Indian Institute of Technology
Kanpur

NP-TEL
National Programme
On
Technology Enhance Learning

Course Title
Advanced Characterization Techniques

Lecture-20

by…
Prof. Krishanu Biswas&
Prof. N.P Gurao
Dept. Materials Science &Engineering

So in the last class we have started discussing about the advanced surface characterization techniques.

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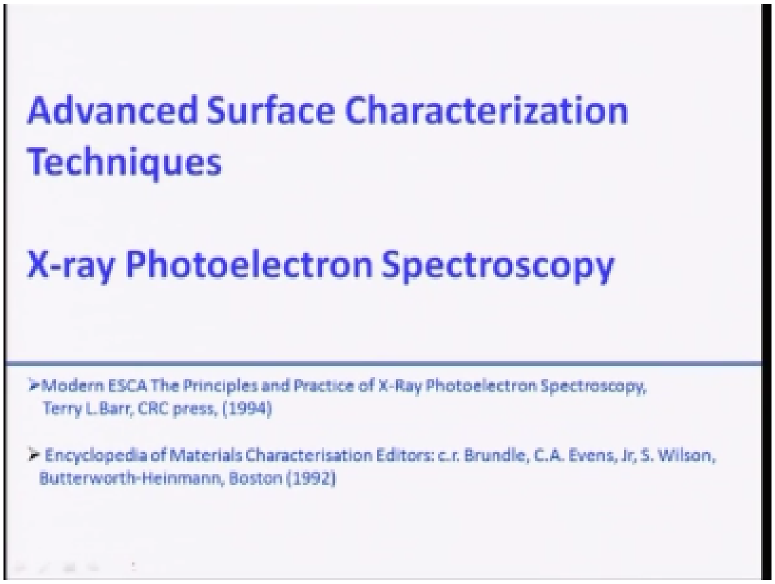

Advanced Surface Characterization Techniques

X-ray Photoelectron Spectroscopy

- Modern ESCA The Principles and Practice of X-Ray Photoelectron Spectroscopy, Terry L.Barr, CRC press, (1994)
- Encyclopedia of Materials Characterisation Editors: c.r. Brundle, C.A. Evens, Jr, S. Wilson, Butterworth-Heinmann, Boston (1992)

And I have introduced to you the subject given different examples from our own studies showing the importance of the surface characterization techniques from the perspectives of material science engineering, so we need to now go it into details of each of these techniques the first one which we will discuss is x-ray photoelectron spectroscopy or what is known as x p.s in the literature many of these slides, which I am going to show you can be actually seen in this first book which is by Terry Barr and published in 1994 but in the encyclopedia also you can get a lot of information's first one.

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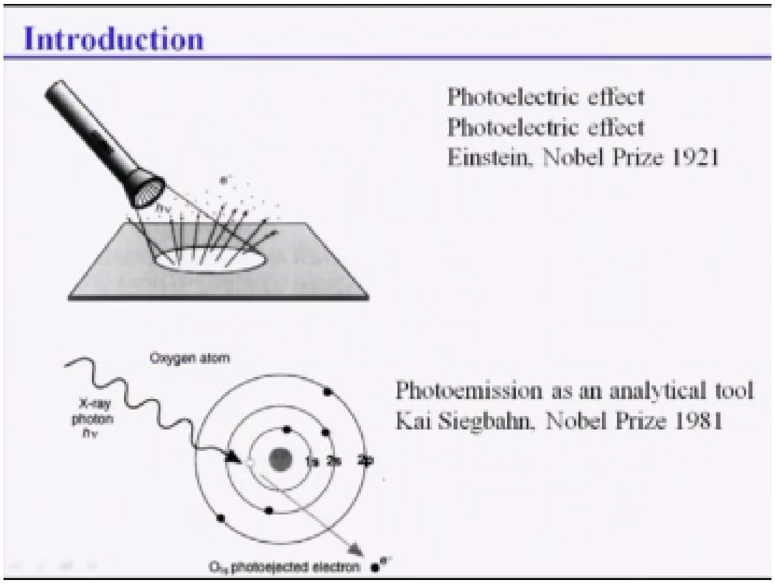

Introduction

Photoelectric effect
Photoelectric effect
Einstein, Nobel Prize 1921

Photoemission as an analytical tool
Kai Siegbahn, Nobel Prize 1981

Is what is experienced as I said it is known as x-ray photoelectron spectroscopy that means you have x-ray source and photoelectron as the output that is very clear is it not, so what is actually done as you know photoelectric effect was discovered long back almost like 90years back in by Sal wat n stein and he received a Nobel Prize because of the discovery in the photoelectric effect normally if a photon of subtle energy suppose H new falls on a photo electrically sensitive material the photo electricity is generated.

Because of the production of electrons that is what is shown in the first slide you see there is a light source with energy of the photon quanta which is coming as energy of H new and this can actually eject out electrons from the photo active elements and that can produce electricity fine so that same thing can be used to make photo electron spectroscopy per source which can be used in the photoelectron spectroscopy is not the photon but an x-ray, so this was done by K slag boon Chuck one in night and he received a whole pies after60 years of Einstein's discovery.

Both of these two scientists are from German and the psychic bond receive nullified in1981 for the discovery of this, so what is done here you have a x-ray photon coming from x-ray source it can be any actual exercise like copper or nickel or chromium or iron and this XL photon falls on a sudden suppose molecule here is an oxygen or certain atomic oxygen atom and then because of his high energy its ejects one electron from the inner cell that is one a cell of the oxygen atom and this electron comes out this electron is basically oxygen.

One electron photo is photo elected electron and we can use this electron to study different kinds of you know behavior different kinds of aspects of these spectroscopy that is what is the key basic principle of the technique in a nutshell what I can say, so and as I said in the last class also AC is known as ESCA electron spectroscopy for chemical analysis but it has different acronyms like XPS X a photoelectron spectroscopy or UPS.

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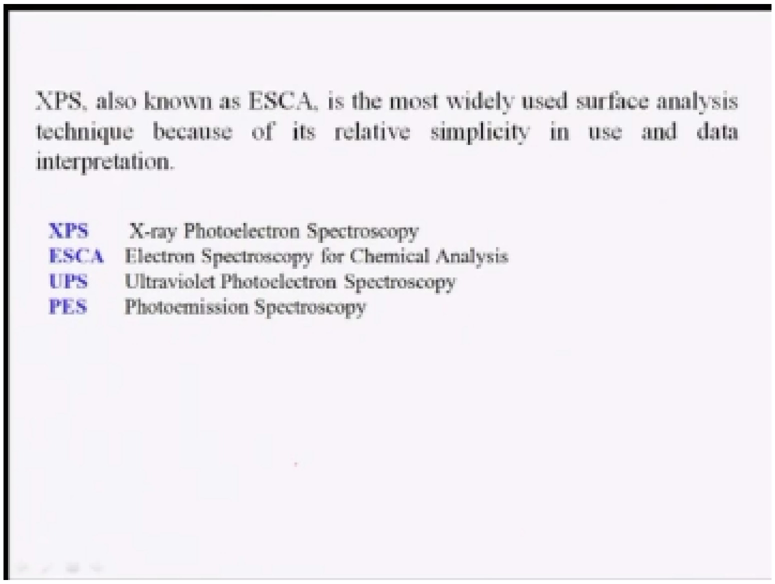

XPS, also known as ESCA, is the most widely used surface analysis technique because of its relative simplicity in use and data interpretation.

XPS	X-ray Photoelectron Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
UPS	Ultraviolet Photoelectron Spectroscopy
PES	Photoemission Spectroscopy

If you use ultraviolet as a source of energy ultra wireless protocol spectroscopy are you can use a photo light like photo, so which can lead to emission of electrons then it is called photoemission spectroscopy, but we are going to discuss these two mainly so we are not going to discuss what will happen if you solder violet or photon light actual and then produce spectroscopy.

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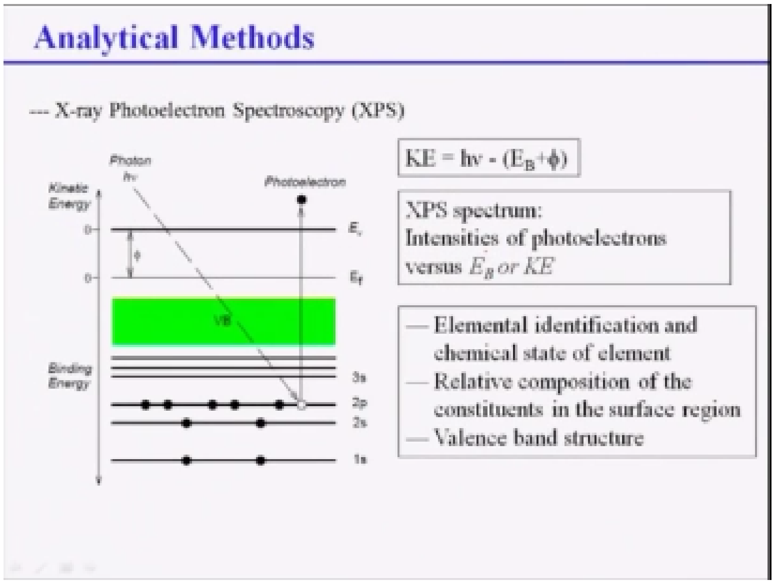

Analytical Methods

--- X-ray Photoelectron Spectroscopy (XPS)

$KE = h\nu - (E_B + \phi)$

XPS spectrum:
Intensities of photoelectrons versus E_B or KE

- Elemental identification and chemical state of element
- Relative composition of the constituents in the surface region
- Valence band structure

Well what is actually the process what is actually there are analytical methods let us know it in terms of energy diagrams what I am showing here is basically energy levels of certain Adam you can see 1s 2s 2p 3slike that, so one is has two electrons to assess two electrons and then to P has six electrons in the shelves, so then you have three years which is unfilled and then you have valence band after that you have a Fermi level so and below Fermi level actually all the specified levels of the energy levels occupied by atoms.

Electrons sorry and then you have EV at a higher level than basically EF by difference of ϕ is known as what function as we know that from the Einstein's theory, so this is what is called kinetic energy this is what is called binding energy now if a photoelectrons or x-ray actually comes at false on this metal atom and it rejects suppose all the electrons need to push out and this electrons then has sufficient kinetic energy to travel through this valence band and wave and pass the Fermi level and come out.

This is known as photoelectron so we can calculate the kinetic energy photoelectron as Hv which is the incident energy of the photon minus EBEB is basically the binding energy + 5y is the work function, so this is work function you know and EB is basically binding energy that is how we denote so that means the binding energy is the energy with which this electron is bound to the nucleus, so that means excess XPS spectra basically can always plot the energy or the intensity of the photo electrons I versus either the binding energy that is EB or the kinetic energy they are related.

As you can see why is that is what function for the material is well known hv is the energy of the incident x-ray that is also when known, so therefore the two things which can vary is the ke or Ev depending on which atom which electron you are rejecting out, so that is why the experience plots basically will be intensity versus either EB that is the binding energy are trendy cannot see that is how the plots are met now what all you can do with this is a basically the principle which I told you that is how things are actually happening inside.

A material and as you know why it is called surface cactus in tool as we know this electron photoelectron which is coming out from the sample will have energies I know something kind a energy not very high, so therefore if it is ejected deep inside the sample then this electron may not want to come out of a sample surface and we cannot analyze that is why we use surface actually calculation this state is used for surface cactus and tulle, now what we can do we can do elemental identification obviously.

Because we know what is the exact energy of the electron which is coming out so you can categorically say which element is present we can actually even tell chemical stairway element that is whether it is a oxidized reduced what kind of state a droid is a neutral we can actually measure the Olympic composition the console in the surface is I an and looking until obtained valence band structure.

In fact now-a-days we can actually do mapping of different elements presents on the surface in the surface, so therefore lot of things can be done in the XP that is YX pace is considered as a versatile tool.

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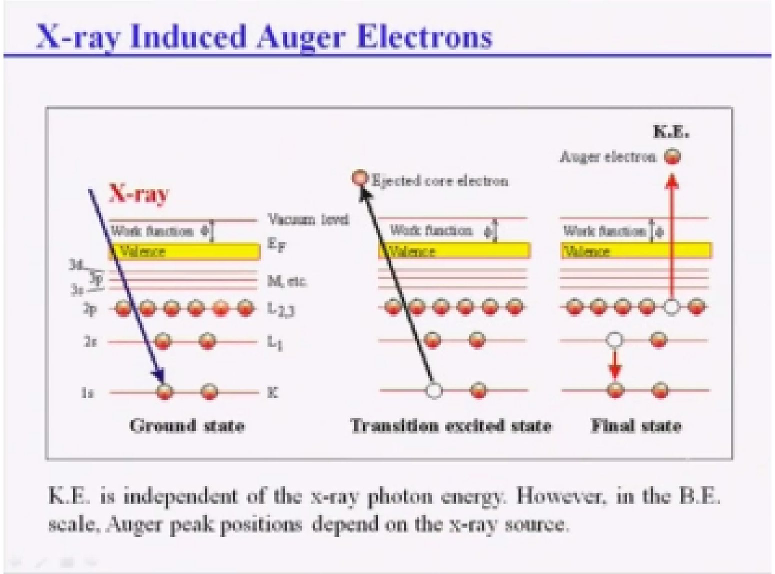

X-ray Induced Auger Electrons

K.E. is independent of the x-ray photon energy. However, in the B.E. scale, Auger peak positions depend on the x-ray source.

Before I get inside into the other things of XPS, let me just explain little bit about watches Augier because all g is also used the purpose, let us see what can be done in orgia, so this is what is this the first picture is basically correspond to the XPS as UCK electron case level l1 l2 3m then the Fermi level then the vacuum level that is EV and this to a differentiated by work function okay, so now it makes a false and eject electron comes out this whole thing is known as XPS right.

Now in this case the last picture the last basically schematic diagram what is happening if you see if this becomes vacant by ejecting the electrons out by the x-rays and higher never left on higher level means suppose at l1 level electron can fall back into the key level and thus creating releasing certain energy when this comes to this summer as you be released and this energy then can be used to knock out an electron at a higher much higher energy level that is l23 this electron will have such official a little bit of kinetic energy.

Not as high as the XPS electron x-ray photo rejected electron but it will of certain energy this electron is known as RG electron, so that is all in a nutshell i can say orgi electron on production is totally different from the from the photo except photo electron spectroscopy here basically jump of the electron from a higher level to lower level leads to production of certain other energy H nu 1 which can basically eject an electron from il-23 say out and that electron comes out from the sample surface is known as og electrons.

So obviously the kind a can see of Auger electron is much lower than the XPS that is why audio spectroscopes always done from this GGN near to the sample surface you cannot actually probe little inside the sample surface whether expiry used to probe the sample surface which is deeper compared the odds here, so that so I experienced a auger these are complemented tool very you know widely used remember GA was discovered by auger, so that is why this process is named after him we are going to discuss this audio spectroscopy in detail.

So let us not talk about this right now but for the sake of your understanding i am just going to tell you what is Auger spectroscopy.

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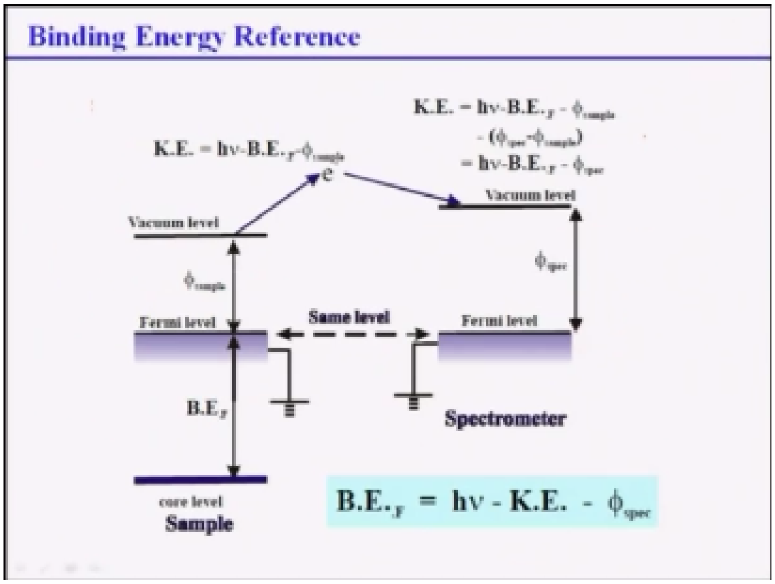
Binding Energy Reference

$K.E. = h\nu - B.E._F - \phi_{sample}$

$K.E. = h\nu - B.E._F - \phi_{sample} - (\phi_{spec} - \phi_{sample}) = h\nu - B.E._F - \phi_{spec}$

$B.E._F = h\nu - K.E. - \phi_{spec}$

Now let us me go back to the XPS again an XPS binding energy difference is like done like this let us do that, so this is sample they have a core electrons then ever binding energy binding as Jimmy this is what the electrons are there then this is a Fermi level as I said EF and there is a work function then you have a vacuum energy level okay, so once the excel falls it basically crosses the binding energy then Fermi level then this work function comes out that, so actually you get G of the XPS as this hv – bf – ϕ of a sample.

So and that is basically then you know if in a case a spectrometer what happens this is a vacuum level and there is a spectrometer work function, so this needs to be you know subtracted so basically it depends the kind a kanji is basically when this comes to the electron falls on a spectrometer kinetic energy becomes like this hv BF - 5SPEC because Q sample by sample fine cept for basically cancel out.

So finally we get binding energies basically equal to x near the electron H nu is the energy of the incident photon the x-ray photon minus the kinetic energy minus the five spectrometer, now you know this is fixed well known in a very particular spectrometer this is the fixed also because we know the way to the incident energy of the x-ray, so basically what is varying is this and this are these two are dependent so now we can actually calculate if I know this the kind of can see or find out the kind of courage.

You can calculate by all basically what you measure is a kind of can see of the electron and that can be used to calculate the a binding energy which is present in the electron, so that is so actually we can characterize the electron which is ejected out.

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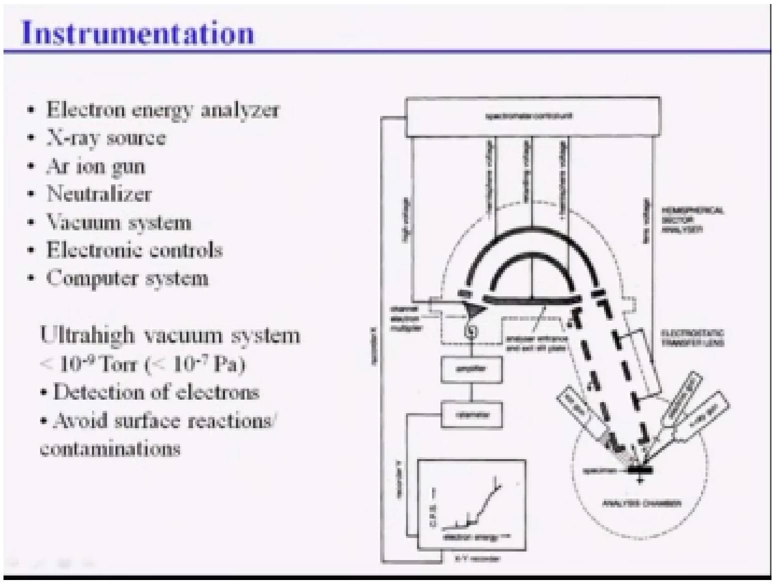

Instrumentation

- Electron energy analyzer
- X-ray source
- Ar ion gun
- Neutralizer
- Vacuum system
- Electronic controls
- Computer system

Ultrahigh vacuum system
< 10^{-9} Torr (< 10^{-7} Pa)
• Detection of electrons
• Avoid surface reactions/ contaminations

How the instrumentation is done we are going to discuss in detail later on but to show you that so what you have is basically your web a lot of different stops are there here this is the basically heart of the system you have a sample of x- ray gun and you can have electron gun basically x-ray as always electron gun and then you have iron gun to basically you know clean the sample surface many times you can use argon ion because this is done inside a vacuum chamber, so once I electron ejector this passes through this electrostatics transfer lens this is what is shown you here.

And then it which basically goes to the hemispherical you know portion and then falls on the electron channel electron channel electron multiplier which is nothing, but basically a get and then it is getting multiplied amplified the signal through when it passes through this multiplier and then it is recorded you know after it passes to the rate meter, it recorded and you get a plot between intensity versus kinetic energy or intensity versus binding energy that is what is shown you here well that is actually simplest possible.

Thing but it is not so then you have a control unit and there are many other stops related to it, but this is what is done remember it is done in a very high vacuum system because he will acknowledge needs to travel through this that's why we need a very high vacuum system back on level should be rid of the – 10 9. And we need also any kind of surface confirmation or the surface reactions.

So that is why you know x- rays energies which are allowed to follow the samples to be Taylor so that there will be no surface reaction or contamination form because of the x-ray falling on a sample surface.

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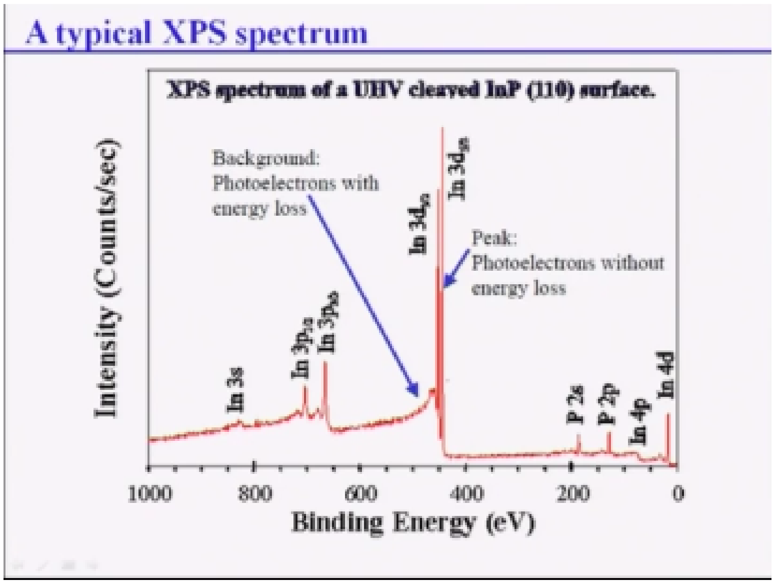

A typical XPS spectrum

Well let me show you atypical xA xB a spectrum I am going to show you two spectrums one from our own other ones from taken from literature as I said in the last class we have been working lots on the hydroxyl apatite and Harris appetite model that is titanium composites, so from the surface the spectrum is taken both from higher appetite and I super titanium composites is basically intensity versus binding energy plot in density is in arbitrary units that is called they basically the energy or the number of counts.

GPS sometimes we call CPS counts per second and Bonnie and is always written in units of electron volts, so as you see we can see different pics as usual any spectroscopy I have a background and apic okay and as most intense peak coming from both the sample is oxygen 1sfollows I have already discussed with you then you have a peak coming from carbon 1s which is basically you set a standard in an XPS because you know all samples of some kind of carbon so you are going to proceed speaks.

So many times the spectrometers actually are basically calibrated using this peak position then because it is a hydroxyl apatite a dissipative formula of ca10 po4 whole 20 h volt oh okay, so as you see there are phosphorous there is calcium that oxygen and the hydrogen normally not detected and you have C oxygen pics calcium pixels here calcium 2 p 3 by 2 calcium 2p ½ we are going to discuss for the meaning of that this a peasant both in hydroxyl apatite a titanium then you have phosphorus pics p 2 p and p 2s coming and this in this positions and all the whether you have basically little bit of titanium pics here you can see carbon one has a carbon 2's will present always.

This titanium peak is not visible here but little bit small peak is visible here, so that is how we can say titanium is present the basically titanium is not present as a metallic state its presence as a oxide of state or basically oxidized state, so that is actually how these XPS spectrum look like and we can analyze different things from this we can calculate the element present the chemical state of the element present and we can calculate the percentage of the particle element present Barry Calcul on area another pics.

We can calculate in fact the chemical shift because of the binding of the elements with any other things a lot of lot of other things can be done which is a part of the topics of this lecture typical XP respect um for indium phosphide 110 surface as you see here you see all.

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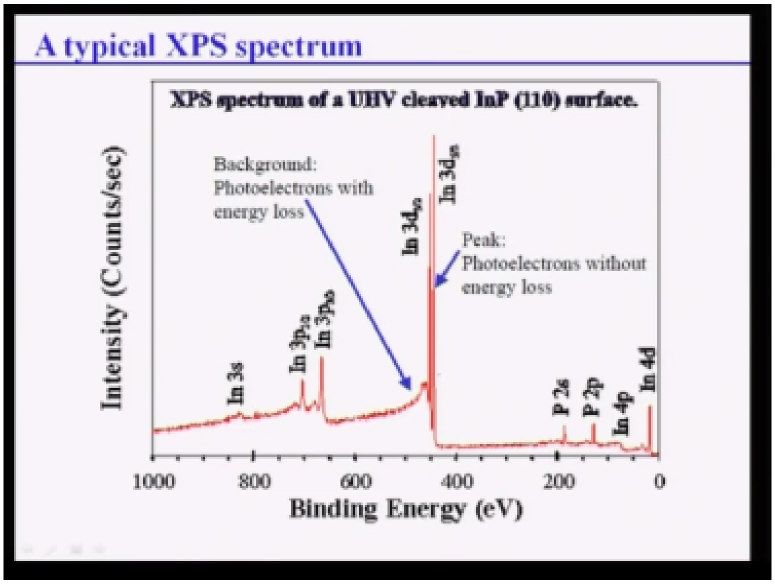

A typical XPS spectrum

For indium phosphates 110 surface as you see here you see all the India one phosphorus pics you see indium 3s indium 3 1 / 2 this is 3 p 1 / 2 this is 3 P the 3 / 5 3 T 3 by 2 this is 3 D 5 / 2 okay this is 3 /2 this is phosphorus p will always have a high binding energies when I indium as you know phosphorus 2's phosphorus 2p phosphorus say indium 4p in the m40 so indium as 3s 3p 3d 4p and 4d phosphorus has 2s 2p which is clearly detected and then you have background in this that is so actually the peaks are they the spectrum looks like I hope things are clear.

In your mind how is PS works and how the spectrum looks like because we are going to use the spectrum.

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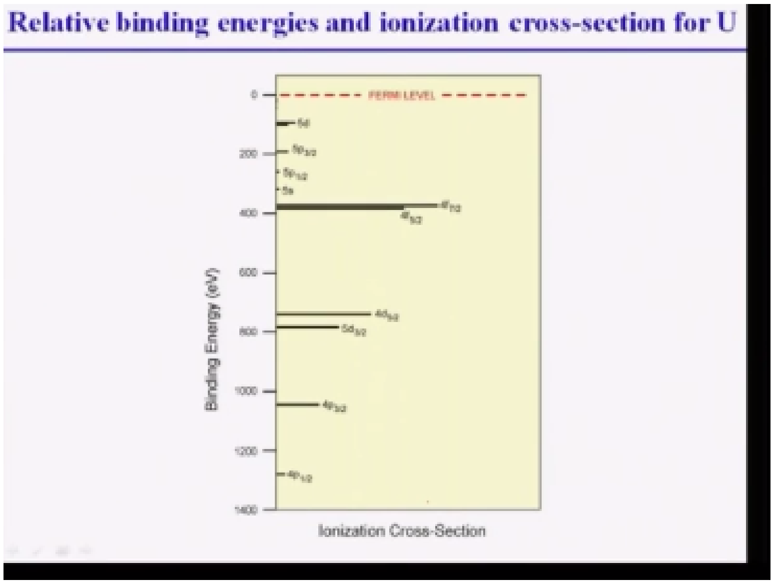
Relative binding energies and ionization cross-section for U

Now to give you more idea let us look at a very high at we number elements like uranium and talk about binding energies and iodine is and cross sections this is binding any of us an across sections as you see here different kind of levels are there you have 4 p-2 spins one half and three by 25 d 3/ 2 okay, 5 d 3 / 2 is small also there and this is different than 5p half 5s and 5d another and if levels are there also is f 5 x 2 f 7 / 2 you can see the anlagen cross sections are very high on a cross section means how much I know energy electrons are created after you ionized.

With this excess very high 44 f electrons followed by five f od that 5d and for p1 s energies are very low for these electrons like 5d 5p and 5d and 5s whether they are very close the Fermi level so that means the electron is photoelectron yield by x rays x spectroscopy will depend on this understand cross section that means this will be higher if for these energy levels for case of I uranium than others so that means we can do such a common axis for all elements and then figure out whether this actually happens in a particular system or not well.

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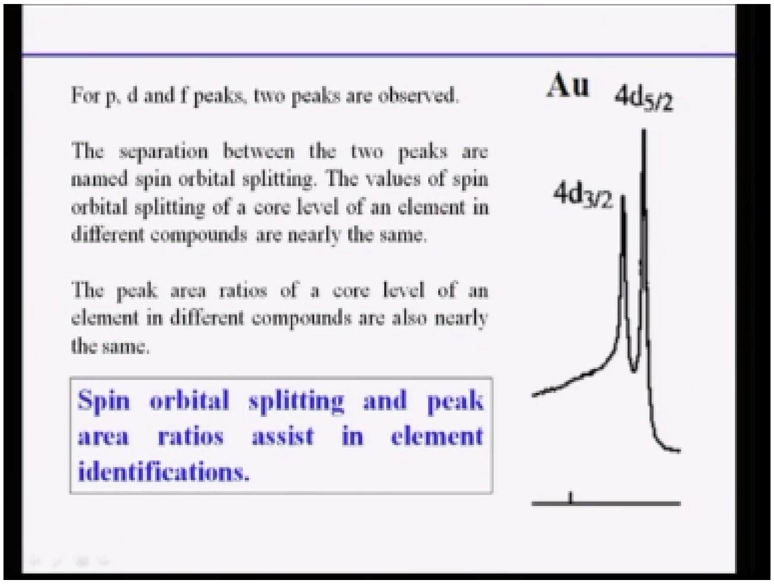

For p, d and f peaks, two peaks are observed.

The separation between the two peaks are named spin orbital splitting. The values of spin orbital splitting of a core level of an element in different compounds are nearly the same.

The peak area ratios of a core level of an element in different compounds are also nearly the same.

Spin orbital splitting and peak area ratios assist in element identifications.

Now let us get into nativities of that as you see for P D and F pics that I always to Pixar observe here you see for gold 34 d 3 / 2 and 4 D 5 / 2 please then I mean these pics are actually comes as a doublet suppressing between these two peaks are named as a spin orbital splitting the palace of the spinner battle pitting up a core level of an electron in different compounds are nearly CM you must remember this is very important that means values of this pin orbital speeding this is the spinner battle pitting value this is for a quad.

I will act on it different compounds are nearly same peak ratios speak as a ratio that mean this is the peak area for these two electrons peak area ratios of a coal level up an electron element in different compounds are also nearly same these two are very important now I want to discuss what is the spin orbital splitting I am going to do that but this is what we observe and we have seen some of this NOS pattern the spin-out is spitting and speak area ratios assist in any mental identification okay.

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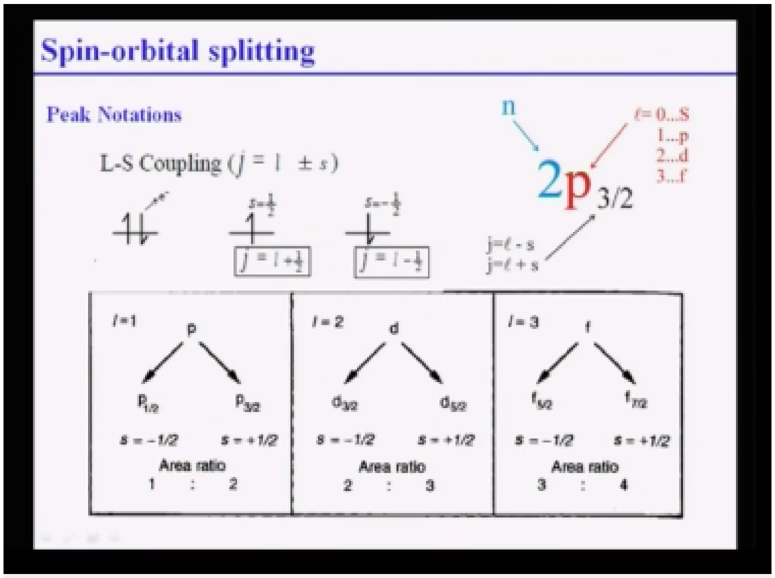

Spin-orbital splitting

Peak Notations

L-S Coupling ($j = l \pm s$)

Now let us look at what is it what is finger battle pitting this is first to tell you how actually done you know electron one has the ops mean or down spin it is 1/2 = 1/2 + up so what we do here basically use something known as LS coupling we do not use only S as you know the principal quantum number n l S all these things you are very or of it so l and S, S actually talks about the spin of the electrons so here we are using L&S coupling so this number j James what is this number 3 /y 2 1 x 2 is basically L +-S as you know S can be either +1/2 or – 1/2 depending on the spin.

So if you have this kind of situations one up and down so one is app is called plus up town is called minus off so in this case when it is up is basically j = l + ½ if it is down the J is going to l minus half okay, so first one the way pixel notice is first is the principle quantum number 2 p okay, as you know one 1s, 2s, 2, 3s ,4p that is how that point of principle quantum number actually goes so first one first digit in a peak nota nation is corresponds to n at the principal condom n second one corresponding to L the magnetic quantum.

Number that is p SDF there are four sets is to know and so that that means s is equal to what is basically s is going to 0 p = 1 d = 3 fa q look 3s = f x3 so that means p = 1so it is two corresponding to n principle quantum I n P corresponds to what one then if it is 1 plus half that is the electron is up spin then is positive so it is become 1 +1/2 = 3 by 2 correct so that is what is here when L=1 that is 4p cells either it is p 1 / 1/2 or p3 / 1/2 if it is p 1 by half that means p 1 -1/2 1 is basically l and - up is basically down spin so that is what is tad and then here this p1

+1 1/2 that is 3 / 2 to 1 is corresponding to the l p = 1 that is this magnetic one number I but y l quantum a non magnetic quantum ,quantum number and 1/2 is basically coming firms up spin so which has been found that area ratios.

That what I have been discussed of these two peaks will be 1 is to 2 that means 3 by 2 will be double and you have a novel idea d to now d I will d correspond to illegally to write so will too so that means d it will be 2 – 1/2 that is d 3 / 2 where- up is cause form to downstream right and otherwise it will be 2 + 1/2 then 1/2 + Upper cross went off spin this is how actually we are designating area ratios of these two split spin orbital spitting is to is to three and then f correspond to l equal to three so L in the 14 + two paths l pd and a low 34 f so as you see 3 -1/2 will be 5 and ½.

So that becomes down spin electron and three plus half will be 7 / 2 that is a last min electron area issues of these two speaks after splitting will be 3 is 24 so in a nutshell this slide is that is why is very important for you to understand in a nutshell we can actually obtain spin orbital splitting information in XPS and this is how things are designated this is how things are actually in a picture marked in the XPS spectrum.

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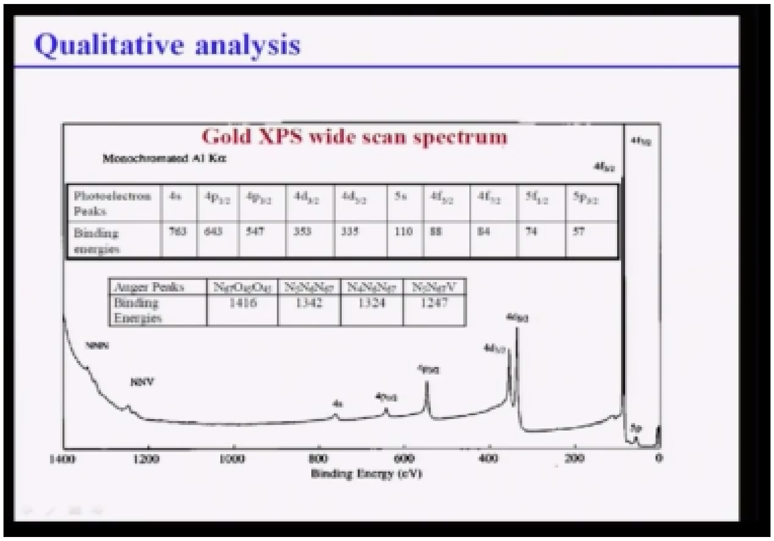

Qualitative analysis

Gold XPS wide scan spectrum

Monochromated Al Kα

Photoelectron Peaks	4s	$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$	5s	$4f_{5/2}$	$4f_{7/2}$	$5f_{1/2}$	$5p_{3/2}$
Binding energies	763	643	547	353	335	110	88	84	74	57

Auger Peaks	$N_{67}O_{45}O_{45}$	$N_5N_6N_{67}$	$N_4N_6N_{67}$	$N_5N_{67}V$
Binding Energies	1416	1342	1324	1247

Now let us look at you know how we can use this for gold has you know it has 4 a's for p for the 5s for f5 f and 5p electrons so what are they you know the binding energy for election is 763 this is what is their 763 4p hop that is down spin is basically 643 this is the 14 p 3 / 2 off spin it is 547 you see the area ratios are 1 is 2 this is 2 is to 1 then 4d 3 / 2 that is down spin this these correspond to illegal too so therefore 1 2 – 1/2 is 3 / 2.

This is what is that this is coming surround 353. I electron volts binding algae and 5 by 2 will come 335 they are very close by area ratio is about how much it is about two is 23 .

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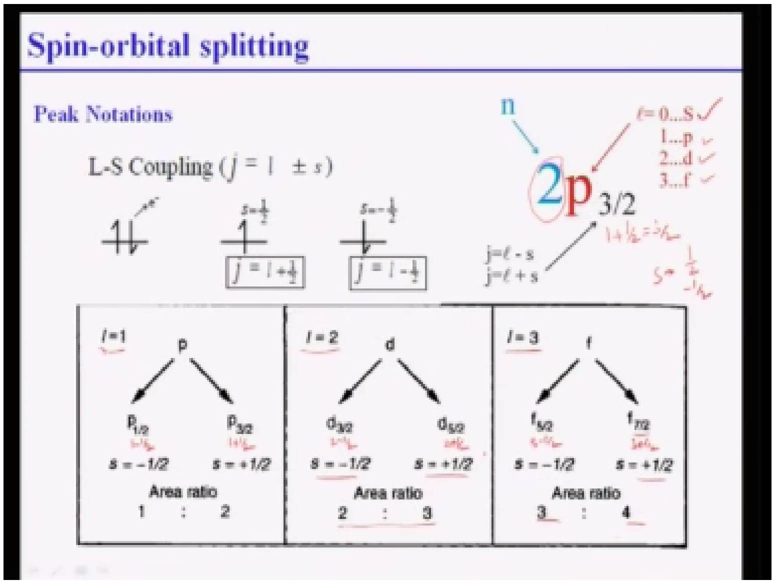

Spin-orbital splitting

Peak Notations

L-S Coupling ($j = l \pm s$)

l=1 p		l = 2 d		l = 3 f	
$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$
$s = -1/2$	$s = +1/2$	$s = -1/2$	$s = +1/2$	$s = -1/2$	$s = +1/2$
Area ratio 1	2	Area ratio 2	3	Area ratio 3	4

Now if you look at 4 f, for F so for AF has 88 and 84 as a binding energies this is the one this is the one very close by 88 and t4 so Л / 2 is 3- 1/2 down spin and seven by two is 3+ up off-spin eraser is 3 is 24 then you have 5p and others many times are not observe 5f and 5p is very 5 piece of the five wave is very close so it is not observed.

But not seen now we can actually use this in oak area ratios for quantitative analysis that is what has done in this case we are used aluminum k α SI x source so in case of assize up if you look at it the bandages for lap of say I am not discussing here but I will discuss letter is n of 0 is 1 116 electron volts and five in six n 67 where when you discuss let us not discuss about this part right now once you come back to we will discuss.

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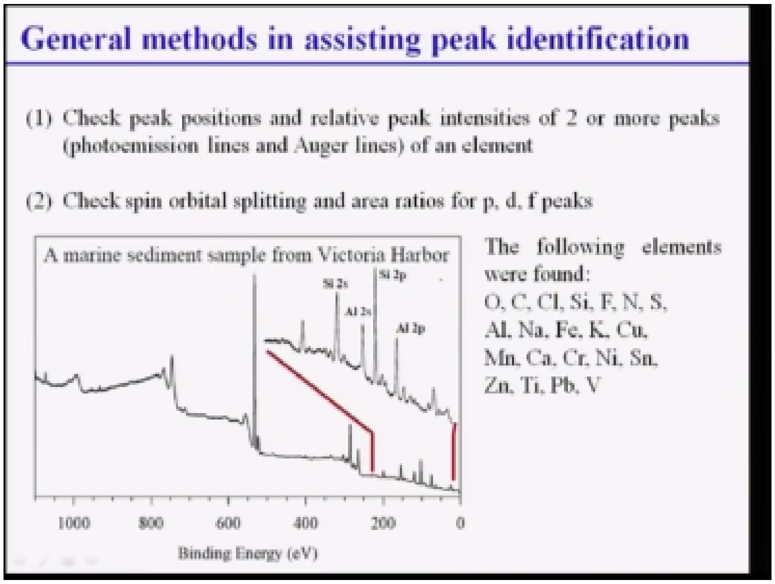

General methods in assisting peak identification

(1) Check peak positions and relative peak intensities of 2 or more peaks (photoemission lines and Auger lines) of an element

(2) Check spin orbital splitting and area ratios for p, d, f peaks

A marine sediment sample from Victoria Harbor

The following elements were found:
O, C, Cl, Si, F, N, S, Al, Na, Fe, K, Cu, Mn, Ca, Cr, Ni, Sn, Zn, Ti, Pb, V

So first let us see how we can identify pics just like x-ray diffraction here we can identify pics so what is the general method first is take pics position and elective intensities of two or more pics both in case of experience and nausea lines of an element takes the spin orbital spitting and area ratios of PDF fasting is the peak position .I relative peak in cities or two or more pics that is what you should do second thing is the spin split is splitting of our area ratios so let us see the following things here.

It is basically the plot is showing for aluminum and silicon you see this is kind of aluminum 2 s so we can actually on the peak position 42s what is the binding energy, so binding energy can be collected aluminum do p also silicon twists silicon to pee but it does not tell about what is the spin orbital spitting okay, so to do that well as to pee hop or 2 p 3 by 2 we have one has to look into the area ratios so as you can see this is aluminum to P so therefore this will be 2 P 1/2 and this will be 2 p 3 / 2 think this will be 2 p 3 / 2.

This will be small one in 2 p 3 / 1/2 silicon is also like that one can detect the and if you ,if you scan the whole thing there are many Peaks first thing is this you can find oxygen carbon chlorine silicon nitrogen since all aluminum sodium so many pics are observed so that is what they done by just taking the peak positions second thing which.

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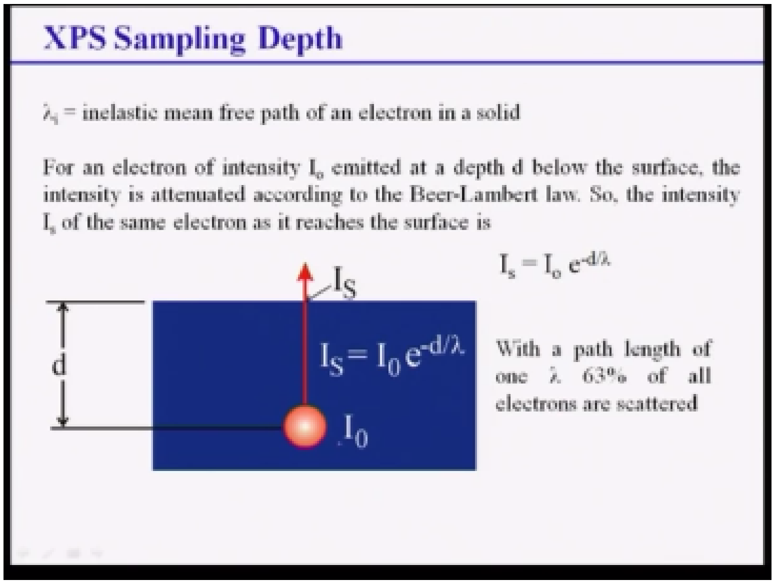

XPS Sampling Depth

λ_i = inelastic mean free path of an electron in a solid

For an electron of intensity I_o emitted at a depth d below the surface, the intensity is attenuated according to the Beer-Lambert law. So, the intensity I_s of the same electron as it reaches the surface is

$I_s = I_o\, e^{-d/\lambda}$

With a path length of one λ 63% of all electrons are scattered

You must know before even going proceed further is what is sampling depth how much information is coming from what to the till what kind of no depth of the sample. So normally this is again we use the same for more like x-rays because it is plantation only but electrons coming out after generation from the sample surface. So if we know the μ I, I means was a particular element elastics mean free path of any element in a solid we can do that.

So for a healing electron intensity of a zero which is created inside the sample at the depth D below the surface the intensity is attenuated I come to the beer slumber long we have already discussed and UV visible spectroscopy. So intensity IS which is coming on the surface is basically exponentially varies with dy λ so with a path length of on λ okay that is you know sixty-three percent of the electrons are scatter, this is very clear when d equal to λ is basically you will to λ is being killed is equal to i0 / e.

So that means 1 by e of a 0 that's equal to 63 % of a zero that is what is said here so therefore you must remember this formula it is I 0 exponential d by λ_0 λ by D okay it is d by λ λ is the elastics mean free path of an electron assault that you must have knowledge first, we must have done this is actually University scattered electron electrons are losing energies so therefore one is to know what is the mean free path of that.

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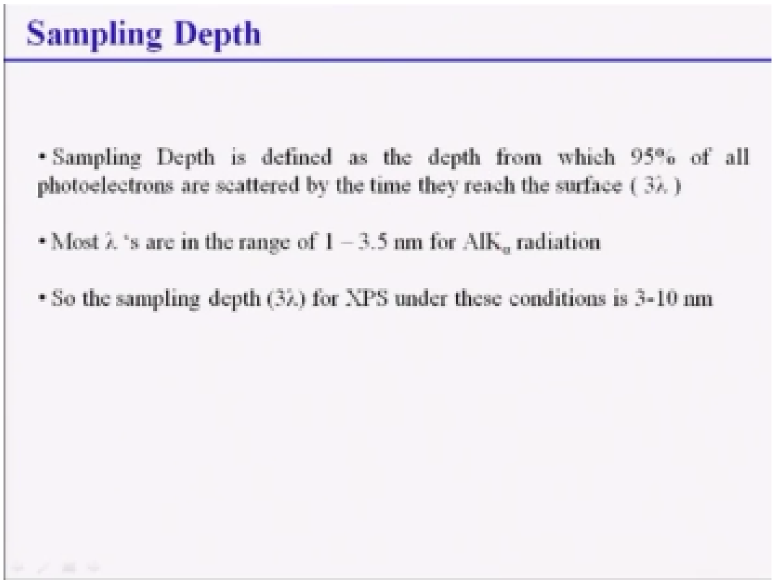

Sampling Depth

- Sampling Depth is defined as the depth from which 95% of all photoelectrons are scattered by the time they reach the surface (3λ)
- Most λ 's are in the range of 1 – 3.5 nm for AlK_α radiation
- So the sampling depth (3λ) for XPS under these conditions is 3-10 nm

This is all available sampling this is identified the depth from which 95% of all photoelectrons are scattered by the time they reach the surface correct. So it is the depth for much 95% all the photoelectron the scatter by the time they reach the surface, so more λ are in range of 1 2 13.5 nanometer for aluminum care edition, so sampling depth T λ for XPS under this condition is about 3 to 10 nanometers the spread is small about 100 am strong depth you cannot get more than that.

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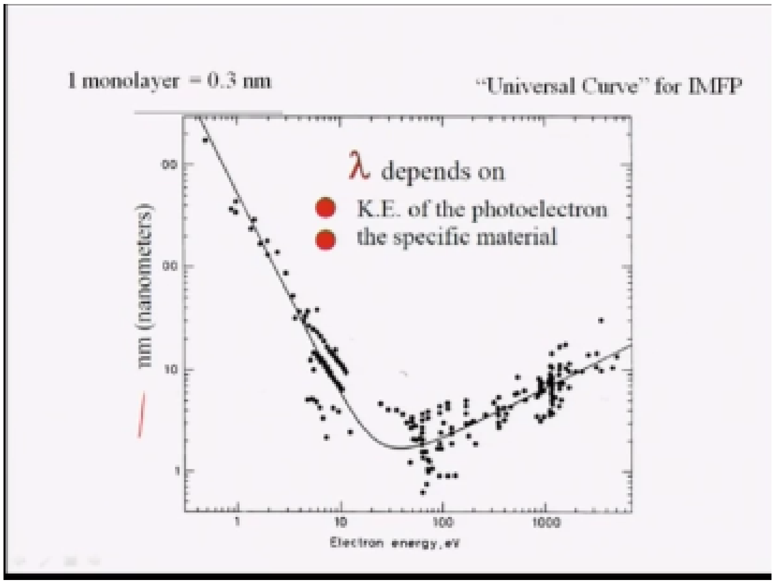

1 monolayer = 0.3 nm

"Universal Curve" for IMFP

λ depends on

- K.E. of the photoelectron
- the specific material

So if you have more layer up 30 am strung okay this is how actually get this is a depth in nanometers electrum energy as you see here depth is very high this is 100 this is thousand as you say this is depth is high when you have binding and is less as obvious there are be more kind against of electron as the mining as it reduces kind a cancel more. So it will be coming out as the binding energy increases it also decreases but for a very high binding energies again in density increase that is because of the you know effect which is different from scattering.

This is basically Universal curve so λ actually depends on the kinetic energy of photoelectrons and the specific elements this is that, so as specific element means what type of element is that is basically the dictates the binding energy.

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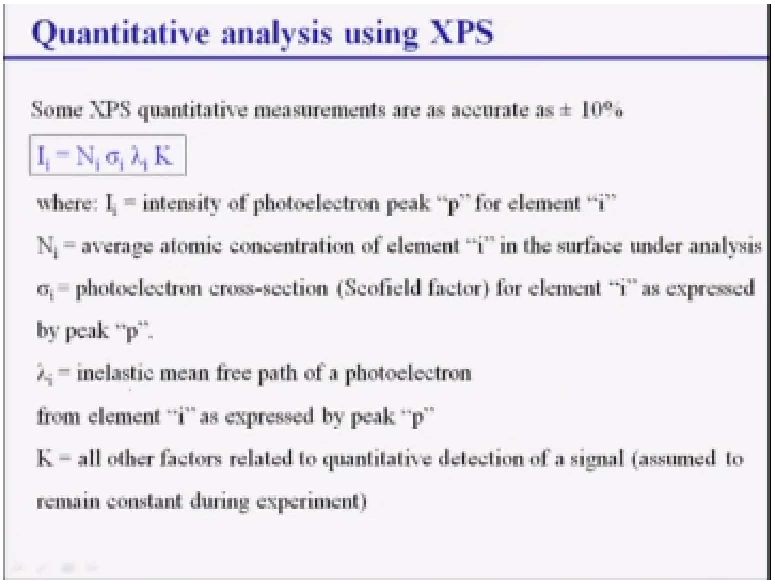

Quantitative analysis using XPS

Some XPS quantitative measurements are as accurate as ± 10%

$\boxed{I_i = N_i \sigma_i \lambda_i K}$

where: I_i = intensity of photoelectron peak "p" for element "i"

N_i = average atomic concentration of element "i" in the surface under analysis

σ_i = photoelectron cross-section (Scofield factor) for element "i" as expressed by peak "p".

λ_i = inelastic mean free path of a photoelectron from element "i" as expressed by peak "p"

K = all other factors related to quantitative detection of a signal (assumed to remain constant during experiment)

So now after knowing all these things because you know sampling depth now we know how the pics to be identified, let us see how quantity balances can be done. Now inexperienced instrument measurements are accurate with level of 10% it is not very accurate errors are putting with ten percent the intensity which is coming our sample surface is a function of n i σ λ ik what is ni ni is the a to me concentration of element I in the surface under analysis that is what I feel you want to measure.

I the indices of electrons peak can you measure be easily ni is the average atomic concentration that is our variable or that is what is actually one to measure so Sigma is what photoelectron cross-section basically is called schofield factor expressed by any peak position P λ i have already discussed is mean free path a photoelectron and case all the other factors dumped in like a quantitative assessment you know it is how many other factors dumped in any DX actually there are factors like you know atomic number difference the flow sense all these factors are dumped in a particular parameter same way k has all other factors.

So basically finally speaking intensity depends on the concentration of the element for electron cross section of the element and the community path of photoelectron these three factors k is normally constant for any experiment, so as if you know this is memorable if you know these two parameters we can calculate in that is what is the quantification done.

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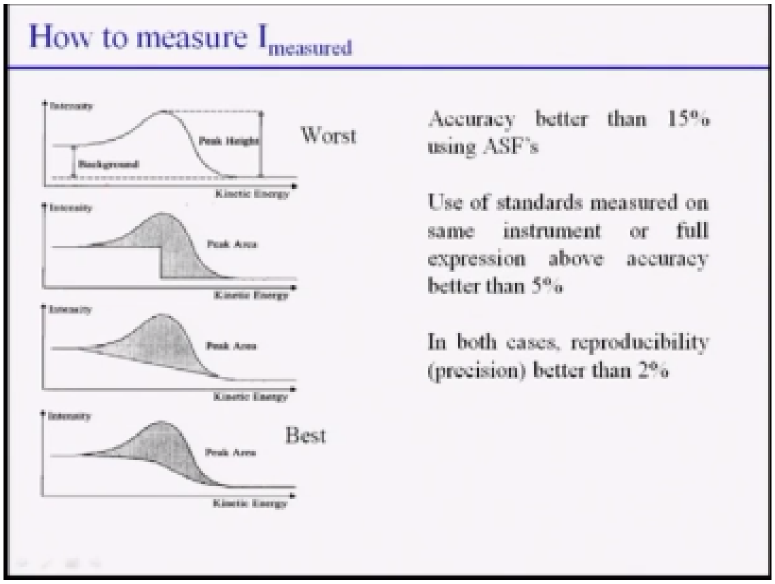

How to measure $I_{measured}$

Accuracy better than 15% using ASF's

Use of standards measured on same instrument or full expression above accuracy better than 5%

In both cases, reproducibility (precision) better than 2%

Now how to measure this I that is what actually errors comes in and that is actually propagates into the analysis, so if you look at this intensity by the kinetic energy shape is like this is not a typical x-ray diffraction peaks little bit distorted. So one has to remove the background to calculate peak height if you fit the background like this like this one this is wrong if you put the background like, this is also not best the best one is to fit the background like this that means background fitting is very important.

So the standard measure on this some instrument or full expression about the equation C can be done if you have a standard but reproducible et is always very high here for two percent so washed cases in this manner when is this best one is this these are the middle that is so actually the human error comes in the picture because depends it depends on how the measurement of the area depends on how you perceive the peak.

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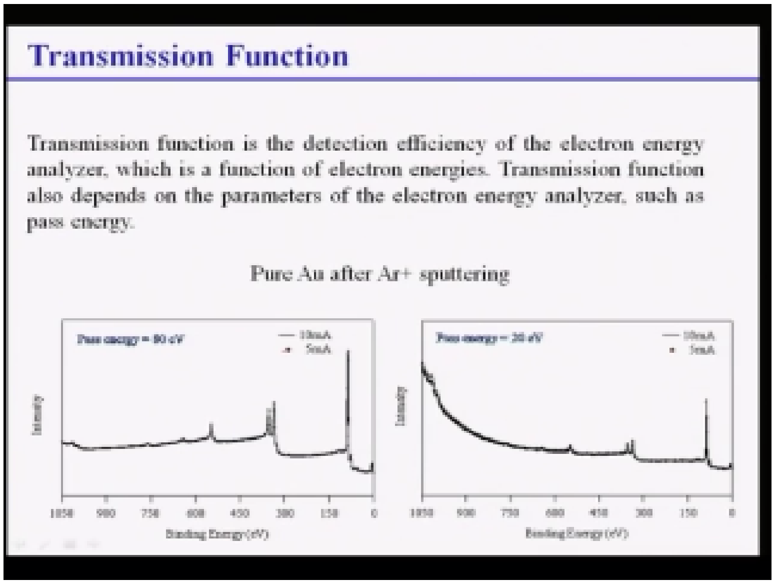

Transmission Function

Transmission function is the detection efficiency of the electron energy analyzer, which is a function of electron energies. Transmission function also depends on the parameters of the electron energy analyzer, such as pass energy.

Pure Au after Ar+ sputtering

Second important thing which you learn is to consider for measurements of this quantum measurement is called transmission function which is basically due to the digital efficiency so this is nothing but detection efficiency of an electron energy analyzer which is function of electron energy tangent function depends on parameters of the electron energy analyzer such as pass energy to give you an idea.

If I pass energy of 8 electron 8electron volts and this is the you know the energies of the beam current and this is done for gold after sputtering as you see the peak, peak height here is this much but when you have a person energy of 20 electron moles peak height is this punch so that means the peak height are the Arian a peaks get affected by the pass energy pass energy basically the energy which is used in the detector to energize is to get to the electrons can be detected very easily.

So this is what is basically dependent on the machine so but you must have a knowledge about that normally sorry you know fixed quantity for a particular setup but one must know what is passion and see how it is going to control to get a good peak position peak of that.

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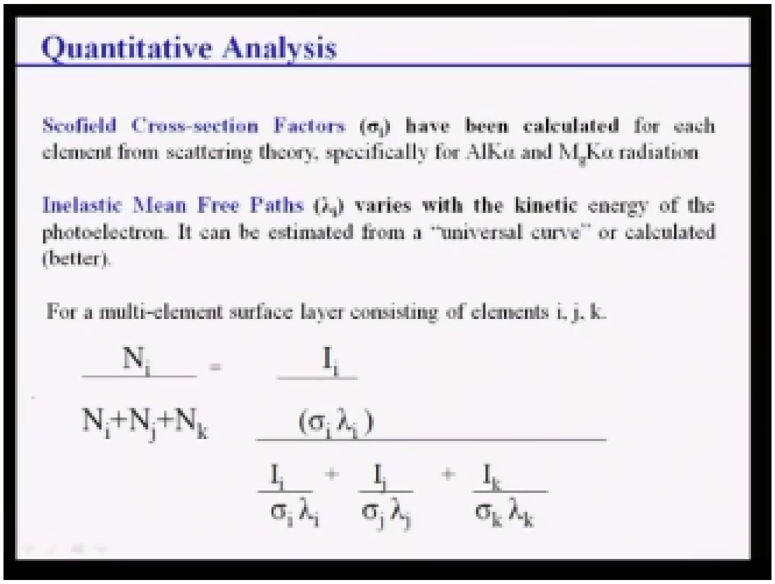

Quantitative Analysis

Scofield Cross-section Factors (σ_i) **have been calculated** for each element from scattering theory, specifically for AlKα and M$_g$Kα radiation

Inelastic Mean Free Paths (λ_i) **varies with the kinetic** energy of the photoelectron. It can be estimated from a "universal curve" or calculated (better).

For a multi-element surface layer consisting of elements i, j, k.

$$\frac{N_i}{N_i+N_j+N_k} = \frac{\dfrac{I_i}{(\sigma_i \lambda_i)}}{\dfrac{I_i}{\sigma_i \lambda_i} + \dfrac{I_j}{\sigma_j \lambda_j} + \dfrac{I_k}{\sigma_k \lambda_k}}$$

Now what is Scofield cross section factor eight this can be calculated for each element from scattering theory basically for you know basically for aluminum and magnesium calliphoridae shin and similarly λ I is varies with the kinetic energy of a photo electron it can be also estimated for universal cap which I have told you Universal curve is this one.

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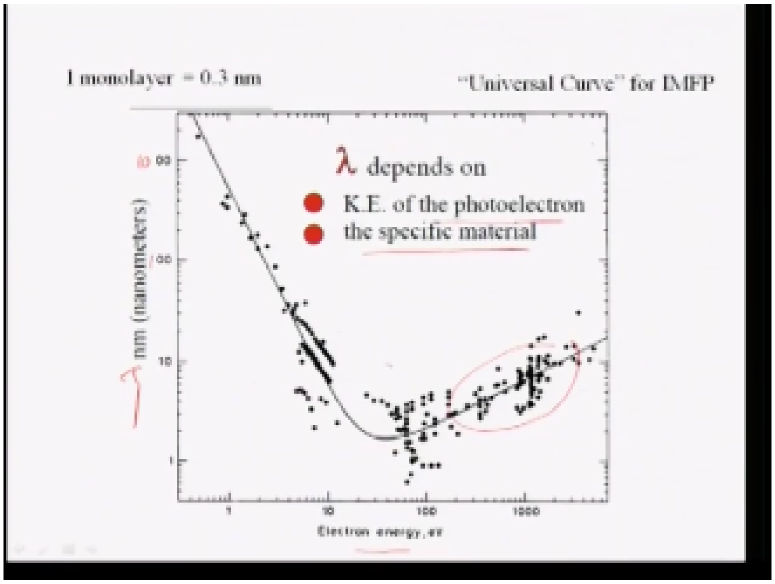

1 monolayer = 0.3 nm

"Universal Curve" for IMFP

λ depends on

- ● K.E. of the photoelectron
- ● the specific material

This is the one this is λ this can be used to calculate all the λ of different elements okay so for a multi-element system Sabella which is normally the case this is we can write down the constants of element ni / ni + NJ + KR j IJ k are three elements so this is how it is done I I i / σ I / λ divided by this is the whole thing the whole divided by this one this is for I this is for Jay this is perky as you see that the factor which comes with capital K has nullified because of the ratio taking so that is so actually done so I can also calculate in J now in Jays NJ / ni + n j + NK similarly in k can be calculated.

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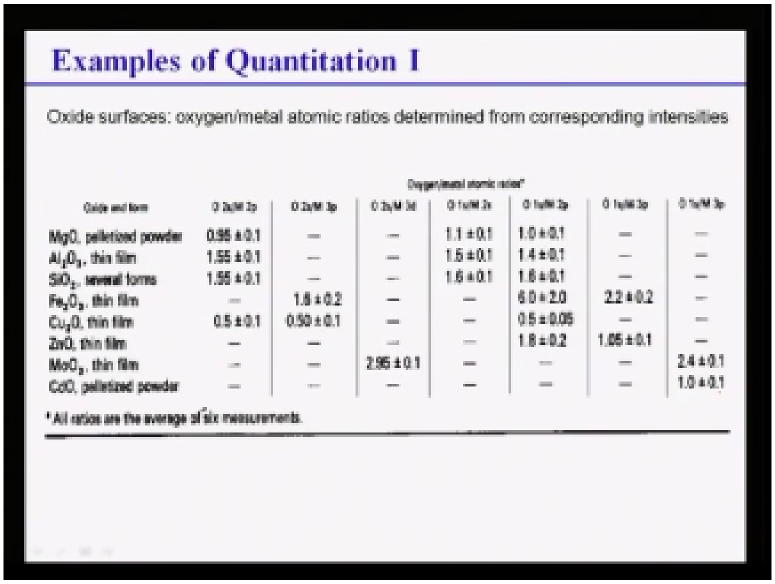

Examples of Quantitation I

Oxide surfaces: oxygen/metal atomic ratios determined from corresponding intensities

Oxide and form	Oxygen/metal atomic ratios* O 2s/M 2p	O 2s/M 3p	O 2s/M 3d	O 1s/M 2s	O 1s/M 2p	O 1s/M 3p	O 1s/M 3p
MgO, pelletized powder	0.95 ± 0.1	—	—	1.1 ± 0.1	1.0 ± 0.1	—	—
Al_2O_3, thin film	1.55 ± 0.1	—	—	1.5 ± 0.1	1.4 ± 0.1	—	—
SiO_2, several forms	1.55 ± 0.1	—	—	1.6 ± 0.1	1.6 ± 0.1	—	—
Fe_2O_3, thin film	—	1.8 ± 0.2	—	—	6.0 ± 2.0	2.2 ± 0.2	—
Cu_2O, thin film	0.5 ± 0.1	0.50 ± 0.1	—	—	0.5 ± 0.05	—	—
ZnO, thin film	—	—	—	—	1.8 ± 0.2	1.05 ± 0.1	—
MoO_3, thin film	—	—	2.95 ± 0.1	—	—	—	2.4 ± 0.1
CdO, pelletized powder	—	—	—	—	—	—	1.0 ± 0.1

* All ratios are the average of six measurements.

Let us see how these are done some examples for oxide surface that is oxygen metal atomic ratios determined for cosmonaut densities MGO palletized 10 shots by metal is basically mg, mg here to pee ratio is this month +- 10 process she okay now all 2 o 3 is also like that Si O to calculate it is you too these are the different and oxygen atoms oxygen energy levels / metal and the levels issues so these are the measurements actually tells us how quantitatively intensities can be correlated.

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Ram Chandra
Dilip Tripathi
Padam Shukla
Manoj Shrivastava
Sanjay Mishra

Editing
Ashish Singh
Badal Pradhan
Tapobrata Das

Shubham Rawat
Shikha Gupta
Pradeep Kumar
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Aradhana Singh
Sweta
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Production Crew
Bhadra Rao
Puneet Kumar Bajpai
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Office
Lalty Dutta
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Bharat Lal

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