Chemistry and Physics of Surfaces and Interfaces

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Lecture - 31
X-Ray Photo-Electron Spectroscopy (XPS)

Hello everyone, welcome back to lecture number 31. In this we will start to look at the X-ray photoelectron spectroscopy. So, in the last lecture we had looked at ultraviolet photoelectron spectroscopy, we have seen the capabilities of it, and now we will move on to X-ray photoelectron spectroscopy, and we will also look at the applications of X-ray photoelectron spectroscopy to understand in greater detail what this spectroscopy can do particularly in the surface science perspective.

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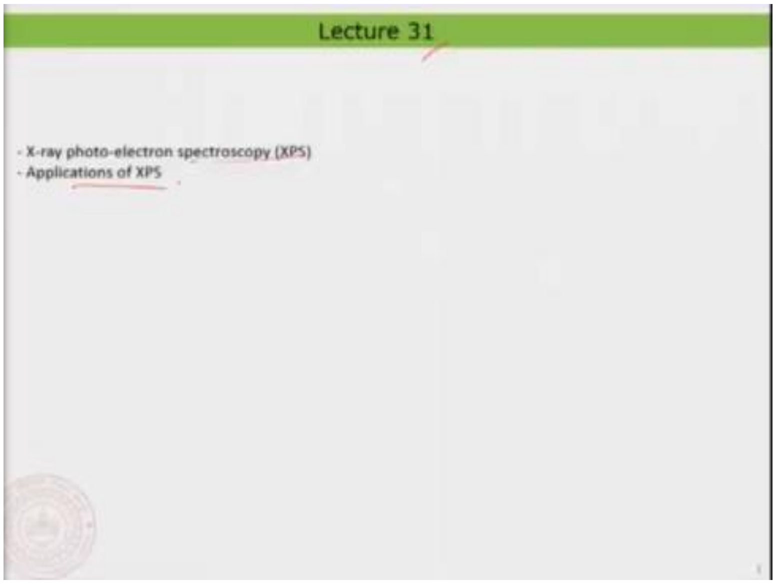

Lecture 31

- X-ray photo-electron spectroscopy (XPS)
- Applications of XPS

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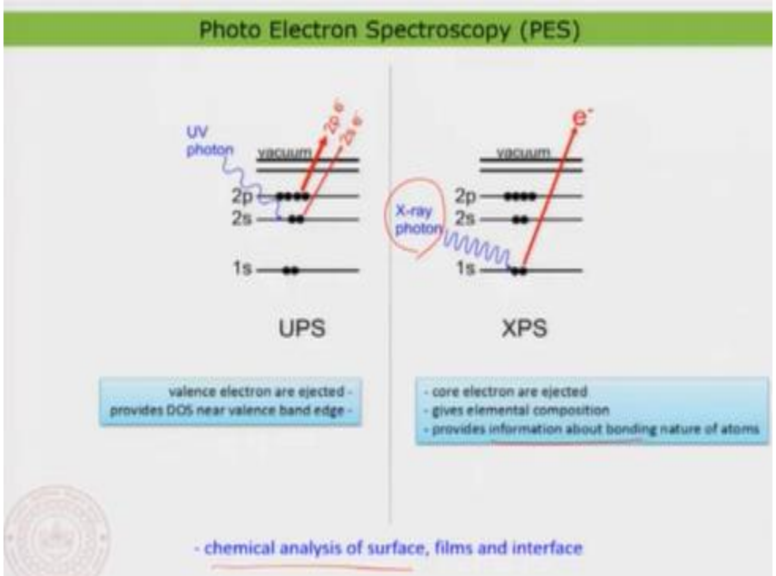

Photo Electron Spectroscopy (PES)

valence electron are ejected -
provides DOS near valence band edge -

- core electron are ejected
- gives elemental composition
- provides information about bonding nature of atoms

- chemical analysis of surface, films and interface

Now you remember that something we have already discussed in the previous class. So, what is here going to happen is that we are going to use an X-ray photon, that means a photon that is higher in energy, which is going to be basically shining onto the or impacting the material and then you are going to basically kick out a core electron. So, that is the interesting aspect. So, you will also see that typically the energy that we are talking about in the X-ray photoelectron spectroscopy is in the order of a few hundreds of electron volt. In the previous case in the ultraviolet photoelectron spectroscope what we dealt with from a few electron volt to a few tens of electron volt. But now today or in this class, we will be looking at a spectrum which is actually much deeper in binding energy. So, that is the difference. But it has some importance as I told you that this spectroscopy is actually something which we can do something like a chemical analysis of the surface films, interface material, whatsoever you are investigating, because the important thing is that the core levels are quite sensitive to the chemical environment of a given element. So, if you are looking at the core level binding energy of a given element that is quite strongly dependent on the by on the chemical environment of this molecule. So, that means we can understand formally the oxidation state of the element itself.

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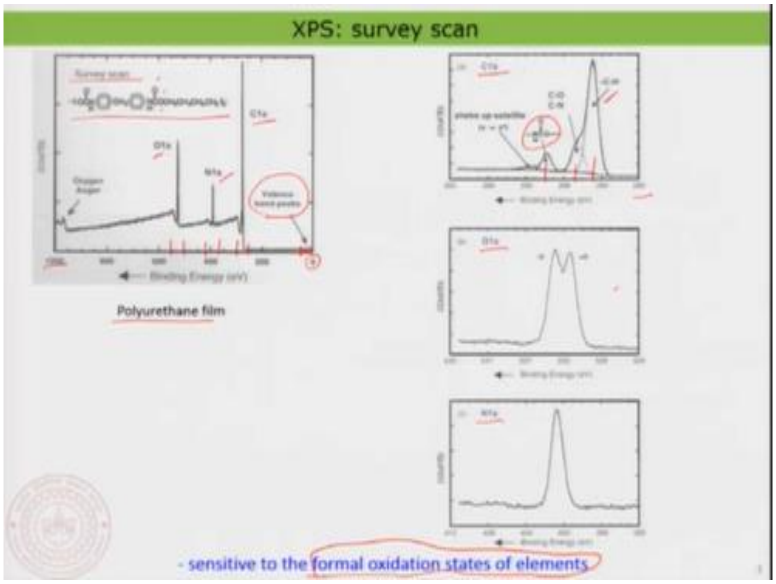

XPS: survey scan

Polyurethane film

- sensitive to the formal oxidation states of elements

So, let us do the experiment. So, like we can take an example and then try to understand it in greater detail. So, I have here a polyurethane film, so this is a thick film. So, here it is nothing to do with our surface or interface. So, I am just taking a very nice example so that is the reason why I do that. So, what you do first you take the film and then you basically scan the energy over a wide range. So, of course here you see that we are starting now from 0 as always then we are going up to about 100 electron volt. You remember in the last class when we talked about the UPS, so typically we were just looking at this range here, and that is also something they are actually showing. Well, I can see also the valence band peak but that is not something we are really interested in this case, what we are really interested is about the core levels of different elements. So, polyurethane so this is basically a single unit of the polyurethane or the chemical composition of the polyurethane and what do I have here in this molecule or in this polymer chain is nothing but carbon, nitrogen and oxygen. Well, you see this scan which is spanning over several hundreds of electron volt is typically known as a survey scan. So, that something you first do to detect what are the elements present inside, no surprise you see carbon, nitrogen and oxygen. But what is quite striking here is that the carbon peak is the most intense and the nitrogen is being intermediate and oxygen is actually somewhere, sorry, the nitrogen is the lowest and oxygen being the intermediate intensity. That clearly tells me that this is some kind of a proportional chemical analysis. So, carbon is the highest that is what I expect, nitrogen the lowest, oxygen the intermediate. So, clearly, I see that I can detect the elements that are present which are carbon, nitrogen and oxygen and then I also see some kind of a composition of the carbon, nitrogen and oxygen and that is exactly what you see by the peak intensity. Already the service scan is quite promising. But now we can look into each of them separately. So, zoom into this small window of energy and if we do that then we can basically understand each of the elements in a greater detail. So, let us do that. So, polyurethane what I am doing is basically I am zooming into the energy of the carbon and this is particularly the carbon 1s level. So, always you would find that in the XPS analysis there will be a particular assignment like this. This is indicating it is a carbon 1s level core level that you are actually looking at and each of the core level will have a characteristic energy. But within the characteristic energy range, you will also see multiple peaks depending on the type of carbon that is available in this particular case, depending on the case. So, here you clearly see that we will look in greater detail in the next slide. But here you quickly look into the system, you already see that I have basically carbon alkyl, carbon I have then I have, aromatic carbon I have. And you clearly see that I can also identify many different peaks and each of these peaks are actually corresponding to different type of carbons that are present within the polymer chain. We look at the oxygen I also expect to see like two different type of oxygen and that is also something I see which is actually at a slightly higher energy. This is the oxygen 1s level and you can also look at the N 1s level, there you see only one particular peak and that is actually corresponding to this aminic nitrogen peak, that is only one nitrogen that is actually present within the molecule and that is the one you are actually detecting. But now you see when you do this kind of an elaborated or some kind of a fine scanning into the region which you are interested in. You can basically detect not just the element; you can actually just detect the different type of carbon and even their proportion. Because always the intensity of the peak is kind of representation, it is not an absolute representation please keep that in mind but it is a kind of representation of the amount of the element that is present. So, that means I have more of that alkyl carbon and then I have something like an intermediate amount of aromatic carbon and aromatic nitrogen and that you also clearly see and then I also have some kind of carbon which is also connected to oxygen. So, that is the carbon that is actually present here. So, that is the interesting thing. So, now oxygen when you look there is only two and nitrogen one, so this is good. So, you can now identify the elements and also the different type of elements and also each element but they are different chemical environment you can analyse. So, that is the interesting thing. So, we are basically just looking at not only the element and also their different possible oxidation states within the system. Now let us try to understand this in greater detail, so that you have a clear idea how to interpret the spectra itself.

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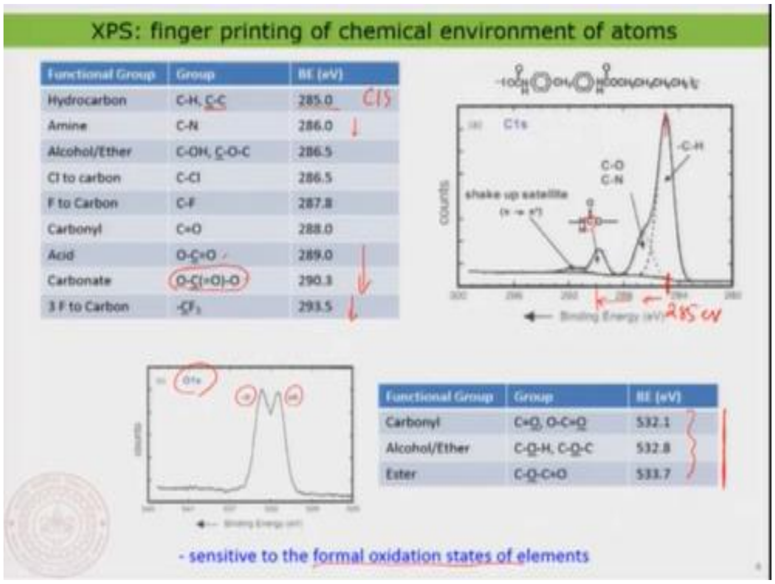

XPS: finger printing of chemical environment of atoms

Functional Group	Group	BE (eV)
Hydrocarbon	C-H, C-C	285.0
Amine	C-N	286.0
Alcohol/Ether	C-OH, C-O-C	286.5
Cl to carbon	C-Cl	286.5
F to Carbon	C-F	287.8
Carbonyl	C=O	288.0
Acid	O-C=O	289.0
Carbonate	O-C(=O)-O	290.3
3 F to Carbon	-CF$_3$	293.5

Functional Group	Group	BE (eV)
Carbonyl	C=O, O-C=O	532.1
Alcohol/Ether	C-O-H, C-O-C	532.8
Ester	C-O-C=O	533.7

- sensitive to the formal oxidation states of elements

Now this is actually a table that will give you an overview kind of chart telling you the typical energy of carbon and also like what would happen if you connect the carbon to a different element and then how it will basically be just looking at. So, this is of course a small guide but of course there are a bigger table available in the XPS database that is also available online and there you can look for more details. So, now what I have here is typically a hydrocarbon, carbon is present at around 285 electron volt. So, this is this is the carbon 1s please keep it in mind carbon 1s. So, that is about 285 electron volt. But the moment the carbon is actually connected to nitrogen, you see the binding energy has actually increased or when the carbon is connected to an oxygen or when carbon is connected to more and more oxygen, you see that the binding energy has increased tremendously compared to hydrocarbon that is what I said compared to carbon connected to carbon, you see about a 5 electron volt shift in the binding energy is observed when carbon is connected to more and more oxygen or when carbon is connected to fluorine for example or chlorine you see also the binding energy is increasing. What is going on actually or why is this happening? You clearly see the carbon is connected to another element, and that element is actually more electronegative in nature. So, carbon is connected to oxygen that is more electronegative. So, what happens is that the oxygen basically draws the electron from carbon and because of this the carbon is actually getting more oxidized. So, that means when carbon is actually connected to more oxygen then eventually what happens to carbon is that the carbon is actually more oxidized. When you have a highly oxidized species of course what happens is the core electron is getting lower screening and therefore it is harder to remove that particular core electron compared to a normal carbon. So, the moment the carbon is connected to more oxygen so what happens is a carbon is getting more oxidized. So, when it getting more oxidized that would eventually means it is harder to basically just kick that electron. It is also to do something like this. When the outer electrons are actually being pulled that means the valence electrons are being pulled by the neighbouring elements then the electrons that are present in the core will basically start to bind more closer to the nucleus. So, their binding energy basically increases. So, in general whenever an element is actually connected to a more electronegative element, then what happen their binding energy of that particular electronic state, in this case the carbon 1s state is actually shifting to a higher binding energy. So, in general the binding energy value is an indicator of whether the element that you are looking is more oxidized, higher binding energy or reduced that means lower binding energy. Now we can look back into this spectrum again of the carbon element, and there you clearly see that the hydrocarbon carbon is actually the 1s which is actually the least oxidized or that should be the most reduced in this case which should give you a binding energy the lowest. So, that is something you can see here, it is about 285 electron volt, and then when the carbon is connected to oxygen or nitrogen you clearly see that the binding energy is shifted as per this table that is also as per your expectation and this particular carbon which is actually the one which is connected to two oxygen and also one nitrogen therefore you would expect it to be shifted to a much much higher binding energy because that carbon is actually in a highly oxidized state. Now you see the reason why these particular carbons are actually just looking at different energies and also now it makes sense for you to how to analyse or how to identify that particular carbon in this case or depending on the system that you are looking at. Therefore, you can clearly clearly identify the element and also the elements chemical environment and that is why I call it that you can basically understand the oxidation state or the formal oxidation state of a given element. Now we can also just see the same for oxygen 1s state. But interesting thing here is in this case you can see that the change in the binding energy as a function of the functional groups or elements that are coming in the neighbourhood is not as strong as you would have expected it for carbon because oxygen itself is a strongly electronegative element. Therefore, you are not expecting to see a huge change but nonetheless you can see that if you have a carbonyl or an alcohol type oxygen, you can basically identify this oxygen clearly. So, that is the interesting aspect. So, you can of course it also has to do with the energy resolution of the device itself. But in the modern XPS technique we can basically just measures at a resolution of about 0.1 electron volt is not a problem. So, therefore you can see that this is actually quite identifiable. So, we can clearly measure the details at an elemental level and also, we can identify the oxidation state of each of the element.

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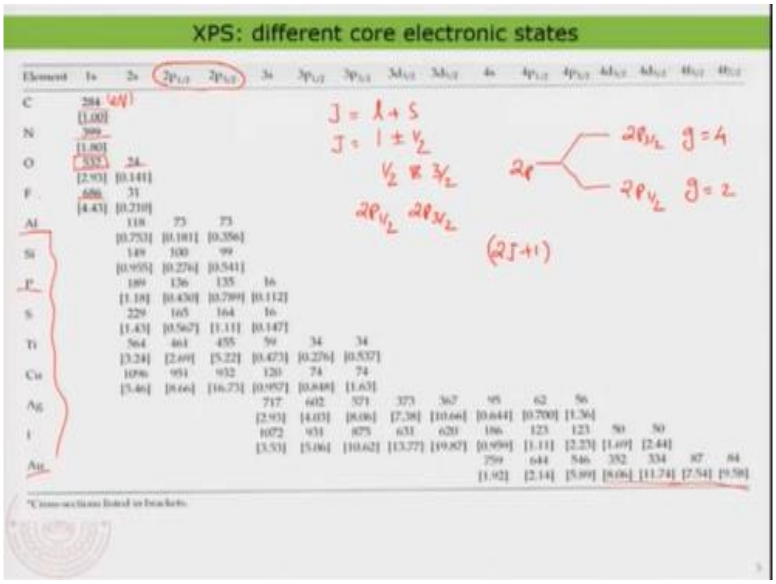

XPS: different core electronic states

Element	1s	2s	$2p_{1/2}$	$2p_{3/2}$	3s	$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$	4s	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	$4f_{5/2}$	$4f_{7/2}$
C	284 [1.00]															
N	399 [1.80]															
O	532 [2.93]	24 [0.141]														
F	686 [4.43]	31 [0.210]														
Al		118 [0.753]	73 [0.181]	73 [0.356]												
Si		149 [0.955]	100 [0.276]	99 [0.541]												
P		189 [1.18]	136 [0.430]	135 [0.789]	16 [0.112]											
S		229 [1.43]	165 [0.567]	164 [1.11]	16 [0.147]											
Ti		564 [3.24]	461 [2.69]	455 [5.22]	59 [0.473]	34 [0.276]	34 [0.537]									
Cu		1096 [5.46]	951 [8.66]	932 [16.73]	120 [0.957]	74 [0.848]	74 [1.63]									
Ag					717 [2.93]	602 [4.03]	571 [8.06]	373 [7.38]	367 [10.66]	95 [0.644]	62 [0.700]	56 [1.36]				
I					1072 [3.53]	931 [5.06]	875 [10.62]	631 [13.77]	620 [19.87]	186 [0.959]	123 [1.11]	123 [2.23]	50 [1.49]	50 [2.44]		
Au										759 [1.92]	644 [2.14]	546 [5.99]	352 [8.06]	334 [11.74]	87 [7.54]	84 [9.58]

*Cross-sections listed in brackets

(eV)

$J = l + s$

$J = 1 \pm 1/2$

$1/2$ & $3/2$

$2p_{1/2}$ $2p_{3/2}$

$(2J+1)$

$2p \to 2p_{3/2}$ $g = 4$

$2p \to 2p_{1/2}$ $g = 2$

Now let me just show you also one important table. So, this is quite useful for you, this will actually be an identifier or kind of a chart which you can use in looking for the position of energy and the type of element and its core level that you want to detect. So, if you want to detect for example a carbon 1s state you know that typically the energy that you are expecting is in the order of 284 electron volt. So, all the energies are by the way in electron volt. Now if it is nitrogen, you see its about 399 electron volt, for oxygen it is 532. But oxygen also can have basically the 1s core level and also can have the 2s score level but that comes at a much lower energy. So, typically you do not look at that what is more interesting is basically this guy here which is the 1s level of oxygen. But now you see also in the bracket here, there is some kind of an indicator given which is actually known as the cross section or the relative intensity. So, carbon is just taken here as one so that means typically the oxygen resonance or the oxygen XPS resonance of 1s level would be more intense. So, three times intense than the carbon for example. So, that is known as the cross section that is also what is given. So, for example fluorine you can look or when you take higher elements gold, I know that I can look at this range here which is basically the 4f or 4d levels, I can look at and so on. So, you can basically select which energy you want to look for and what element you want to basically identify. So, typically you would have a slight idea when you start doing your experiment what are the type of element that you are going to detect and once you have that idea then you can use this kind of a table in understanding the position of the energy. So, this is kind of a help. But you also notice that for a few elements like oxygen, fluorine or many of them you actually have not just one type of 2p, it also has something like a strange notation. So, what is basically that representing? So, for bigger elements you are also expecting basically or that means core levels that are not just s states you are also expecting something called as a spin orbit coupling that means you are basically exciting an electron, and once the electron is excited then there is actually a spin orbital coupling and due to that spin orbital coupling you will have basically new quantum number that represents. So, that is actually the spin orbit coupling quantum number is basically known as J which is actually l + s where l represent basically the orbital angular momentum and s represent basically the spin angular momentum, and for p state you will have basically like l is equal to 1 and I also have basically plus or minus half for the spin of electron that basically means I can have two J values; the j values are half and 3/2. So, that is the reason why you see basically the 2p states are represented either 1/2 or 2p 3/2. So, these are basically the two spin orbital states and this would be basically always be observed in the elemental analysis or when you do the XPS spectrum of higher elements. So, for example if I would do for aluminium or if you do it for phosphorus whatsoever you can see basically can find it in this table you would start to find this. And now there is also something interesting that you have to notice that means the 2p state is basically now split into, so this is basically the 2p and due to the spin orbit coupling so it is basically split into 2p 1/2 and 2p 3/2. Now you can also calculate basically the degeneracy of this state and the degeneracy can be calculated using 2J + 1. So, you can plug in the J values here and then you would find that the degeneracy is actually equal to 2 for this and the degeneracy for this is actually 4. This would means that always the p 3/2 level will be much more intense compared to the p 1/2 level. So, in this particular case it will be a ratio of 1 is to 1 between the half p 1/2 and p 3/2. So, this is basically representing due to the degeneracy of the different levels. So, please also keep that in mind. So, I will show you some spectra where you can clearly see this kind of spin orbital coupling and also the different peaks that are originating from the spin orbit coupling; and we can clearly use this kind of understanding in measuring the elements inside. So, we need to keep this in mind while we look at the elements, particularly the elements like these ones. So, for carbon and nitrogen it does not matter because we are looking at the 1s core level.

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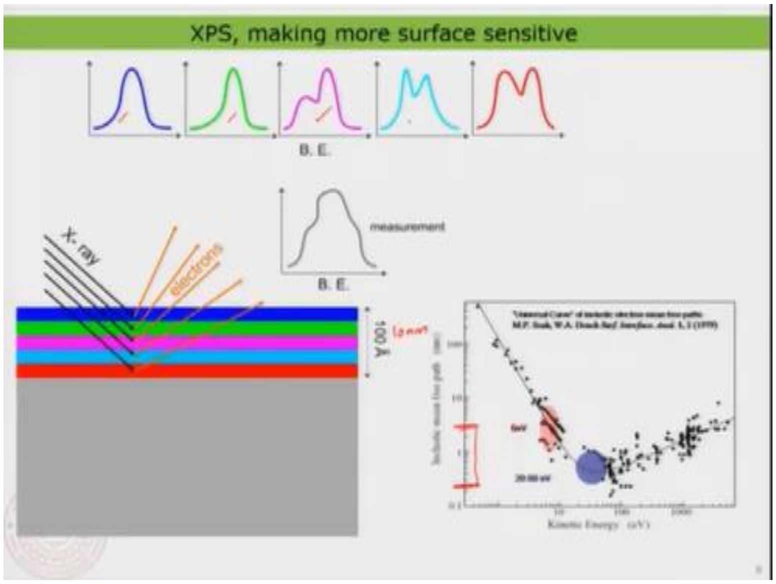

XPS, making more surface sensitive

So, now let us also look at a few important aspects here. So, we have already talked about in the beginning that this kind of technique, the photoelectron spectroscopy is quite surface sensitive because most of the time what you are basically measuring is all in this region. So, that means it is typically a few nanometre around the surface. So, that is what you are basically measuring. So, that means it is a surface sensitive technique. But now imagine that you have a kind of sample which is like this that within this 10 nanometre so this is 10 nanometre I have 5 different type of material that are actually just sticking on top of each other. So, that means I have actually just made within this 10 nanometre five different materials each having two-two nanometre thick. Here, we are having a trouble. Of course, if it is just one type of material sticking on a surface no problem, we can nicely do the experiment, and we can get the spectrum of that particular material on the surface. But this is a very special case where I try to generate a thin film of different materials which are stacked on top of the other. So, now what happens? If I would measure the spectrum, I would get some kind of a spectrum which is basically kind of the sum of all these different type of spectrums. So, what I would have expected from this blue material is this, from the green material is this; and from the magenta material is this and from the cyan is this and the red is this. But now what I am basically seeing in the actual measurement is basically a sum of all these things together, that is bad. So, if I have special requirement where I want to basically measure this kind of heterostructures then I need to make actually the XPS much more surface sensitive that means I want to basically measure just materials property from a very very thin layer. That means a monolayer or from by layer. Is it possible? Yes, it is.

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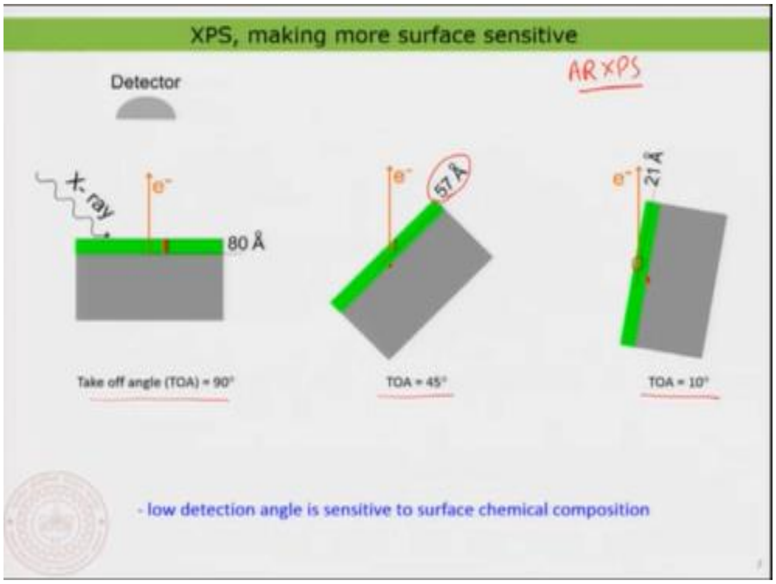

XPS, making more surface sensitive

- low detection angle is sensitive to surface chemical composition

We can do a technique which is actually known as an angle resolved XPS. So, that is something which is generally known as angle resolved XPS. What you do is that you basically just rotate the sample with respect to the detector. So, now whenever I talk about general XPS detection is always about the surface being like that and the detector is just on the top. So, this is something known as a take off angle of 90 degree. So, that means the electrons are taking off from the surface perpendicular to the surface. So, it is actually known as a take off angle of 90 degree. But now I know that typically that everything within this region is something that I am going to measure. It is of course 8 nanometre it is surface sensitive but you see like it is about 80 nanometre. But the moment I tilt the sample so that means if I would just do an experiment at a take off angle of 45 degree. Then what happens is the length that the electron travels is still the same as previously. But since the electrons that have started from here in this part is somewhat not escaping the surface particularly when you take the electrons that are coming at a take off angle of 45 degree or when I have a take off angle of 10 degree you basically see everything that is at the interface is not detected but something which is at the closer to the surface is what is detected. So, that means when you do an angle resolve X-ray photoelectron spectroscopy you are extremely sensitive to the surface. So, that is quite striking and interesting. Because now I can basically measure the sample that I have showed you in the previous case extremely something at the surface. So, I have also given a scaling here as you make actually the angle smaller and smaller, the so called take off angle smaller and smaller your detection is basically becoming extremely closer to the surface.

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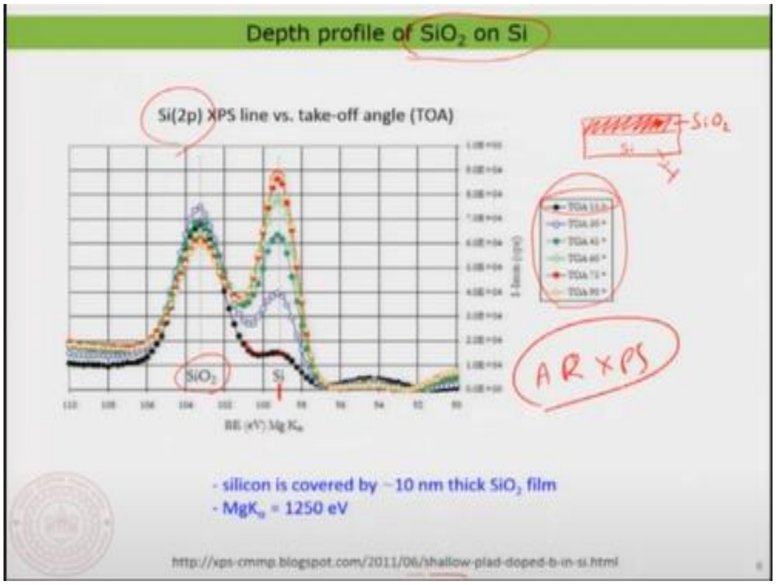

Depth profile of SiO_2 on Si

- silicon is covered by ~10 nm thick SiO_2 film
- MgK_α = 1250 eV

http://xps-cmmp.blogspot.com/2011/06/shallow-plad-doped-b-in-si.html

So, now I have an example here so I have taken it from internet source this is not a publication so, far. But it is a beautiful example where what they have done is XPS on a silicon dioxide deposited on silicon surface. So, what typically, the thickness of the silicon dioxide is about 10 nanometre on top of the silicon so this is the natural silicon dioxide on top of a silicon. And now what I am doing is an experiment where I am looking at the 2p core level of the silicon, and I am doing the experiment as a function of the take off angle. So, the yellow spectrum that means this spectrum here is the one which is actually recorded at a normal take off angle. So, that means the detector is exactly on the top and then you start to basically detect the rotate the sample and then start to detect. So, the take off angle is actually getting smaller and smaller. So, what you see is something very striking. When you have a take off angle of 15 degree you see that this is the spectrum where the silicon resonance. So, the first resonance, the one at a higher binding energy is actually from the silicon dioxide because you would expect it that silicon is connected to oxygen. So, the silicon 2p should be at a higher binding energy, silicon is about 99 electron volt that is because it is pure silicon. And when you have a take off angle of 15 degree what you clearly see is that I can only detect the silicon dioxide, and the silicon peak is almost vanished, that means this was somehow the construction of our material. So, this is basically the silicon and then I have basically on top of it, the silicon dioxide. This is the silicon dioxide and now you see as you tilt the sample, I am only getting information from the silicon dioxide and the silicon is actually just kind of not possible to detect. So, this is quite beautiful. So, if you do the angle resolved XPS you are basically more sensitive to the surface. So, you are extremely sensitive to the surface and therefore you can basically detect what is going on at the surface directly. And that is why XPS is quite a celebrated technique in surface science. So, you will also see like I will show you a couple of more examples and also, I would familiarize you a few more new interesting materials that is clearly forming on surfaces, there we will use XPS as a tool in detecting whether we can in understanding the chemical nature of those materials that we form. Thank you very much for your attention and I see you in the next class with more examples on XPS. Thank you very much.