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NP-TEL
National Programme
On
Technology Enhance Learning

Course Title
Advanced Characterization Techniques

Lecture-21

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So we have been discussing about quantitative analysis using XPS.

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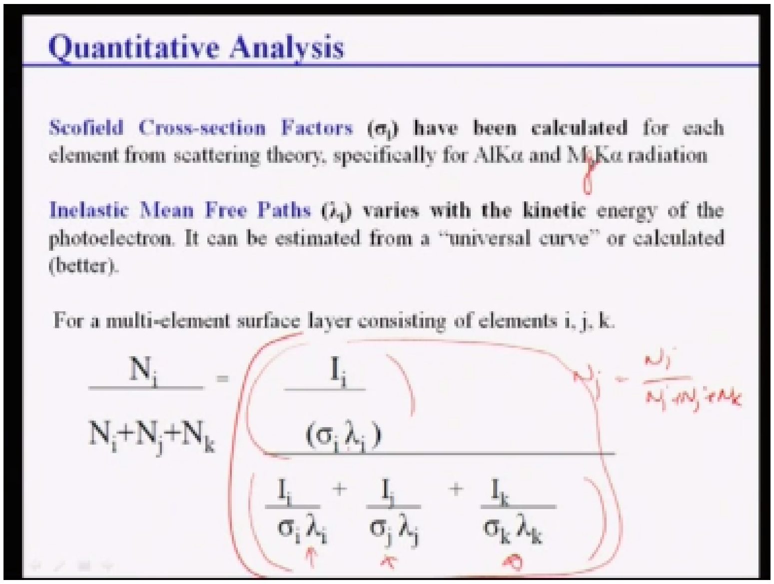

Quantitative Analysis

Scofield Cross-section Factors (σ_i) have been calculated for each element from scattering theory, specifically for AlKα and MgKα 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.

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

$$N_j = \frac{N_j}{N_i+N_j+N_k}$$

Quantity of analysis is very popular in XPS in the sense that we can obtain very high quality informations and I have already discussed you about the way quantitative analysis is done basically when you have multiple elements on the surface layer of an material and if this elements can be represented by I j and k then i can write down the ratio of n I / n i+ NJ + n k =

this expression which I have written here basically it is if we look at it properly it is in ratio of I divided by σ λ for the Pacific element / the ratio of the same edition of the ratios of all.

The elements and the by this way ,we can measure the basically the particular element concentration in the surface layer so what is needed to be measured is the intensity and I have already told you how intensities are to a measure using very nice approach but let us see some of the examples.

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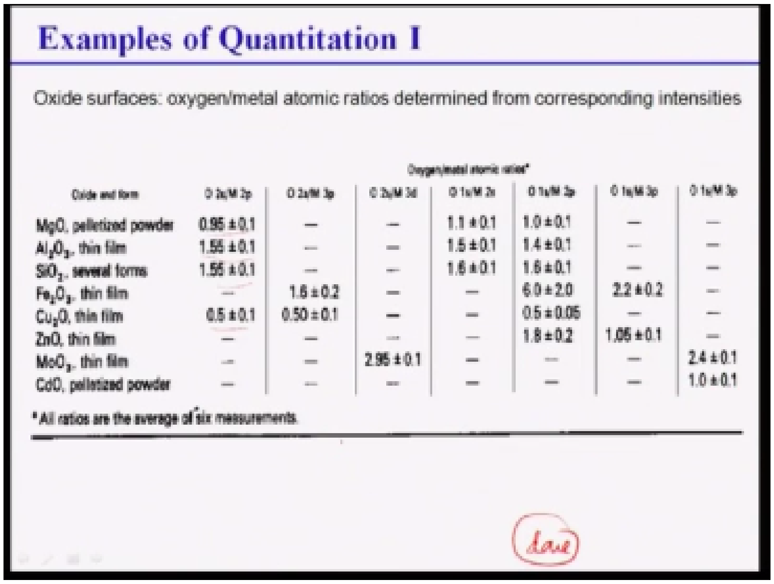

Examples of Quantitation I

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

	Oxygen/metal atomic ratios*						
Oxide and form	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	—	1.6 ± 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.

I am going to show you the examples of oxygen metal atomy ratios determine form from the corresponding intensities if you take magnesium oxide first case MGO so it is a pelletized powder ratio between oxygen to a speak / oxygen in a metal 2p peak is the concentration is almost 0 . 95 +- 1 as you know 10% is the approximate error in case of these quantifications and obviously oxygen 1 s / module 2 s balance - m to acs equally almost like 1.1 +- . 1 similarly oxygen 1/ by metal to PS 1 +-. 1 and we can keep on doing this for aluminum oxide l23.

Thin claims slip the silicon dioxide fe2o3 you too jarring oxide, dioxide trioxide and carbon oxide and these issues are actually average of six measurements and this is a very reliable so one can actually obtain from the ratios exact you know oxygen to model a Mo ratios for the particular oxide.

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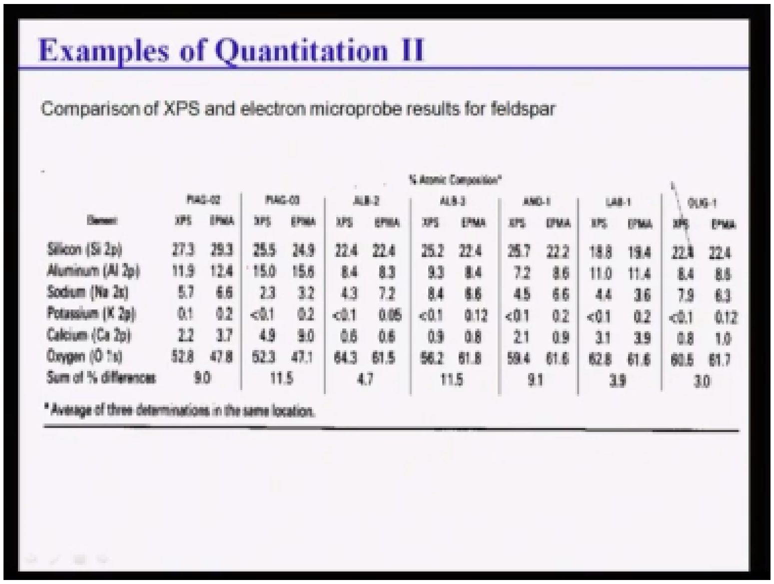

Examples of Quantitation II

Comparison of XPS and electron microprobe results for feldspar

	% Atomic Composition*													
	PLAG-02		PLAG-03		ALB-2		ALB-3		AND-1		LAB-1		OLIG-1	
Element	XPS	EPMA	XPS	EPMA	XPS	EPMA	XPS	EPMA	XPS	EPMA	XPS	EPMA	XPS	EPMA
Silicon (Si 2p)	27.3	29.3	25.5	24.9	22.4	22.4	25.2	22.4	25.7	22.2	18.8	19.4	22.8	22.4
Aluminum (Al 2p)	11.9	12.4	15.0	15.6	8.4	8.3	9.3	8.4	7.2	8.6	11.0	11.4	8.4	8.8
Sodium (Na 2s)	5.7	6.6	2.3	3.2	4.3	7.2	8.4	8.6	4.5	6.6	4.4	3.6	7.9	6.3
Potassium (K 2p)	0.1	0.2	<0.1	0.2	<0.1	0.05	<0.1	0.12	<0.1	0.2	<0.1	0.2	<0.1	0.12
Calcium (Ca 2p)	2.2	3.7	4.9	9.0	0.6	0.6	0.9	0.8	2.1	0.9	3.1	3.9	0.8	1.0
Oxygen (O 1s)	52.8	47.8	52.3	47.1	64.3	61.5	56.2	61.8	59.4	61.6	62.8	61.6	60.5	61.7
Sum of % differences	9.0		11.5		4.7		11.5		9.1		3.9		3.0	

*Average of three determinations in the same location.

If you compare this experience measured quantities respect to the electron microprobe things will be much clearer to you let us talk about silicon and this is silicon 2p so that means it is basically silicone dioxide so XPS gives you 27.3 percentage whether electron microprobe gives you 29.3 just differ by 2p percentage in different you know wavelengths this is an aluminum you know lab different kind of careers so you can see the values they are very close by not differing much similarly for calcium potassium sodium aluminum.

And if you look at some of the passage of the difference is nine percent here is about 11% there it is maximum actually 11.5 % so that means experience gives you reasonably good data in terms of compositions although electron microprobe is better but. I know electron microprobe uses of electron microprobe is not easy in the sample has not prepared properly and also electron microprobe analysis requires standards which is not the required for XPS but that is why experience is easier but cost of the instrument for the express is much higher.
Than the electron probe so that is some advantage let us talk about errors.

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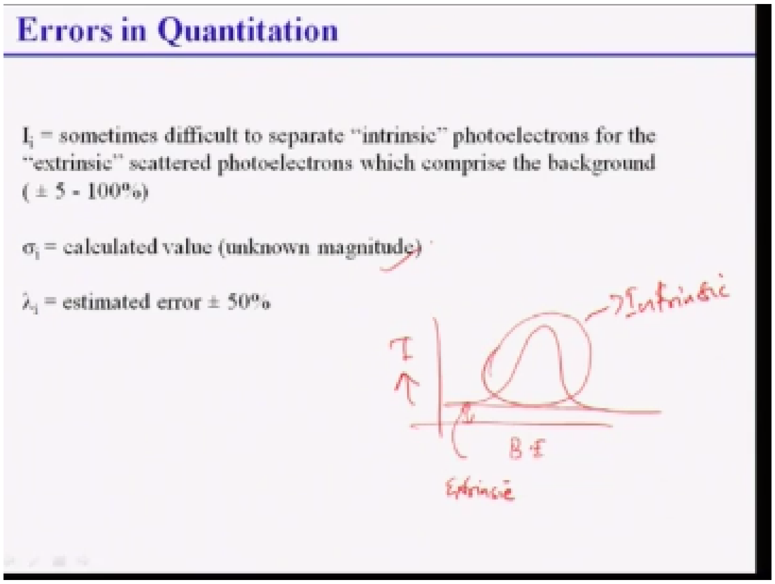

Errors in Quantitation

I_i = sometimes difficult to separate "intrinsic" photoelectrons for the "extrinsic" scattered photoelectrons which comprise the background (± 5 - 100%)

σ_i = calculated value (unknown magnitude)

λ_i = estimated error ± 50%

As I said error is approximately 10% so, I basically the error comes upon the intensity measurements so what is the problem there this is basically difficult to separate the intrinsic photoelectrons for the extrinsic scatter photoelectrons which comprise the background that means there are extensive photoelectrons which forms a background of the XPS intensity versus you know this binding as a peak so that means there is a background and so this background basically comes from the extrinsic photoelectrons exchange sick.

Whether the intensity peak comes from in intrinsic photoelectron the basic problem is to differentiate between them that means basic problem is lies in fitting the background properly because in density calculation will depend upon how you remove the background and that is why actually error tips in and this error can be approximated to be over +-5 % 5 to 10 % second important can be coming from the σ I which is normally calculated from upon this plot which have shown you and thus then there is basically meant error of magnitude is unknown most purchases lastly error can come from the λ. I estimated error and I have already shown you how λ is calculated.

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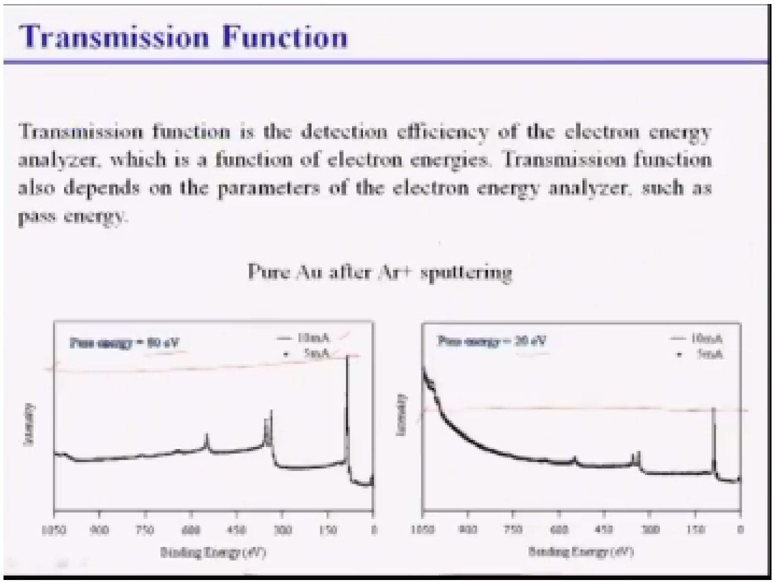

Transmission Function

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

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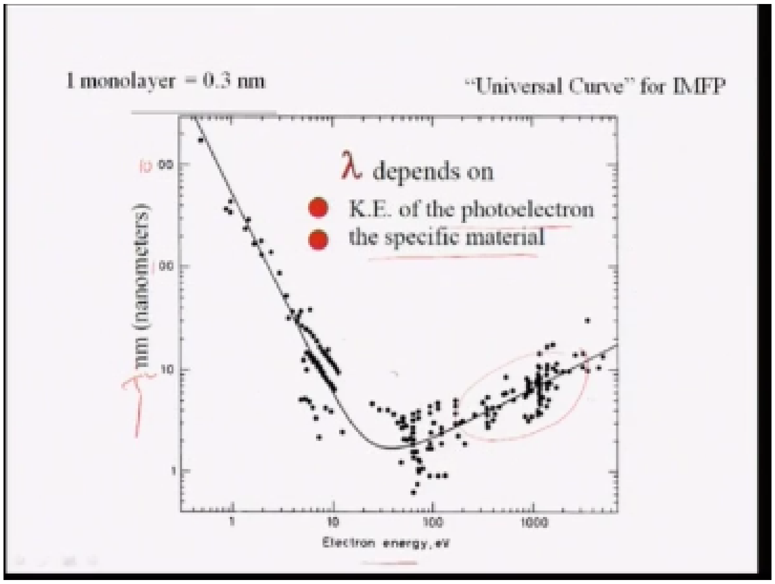

1 monolayer = 0.3 nm

"Universal Curve" for IMFP

λ depends on

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

Let me go back yeah this other λ I calculated this is the master plot a new versa curve and obviously measuring this λ is if there is a small error and then it can lead to error in calculation of the compositions but most importantly this is you need to take care very well otherwise error can be high σ is normally error is unknown mind to do so we cannot really predict λ I can be calculated precisely estimate it very precisely so there is no problem there well after giving you some idea about the quantification let me just talk about some other very important issues of XPS.

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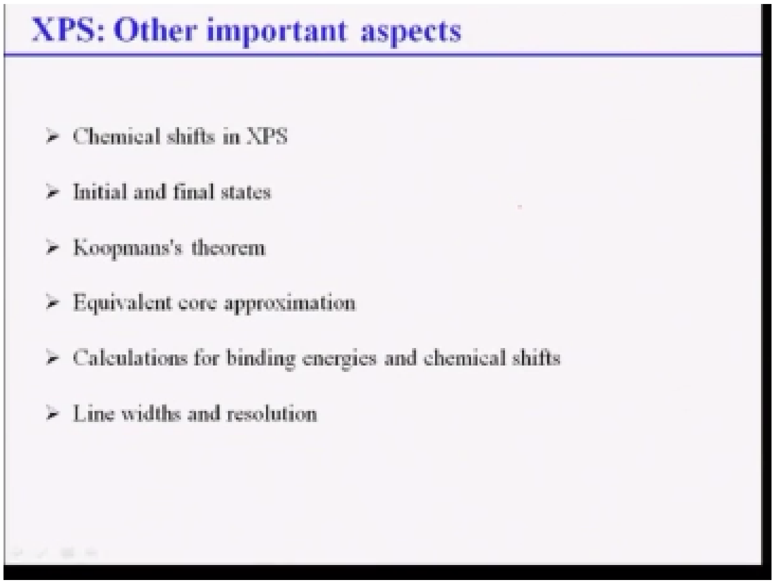

XPS: Other important aspects

- Chemical shifts in XPS
- Initial and final states
- Koopmans's theorem
- Equivalent core approximation
- Calculations for binding energies and chemical shifts
- Line widths and resolution

Most important one is obviously chemical shift in XPS that is why this particular technique is famous for chemical shift means the chemical change of electronic state or a chemical state you can define when something is some metal is reacting with some oxygen nitrogen or what are other elements together then obviously we needs to we can also find out when some reaction is going on whether initial state and final state and we also need to discuss about Koopmans's theorem which is very good.

In analyzing this chemical shift and we can calculate actually this chemical shift using formula finally obviously one is to know the line width resolution for a particular expression instruments so let me first discuss my chemical shift.

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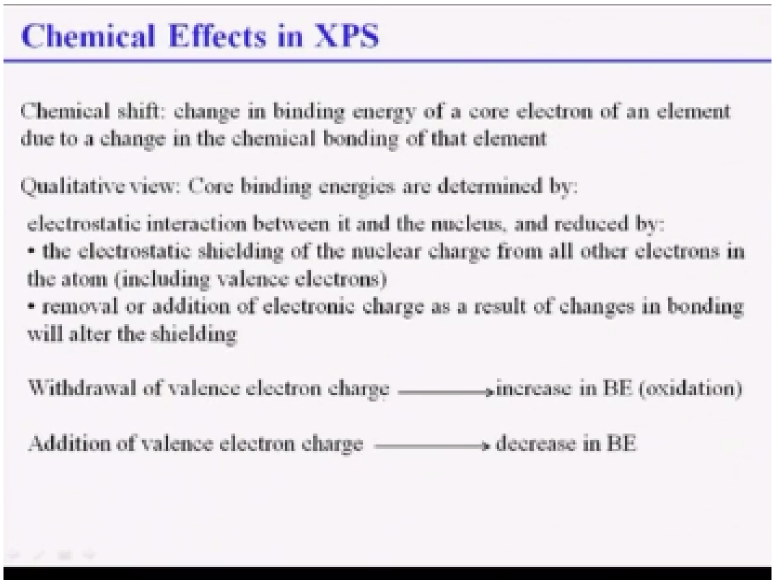

Chemical Effects in XPS

Chemical shift: change in binding energy of a core electron of an element due to a change in the chemical bonding of that element

Qualitative view: Core binding energies are determined by:

electrostatic interaction between it and the nucleus, and reduced by:
- the electrostatic shielding of the nuclear charge from all other electrons in the atom (including valence electrons)
- removal or addition of electronic charge as a result of changes in bonding will alter the shielding

Withdrawal of valence electron charge → increase in BE (oxidation)

Addition of valence electron charge → decrease in BE

Which is very important from the space point of view what is the chemical shift actually chemical shift means change in a binding energy of a core electron of any element T to change the chemical bonding of that element that means when there is bonding between two elements that is going to be changed or the binding energies of the core electrons and this leads to shifting of the peak position in the x-ray spectrum I hope this is clear.

I will make it clear by giving some examples also what it is the quality review of this quality of these coal mining areas are normally determined by what electrostatic interaction or combing interaction between the electrons and the nucleus as you know the nucleus a positively charged species electrons are negatively charged species so there is an columbic interaction between these two so this interaction is what is basically leading to the core binding energies now this can be affected or reduced rather by two things one the electrostatic stealing of the nucleus charge from other electrons present.

In the atom that you know if there are other electron beam the atoms that can act a shielding then here between the core electron and the nucleus secondly, there is the first factor and there is a predominant factor second factory the removal or addition of the electronics charge as a result of change in the bonding that will also alter the shielding actually so that means first one is a shielding of the nuclear charge second one is the removable edition of the electronic charge because of the bonding that can also alter the shielding yes as an extra electron comes that can alter the shielding.

So these two actually are the inner code binding energies actually depending on these two factors so whenever we add an electron or remove an electron from the core shells of the atom there is going to be change of the union charge or change of the binding energies so this means if you have we develop electronics charge that is a increase in the binding energy and this is also obviously known as oxidation if you take out some electron out of a species it is called oxidation and if you iron valence electron charge into it is called it specifically need.

To decrease in bending and this is nothing but read action okay, this is basically can be taught in this way suppose you take a sodium and the chlorine we know the sodium and chlorine reacts and form sodium chloride which is a common salt now how the reaction happens you know very well should ,I am actually gives away one electron from the outer shell and this same electronic accepted by the chlorine and this process sodium become + charge and to become negative charge and then these two oppositely charged pics .

I get attracted because with coulomb interaction and forms a bond in this process both the binding energy of sodium and all the binding energy of the binding on two electron the sodium and binding energy of the electron the chlorine gets affected and the cause of these issues we are going to see a chemical shift, I hope, I am made you understand clear now let me give an example in that way let us talk about Madeline oxide you know this we're talking about materials engineering so it's better talk of metal monoxide .

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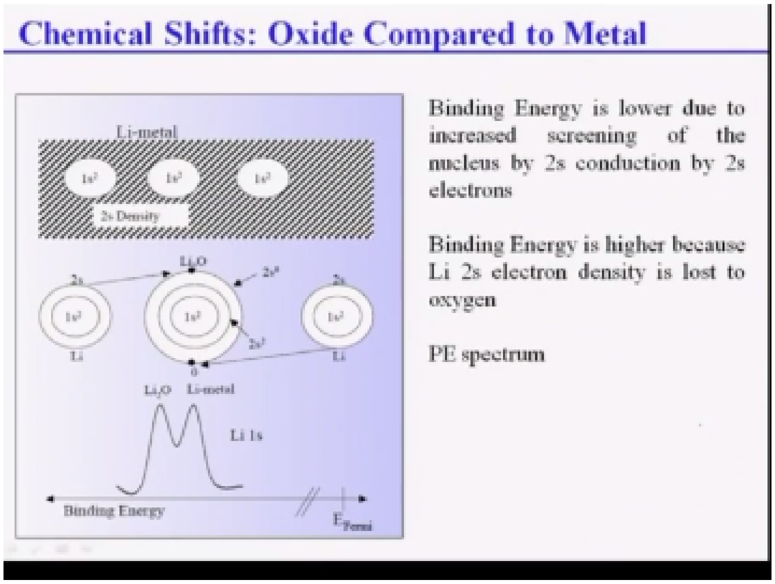

Chemical Shifts: Oxide Compared to Metal

Binding Energy is lower due to increased screening of the nucleus by 2s conduction by 2s electrons

Binding Energy is higher because Li 2s electron density is lost to oxygen

PE spectrum

Let us talk about a simplest possible metallurgist the lithium we has three electrons in its outer cell there are two electrons the one is orbit and that is one is two and one electrons in the two years of it so basically 1 s 2 to s 1 now that means what if we look at the electron density the 1 s to 1 s to the two electrons then three electrons so if ,I basically have a plot of intensity versus bond energy you will see this speak for lithium 1s right now what happens when lithium gets oxidized lithium this oxidized it forms li 2 0 that means two electrons comes from the two lithium charges are two item actually gives a one electron each.

To the oxygen atom so the oxygen become doubly negatively charged and two lithium ions become singly positively charged and that is so actually the these two opposites attract and form zip compound now what is the structure of a lie to coastal as one is 2 then 2 s 2 and 2 s 6 okay, so two s6 basically for the oxygen as you know there is no six electrons nor 2s but because you have added to it you know for two electrons in oxygen so there are oxygen has four electrons in a two-piece we are two electrons outer cell.

So the four electrons four + to become six so that leads to change in the binding energy of the co electron of the lithium so that means lithium binding energies gets shifted to the left side and we start saying lowering of the binding energies and this is due to its increased killing of the nucleus by 2's conduction electrons the buying energy higher because Li 2's electricity is lost to the oxygen because basically bending and the increases this way not dot if you increase this way this is a Fermi surface energy so binding energy is basically higher because Li 2 s electrons to s electrons are here there is only one to a select on there are 1 2 is to 1 is 2 electrons level and two is one electron to wait level so because these two a single electrons density is lost so there is change in the ceiling of the electrons and this leads. To change in the binding axis correct.

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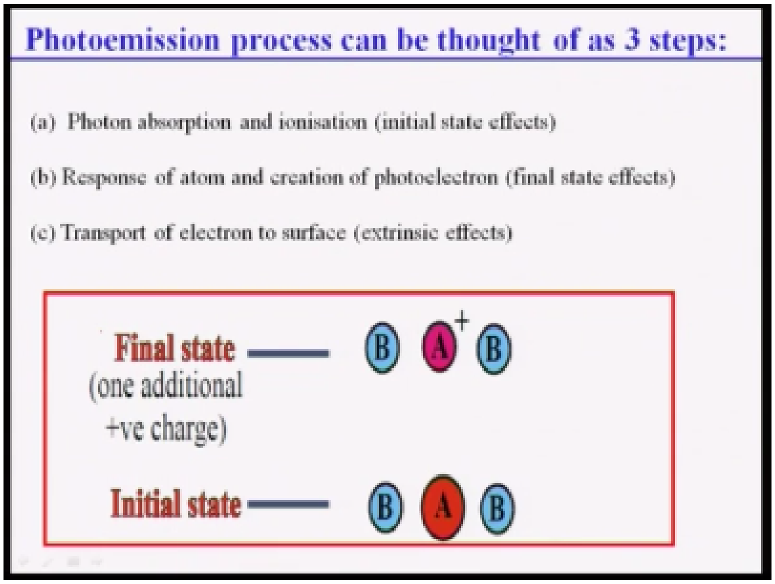

Photoemission process can be thought of as 3 steps:

(a) Photon absorption and ionisation (initial state effects)

(b) Response of atom and creation of photoelectron (final state effects)

(c) Transport of electron to surface (extrinsic effects)

Final state (one additional +ve charge)

Initial state

So this can be taught in different little bit different way because the photoemission actually can be thought of consisting of three tips steps first is the photon absorption that means except photon comes it get absorbed then this leads to ionization that means when, I will get absorbed at the electron gets ejected at least ionization this is called initial state effects second k second thing is response of the atoms in the case of the photoelectron that means ionization has happened how electro has got removed that is why this will happen and this leads.

To increase in a photoelectron, I understand the photoelectron comes out with extra mechanical energy now third step can be thought of transport of these photoelectrons in the surface and this is what is in the extreme Sigh effect this is doesn't depend on the you know particular atomic pcs it depends on the surface layer thickness and many other aspects so first is this absorption XXL photon get absorbed and this is causes an additional material ionization means removal of the electron from the outer set up on the ionization rather and this leads to in a second step the photoelectron generation and then photoelectron moves so therefore finance tell is one additional positive negative positive charge initially stated bab and then you have a positive charge attached because of this ionization .

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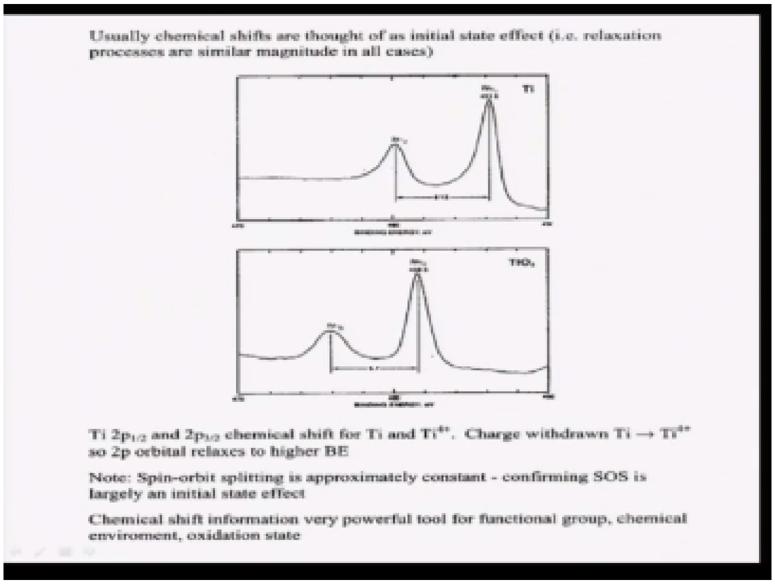

Usually chemical shifts are thought of as initial state effect (i.e. relaxation processes are similar magnitude in all cases)

Ti $2p_{1/2}$ and $2p_{3/2}$ chemical shift for Ti and Ti^{4+}. Charge withdrawn Ti → Ti^{4+} so 2p orbital relaxes to higher BE

Note: Spin-orbit splitting is approximately constant - confirming SOS is largely an initial state effect

Chemical shift information very powerful tool for functional group, chemical enviroment, oxidation state

It usually chemical shifts are thought of as initial state effects initial state means ionization as you see here it is state effect state effects relaxations basically is a nothing relaxation process you will add to any other election process in this case I don't know that you can see this is a titanium this is a titanium dioxide titanium has 2 p 3 x 1 x 2 this is 2 p 1 / 2 and this is comes around 460 by 8 electron / binding energy and this is 2 p 3 ./ 2 this is which is basically thinner about a splitting of the two peaks and this comes around 453.

So difference between these two is actually 675 660 7.5 something like that so the chemical shift for TI and TI for basically charged with when they say ti ti P t io2 well yeah let us see what happens in there when this is I am this is 66 6.75 so this is 6.75 electro ball now if I for M tio2 basically. I have a change in the state electronic state of titanium from TI 0 to pi/4 + so the ti 2p ½ this is 2p ½ and this is di 2 p 3 / 2 you see the distance between these two has reduced to 5.7 electron volt so that means binding energies are the other the thin orbital splitting of these two P levels p 2 and ½ and p2 both you and ½ as reduced so the spin or less spitting approximately you know constant not confirming it says let us say chemicals information very powerful tool for functional group and oxidation states.

So you know this is basically can be thought of and relaxation process which is basically due to ionization of the initial step now what is now.

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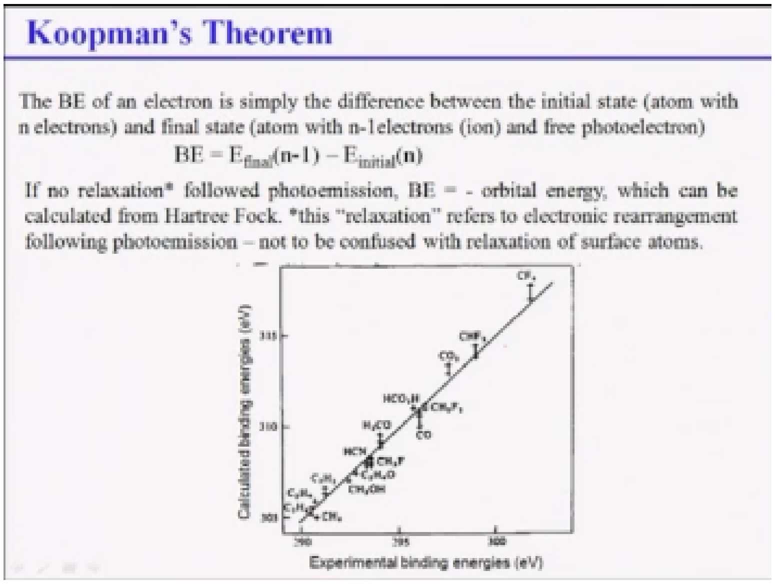

Koopman's Theorem

The BE of an electron is simply the difference between the initial state (atom with n electrons) and final state (atom with n-1electrons (ion) and free photoelectron)

$$BE = E_{final}(n-1) - E_{initial}(n)$$

If no relaxation* followed photoemission, BE = - orbital energy, which can be calculated from Hartree Fock. *this "relaxation" refers to electronic rearrangement following photoemission – not to be confused with relaxation of surface atoms.

Let us talk about what is a Koopmans's theorem after knowing the what is the chemical shift you know cumin serum says the binding energy of an electron is simply the difference between the initial state and the final step that means what is the initial state initial state is the atom within electrons and final state is atoms with n - electron may more than one who knows that is n - 1 electrons ions and + 3 electrons so that means in the initial state you have fully you know all the electrons are present in the whatever electron is defined by the atomic number of the element within the shell and the final state.

You have removed the electron because of the because of the you know charging because of the annotation effect so you have n - 1 electron writer suppose one has got removed and this extra electron will come as a free photoelectron so what is the binding energy change binding energy is basically n -1 / by initial n that is what is basically the equation which is used by Koopmans's so you have no relaxation followed photo mission there is no relaxation so binding is nothing but orbital energy which can be calculated from hat trick for theory which is available basically the plot of that this election is nothing but electron attachment following the photo emissions please do not get countries to use relaxation of a surface atoms.

Now if I plot exponential binding energies with the calculated binding energies like this if you if you look at carefully this char they fall on a straight line almost passing to the origin so this is CH 4 CH 22 h 6 and 0 c 2 h four different kinds of organic compounds up to CCF for so one can actually see the experimental binding energies and the and the capital demand they are same so that means coupons theory predicts what is to be estimated or calculated based on this theory and then measure so this is true.

So please try to remember this equation when there is a notation this is how we can calculate here we have not considered that 3 electron we thought this is not any effect because of a relaxation.

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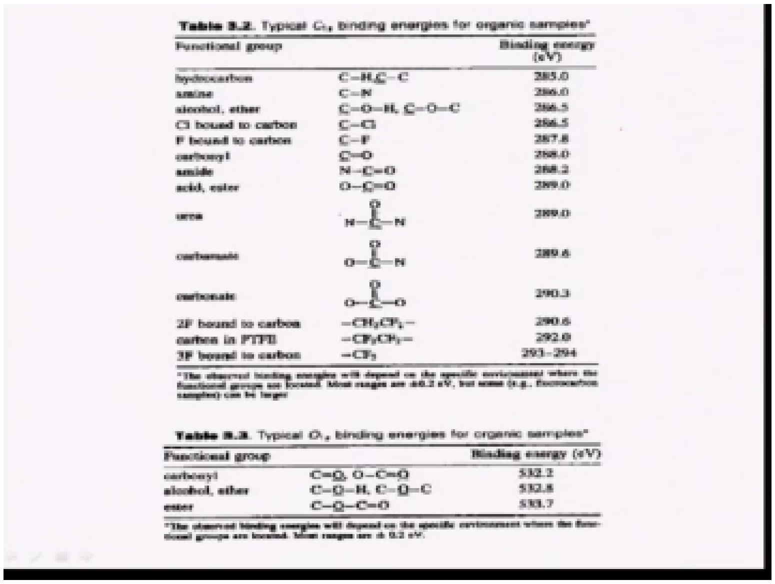

Table 8.2. Typical C_{1s} binding energies for organic samples*

Functional group		Binding energy (eV)
hydrocarbon	$C-H, \underline{C}-C$	285.0
amine	$\underline{C}-N$	286.0
alcohol, ether	$\underline{C}-O-H, \underline{C}-O-C$	286.5
Cl bound to carbon	$\underline{C}-Cl$	286.5
F bound to carbon	$\underline{C}-F$	287.8
carbonyl	$\underline{C}=O$	288.0
amide	$N-\underline{C}=O$	288.2
acid, ester	$O-\underline{C}=O$	289.0
urea	$N-\underline{C}(=O)-N$	289.0
carbamate	$O-\underline{C}(=O)-N$	289.6
carbonate	$O-\underline{C}(=O)-O$	290.3
2F bound to carbon	$-CH_2CF_2-$	290.6
carbon in PTFE	$-CF_2CF_2-$	292.0
3F bound to carbon	$-CF_3$	293–294

*The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ±0.2 eV, but some (e.g. fluorocarbon samples) can be larger.

Table 8.3. Typical O_{1s} binding energies for organic samples*

Functional group		Binding energy (eV)
carbonyl	$C=\underline{O}, O-C=\underline{O}$	532.2
alcohol, ether	$C-\underline{O}-H, C-\underline{O}-C$	532.8
ester	$C-\underline{O}-C=O$	533.7

*The observed binding energies will depend on the specific environment where the functional groups are located. Most ranges are ± 0.2 eV.

These are the only if different values typical chemical see one is values and these are taken from those books as you see here for harder carbon that is CH CC bond okay, it is finding as is 285 a mines this seek nitrogen 26 alcohols has C-O-H of C-OC both possible to 86.5 electron volts flew into carbon is very important 26 / 1.8 carbon and says basically C-0 N-C Double 02 e 892 89.6 RC f 33 more thick full item 12 carbon is 293 to 294 that is this is a very generic table available in the literature most values are actually +-. 2 electron role.

That is why this measurement says focus of oxygen binding energy specifically up or look at carbon y l groups see double O of C double o 532 alcohols a 35-32 star CA 533. So if one can actually measure this is kind of binding energies using XPS well we can actually explain this chemical shift as I said chemicals is very important using charged sphere model is not very difficult to do.

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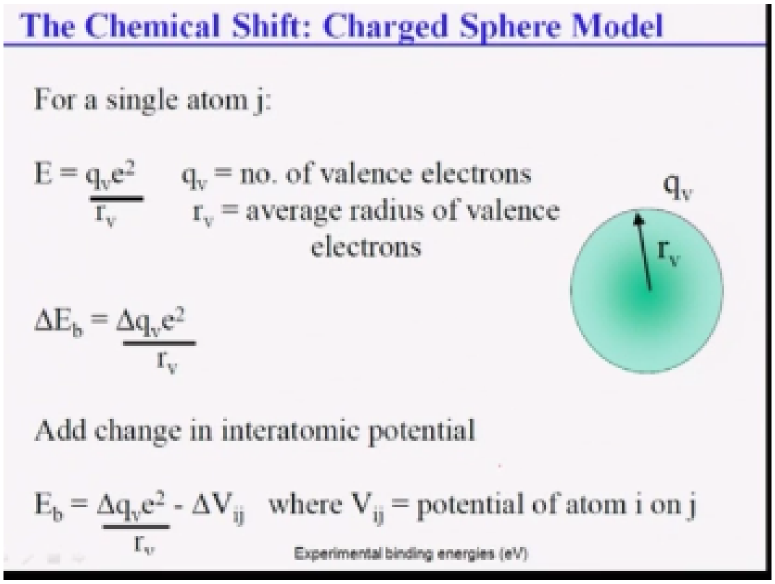

The Chemical Shift: Charged Sphere Model

For a single atom j:

$E = \frac{q_v e^2}{r_v}$

q_v = no. of valence electrons

r_v = average radius of valence electrons

$\Delta E_b = \frac{\Delta q_v e^2}{r_v}$

Add change in interatomic potential

$E_b = \frac{\Delta q_v e^2}{r_v} - \Delta V_{ij}$ where V_{ij} = potential of atom i on j

Experimental binding energies (eV)

For a single atom suppose which has certain number of electrons the electrostatic potential is basically given by Coulomb's law QB ,QB is the you know number of Q charges into electron $^{2/}$ RV armies the distance away the radius of valence electrons q is the number of electrons and always respond so change in the binding energies is obviously change in the average number of electrons is nothing no effect of these two they do not get changed so if I add the change in the inter-atomic potential because of this change in the binding energies then EV becomes VJ - and then this is the plats quantity Δ q v square algae as you see here .

So is the potential of the atom I on JY that means when suppose in B and Cl so if Na gets 1electron removed so because of that is a change in a binding energy now when this Na +charge and this electron is taken by 2n it comes close to crowing that is a potential change so one needs to basically use this Δ v IJ along with the change the binding energies to calculate the exact binding energy of this sodium iron in neighborhood of the chlorine iron that is what actually is calculated to in this model. Now to give you some more examples of chemical shifts that is what makes your understanding clear.

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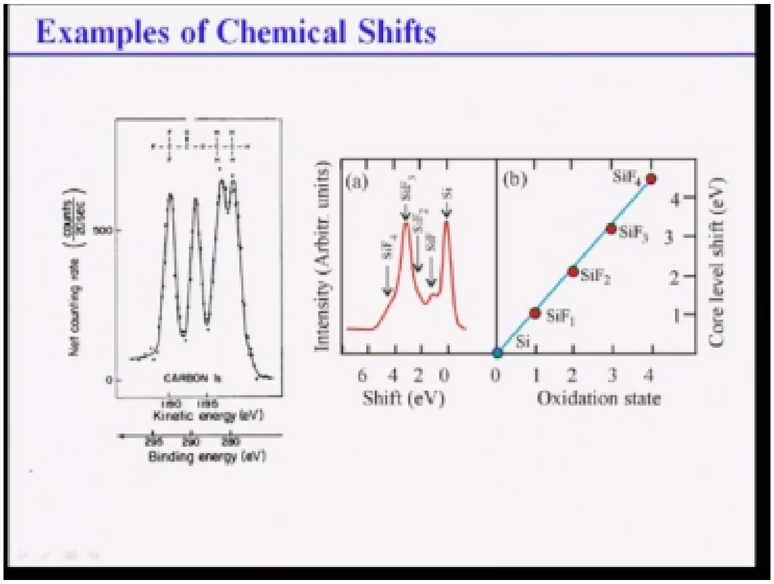

Examples of Chemical Shifts

Let us suppose carbon 1s in this compound C-O-H I do not exactly remember this is a three-floor in groups one carbonyl group and then there are C-H bonds so carbon one is if you look at it this is this is the typical you know spitting and these are the two this s and 2′. I think so carbon speak actually has this kind of shapes now if I look at the silicon as pure silicon is here so as you see this is close to almost zero and silicon f IF ,IF to SI f three SI f 4 so as you keep on you know having more and more fluid ions attached to silicon from one to four the chemical shifts it increases.

So by this way actually one can determine what is the exact state of the atom so if I fought the oxidation state vs core electrons shift silicon has no oxidation state 0 silicon f1 has one oxygen state + 12 14 electron shift SI f 22 SI f 33 SI f 4 is little bit higher for so that means there is a linear relationship between oxygen state. And the core level electrons secondly like the example I am giving a metal like oxygen metallic iron with fe2o3 hematite.

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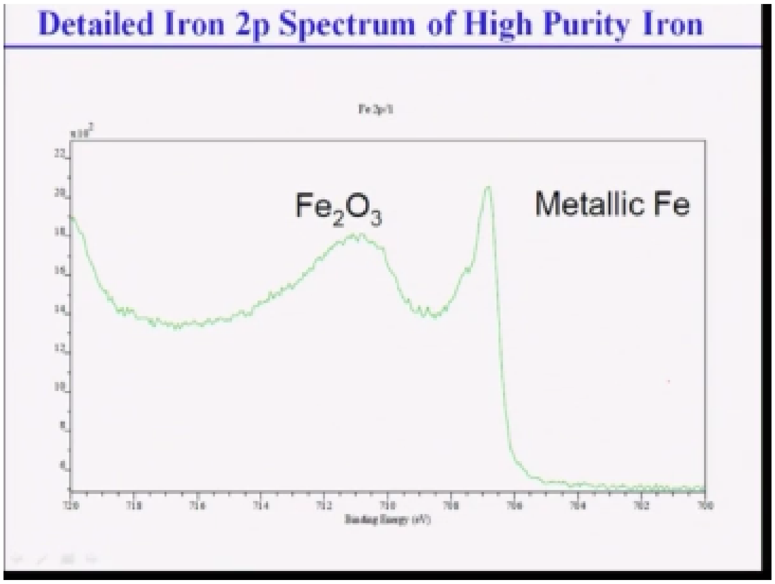

Detailed Iron 2p Spectrum of High Purity Iron

What you are showing is a p21 / ½ to p1 / ½ as you see metallic iron has binding energies of around 707 well iron oxide is broad peak like this and binding energies of the peak is about 711 so that means there is a change in the shift towards higher energies as we have pole already for metallic iron to the iron oxide let us see an example so in order to give you a F 2 or 3 and fe 2 o 3 basically what ap is three state + 3 + o is oxygen is +- 2.

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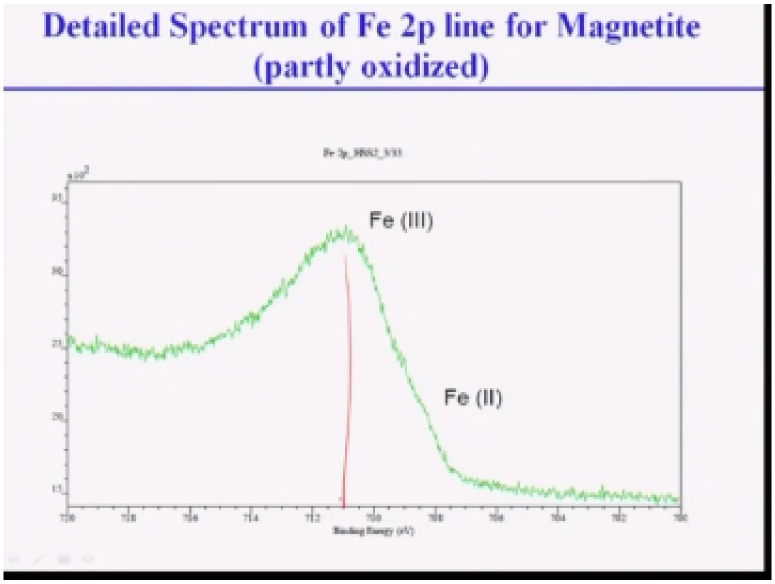

Detailed Spectrum of Fe 2p line for Magnetite (partly oxidized)

So if I look at this is what is a F this is a three if it you will come somewhere here you can see that small peak fe 2 comes actually in a few oxide iron oxide so that means we can actually clearly say there is no class two states all oxygen's are actually pass three state.

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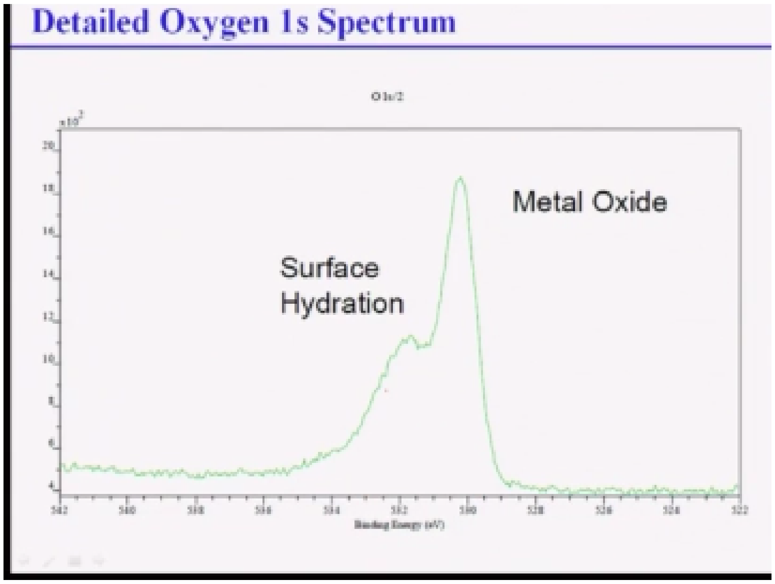

Detailed Oxygen 1s Spectrum

Let us talk about oxygen norm in case of oxide and surface hydration you have metal oxide this is oxygen s ½ so if you look at oxygen one is half if you look at this is the metal oxide. I do not remember what is the metal oxide but if the hydration happens on the surface is not oxidation but surface hydration the peak will come very close by this is 5 30 0 . 5 this is 5 32 x is that also can be interpreted out in XPS.

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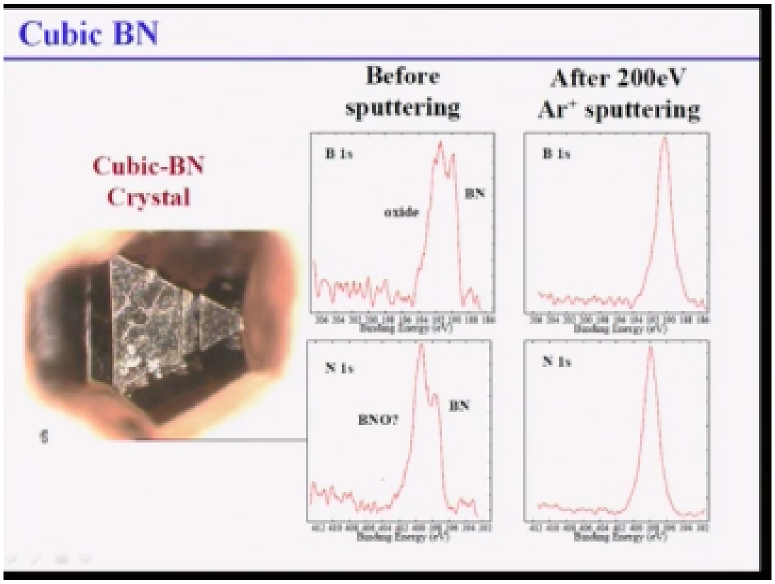
Cubic BN

It is cubic boron either is a very hard material which is used let us see what happens when you do the spectrum before. I earners the our guns plan sputtering and after hands pattering will be so both born one speaks you to see this is BN this is oxide before sputtering there will be some oxide obviously boron oxide but if you sputtered you clearly see only right quick that is why basically sputtering is used now if you do not spot a nitrogen happen I do not know one is this is BN this oxide so we do not know this is not a boron nitrogen oxide.

This is basically carbon oxide v 2 o 3 or something if we do the sputtering you skip to see only the be nitrogen peak corresponding to be n so that means this is very clear that shift of the coma of the of the or the chemical shift of the boron and nitrogen one is peak positions also function of even oxygen presence on a surface so that can lead this of oxide formation as in a pirate another example.

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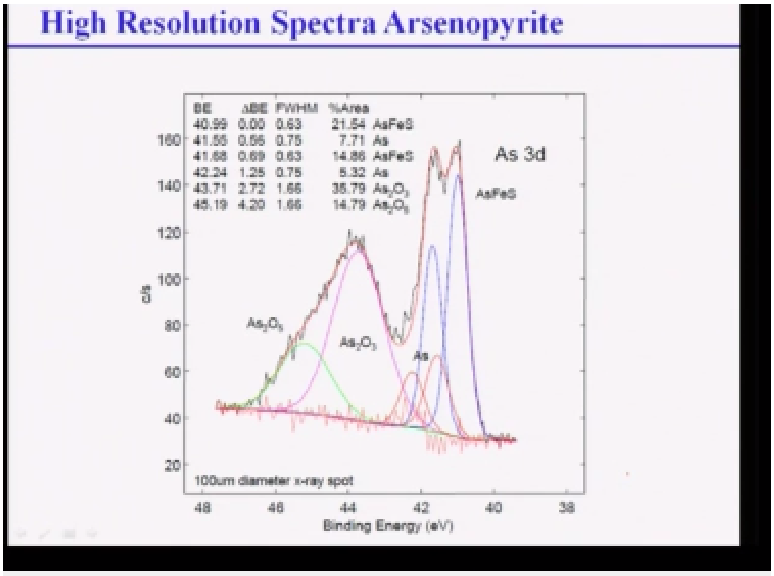

High Resolution Spectra Arsenopyrite

BE	ΔBE	FWHM	%Area	
40.99	0.00	0.63	21.54	AsFeS
41.55	0.56	0.75	7.71	As
41.68	0.69	0.63	14.86	AsFeS
42.24	1.25	0.75	5.32	As
43.71	2.72	1.66	35.79	As_2O_3
45.19	4.20	1.66	14.79	As_2O_5

If you look at arsenopyrite you have suppose a cynic iron of sulfide that is what is called arsenopyrite so this can be fitted actually this is done with 100 micron diameter x a spot and then we have also showing you our cynic oxide to oxygen state arsenic 203 and arsenic 205 here you see the two pics one is correspond arsenic as atom to iron and this is arsenic 3d actually not arsenic yeah, so you have basically splitting and this is distinctly different from these two so arsenic 02, 02, 03.

So that means in this sample actually have both arsenic sulfide arsenic iron sulfide as well as arsenic oxide 0302 as a h 2 o 3 both are put they are present.

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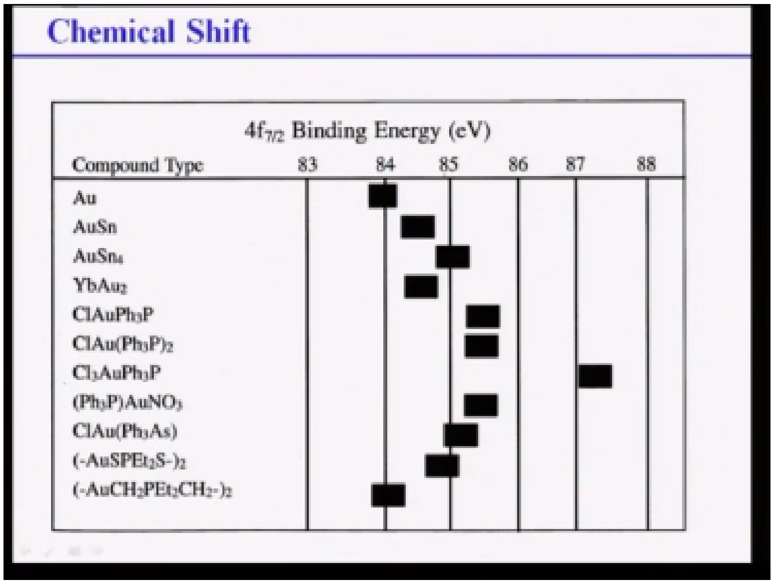

Chemical Shift

Now to not sell after giving all our examples, I just want to show you some in a chart where this can be you know chart. I only told this is basically for f 7 /2 binding energies of gold and some gold compounds shown from top to bottom goal actually has a binding edges of 84 if you have binding compound 2 atomic it is increases 84.5 Golden another compound s and 485 it TM gold what happens it will be am gold partum gold you two again sits very close to ASM ,RO phosphoric acid phosphoric is basically comes here 85.5 this is again same thing but three irons there is no change in this in the in the position.

Since you receive phosphoric acid phosphate group actually or on I tried this comes same place so this one decreases here these two a same three oxide change so phosphate group does not change the electronics binding energies up to f4 f 7 / 2 but if you change turbine 3 and the phosphate group remaining same it gets increased for 87.5 chloral RO phosphate three AAS arsenic decreases similarly iron I know complex compounds also change so that means the force F 7 / 2 binding energies can be you know used as an marker.

What kind of gold compounds are PPR present in the sample that is very clear one can actually use this technique to measure even oxide thickness it is possible let us see you for temples by aluminum has always some 11 surface.

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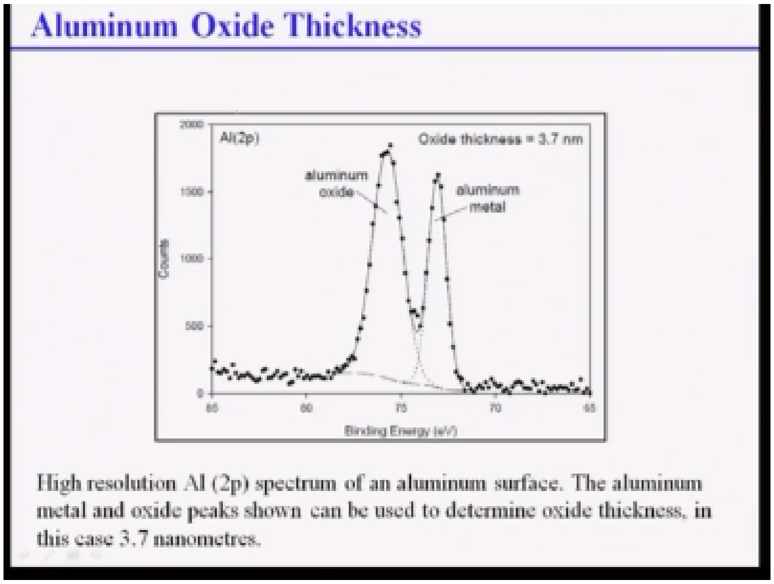

Aluminum Oxide Thickness

High resolution Al (2p) spectrum of an aluminum surface. The aluminum metal and oxide peaks shown can be used to determine oxide thickness, in this case 3.7 nanometres.

You cannot remove it so if you look at Al to P pics there will be obviously this is aluminum metal and this aluminum oxide when the oxide thickness about 3.7 hi loosen victim of aluminum surface the aluminum metal oxide pics soon can be used to determine the oxide thickness how it is to be done.

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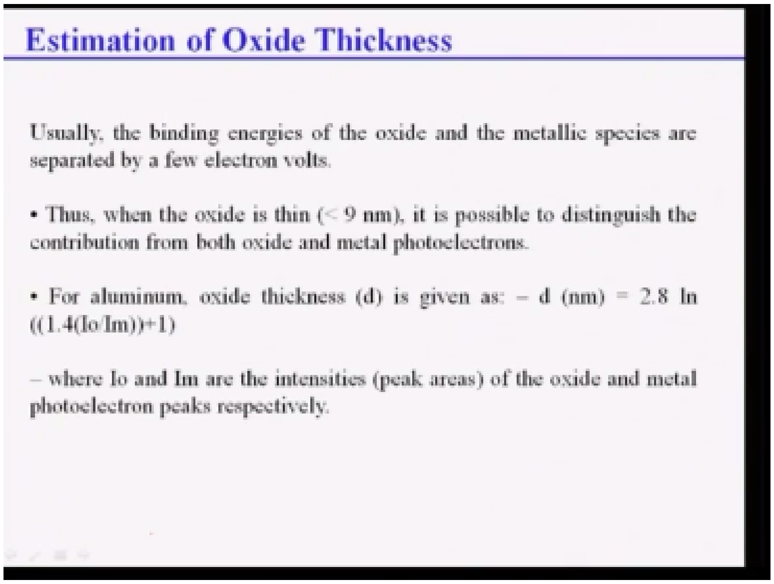

Estimation of Oxide Thickness

Usually, the binding energies of the oxide and the metallic species are separated by a few electron volts.

- Thus, when the oxide is thin (< 9 nm), it is possible to distinguish the contribution from both oxide and metal photoelectrons.

- For aluminum, oxide thickness (d) is given as: – d (nm) = $2.8 \ln((1.4(I_o/I_m))+1)$

– where I_o and I_m are the intensities (peak areas) of the oxide and metal photoelectron peaks respectively.

Let us see usually binding ends of oxide and the metallic pieces are separated by feel electron volts thus when the oxide is very thin less than 19 nanometers it is possible distinguish the contributions actually from both oxide and the metal photoelectrons it will be less thick pile Aluminum oxide thickness is normally given x 2.8 log of 1 .t for i 0 by m + 1 this is ions are in 10 cities of the pics of oxide and a metal that means D is for aluminum is given by this formula Ln 1 / 1 . For i 0 x i M x a + 1.

That is how I actually used so I you is basically intensity of the oxide peak and, I am as the intensity of the metal p so that means if, I know intensities these two or the oxide and metal pics I can put in here and find out the basically the thickness and this is only possible and thickness is less than and I nanometers if it is more than that then this may not possible to distinguish between these contributions and this fails this is done for many other oxides so in the last actually few minutes. I am going to discuss about instrumentations what is done so what I have shown.

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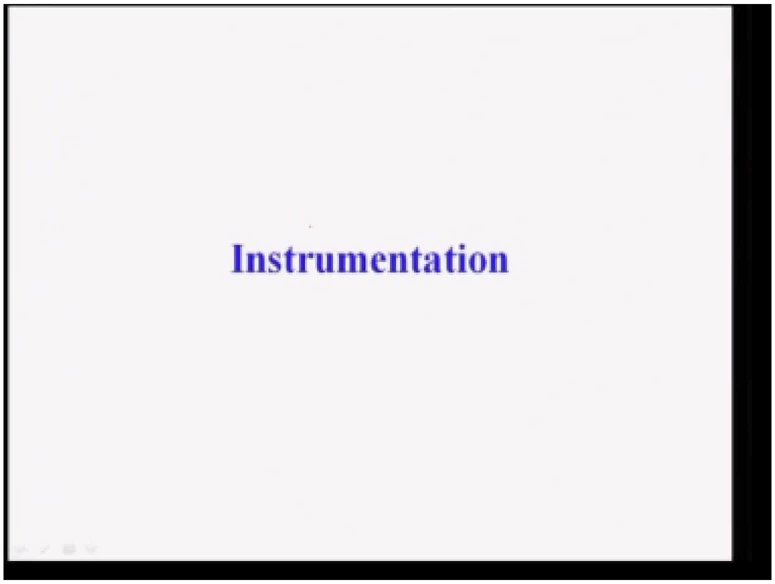

Instrumentation

You in the nuts Dale is basically XPS as a technique and to be used for you know fingerprinting like you can detect certain elements electronic states of the element present very well and also even we can distinguish between the spin orbital speeding up a particular orbital like to PR for 3 p-11 F D orbital's we can distinguish very clearly. I have done with that then we can use experience to measure the compositions very well we have shown.

You how it can be done finally what last few and all 10 to 10 minutes I have shown you that XPS can actually use to determine the chemical shifts when some reactions happen with two pieces like Madeleine oxide metal and nitride are metal and I try like ba cubic boron nitride we can actually determine very precisely those states last thing that what I am going to discuss the instrumentation is very complex let me tell you in the XPS.

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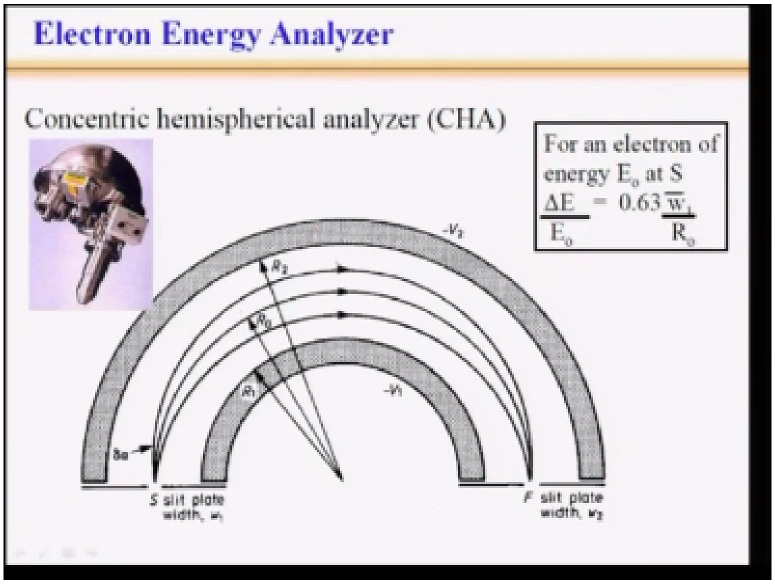

Electron Energy Analyzer

Concentric hemispherical analyzer (CHA)

For an electron of energy E_o at S

$$\frac{\Delta E}{E_o} = 0.63\frac{w_1}{R_o}$$

The machine itself a very costly it is about 4 to 5 crores and very few lavatories in India pushes this kind of instruments what is the basically electron energy analyzer is basically it's the heart of the instrument is basically electron ionization we have a x-ray source in this instrument in this particular instrument and this x rays falls on a sample tonight as the photoelectrons and these photoelectrons then are captured or rather they not basically you know capture in a different manner and then their energies are measured and this is done by electron energy analyzer.

The most important one is constantly camera image particular analyzer here you can see here this is r1 r2 there are different concentric you know radius regions are used here r0, r 1,r 2, r 1 is basically natively charge and act is also negatively charged by different and there is a slit plate here you can see with w1 w2 depending on that the electrons actually moves in this and then get detected so for in electrons of energy 0 at s the split slit width Δ / E is basically . 6 3 / w 1 /y Archer w1 is basically the width at of this I think this width / rj's this constant a cycle radius hybrid constant cycle ½ this radius R ½ diameter.

This is the formula what can actually separate out different Δ e values so you have if you have to have different Δ values you have to either have different wi w 1 or are zeros so that is why different are zeros are shown here one can actually very the r0 c second thing is that.

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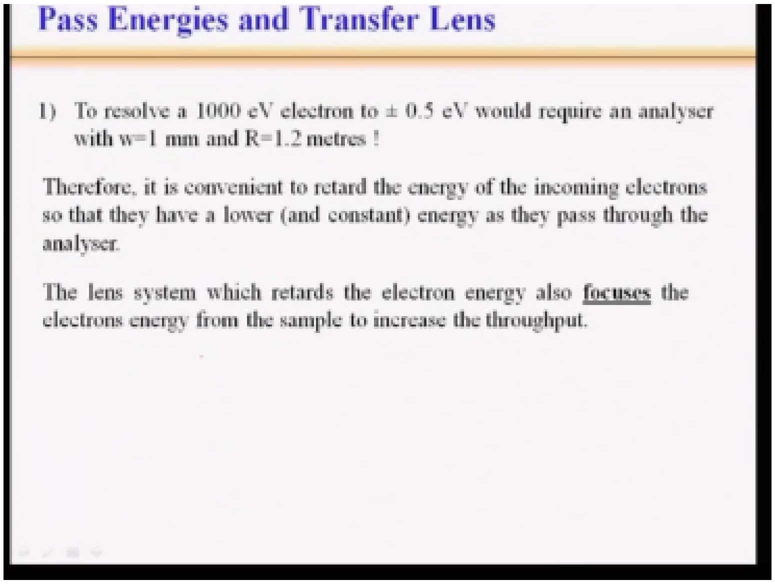

Pass Energies and Transfer Lens

1) To resolve a 1000 eV electron to ± 0.5 eV would require an analyser with w=1 mm and R=1.2 metres !

Therefore, it is convenient to retard the energy of the incoming electrons so that they have a lower (and constant) energy as they pass through the analyser.

The lens system which retards the electron energy also **focuses** the electrons energy from the sample to increase the throughput.

I discussed about this path energies and transport lengths you need to have very high resolutions in XPS because binding energies to be measured can refer by about .5 electrons volts so that is why we require analyzer with w = 1 millimeter and r equal to 1.2 meters you can understand small width but large radius that that means I know it is convenient to return the energy of the incoming electron so that they have a lower energy as they pass through this analyzer this is what is basically used in a pass energies lens system.

Which normally use three in the square in system it helps us heater the electron energy and also allows us to focus the electron energies you know from the sample to increase the throughput so it electron energy and also allows us to focus that otherwise you cannot get it absorb it must be focused so electrons can you focus very easily because the charged particles there is no problem.

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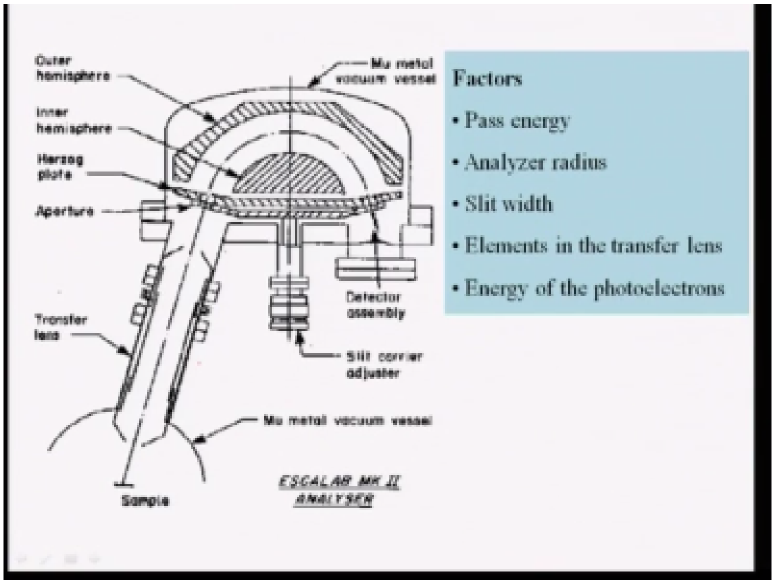

Factors

- Pass energy
- Analyzer radius
- Slit width
- Elements in the transfer lens
- Energy of the photoelectrons

And there are other issues also I am showing you the schematic picture which, I obtained but not very good but it can be seen here as you see basically is nothing but this is present in mk2 analyzer metal vacuum vessel sample is here and the falls like this and gets transferred they are electrons photoelectrons and then there are different plates they say aperture here through is electron pass through this is the Uni-sphere this is out a hemisphere that is what I have shown you just now history hemispheres here.

In an out n ^{2} r 1 and r r 2 and inside this electron moves and gets detected this is a detector assembly and this is the slit adjuster there is a slit here the slit pins this leads this can be adjusted using this adjuster and that is what is done so one of the factors we responsible for whether in electronic pass energy of the of this system radius r1 r2 slit width w1 w2 elements in the transport lens and energy of photoelectrons that transport lens is a transport lens so there are a lot of elements which is allowed to focus they left on.

So that you can pass through the aperture and falls and move inside this hemispherical region well another important.

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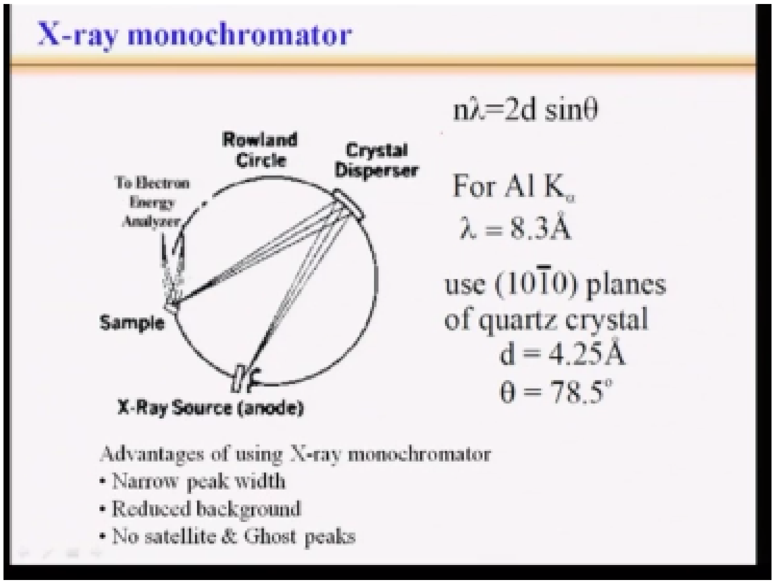

X-ray monochromator

$n\lambda = 2d \sin\theta$

For Al K_α
$\lambda = 8.3Å$

use $(10\bar{1}0)$ planes
of quartz crystal
$d = 4.25Å$
$\theta = 78.5^\circ$

Advantages of using X-ray monochromator
- Narrow peak width
- Reduced background
- No satellite & Ghost peaks

Thing of the parliament is the monochromatic XM monochromator is basically monochromator I the exodus this is done by blacks law as you see here Black's law is in λ 2 L sin θ if used aluminum k α has eight point is the λ and if you was plates d become this and theta is this so by using different plates different crystal place actually we can motorized we can get exactly the same you know only the aluminum k α and not any other cave our K α 2 we can do.

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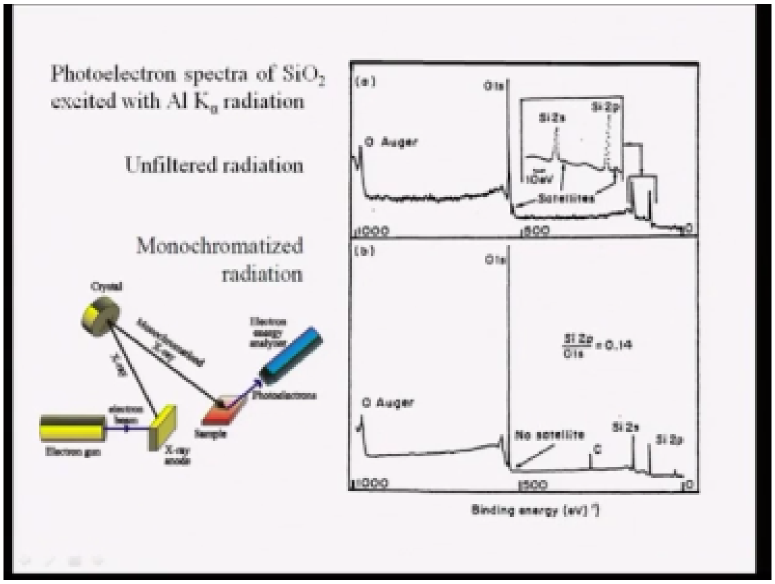

Photoelectron spectra of SiO_2 excited with Al K_α radiation

Unfiltered radiation

Monochromatized radiation

That lastly the photoelectron spectra this is actually the whole set of loops like as you see here you have electron gun electron being false exercise annihilated except falls on a sample okay Monica XA falls on him this tile that still more context three comes it is false on a sample and the photoelectron generated and then measured in this so this is basically the x-ray so thing and this is what is the photoelectron generator now one can actually get lots of things obviously one can get this is silicon and carbon pics.

One can get audio also here but when we discuss separately about the electrons and I just want to finish it up using showing that if you saw the fastener Jesus as you change a person algae from 10 to 80 electron volts what happens to the particular pieces like PTR polyethylene θ flap which is used in the bottles this all this plastic bottles are actually matter of this and.

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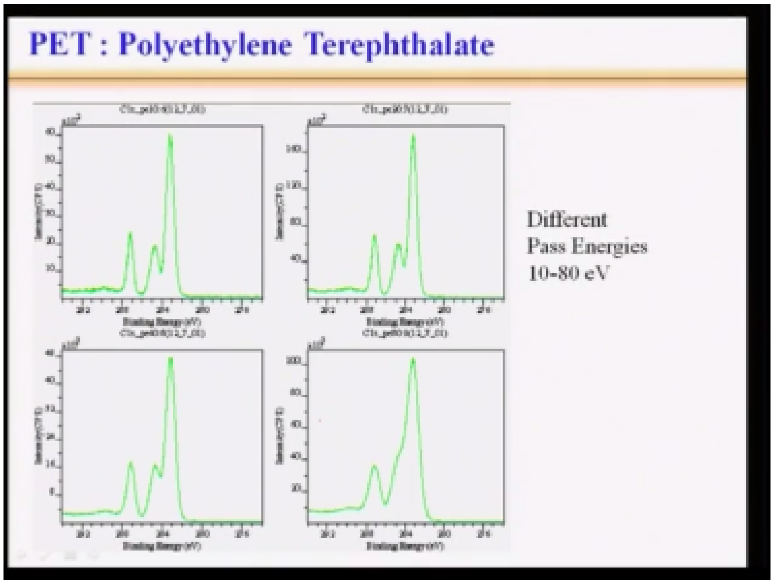

PET : Polyethylene Terephthalate

Different Pass Energies 10-80 eV

You can see one speaks how it gets shifted I which gets affected by this way finally if you say what a tickly electron volt pass energies we get a rise nice this peak positions of the carbon 1 s very easily so with this, I just close this discussion on the on the x-ray photoelectron spectroscopy in the next class. I am going to discuss about the osseous spectroscopy.

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