearly what you are measuring is the density of state or the variation of the density of state of the material itself. So, this is basically my valence band and this is my conduction band and you clearly see that I could measure the density of state of the material in an explicit way so this is quite beautiful. But now something interesting that you also have to notice that when I basically just measure the density of state of the material of the two different type of island. So, there is one island that is looking like upward pointing triangle. And another one which is looking like a downward pointing triangle and the one they are actually called as the faulted and unfaulted type of triangle, I just tell you what it is but when you measure the spectrum on top of the different type like if I would basically measure on this island or this island then I see there is a small variation in the density of state. Well, that is something which is much important or most important in tunnelling spectroscopy because it is a local measurement and you have an atomically sharp tip you are actually able to do the spectrum on a given island. So, you image and then you select an island and then you can basically just place your tip on top of an island and then measure the spectrum. This is very very important. This is impossible with any other technique because you will also study in the upcoming lectures another technique called as ultraviolet photoelectron spectroscopy which is also a technique to understand the electronic structure of material but that is something like a measurement which you average over enormously large area. So, therefore, this spectroscopy is really single molecule or single atomic level. You are ideally just going on top of an atom because your tip is as sharp as an atom, so you place your tip on top of an atom and you basically run the I-V characteristics and then you record the spectrum. So, this is something spectacular about tunnelling spectroscopy that you can really measure one by one. No other technique would be able to do this and that is also the reason why this is actually a much celebrated tool in the modern days which is also known as a tool which is actually much suitable for nanotechnology the development of nanotechnology and that is also the reason why you see that this technique has gained a lot of interest immediately within the five years of its discovery. That story I have already told you now what for us important is that you see that depending on the type of island that you look you basically see that there is a variation in the density of state. That is something quite important because if you want to basically use these islands. For example, cobalt island can be used as a catalyst or it can be used in an electronic application but if I want to basically use the different type of cobalt islands for some purpose. But then it is quite important for me to know the electronic structure because the conduction band the valence band density of state is directly related to the reactivity for example, if you consider the chemical applications. Or how what strong is the density of state of the valence band and the conduction band is also something to do with the transport of the material, the transport of charge carriers in the material and so on. So, there are very very important aspects that you would actually consider inside when you measure the electronic properties. Now let me also take a minute in in just explaining you what is this faulted and unfaulted or why there should be a difference in fact. Now if you recollect in our one of our discussion, we have actually talked about packing of materials. So, like of course you know that the copper 111 surface is actually a hexagonal surface, where you have the atoms placed like this. So, this is basically the copper atom that is going like that and now when you add the new cobalt atom on top of it. So, I am just going to basically just take again red for the cobalt atom I can actually add the cobalt atom in this point or I can add the cobalt atom actually at this point, it is different. One is actually the so, called FCC site, and the other is basically the HCP site. That means one is actually that you have an ABC type of packing and if I would add so if I would add actually the cobalt atom in the FCC site, then I have basically an ABCABC type packing and if I would add the cobalt atom in the HCP site, then I have basically kind of ABAB type of packing. So, that means if the cobalt atom is coming to the FCC site, then that then based on and all the cobalt atom is basically placed at the FCC site in an island. Then it will be called as a faulted island and then faulted island and if the cobalt atom is actually just occupying only the HCP site, then they would be called as an unfaulted island. So, that is the difference. So, depending on how the growth happens on the surface then you would basically just end up in forming the faulted or the unfaulted islands. So, well the symmetry is same. So, this is of course due to the fact that both the HCP and FCC sides are threefold in in symmetric and that is the reason why you would basically seeing that they are both triangular in nature but their orientation will be different because both are having either an upward symmetry or a downward pointing triangle. So, the HCP for the FCC sites are pointing like this and the HCP sites are pointing basically like this and therefore the growth also would look like that. But now what is spectacular? What is more important in our case is that the faulted and the unfolded islands they have a clear difference in their electronic structure. Is in it surprising? Yes, it is surprising, what is very striking here is that the way the cobalt atom is binding to the copper atom is the origin of this differencing. In one case in the faulted case the cobalt atoms are actually binding in a slightly different way or slightly different adsorption energy or the binding energy is different therefore their interaction is different and due to the fact that the unfolded and the faulted islands have a slightly different density of state. It is looks like kind of everything is shifted left and right and that means the binding energy of this particular band that is originating from the d in fact in this case are actually having a slight difference in their density of state.

So, that is the interesting aspect about it and that is a reason also why scanning tunnelling spectroscopy is quite important because you can clearly go and do the measurements at a local level. So, this would not be other ways possible in an in a normal case. Now let me show you a few more example of the same type of spectrum recorded on islands that are having different size. Now you also see here that I have different size for the island. So, some are looking like larger triangles, some are looking smaller and so on. So, in this particular reference; so, you can see the details more in detail in this. You see that they have actually measured the tunnelling spectrum on islands having different shape and size. Well cobalt island as you see here is just nothing like a small nanoparticle of having triangular shape. Now you see that the spectrum recorded on all these different kinds of islands are looking quite different in terms of their band which is actually shifted with respect to each other. So, that also means that there is a strong dependence on the island size itself. This actually due to the fact that the smaller islands are having a little bit huge relaxation or strain within the islands compared to a large island. So, we also talked about it in the case of cobalt on copper 111 surface it is not that bad, because we have already talked about that in the case of cobalt the strain at the interface is about 1.3%, so we do not need to worry much. But still when you actually just prepare a smaller island all the atoms in the islands are actually much more relaxed or much more strained than the islands that are formed at than the larger islands. This is actually meaning that whenever you have actually a larger islands the strain within the island is much more relaxed and that is a reason why you find that in general that the electronic structure or the electronic property itself of the island is also varying as a function of the island size itself. It is quite interesting to understand and this again an opportunity that is only possible when you do this experiment with the help of scanning tunnelling spectroscopy and no other technique can actually just go down at this at this atomic at this position as you see in this case.

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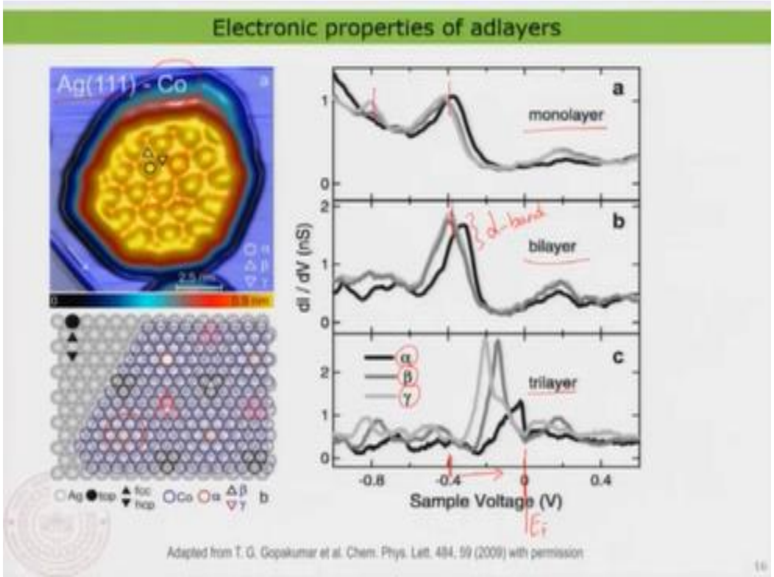
Electronic properties of adlayers

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Well, now let us look at a few more examples. So, this is again an example that we have talked about. This is again cobalt atoms or cobalt adlayer deposited on silver 111 surface. You remember that the cobalt on silver 111 surface is actually an interface which is having a very very very high strain and therefore we have also said that they do show a kind of moiré pattern on the surface. Due to the fact that they are actually having different type of adsorption for different atoms on the surfaces. So, that is actually due to the strain. Now something interesting that we have already looked at the microscopic structure is something clear to you and you also know the origin of this moiré pattern but now something interesting is that we have also performed some experiments by looking at just the monolayer of cobalt and then bilayer of cobalt and a tri layer of cobalt. What is striking is that the monolayer and bilayer and tri layer you see there is a strong variation in the density of states. So, this particular peak, so this is the same peak as you have also seen in the previous example. So, that is d band that is the one which is strongly affected due to the fact that there is some kind of a strain within the system. And in the monolayer, you see that that particular state is actually at about 400 milli electron volt. And as you increase the layer thickness you see that is basically shifted down to a much lower energy with respect to the fermi level. Because 0 is always in tunnelling spectrum representing the fermi level and now you can see basically as the layer thickness increases that particular band is being shifted to a very high energy a very low energy with respect to the fermi level. So, this is quite interesting. So that is again is understood basically due to the fact that in each layer there is a relaxation in the strain because you know that at the monolayer there is about 13% strain that you deposit the strain energy that you deposit at the interface and due to the fact that all the atoms are much more relaxed at the interface you if you recollect, we have also talked about that and the atoms are actually much more relaxed at the interface. And as you basically grow the island higher then what happen the cobalt atoms are coming to the bulk lattice. And due to that fact, you would basically see a strong shift in the density of state. And therefore, what I want to say is that this particular band, so this is actually due to the d band it is a d band originating from the d orbitals of the atoms that is forming the material. So, the d band is strongly influenced by the distance between the cobalt atoms. At the interface it is actually much slightly compressed. If you recollect this was actually slightly compressed and as you go out and then when you come to the tri layer the atoms are actually coming back to your equilibria position as in the bulk. Therefore, you see this strong shift in the density of state of the material. So, that is quite interesting and one can also now interestingly do is something like record the spectrum not only adjust arbitrarily on top of the island, you can also basically record that at different positions. You can record at this position or you can record at this position or you can record at this position. What are they? We have already seen in the microscopic structure that depending on where the cobalt atom is sometime you have the cobalt atom sitting on top of a silver atom or sometime you have the cobalt atom sitting on the HCP site or sometime it is sitting on the FCC site and that is what this Moiré pattern different protrusions or voids in the inside the Moiré pattern represent and depending on that if you would basically record the spectre at in depend at different position. You also see that there is a striking difference in the position of the d band, this is also very interesting. So, that also tells how the atoms near the top site or near the HCP or FCC site is basically relaxing with respect to each other is what you find clearly in this kind of spectrum. So, now you see how specific this spectrum is perfectly done. So, you are basically placing the tip exactly on top of this cobalt atom or you are placing the tip exactly on top of this particular cobalt atom or on this and you are recording the spectrum. So, this opportunity is not possible or never there for other systems and therefore tunnelling spectrum is quite celebrated in understanding the electronic structure of materials at an atomic scale. Good so let us look at a few more examples. So, then we have a clear understanding.

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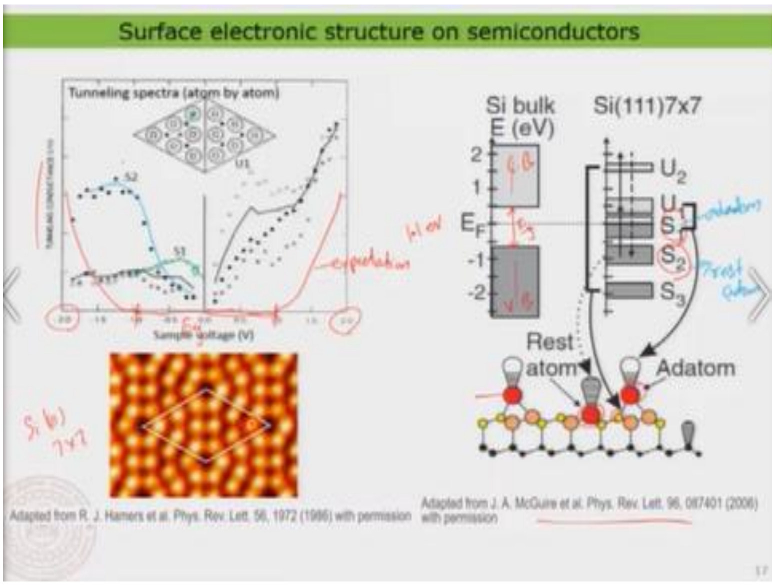

Surface electronic structure on semiconductors

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So, here I have taken actually a more complex surface that is actually our silicon 111, 7 by 7 reconstruction, so you have already seen the image. So, this is basically it and then we already know that this is basically corresponding to an adatom so that something we have seen. Now when you record the spectrum on this again, we can record on individual atoms. So, I can record basically on top of the adatom or I can record basically in between these regions. So, these are all corresponding to different kind of silicon atoms, either the adatom or the atom which is just below the adatom and so on. Now what is quite interesting is that when you record the spectrum on the silicon surface what you suddenly see is that it is looking somewhat like this more complex, as you see in the spectrum again you see the tunnelling conductance as a function of voltage. This is recorded from minus 2 to 2 volt and then you see that there is quite some variation in the density of state near the fermi energy. Well, that is quite surprising because if you would ask a question how does the silicon density of state look like and then you would say that well silicon is known to be a semiconducting material, then that semiconducting material has a characteristic band gap this is Eg that is a band gap. And typically for silicon for an intrinsic silicon semiconductor silicon it is about 1.1 electron volt. So, that is what the typical number is. Well, it also going to vary depending on the doping and things like that but I am just considering a case like that. But then what you would have expected to positive side about one electron volt or here I would have expected to see a spectrum which is just looking like this somewhere here like this. This is what I would have basically expected. This is the expectation. Why is that? It is because I know that when I take now a tip which is metallic and a semiconductor then I should not be able to see any kind of density around this region, because this region is basically corresponding to Eg, that is actually the gap. So therefore, for a semiconductor in general in a tunnelling spectrum what I would have expected is basically having a gap region and then the density increases because you can see again here. I have actually arbitrarily chosen some kind of a constant density of state for the valence band and the conduction band. But that is not what I see, I see much more variations I see depending on the atom that I record the spectrum, I see more features inside the spectrum. Then the question that you ask where are they coming from or what are they? Well, they are surface states. That is what I told you, silicon 111, 7 by 7 reconstruction, you have a lot of atoms that are on the surface and each atoms are not having their real coordination as you would expect in the bulk. That is a reason, why you are expecting depending on the type of surface atoms, because we have already seen this in the previous lecture that you have adatoms you have actually atoms that are sitting in between or you have atom which is known as a rest atom. There are many different type of atoms that are available on the surface. But of course, we see in the STM more clearly the adatom on the surface that is basically this one but everything else is also kind of not visible in the STM. But now depending on the atom that each atom would contribute a type of surface state inside and this is what is schematically represented. So, you can also look at this literature for more details. But you see that there are strong surface state, two surface states that are coming basically from the adatoms this is S1 and S2 is basically coming sorry, so, the S1 is basically coming from the adatom and the S2 is basically coming from the rest atom. That is a reason when you record the spectrum you find when you record the spectrum on top of this part; so, that is what is depicted by this square you see that there is actually a peak somewhere around this energy. But now when I record the spectrum somewhere in between that is actually the dot spectra; so the dot spectra, then you see that there is actually a variation that goes like this. That means there is a state here. So, that is basically the S1 so, S1 is originating from the adatom and the S2 is basically originating from the rest atom that is the atom that is coming in between. So, depending on this you can basically see much more detailed features within the spectrum.

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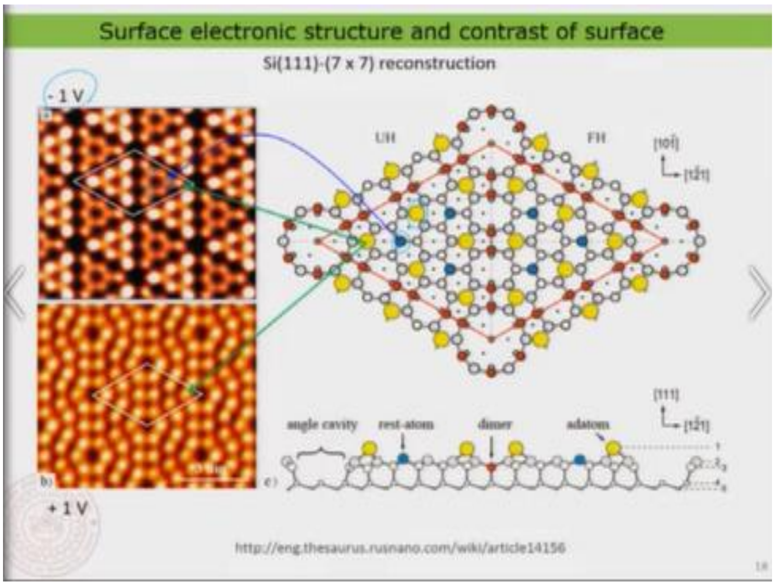

Surface electronic structure and contrast of surface

Si(111)-(7 x 7) reconstruction

http://eng.thesaurus.rusnano.com/wiki/article14156

So, you can also therefore have a look at the structure of the silicon 111, 7 by 7 reconstruction itself, where you clearly know what is basically the adatom and the rest atom. And this is basically the rest atom and this is the adatom and you are basically recording your spectrum these independent atoms and depending on the independent atoms you clearly see that there is a strong variation in the density of state near the fermi energy. And now you also see that I can basically switch the voltage between negative and positive then you also see that the contrast is basically varying because as you see in the spectrum in the previous slide that you clearly see that when you record the spectrum on the rest atoms, there is a strong density in the for the unfilled level near the fermi energy. That is the reason why now when you record the image at negative voltage you basically see that even the rest atoms are coming up bright.

Now here these are actually the this is the adatoms so that I have already indicated and the one in between is basically the rest atom. So, you can clearly now see them depending on the voltage and that is actually due to the fact as you see there was a state S2 present particularly for the rest atom and that is the reason why you see them clearly when you do the imaging at negative voltage. So, that means the voltage is also very important for the imaging. So, depending on the voltage you can also now visualize these electronic states and that is the reason why the contrast is also changing. And on the positive side everything is only contributed from the adatom, so that is the reason why mostly you see only the adatoms in the positive contrast but in the negative contrast you have the S1 and the S2 and they both are basically visible in the spectrum. Well, look I think this is a more complex example but you can try to understand or maybe even read a little bit further in this literature or also the literature that I have seen given in the previous slide. And you can understand it better or maybe we will also work out this problem a bit greater in detail in the assignments. Thank you very much for your attention and I see you in the next class with more examples.