Chemistry and Physics of Surfaces and Interfaces
Prof. Thiruvancheril G Gopakumar
Department of Chemistry
Indian Institute of Technology – Kanpur

Lecture -30
Ultra-violet Photo-electron Spectroscopy (UPS): Applications

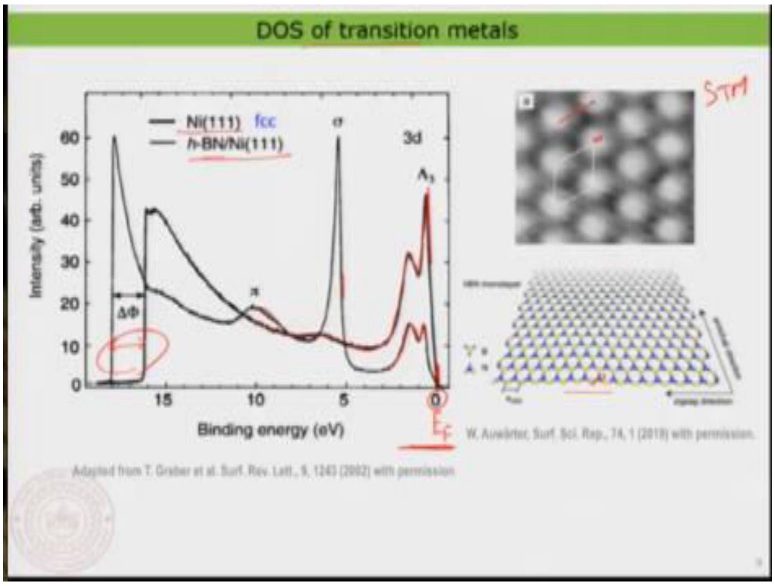
(Refer Slide Time: 00:24)

Lecture 30

- Photo-electron spectroscopy (PES)
- Applications of UPS

Hello everyone, welcome back to lecture number 30. So, in this, we will continue looking at the applications of UPS, ultra-violet photo-electron spectroscopy in the last class, we have looked at gold as an example. And then we have also just seen the capabilities and its application in a metallic surface. But today, I will like to show you a few more examples, so, that we can clearly see, the scope of this kind of spectroscopy. But, before I start one thing that I would also like to mention here is unlike in the scanning tunneling spectroscopy. We will see that clearly in an example, which is coming up that there is not a huge averaging effect in this particular case, because this spectroscopy is not local, it depends quite a lot on the excitation spot of the photon. And therefore, you basically just see an image that is coming from or the collection of the data that is coming from about several hundreds of micro meter squares. So, that basically means, it is actually kind of an averaged data than local data like we have seen in this scanning tunneling spectroscopy. So, just keep that in mind, I will show you this with the help of an example. So, you will understand that in greater detail.

(Refer Slide Time: 01:44)



DOS of transition metals

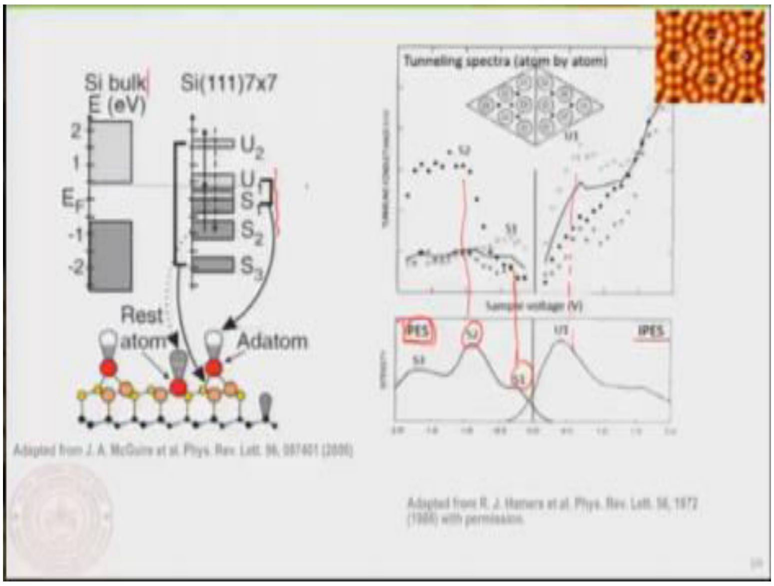
Adapted from T. Greber et al. Surf. Rev. Lett., 9, 1243 (2002) with permission

W. Auwärter, Surf. Sci. Rep., 74, 1 (2019) with permission.

So, now, let us have a look at a slightly different materials. So, like what we have looked at was a normal metal like gold in the previous class, but here I have nickel 111 surface which is known to be a quite reactive surface and also known to be quite an unstable surface; you cannot just keep it clean for a long time because, it is very reactive. So, now, when you look at this, so, here I have 2 spectra. So, like the spectra that is taken on the nickel surface itself is basically this one. So, this is actually the bold one which goes like this. So, this is basically the density of state. What is quite striking here? In this case, again binding energy and this zero would therefore, represent basically, the Fermi level and what you clearly see is that the density near the Fermi energy is not any more looking like a normal flat function as you have seen in the case of gold, Instead, it is looking much more spiky like this. So, this is quite interesting, because the nature of this density of state near the Fermi energy would decide how reactive a materialists. For example, gold is known to be a normal metal, because you see that the corrugation in the density of state is quite flat near the Fermi energy. So, any electron or any particular electron that is close to the Fermi energy is the one having the lowest binding energy. And that is the electron which is actually capable or involved in a chemical reaction when this particular surface is exposed to something. So, the sudden effect that happens on the surface is quite, a strongly dependent on what is around the Fermi energy. And that is itself the reason why the valence band is quite the decisive factor in many of the properties. The chemical reactivity of the transport property of whatsoever you name or the magnetic property whatsoever you name, it basically strongly dependent on the density of state near the Fermi energy, because, that is the electron that is readily available from the surface for any kind of chemical reaction or transport or whatsoever you mean. So, now, you clearly see that nickel is having a spiky density of state. That is actually due to its chemical nature itself, but that is an indicator, thatthis nickel is going to be much more reactive than a gold 111 surface. For example You have already seen that there is no spiky density of state near the Fermi energy. So, you will actually just see for most of the catalytic material, the density of state near the Fermi energy is much more corrugated than of flat density like in the gold 111 case or an in general gold. So, that is why understanding this kind of electronic structure of the valence band is quite, quite important for understanding the meaning property itself and that actually is what the application of UPS in general or in general, understanding the electronic structure of the valance part. Now, here in this particular example, I have actually just also chosen this example, because you can see now, you can take the nickel 111 surface. And I can deposit something on top. So, this is basically something known as a boron nitride. So, this is the schematic you can see, it is also kind right now, a currently celebrated 2 dimensional material, it is made up of boron and nitrogen and they have a similar structure like the grapheme, but here the nitrogen and boron are actually connected in a hexagonal manner. So, this is actually a 2 dimensional material consists of 2 different type of elements here. So, this general therefore, look like the graphene. So, but now, you deposit this molecule or prepare this material on top of the nickel 111 surface and then you can do the UPS, ultra-violet photo-electron spectroscopy. So, you clearly see that new features are coming up. So, of course, these 2 features near the Fermi energy is truly coming from the nickel 111 surface itself. Because, I have told you that whatever we are measuring is just from a few layers near to the surface. So, that means nickel is still visible to the ultra-violet photo-electron spectroscopy and therefore, we see something from that, but after that about 5 electron volts, you can see there are strong bands that are actually coming from the material itself. So, you can now clearly understand just by comparing the density of state of the nickel. And also the density of state of the h BN deposited on top, you can basically by comparing, you can understand clearly how the density of state basically changes as a function of or as when you deposit something on the nickel. So, you can clearly do this. So, this is basically how the density of state would look like 4 different materials, you can clearly do it for any different type of material. And they can use it for understanding their electronic structure in general. You can also, for example, compare the change in work function. That is something interesting because if you know the photon energy, so that is what I have told you in the beginning. So, if you know the photon energy, then they can clearly also calculate the work function if work function is unknown.

Now, what you see is that when you deposit the boron nitride on the nickel 111 surface, what you clearly see that there is a change in the work function. So, this change in the work function is due to the fact that the material property itself is changing. So, that is something you can also measure in ultra-violet photo-electron spectroscopy clearly. So, that is something that you can and do with this kind of spectroscopy. So, nice, this is good. So, you also have here an STM image, just to show you how the microscopic structure of the boron nitride look like. So, you can also clearly see that is the moire pattern, what you are seeing, but in inside, you can see like tiny, bright dots, which are also looking like hexagon that is clearly the one which is originating from the boron nitride mesh itself. So, these big ones are nothing but the moire pattern. So, that is good. So, you can deposit the material now, you can now do the scanning tunneling microscopy, understand their microscopic structure, you can also do basically the ultra-violet photo-electron spectroscopy and understand the electronic property of the valence band. So, this is good. So, this is nice. Now, we are actually just making things more collectively; and we are actually, understanding things more in a consolidated way. So, that is nice.

(Refer Slide Time: 09:01)



Adapted from J. A. McGuire et al. Phys. Rev. Lett. 96, 097401 (2006)

Adapted from R. J. Hamers et al. Phys. Rev. Lett. 56, 1972 (1986) with permission

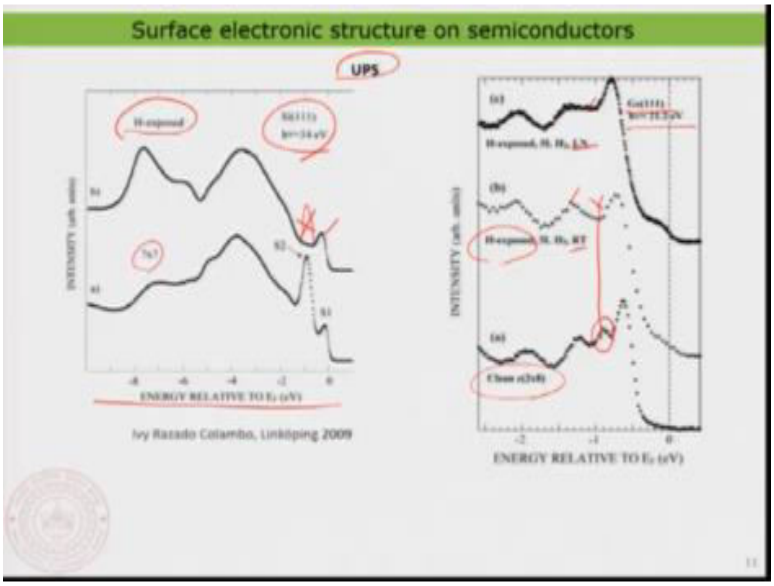
I want to show you also a comparison here and also just to use UPS and STS, in comparison to understand the electronic structure of semi-conducting surface. So, this is something that we have already talked about. So, we have here the silicon bulk expectation is this, but the interesting thing is that the silicon 111 is actually would go undergo a reconstruction and therefore, you basically expect something like these kind of surface states. So, the S 1, S 2 are some surface states that is near the valence band and U 1 U 2 are basically some surface state that is near the conduction band. So, we have already seen that in the STS so, we have seen that we can collectively or we can individually measure by just moving your tip next to an atom. And you can measure the electronic structure at an extremely localized fashion that means at an atomic scale, we can measure and we have also discussed that is quite important, because you can clearly understand the origin of this different kind of electronic structure of where they are clearly originating and so on. But, now, I also want to make a comparison of the STS that you measured to a photo-electron spectroscopy.

Well, this is actually known as inverse photo-electron spectroscopy. We will study that in a minute that is just the opposite of photo-electron spectroscopy, but just keep it in mind that when I just measured the photo-electron spectroscopy, you clearly see that I can measure the S 1 and S 2. So, this actually do correspond to each other. So, you can see although, the UPS is actually a bulk measurement.

I can still see on the surface. This is present. This kind of surface states are present and therefore, I can clearly measure that. The only difference is the broadening so, of course, I can see the signature there appearing like more like a shoulder, but they are broader than of course, what you measured basically in this scanning tunneling spectroscopy, but nonetheless, we can basically just measure that. So, similarly, the U 1 is also just kind of present here, there is slight variation in the energy, because in photo-electron spectroscopy, you do collect things from a larger area. So, therefore, this averaging effect is there. So, this is what the techniques when you compare the scanning tunneling spectroscopy and the ultra-violet photo-electron spectroscopy. One is extremely, localized. So, that means, you can go on an atom and then do the spectroscopy.

And the other one gives you an information about a larger area. So, therefore, you would find that tunneling spectroscopy is rather difficult to do. Because this is something that one need to do atom by atom to understand, but just for a quick understanding about the electronic structure of a film, one would not basically immediately apply the tunneling spectra, rather you quickly check with ultra-violet photo-electron spectroscopy because this is much more, much quicker or easily accessible than a tunneling spectroscopy, for example. So, that is where like, ultra-violet photo-electron spectroscopy is still very popular. Although, this is an older technique than tunneling spectroscopy, it is very popular. And this has been very, very routinely used by surface scientists in understanding the electronic structure of materials in generally.

(Refer Slide Time: 12:49)



Surface electronic structure on semiconductors

Ivy Razado Colambo, Linköping 2009

So, now we can look at a few more examples so, to do kind of understand the capability of ultra-violet photo-electron spectroscopy. So, this is again UPS. What I have here is actually a silicon 7 by 7 surface and now, what you are seeing is the same kind of spectrum like you have seen in the previous slide, but in a larger scale of windows, that means I am looking at deeper and deeper binding energy of electrons. So, that means, I am looking deeper into the valence band for example. Again, you have the S 1 and S 2. So, these are the surface state and then as you go deeper, you start to get actually the normal states that are corresponding to the silicon itself. But now, what I want to show you is that if I would basically just do a hydrogen exposure that means you prepare the silicon 111 surface, of course, it is 7 by 7 reconstructed. And then if you would basically deposit hydrogen on top of the silicon 111 surface, what do you find something interesting and that is also why I want to show you this example, because you can basically see what is going on the surface. You clearly see is a suddenly you see that this peak is missing now, the S 2 peak is basically missing now that is quite interesting. So, if you recollect, that S 2 is basically originating from the add atom on the surface.

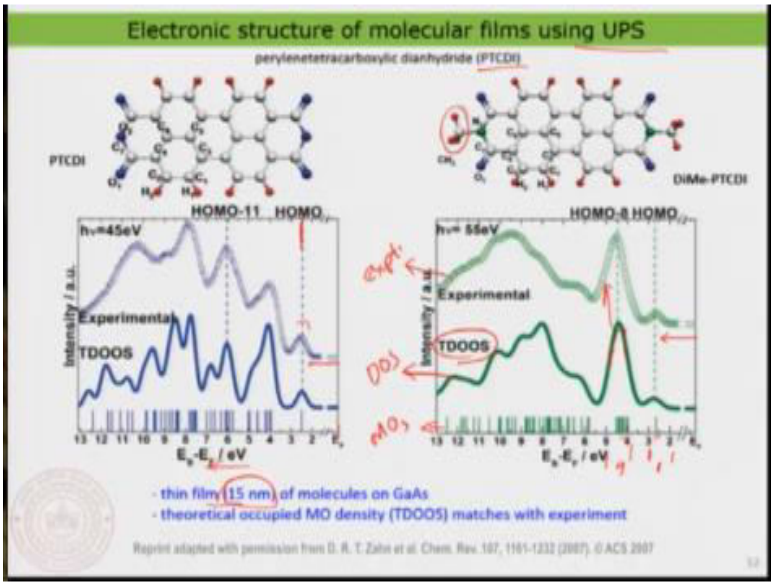
So, this is indicating that now, when you deposit the hydrogen atoms on the surface or hydrogen on the surface, then basically all the surface atoms are getting passivated or getting saturated by the hydrogen atoms. So, that means now, the surface is kind of saturated and therefore, you kill the surface state S 2, but S 1 is basically coming from a silicon atom that is sitting a little bit inside and not just on the very first layer and therefore, that is not affected.

So, they persist, but the other one is actually kind of killed just because you have the hydrogen passivation, so, this is clearly something very interesting. Now, you can use this kind of spectroscopy and clearly look at the surface, and understand well what kind of chemical change has gone on and what is actually where specifically it has happened.

Well, of course, now, our understanding is better, because we have used scanning tunneling spectroscopy and photo-electron spectroscopy to clearly differentiate where this S 2 and S 1 are coming from originally, before scanning tunneling spectroscopy, it was not known where the S 2 and S 1 are originating from, but now, we clearly know it. And once you know it, so, that means a combination of this kind of spectroscopy would give you a huge and very useful information about the interface and the surfaces itself. I have one more example here, which is again a germanium 111 surface, which is also a very popular semiconducting material and you can see here this is actually a clean 2 by 8 reconstructed germanium 111 surface and upon hydrogen passivation, you can clearly see some of the peaks are missing. So, this speak is basically missing. So, these 2 are the same spectrum. One is done at liquid nitrogen and the other one is done at room temperature. But you clearly see is that one of the particular peak is actually vanished upon hydrogen exposure, which is indicating that you have clearly a kind of surface passivation and the surface atoms are now reacted to the hydrogen that you have exposed onto the surface. So, that is the interesting see, I think well that is quite nice.

You can also notice that all the time, whenever you do the spectrum, there is a photon energy is actually given and once the photon energy is given, you can also calculate the work function of the material; everything is nice, you have a quite and detailed understanding about the surface and interface of materials.

(Refer Slide Time: 17:10)



Electronic structure of molecular films using UPS

perylenetetracarboxylic dianhydride (PTCDI)

- thin film (15 nm) of molecules on GaAs
- theoretical occupied MO density (TDOOS) matches with experiment

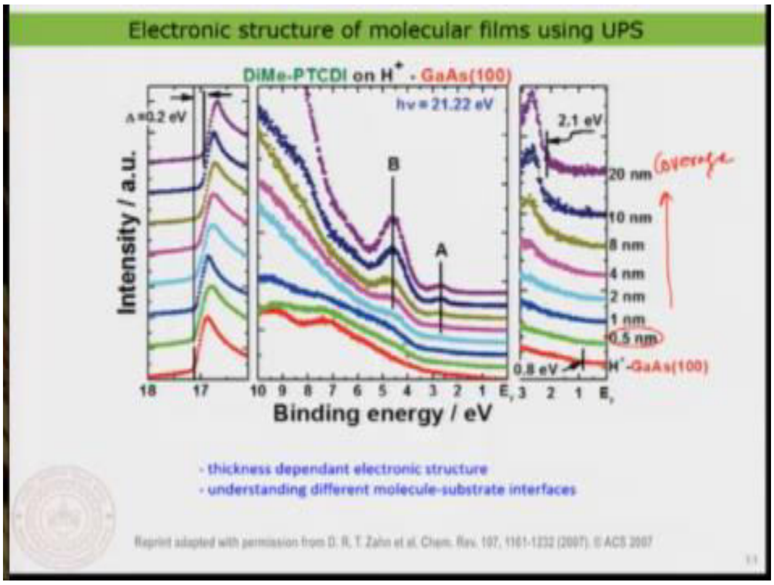
Reprint adapted with permission from D. R. T. Zahn et al. Chem. Rev. 107, 1161-1232 (2007). © ACS 2007

Now, what I want to do is I want to basically just focus on the application of UPS in molecular thin film. So, here 2 very nice examples, I have chosen because this molecules have chosen is actually because they have been also kind of celebrated molecules in the semiconductor industry based on molecules, generally known as PTCDI. And then you can see the both the molecules are the same, except having this small methyl functional group in one of the case. So, that is it.

Now, what we want to do? We want to do is basically just the ultra-violet photo-electron spectroscopy of the molecular film, but here what I am doing is actually just a big film. So, that is also something that you have to see. Now, our perspective has also changed. When you look at scanning tunneling spectroscopy or scanning tunneling microscopy, you are always trying to look things in a greater detail. You are trying to look what happens to the molecule when it adsorb; what is the electronic structure of a single molecule and then so on. Those are the kinds of questions, that you put forward when you try to do scanning tunneling spectroscopy or scanning tunneling microscopy. Because it has that possibility. But when it comes to ultra-violet photo-electron spectroscopy, you go a little bit more bigger. That means, in this case, I am actually just looking at a 15 nanometer thick film of molecule on a gallium arsenide surface. And now, I can basically measure the density of state of the molecule. So, you can see clearly that this is the binding energy. The binding energy is basically increasing and somewhere here, I have the Fermi level. But clearly in the experiment, you see that for some region about 2 electron volt, there is no density of state or there is no electrons coming out of the material, because it is clear, it is an semiconducting organic molecule, which has a clear Homo-Lumo gap. And because of that, you clearly have this kind of flat no density near the Fermi energy. And as you now go deeper in energy, you can see basically you have started to get the first peak and that is actually corresponding to the homo of the molecule.

And that is also something you remember that we have talked about or we have discussed basically in the case of scanning tunneling spectroscopy as well. Now, you can see clearly that I am doing the spectroscopy, the UPS on 2 independent molecules on gallium arsenide, a thick film and you clearly see that this molecule that the methylate molecule is having a much higher gap from the Fermi energy. So, that means the first molecular resonance is coming about 2.5 electron volts with respect to the Fermi level. And in the other case, it is actually a little bit less. So, that is the clear difference that you want to do to make between these 2 molecules. So, in general, you can basically measure the density of state of the molecule. So, what you are also seeing here, this one is actually the theoretical calculation to make some kind of a comparison. And the comparison is also kind of nicely matching with the density of state of the molecules. So, these are the discrete densities. So, you can see, these lines are actually telling the discrete homo, homo – 1 and so on. And this plot here is actually the density of state itself. So, that means, you are basically plotting how many electronic states are present in a given window of energy. So, that means you can see here, there is no state; between 3 and 2, there is one state. And between 4 and 5, you see, I have basically about 8 or 9 states, for example. So, that is how you calculate the density of state. So, you can look at that. And that is actually what is corresponding more closer to the experiment than the line that just drawing the MO diagram, for example. So, this is the MO diagram. So, just for your understanding, I am just putting the MOs and this is the calculated density of state. And this is the experiment; the experimental measurements, so this is nice. So, now, you can make the clear correlation between them.

(Refer Slide Time: 21:47)



Electronic structure of molecular films using UPS

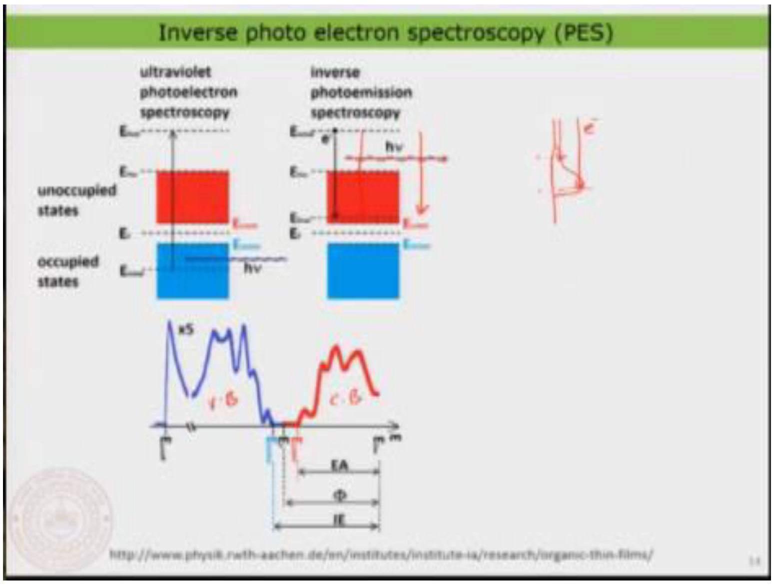
- thickness dependant electronic structure
- understanding different molecule-substrate interfaces

Reprint adapted with permission from D. R. T. Zahn et al. Chem. Rev. 107, 1161-1232 (2007). © ACS 2007

Now, what I want to do is I want to show you also a few more examples. So, it is basically just showing you like I can also just now study the electronic structure evolution as a function of thickness. The problem, so, it is again, somewhat similar molecule like what we have seen in the previous case, the same molecule, but now what I am doing is basically I am just depositing and increasing the thickness of the layer.

You can see here is 0.5 nanometer showing that a sub monolayer coverage and here the coverage is basically increasing. Coverage is basically increasing. And then as the coverage increases, you can see the electronic structure is also slightly modifying. So, that is something you also have seen in the case of tunneling spectroscopy that at the interface, there is strong influence of the surface, but as you go thicker and thicker, you basically just start to see the more molecular type structure. And but here in UPS, this is much more feasible because this is a technique which is really meant to do that kind of thing compared to tunneling microscope, because tunneling microscope is not very capable of measuring things that are like 20 nanometer thickness and so. It is actually just due to the stability of the instrument and the imaging itself. But here, you can clearly do that.

(Refer Slide Time: 23:06)

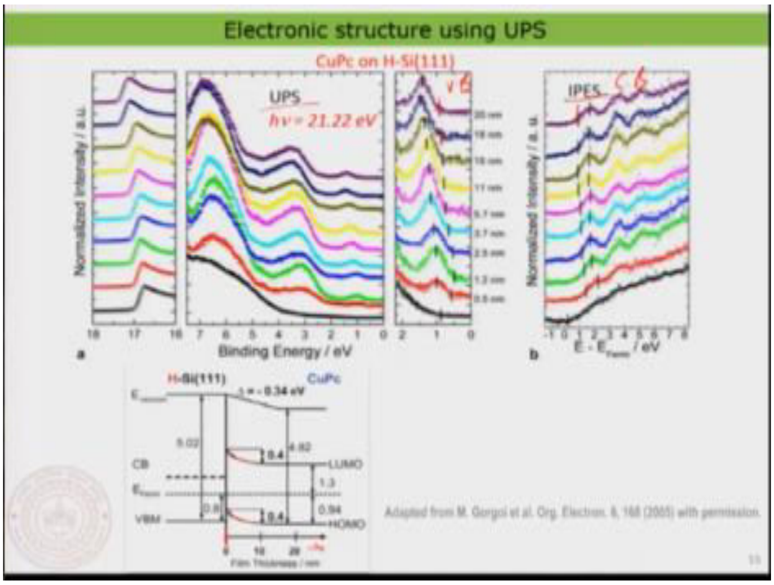


Inverse photo electron spectroscopy (PES)

http://www.physik.rwth-aachen.de/en/institutes/institute-ia/research/organic-thin-films/

Now, what I also want to show you is that you can actually just not only measure the ultra-violet photo-electron spectroscopy. By removing electron, you can also do the opposite of the photo electron spectroscopy. By injecting an electron into one of the electronic state, you can basically just get a photon out of the material, because if you are injecting an electron into a given level with a certain energy gap, then that amount of photon or the photon that is corresponding to that particular energy would be emitted by the material. So, you can now basically just inject electron into the material and then look at the photo emission from the material. And that is actually something known as inverse photoemission material. Just to have an understanding, let us see, I have here a density of state of the unfilled level, which is just looking like let us say, like this. And then you know, basically, that when I am injecting electron into this part, this particular energy, you see clearly that the density is lower. And if you are injecting electron into this particular density of particular energy, you clearly see that the density is actually higher. So, that means the amount of photon that is that will be emitted by the material will also be dependent on the density of state to which the electrons are actually injected. So, therefore, finally, what you can also see is that you can see the valence band and the conduction band if you would basically combine both the ultra-violet photo-electron spectroscopy and inverse photo-electron spectroscopy together. So, that is the strength of this technique.

(Refer Slide Time: 25:00)



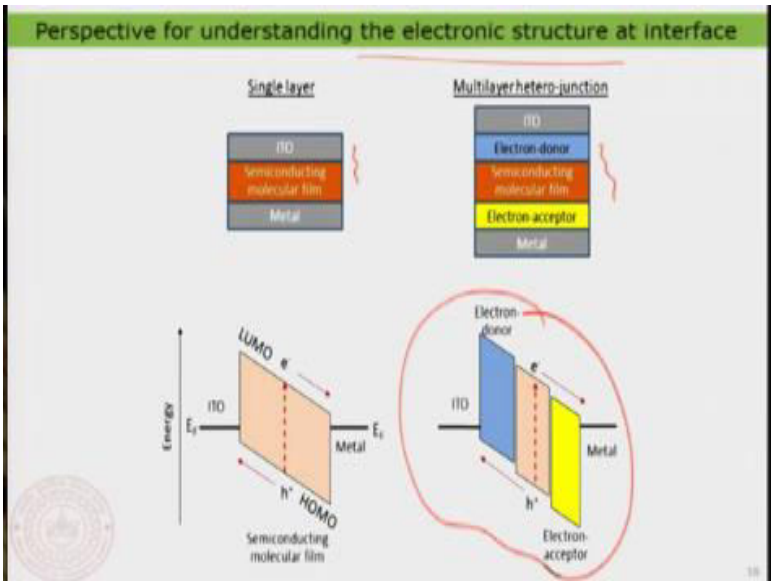
Electronic structure using UPS

Adapted from M. Gorgoi et al. Org. Electron. 6, 168 (2005) with permission.

And I have here is a molecule which is actually known as the copper Pc molecule which is actually phthalocyanine molecule, a copper phthalocyanine molecule deposited on silicon 111 surface and here is actually a UPS which is carried out as a function of thickness and also an inverse photo-electron spectroscopy carried out as a function of thickness. And then what you clearly see is that as the thickness increases, the onset of the density of state of the valence band is basically shifting away from the Fermi energy and also similarly, the onset of the conduction band. So, this is basically representing the conduction band and this is representing the valence band and the onset of the conduction band is also basically bending in this way. So, that means the Lumo and the homo of the molecule with respect to the surface density of state is actually just changing as the interface is basically going. So, this is something represented the film thickness. So, this is basically the interface and as the thickness of the film is basically increasing, you can clearly see that the molecular homo-Lumo is also changing with respect to the conduction band and valence band of the surface.

That is something I have already told you this is something that we would expect and that is something, we can also now clearly measure experimentally, if we combine now, the UPS and IPES, the inverse photo-electron spectroscopy. So, together, you see clearly that we have a great understanding about the interfaces.

(Refer Slide Time: 26:49)



Perspective for understanding the electronic structure at interface

And of course, I would basically just put it into a perspective that understanding electronic structure of interface is quite, quite important that is something I have already told you also in the previous classes. that if you want to construct junctions, for example, this is actually a layout for the solar cell with just simple a single layer active material or by layer hetero-junctions and so on. So, everywhere what you are interested is basically to understand the electronic structure of the interface and that actually decides the efficiency or the efficiency at which the electron or the hole is basically transported to the electrodes. And therefore, it is quite, quite important that we understand clearly the interfacial electronic structure and that is exactly what I have showed you in the previous example of any hetero-junction, it can be like in molecular semiconductor hetero-junction or semiconductor metal hetero-junction.

Whatsoever is your interest, you can basically clearly understand it using ultra-violet photo-electron spectroscopy because ultra-violet photo-electron spectroscopy is also giving you a little bit more global picture than scanning tunneling spectroscopy. But scanning tunneling spectroscopy is also something one can actually use for understanding things at an atomic level. Thank you very much for your attention and we will meet in the next class. Thank you.