Nano structures and Nano Materials: Characterization and properties

Prof. Kantesh Balani
Prof. Anandh Subramanian
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 40

X-Ray Photoelectron Spectroscopy (XPS)

In this lecture, we will learn about x-ray photoelectron spectroscopy, as we realized there are three terms out here, x-ray photoelectron and spectroscopy. So, in this particular process we utilize x-rays to excite a particular material, then utilize the effect of photoelectron like have the photoelectron get emitted from the surface. And from then we achieve a spectrum or being able to analyze the spectrum that is spectroscopy.

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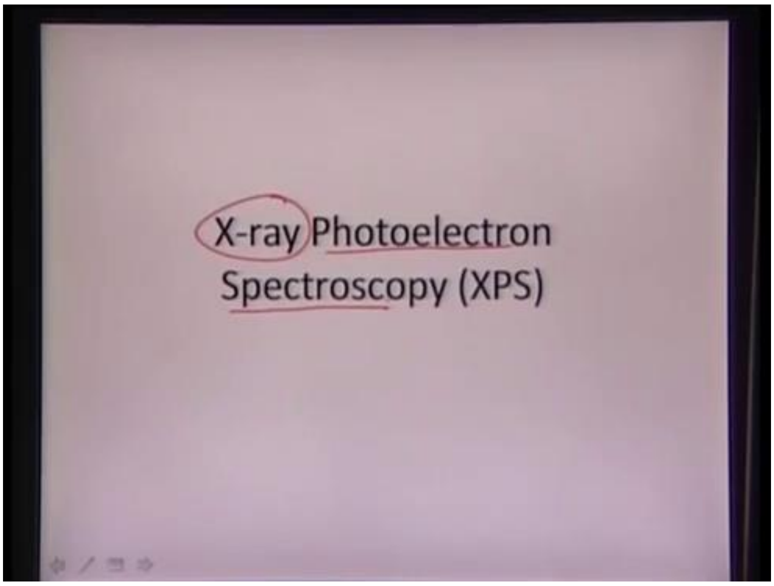

X-ray Photoelectron
Spectroscopy (XPS)

So, we are utilizing x-rays and then from that we are generating a photoelectron and from the photoelectron we are basically going on to achieving a spectrum. To eventually analyze the overall spectrum and find out the chemical composition of a particular material.

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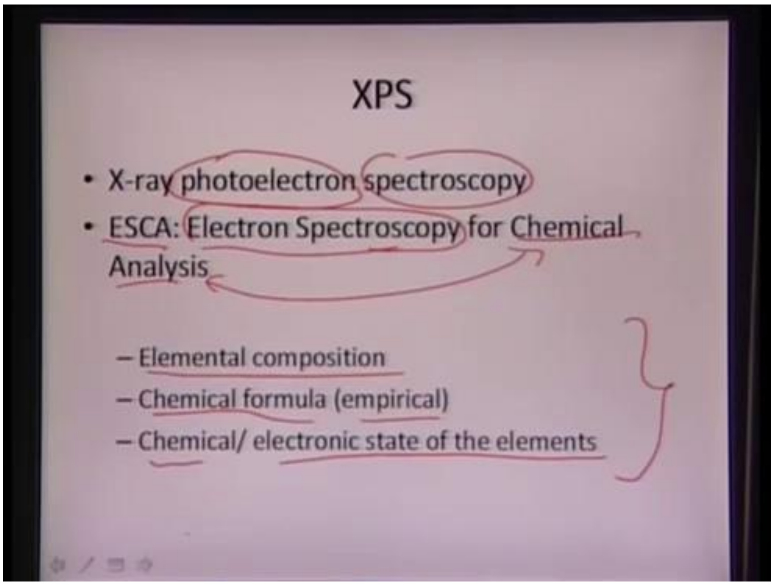

XPS

- X-ray photoelectron spectroscopy
- ESCA: Electron Spectroscopy for Chemical Analysis
  - Elemental composition
  - Chemical formula (empirical)
  - Chemical/ electronic state of the elements

So, in this XPS electron, XPS is also called ESCA that is electron spectroscopy for chemical analysis. So, in this particular technique we utilizing x-ray to excite a particular material, then generate photoelectrons and eventually get a spectrum to finally, evolve with the chemical analysis. It is also called electron spectroscopy, because electron which is emitted as the photoelectron, that is being captured for the eventual chemical analysis of a particular material.

So, via XPS we can analyze its elemental composition because eventually come up with a chemical formula which is empirical in nature and also we can determine the chemical or electronic state of the elements. So, these are the advantages of utilizing XPS because in XPS it is highly dependent on the electronic state of the element as well. So, we can easily determine, what is the overall nature of a particular element and what is its electronic state. Thereby, we can also calculate what its chemical formula?

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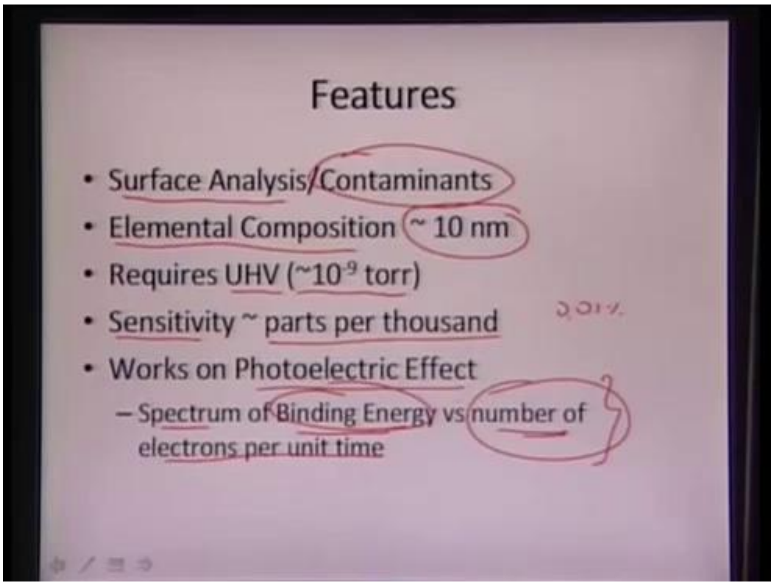

Features

- Surface Analysis/Contaminants
- Elemental Composition ~ 10 nm
- Requires UHV (~10^{-9} torr)
- Sensitivity ~ parts per thousand
- Works on Photoelectric Effect
    - Spectrum of Binding Energy vs number of electrons per unit time

0.01%

And coming to the features of XPS it can it is highly surface sensitive, so we can perform a surface analysis. We can eventually also see, what is the contaminants that are present on the surface of a material? And we can also determine the elemental composition which is limited to the top 10 nanometer of the surface. And since, the electron which are emitted they are low energy electrons and to detect those electrons which are coming out of the surface without any collisions, inelastic collisions. We require a ultrahigh vacuum, which is to the order of 10 to the power of minus 9 torr.

So, that much a vacuum level is required by the system, so that electron which is coming out of the surface of a material. That comes out without any inelastic collisions and the mean elastic free path, the mean free path of the particular electron is to the order of many, many kilometers around 30 or 40 kilometers. So, that is the reason that the electron can traverse and it can come back to the detector.

And its sensitivity is parts per 1000, so we can go up to 0.01 percent of a particular material. And then works on the photoelectric effect and that photoelectric effect is being initiated via application of x-ray photon. And then, it provides a spectrum of the binding energy versus the number of electron which are being emitted per unit time. So, from these two phenomena of finding the binding energy versus the number of electron, which are being generated per unit time. We can get a spectrum that that is helpful in analyzing the overall spectrum via XPS.

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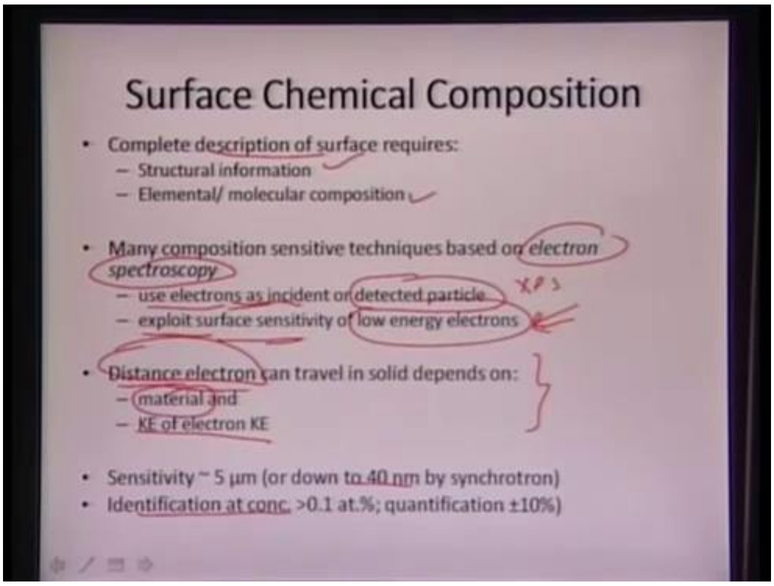

Surface Chemical Composition

- Complete description of surface requires:
  - Structural information
  - Elemental/ molecular composition
- Many composition sensitive techniques based on *electron spectroscopy*
  - use electrons as incident or detected particle
  - exploit surface sensitivity of low energy electrons
- Distance electron can travel in solid depends on:
  - material and
  - KE of electron KE
- Sensitivity ~ 5 μm (or down to 40 nm by synchrotron)
- Identification at conc. >0.1 at.%; quantification ±10%)

And surface chemical composition basically, if you want to go for describing the complete description of the surface, we can get a structural information we also need elemental or molecular compositions. And there are certain techniques which are dependent on the electron spectroscopy such as, ESE as well. In those, in ESE we utilize x-rays, but there are certain technique, where we can use electrons as incident. And in this case, XPS we are utilizing electrons as the particle which is being detected

And that electron is the low energy, it can be low energy particle which is coming out, so we can utilize them in exploiting the surface sensitivity. So, we utilize the low energy electrons and then they are highly sensitive such as, auger electrons or photoelectron. And from that we can limit the interaction with the material to the order of few angstroms or nanometers.

And then the overall sensitivity goes up by a huge number because they are low energy electrons and we can exploit to eventually find out the surface sensitivity. And again the distance the electron is travelling it depends on the kind material it is interacting with. If material has much higher density, then there will be many, many more number of collisions on the surface itself and the penetration of electron into the material will be very, very less. And the kinetic energy of electron which is coming out will be very high if the binding energy is very low. So, that thing is also that thing is also very essential in terms of finding out what is the kinetic energy of the out coming electron.

Since, the electron is to come out from the shell and if the binding energy is very high, then the overall kinetic energy will be very, very less. So, that is the overall thing which distance electron will travel depends on and sensitivity is to the order of very, very less its actually. It can go down to around 40 nanometer by synchrotron facility and identification at concentrations greater than 0.1 atomic percent and with a quantification of plus minus 10 percent.

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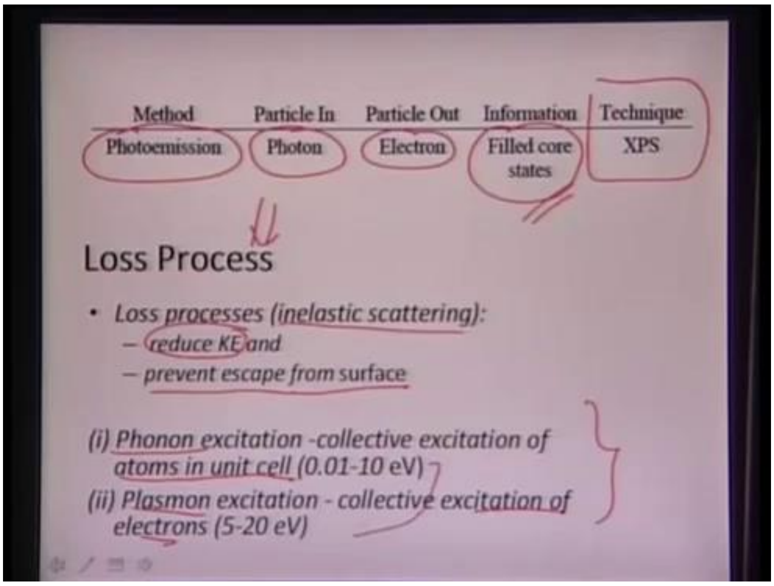

Method	Particle In	Particle Out	Information	Technique
Photoemission	Photon	Electron	Filled core states	XPS

Loss Process

- *Loss processes (inelastic scattering):*
  - *reduce KE and*
  - *prevent escape from surface*

(i) Phonon excitation -collective excitation of atoms in unit cell (0.01-10 eV)

(ii) Plasmon excitation - collective excitation of electrons (5-20 eV)

And in this particular method we utilize photoemission, so we are incenting a photon and particle which is coming out is an electron. And basically, we see excitation of electron and then that basically other electron fills up the core electron. And then, it finds out the what is the status of the filled core, what are the filled core levels and this overall technique is being utilized in the XPS. And there are certain loss process which are also associated in the XPS those arise because of the inelastic scattering and because of inelastic scattering, there is reduction in the kinetic energy of the electron.

And also it might trap the travelling electron, it may prevent the escape of electron from the surface. These are also some of the things which can happen and those inelastic scattering can occur either via phonon, plasmon. So, those excitations can also absorb certain energy, in terms of their excitation as atoms in unit cell or excitation of electron. So, and they also have a different energy levels out here.

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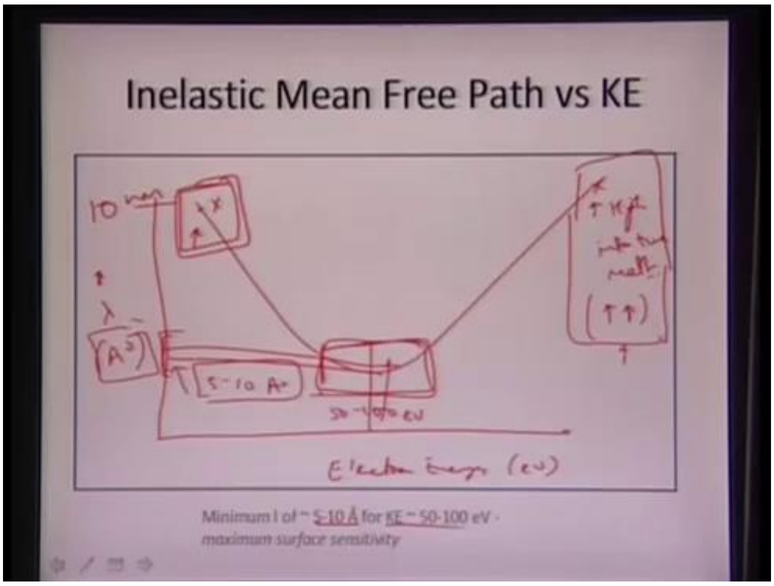

Inelastic Mean Free Path vs KE

Minimum l of ~ 5-10 Å for KE ~ 50-100 eV - *maximum surface sensitivity*

And coming to the inelastic mean free path versus the kinetic energy, we can see that if we start drawing a mean free path. So, we have mean free mean free path which is denoted by lambda and it is given in distance such as, angstrom and then we have say electron energy in EV. So, we see that when the electron energy is very, very less the electron will undergo many, many collisions and when the electron energy is very, very high it will penetrate much deeper into the material.

So, for higher energy electrons we will see that there are very high interactions because higher energy of electrons will allow the much more penetration of the electron into the material. So, what will happen that now, electron will basically once it has to come out of the surface it will undergo many, many collisions. What happens? If lower levels is that it is such a low energy that it just after certain inelastic collisions it basically, dies away. So, that is the problem with the electron energy, at lower energy it can just keep going further and further into the material.

And basically it will get much, it will just keep colliding with the things around and it will such a low energy. It will just deflected by the electrons which are nearby and the energy is not sufficient to basically, collide with some other material and lose its energy. And in this case, it is such a high energy that it will keep traversing to a very high distances without affecting its energy. And then basically, this energy keeps trying later on, but at in this particular location we are seeing the mean free path is very, very low.

So, what is happening is if we can attain a particular electron with certain energy we are observing the minimum mean free path. It means the electron will collide with surface and it will come out only from this particular regime. And we realize that this this amount is around 5 to 10 nanometer, 5 to 10 angstroms and this particular part can go as highest may be say around 10 nanometer. So, if we can capture an electron within this particular regime, which is predominant for may be electron energies to the order of 50 to around 100 EV.

We can capture an electron with a very low mean free path and we can get this much sensitivity for the particular process. So, this tells the importance of the mean free path versus the electron energy or the electron kinetic energy out here in this particular case. So, we are getting a minimum mean free path of around 5 to 10 angstroms or kinetic energy to the order of 50 to 100 EV and that will provide us the maximum sensitivity. So, that is the key part around here that we can also get very high sensitivity in this particular case.

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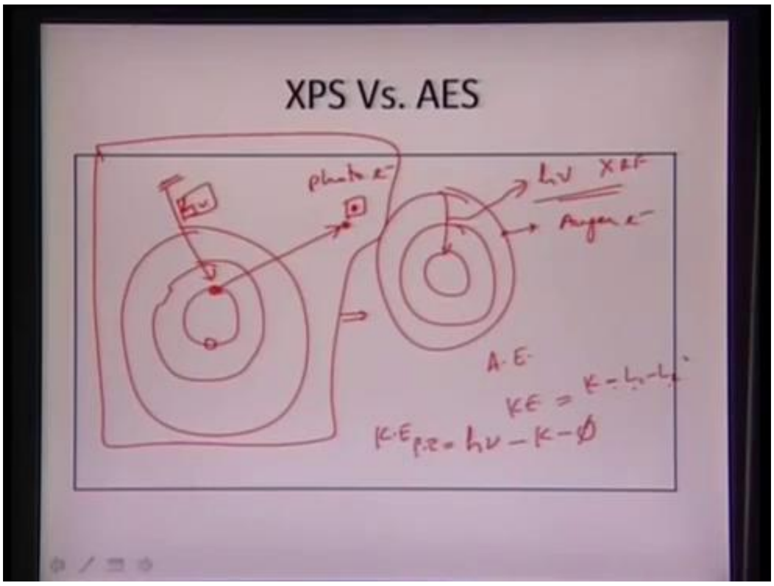

XPS Vs. AES

Now, in one of the earlier lectures we have studied about the auger electron spectroscopy and in there we realize how relaxation process can lead to a auger electron. So, we see that we have certain shells out here, we have certain shells out here and then we excite a particular electron. We had core shell electron, we supply a beam of photon with energy h mu and then we see that this particular electron is knocked away. And, since this is knocked away what can happen is later on, that it can 1 electron can jump from higher energy to a lower energy. And then it can basically, supply certain h mu that will go out as x- ray fluorescence.

The electron which is emitted out is nothing but the photo photoelectron which is basically emitted out. And this energy can again be absorbed by electron in higher shell and that can come out as a auger electron. So, we see that this particular electron which is coming out is a photoelectron and we are interested mostly in this part because we are capturing the energy of the photoelectron. And the auger electron the basically, its kinetic energy was dependent only on the shells, which were belonging to the k shell and l 2 and l 2 shells.

So, we had something like this that the energy or kinetic energy of the auger electron was dependent on the binding energy of the k shell minus binding energy of the l 1 and minus binding energy of the l 2, but in this particular case since, we are bombarding with certain energy h mu. And that particular energy is being utilized to knock off that particular photoelectron. The kinetic energy of a photoelectron basically, depends on the applied energy as well.

So, we had h mu minus the binding energy of the k shell minus some work function required to go from to escape to the Fermi level to the vacuum level. So, how this thing is particularly happening is we did see that, that we have h mu which is interacting with the core shell. And that core shell electron is basically, being knocked off as a photoelectron, so that is what we did see that.

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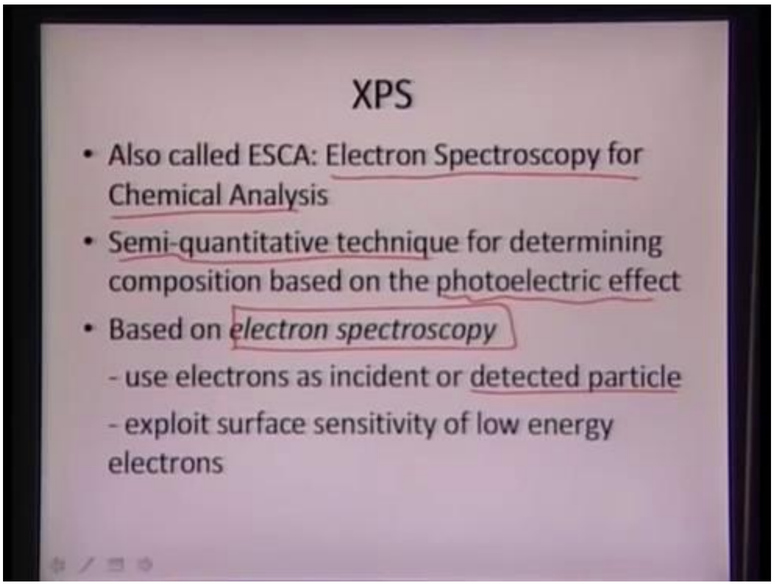

XPS

- Also called ESCA: Electron Spectroscopy for Chemical Analysis
- Semi-quantitative technique for determining composition based on the photoelectric effect
- Based on *electron spectroscopy*

  - use electrons as incident or detected particle

  - exploit surface sensitivity of low energy electrons

An XPS as we said earlier it is also called electron spectroscopy for chemical analysis. It is a semi quantitative technique for determining the composition based on the photoelectric effect. And it is based on the electron spectroscopy because we utilize electron as a detector and we are using the detective particles as electrons and they are able to exploit the surface sensitivity, because the signal is coming out only from the top 5 to 10 angstroms of the surface.

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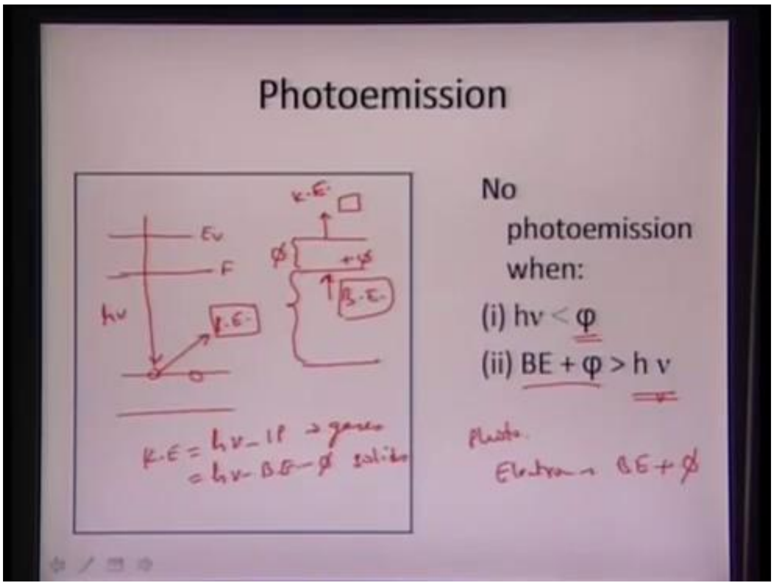

Photoemission

No photoemission when:

(i) $h\nu < \varphi$

(ii) $BE + \varphi > h\nu$

Photo Electron → BE + φ

So, seeing about the photoemission part, we had this vacuum level and then we go on to the Fermi level and then we see the k shell or the core level shell electrons. So, we see that the core hole is being created, we take this core hole and that thing is being eliminated once we apply some h mu. That electron basically, goes and escapes as a photoelectron and again going from the binding energy up to here, it has to come to overcome the binding energy plus it has to utilize certain work function.

To be able to achieve certain energy still with its cell and that thing is nothing but the kinetic energy, which is being possessed by the photo electron. So, once this particular photo electron is getting emitted, it has to overcome the barrier of the binding energy of a particular shell. And then overcome the certain work function and then the remaining energy. So, we have total energy of the of the photoelectron kinetic energy is equal to h mu minus ionization potential, for gases and it is equal to h mu minus binding energy minus some work function for solids.

So, we say that photoemission will occur only when our h mu is greater than the work function and then binding energy plus work function is smaller than the h mu. Then we have a photoemission or in other words we do not get any photoemission, when h mu is lesser than work function and BE the binding energy plus work function is greater than h mu. So, for photoemission we need to have the electron to overcome the binding energy plus the work function, which is required for its emission. And that basically, comes out to be the kinetic energy the remaining energy becomes the kinetic energy of the electron. Once, it is being ejected from the vacuum level, so this what the overall process.

We have a incident photon which strikes on to the core shell, knocks off an electron and that electron is to overcome the binding energy plus certain work function for solids in being able to escape from the surface. So, that is basically overcoming binding energy plus some work function to basically, emerge from the to a vacuum level. So, that is what photoemission is all about.

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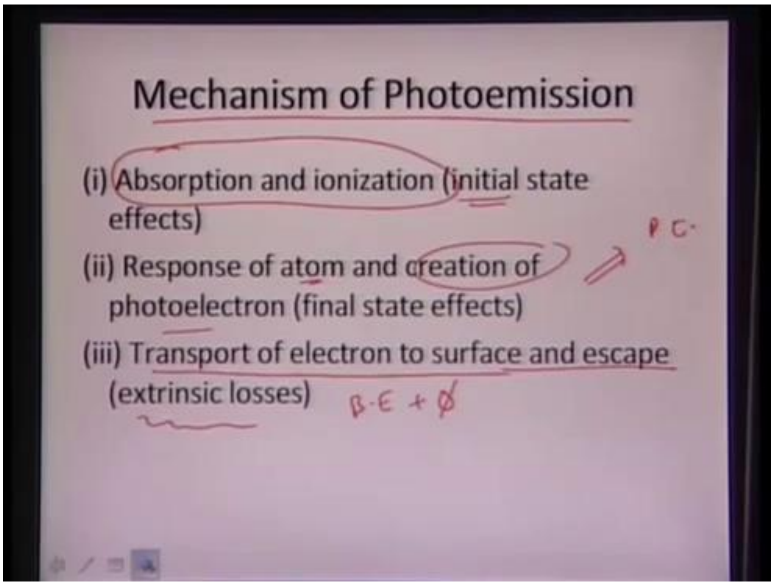

Mechanism of Photoemission

(i) Absorption and ionization (initial state effects)

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

(iii) Transport of electron to surface and escape (extrinsic losses)

P.C.

$B.E + \phi$

So it is defined in three steps mechanism of photoemission, we have first of all the absorption and ionization. So, that creates the initial core level hole and now the material has to relax itself. So, there is some response of the atom in terms of creating the photoelectron. So, we have emission of photoelectron here and now the third thing is the relaxation the transport of electron to the surface and escape. So, in this case it is overcoming the binding energy plus some work function that becomes the extrinsic losses of the particular electron that comes via phonon or phonon and plasmon interaction.

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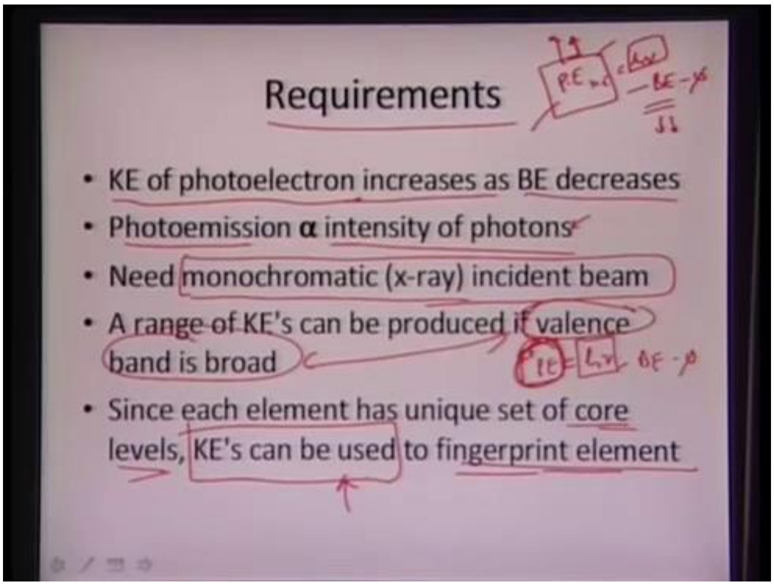

Requirements

- KE of photoelectron increases as BE decreases
- Photoemission α intensity of photons
- Need monochromatic (x-ray) incident beam
- A range of KE's can be produced if valence band is broad
- Since each element has unique set of core levels, KE's can be used to fingerprint element

$K.E = h\nu - BE - \phi$

$KE = h\nu - BE - \phi$

And now the requirement of the XPS in terms of leading to photoelectric effect. So, we have this kinetic energy of photoelectron it increases as the binding energy decreases. It is very obvious because we are applying the kinetic energy of a photoelectron is equal to h mu minus binding energy minus the work function. So, obviously if our binding energy is getting lower and lower the overall, kinetic energy will keep increasing to the extend. And again the photoemission is proportional to the intensity of photon.

So, if we have more number of photons there are more number of electrons which will go out as a photoelectron. And in this particular case we need a monochromatic x-ray, monochromatic x-ray incident beam why because if we have a variety of x-ray beam then the overall energy will be very, very different. So, we have PE is equal to h mu minus BE minus work function. So, for h mu itself is varying it is very difficult to trace, what is the overall kinetic energy of the photoelectron.

So, in that particular case the detection would not be that good and we would not we will get a variable in terms of the kinetic energy values. And that will basically, tell us the electron is coming from somewhere else where else, it is coming from a specific chemical. So, that one we need to have monochromatic x-ray source, so we know what is the incident energy. And that will basically, decide the energy of a out coming photoelectron.

And that will help us correlate, what is the relation between the two and that particular difference will tell us the exact chemical nature of the particular element. And range of kinetic energy can be produced if the valence brand is broad, so depending on the valence band itself. Since, the material has to overcome the work function as well and it has to overcome the binding energy as well.

So, the valence band is pretty broad then again the kinetic energy will be lower and will get a range instead of a unique value. And again the each element has a unique core set of core levels, so that kinetic energy can be easily used to fingerprint an element. So, once we know what is the binding energy? What is the core energy levels? Then we can obviously find what is the element and what the kinetic energy the exciting electron will possess. So, that provides the overall requirements of the XPS process.

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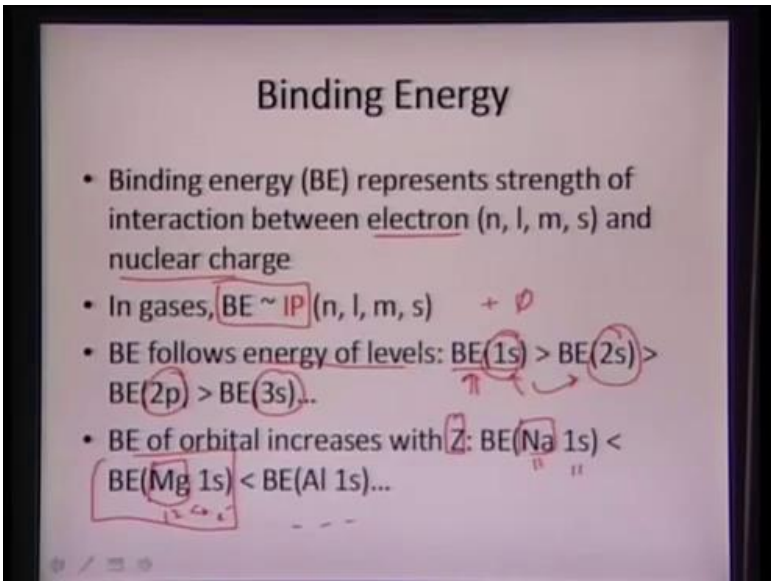

Binding Energy

- Binding energy (BE) represents strength of interaction between electron (n, l, m, s) and nuclear charge
- In gases, BE ~ IP (n, l, m, s) + ϕ
- BE follows energy of levels: BE(1s) > BE(2s) > BE(2p) > BE(3s)...
- BE of orbital increases with Z: BE(Na 1s) < BE(Mg 1s) < BE(Al 1s)...

And again binding energy represents the interaction between the electron and the nuclear charge. And in gases our binding energy is equal to the ionization potential, but in case of solids it has to also overcome certain work function. So, binding energy will be the overall energy which electron has to overcome will be binding energy plus some work function. And binding energy will follow the level such as BE binding energy of 1 s shell is much higher than 2 s shell. That is the reason first electron goes to 1 s level and then once the 1 s level is filled it starts filling 2 s level.

So, this one is the highest binding energy and similarly, follows on 2 p 3 s and so on and again binding energy of the orbital increases with the atomic number. So, for a similar row of elements if we have sodium, magnesium, sodium will have the lower binding energy because here the nuclear charge is around of 11 and then we have electrons also 11.

So, as soon as the charge gets increasing like in magnesium we have 12, atomic number 12, so we have 12 nucleons basically neutrons and protons that are attracting the electrons. So, in this particular case the binding energy is much higher similarly, it goes on like that. So, we have binding energy increasing with the atomic number and also it also follows the energy levels, so that we have 1 s will have much higher binding energy than that of a 2 s and then 2 p and so on.

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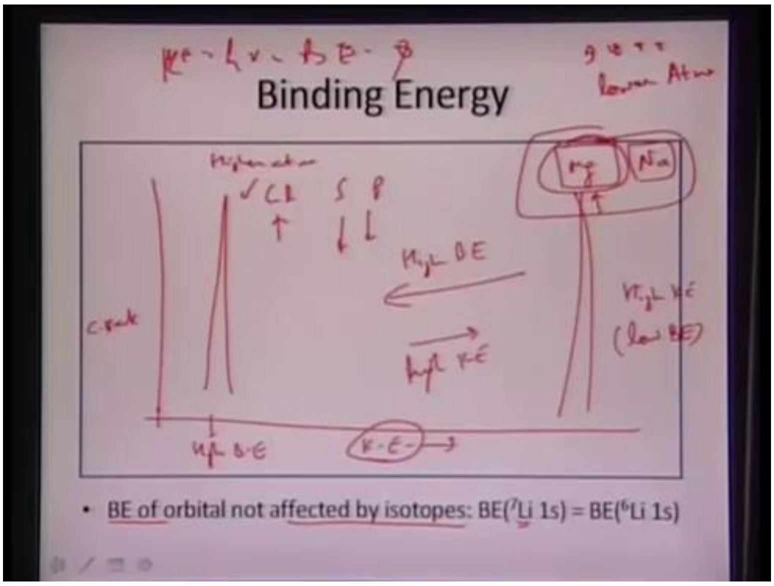

Binding Energy

- BE of orbital not affected by isotopes: $BE(^{7}Li\ 1s) = BE(^{6}Li\ 1s)$

So, again we also see that the binding energy how it basically changes. So, if we have certain counting rate on the on the y axis counting rate or may be some intensity and in this we have a kinetic energy. So, we are seeing the binding energy, the binding energy increases as we have lower atomic number for a particular row of elements. So, we see that the kinetic energy will be very, very low for element with a higher atomic number. So, we have higher atomic number will have a lower kinetic energy.

This is the kinetic energy because this one will have a higher binding energy say we had a chloride, we had a chlorine and then we see it that it will have very low the electron which is coming out chlorine will have a lower kinetic energy. Then say material which was say magnesium, so it is it is much easier for the electron to come out in magnesium. Whereas, it is much difficult for the electron to come out in chloride.

So, that is what the problem is that the kinetic energy of easily releasable electron such as, Na or magnesium it is very easy for the electron to really come out in sodium and magnesium. So, they will possess very high kinetic energy since, they have lower binding energy of the electron. And similarly, like for the material such as chloride, chlorine or sulphur or phosphorous they again they have the atomic number is much higher. So, their kinetic energies will be much lesser than those of magnesium or sodium.

And basically, we have seen higher binding energy in this direction and higher kinetic energy in the this direction because that is what we always say its kinetic energy is equal to h mu minus the binding energy minus the potential of the material. So, that is what we are able to see that is binding energy is being affected by the atomic number of the material, but again binding energy of the orbital it will not be affected by isotopes.

Say, binding energy of lithium, in case of lithium we know that what is the overall number of nucleons and protons out there, so the attraction which with which it will attract the electrons will be the same. It does not matter if lithium has, so many number of electrons on the surface. It will have the same binding energy because the way nucleons will nucleus will keep returning those electrons will be same. So, we have binding energy of 7 lithium 1 is similar to that of 6 lithium 1 s.

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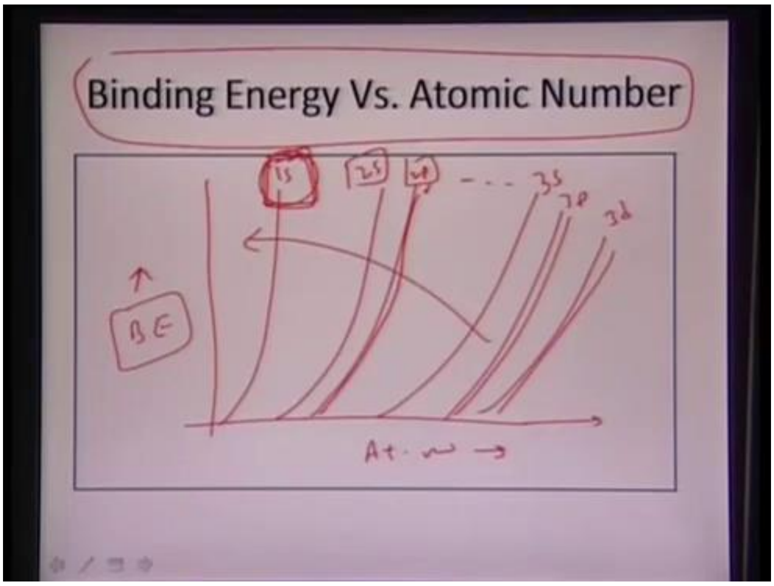

Binding Energy Vs. Atomic Number

And again, seeing the binding energy with respect to atomic number, we will see that the binding energy will in this direction and then we have atomic number in this direction. So, we see that the 1 s shell basically comes out like this and then 2 s 2 p will go on like this, 2 s will be like this and 2 p it may there may be again some splitting between the shells. So, we will see 2 p will have basically splitting out here and then again 3 s and then again 3 p will have again the splitting part. Again, it can be 3 d will have again splitting, 3 s 2 s something like this will observe in case of particular materials.

And these transitions are basically the way the binding energy is defined and, so binding energy was electron atomic number is something like this. That 1 s will have the highest binding energy if we take particular material, then we can say definitely that 1 s has the highest binding energy than the 2 s and then the 2 p and so on. And that is what we were seeing earlier as well, that is what we have studied earlier as well.

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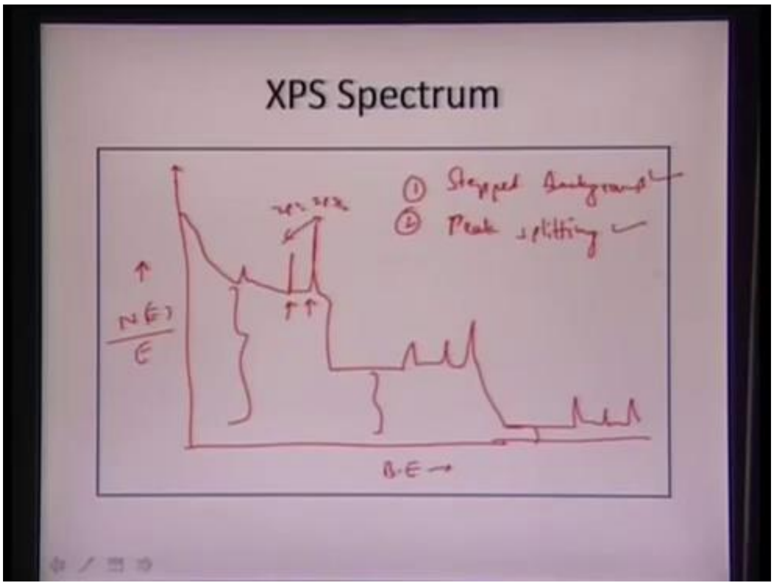

XPS Spectrum

So, and coming to the XPS spectrum we count the number of electrons per unit time, with respect to the binding energy of a particular material. So, we see a spectrum which is which appear more like this, we see much higher background in certain material and certain splits like this. And then certain change in the back ground scale and then again certain scale will go on like this. So, we are seeing binding energy like this and then number of electrons which are again it is being again normalized by the energy levels out here, so we some spectrums something like this.

So, we see that background is basically keeps changing for different levels and again we are seeing certain peaks splitting, so say this was for 2 p 1 by 2 and then 2 p 3 by 2 we see some splitting of the peaks at certain locations. So, this is what basically happens that we have a step background and then second case we have splitting of the peak. So, we have peak splitting as well, so we are seeing these two parts peaks splitting in the stepped background in this particular case. And why does this happen we will see as we go along so this is let us see.

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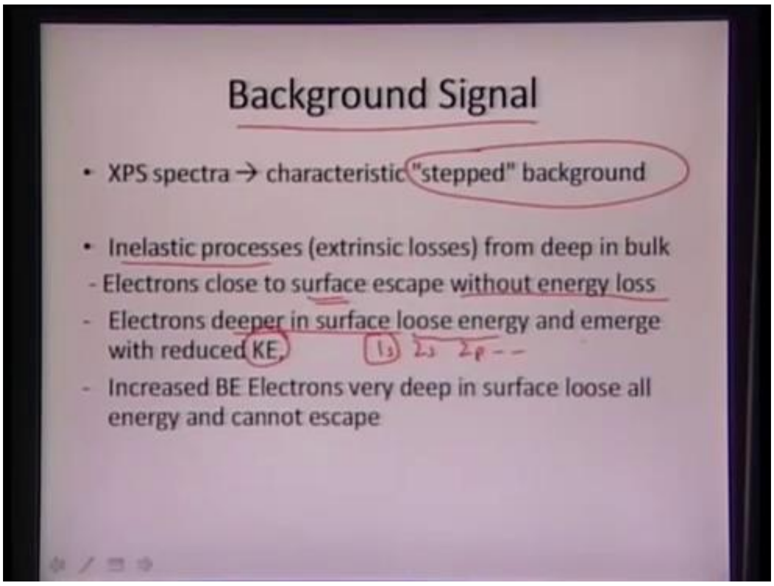

Background Signal

- XPS spectra → characteristic "stepped" background
- Inelastic processes (extrinsic losses) from deep in bulk

- Electrons close to surface escape without energy loss
- Electrons deeper in surface loose energy and emerge with reduced KE
  1s 2s 2p - -
- Increased BE Electrons very deep in surface loose all energy and cannot escape

And in the background signal it generally in the XPS spectra we see a stepped background. This happens because of the inelastic processes and basically what happens electrons which are close to surface they can escape without energy loss. And electrons which are much deeper in surface will lose energy and emerge with reduced kinetic energy. So, that is what is happening that once we have an electron say a binding energy which is the binding energy of very high such as 1 s electron.

And those electrons will undergo very, very high collisions and they will go much because it is the much higher binding energy, it undergoes it emerges with a very low kinetic energy. Since, it is a very low kinetic energy it again starts interacting with the material and depending on its mean free path it encounters many, many elastic collisions. And as we had seen earlier that a certain energy range of electrons will have the minimum mean free path.

It basically, starts losing energy in terms of inelastic collisions and that part is basically emerging in the 1 s much strongly than that of a 2 s and then 2 p and so on. So, electrons which have which have very lower binding energy such as 2 p 3 s 3 d all those shells they tend to show very low binding energy, so very low background.

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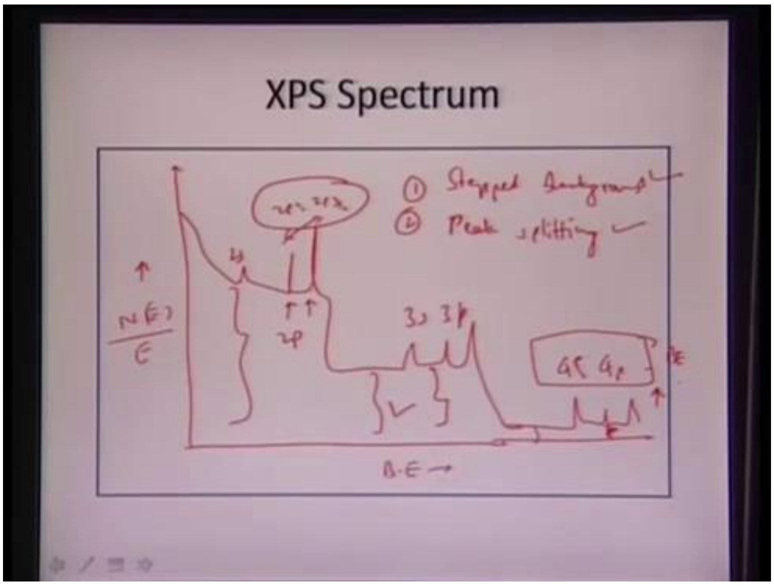

XPS Spectrum

So, in this particular case if we see if this is for 2 p or 2 s or that particular level this will be 3 s 3 d 3 p and then we have 4 s 4 p and so on. So, this particular thing basically comes like this that we see particular level of background in certain materials. This one might be for say 2 s, this one might be for 2 p and then again we keep going down.

And then we again see certain more interaction in terms of 3 s 3 p with varying level of background. And as we see, that for higher shell for higher electronic orbitals we are seeing that the binding energy is very, very low. So, that is the reason the background also is very, very low because electrons are coming out at very higher energies and it is easier to detect those higher energies.

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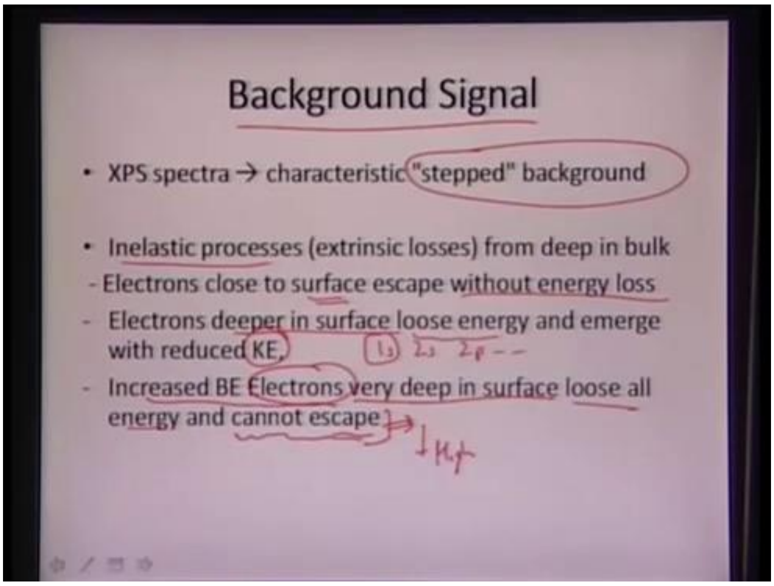

Background Signal

- XPS spectra → characteristic "stepped" background

- Inelastic processes (extrinsic losses) from deep in bulk
- Electrons close to surface escape without energy loss
- Electrons deeper in surface loose energy and emerge with reduced KE, 1s 2s 2p - -
- Increased BE Electrons very deep in surface loose all energy and cannot escape → ↓ K.E

So, that is the reason we are able to see a stepped background because the overall intensity at which the electrons will come out, will depend on the binding energy of the particular material. So, that is the reason we see that 2 s will have much higher background than 2 p and generally 3 s shells will have much lower background than that of 2 s or 2 p and so on.

And again increased binding energy electrons will go very deep in surface and they lose all the energy and it becomes very difficult for them to escape. So, that is the reason since they have you know very low energy left with them because of their increased binding energy it tends to have a very higher background. So, that is the reason we are not getting all the electrons back, which we which were released. So, that is the reason it gives out a low, low energy electron as a higher background.

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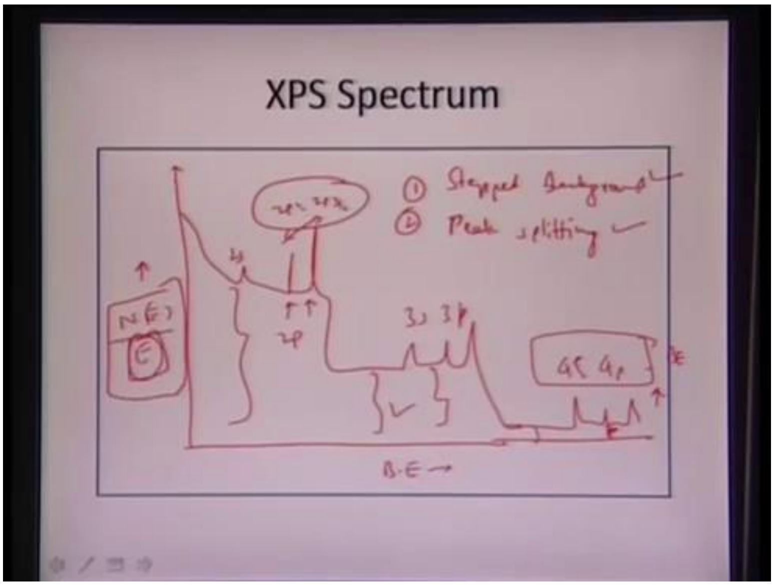

XPS Spectrum

And that is the reason we tend to basically normalize it with respect to the energy level. So, we have number of electrons which are emerging with respect to, the energy and that basically gives out a better signal out there.

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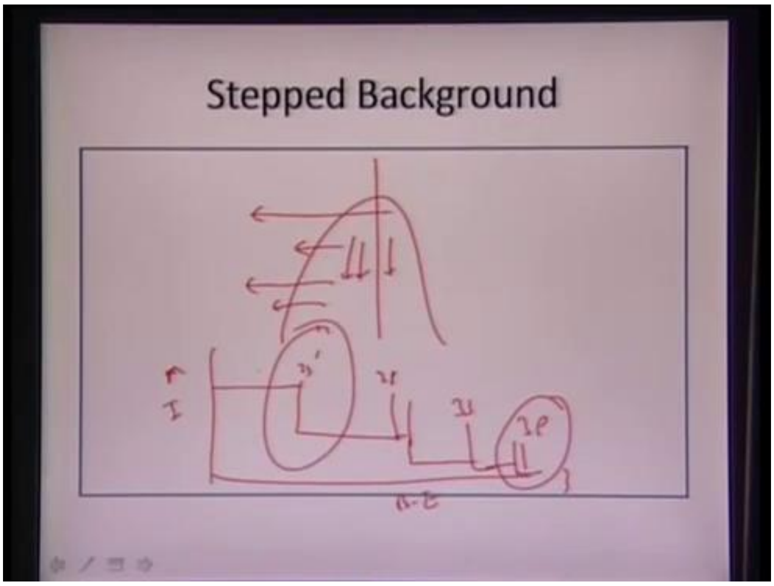

Stepped Background

And as we see as we saw earlier that if you have a particular surface and then the electrons which are coming out from surface they are generating more intense. And as soon as, we start going much deeper into the material, we see that intensity will keep decreasing, but at the same time the 2 s will have a very low kind of energy left with it. Then again we will have 3 s and then 3 p and then 3 s and so on.

So, we tend to see a stepped background which will the stepped background will appear more like this, we will have splitting for the this is say for 2 s. Then for 2 p we will have again a splitting and then we see some background like this and then again 3 s and then 3 p and so on. So, we had this binding energy like this and then the overall intensity in this particular direction and that is what we see. That the 3 p will show the least background whereas, 2 s and 2 p electrons will show a highest background.

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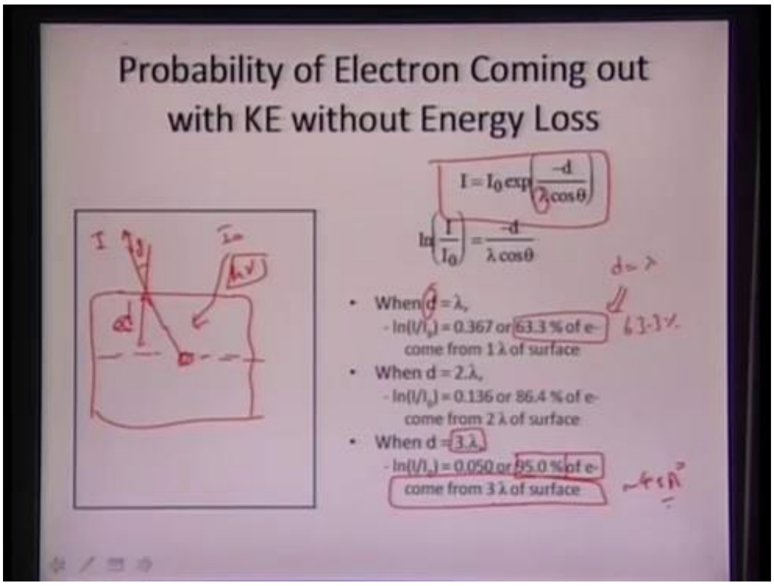

Probability of Electron Coming out with KE without Energy Loss

$$I = I_0 \exp\left(\frac{-d}{\lambda \cos\theta}\right)$$

$$\ln\left(\frac{I}{I_0}\right) = \frac{-d}{\lambda \cos\theta}$$

- When $d = \lambda$,
  - $\ln(I/I_0) = 0.367$ or 63.3 % of e- come from 1 λ of surface
- When $d = 2\lambda$,
  - $\ln(I/I_0) = 0.136$ or 86.4 % of e- come from 2 λ of surface
- When $d = 3\lambda$,
  - $\ln(I/I_0) = 0.050$ or 95.0 % of e- come from 3 λ of surface

And again coming to the probability of electron which is coming out with certain kinetic energy without energy loss. So, that particular intensity is given by i is equal to i naught exponential of minus d by lambda cos theta, what is happening is we are taking a particular incident beam, incident photon and the way it is interacting with the material. And it will have certain depth till which it goes, that depth is basically given by say a particular distance d and then we are achieving certain, we are applying certain photon and that basically photon is getting use.

So, we have h mu which is being incidenting on the material, then we have photon which is getting released with certain angle. And that is what is defining the overall release of electron from the material. So, this is the overall depth from which the electron can skip, so we have h mu the energy of the photon, incident photon and that is interacting with the material. And the intensity which is coming out is being defined as i, so i naught is the incident and i is the intensity which is coming out.

So, we see when d is lambda, when the depth d is equal to lambda which is equal to the wave length of the incident thing, incident beam. And then we get i by i naught it basically, comes out to be 63.3 percent which means, that when the depth is equal to lambda we are getting information from 63.3 percent of the depth. So, as we go along and we see d is equal to 2 lambda and d is equal to 3 lambda. Basically at 3 lambda we are seeing that the most of the information is coming from a depth of around 3 lambda. So, we are getting around 95 percent of the information which is coming out from the 3 lambda surface.

So, this tells us that how closely it basically dependent on the incident beam energy. So, the overall information which is emerging it is only from the distance of 3 times lambda. So, if you can choose the lambda accordingly, say in certain case we want to have lambda of around 1.54 angstrom such as, for copper k alpha radiation. Then we can see that the overall information will be limited only to around 4.5 angstrom. That decide the overall sensitivity, so if we are able to capture the information only from a surface specific layer 4.5 Angstrom.

So, that tells us how much we can really able to contain the information, the chemical information from only a couple of less than a nanometer layer, less than a nanometer. And then we can get the overall depth information from around 4.5 angstrom in case of copper k alpha. So, that is what tells us the probability of electron which is coming out with kinetic energy.

So, this tells us that how closely it basically dependent on the incident beam energy. So, the overall information which is emerging it is only from the distance of 3 times lambda. So, if we can choose the lambda accordingly say in certain case we want to have lambda of around 1.54 angstrom such as, for copper k alpha radiation. Then we can see that overall information will be limited to around 4.5 angstrom that decides the overall sensitivity.

So, if we are able to capture the information only from a surface specific layer 4.5 angstroms. So, that tells how much we can really are able to contain the information, the chemical information from only a couple of less than a nanometer layer, less than a nanometer. And then we can get the overall depth information from around 4.5 angstrom in case of copper k alpha. So, that is what tells the probability of electron, which is coming out with kinetic energy without energy loss. And that thing how much it is dependent on our incident beam and the overall lambda which defines the beam incident photon beam.

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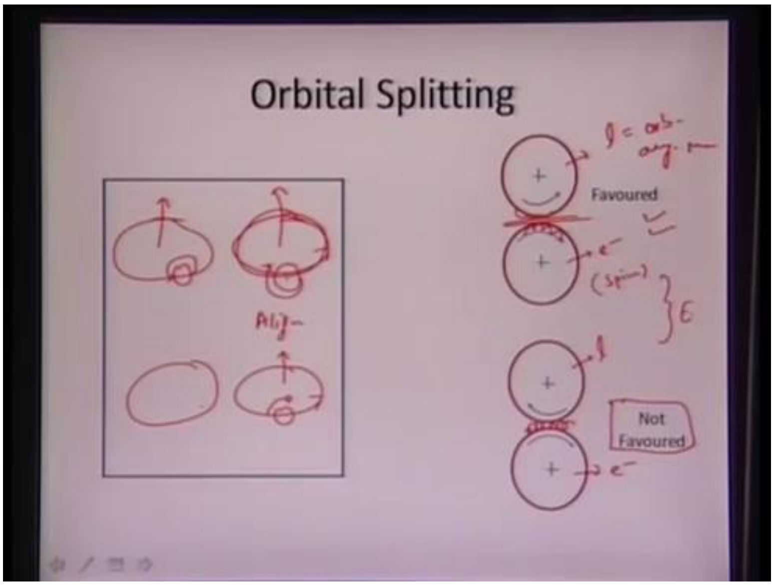

Orbital Splitting

And again, in this case we observe orbital splitting we have orbital angular momentum and then we have also electron, which is being spinning on its shell in a certain direction. So, we see there can be some favorable state and there can be some unfavorable state. So, we have say if we have the orbital which is moving in this direction and since we have electron, which is moving exactly opposite to it, spinning exactly opposite to it the it is much more align.

And this one will face much lesser resistance during the spinning, but if we had the moment something like this of the angular momentum more like this. And if we have the spin the same direction, at certain location it will cause some friction between them. To present it more schematically it is more like this, if we have the overall angular momentum orbital angular momentum going in one direction. And this is for the electron this is for the l or the orbital angular momentum.

Then this is much more favored because now, there will be no resistance at this particular location. They are rolling in just one above the other and they would not assume any friction, but in one case and the other case if we this our l in this direction and the electron is spinning in another direction. Then we can obviously, see that there will be some friction which is being generated out here. So, that stage is basically unfavorable or not favorable.

So, the alignment between the orbital angular momentum and the spin of an electron, so we have spin of electron and the angular momentum. So, they should be aligned properly for it is favorable and or unfavorable and that basically leads to the difference in the energy levels that causes basically the splitting between the orbitals.

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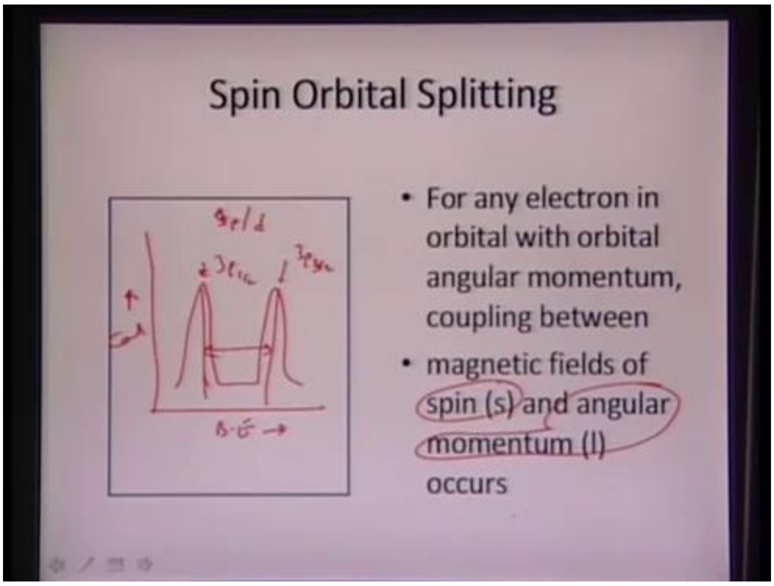

Spin Orbital Splitting

- For any electron in orbital with orbital angular momentum, coupling between
- magnetic fields of spin (s) and angular momentum (l) occurs

So, if we had say we have particular material, then we will see that it will show some splitting in the 3 p and 3 d may be in p or d orbitals. And say in particular case, we have this binding energy, so it will show certain splitting say for 3 p and say for 3 p 2 by 3 by 2 and this is will be 1 by 2.

So, we can see the counts in this direction the binding energy in this direction we will see some splitting, which might be happening between the two or in this two location. So, for any electron in the orbital with orbital angular momentum. So, coupling between the magnetic fields of the spin and the angular momentum basically, causes the splitting between the two and how does this splitting really occurs is?

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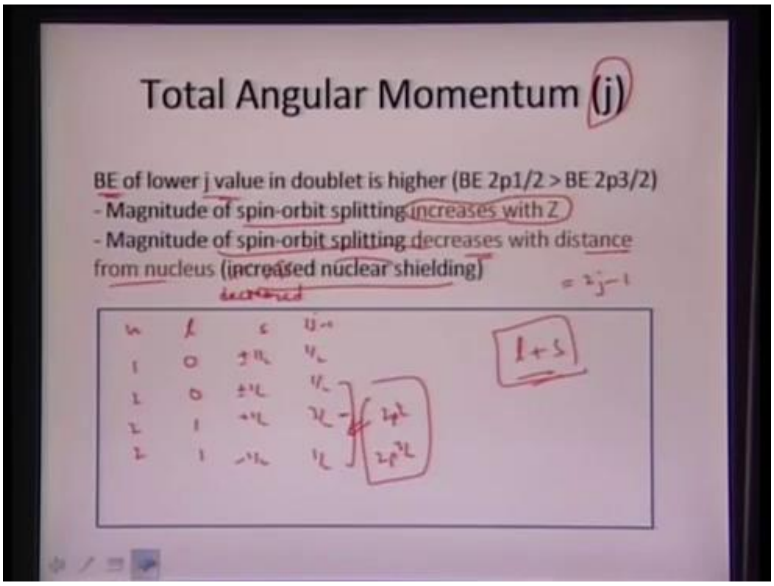

Total Angular Momentum (j)

BE of lower j value in doublet is higher (BE 2p1/2 > BE 2p3/2)
- Magnitude of spin-orbit splitting increases with Z
- Magnitude of spin-orbit splitting decreases with distance from nucleus (increased nuclear shielding)

decreased

= 2j − 1

n	l	s	j
1	0	±1/2	1/2
2	0	±1/2	1/2
2	1	+1/2	3/2
2	1	−1/2	1/2

2p1/2
2p3/2

l + s

We already discussed it earlier, but the overall thing is overall thing out which is determines here is, that the binding energy of the lower j value, j defines the overall momentum of it the total angular momentum is defined by j. And it leads to degeneracy and degeneracy is basically given by 2 j minus 1. So, if we have this n l and the spin and the overall value will come out to be something like if 1 2 2 say 2. Then we have l is 0 in case 0 1 1 the spin can be plus minus half in this case plus minus half, plus half, minus half.

So, we have we get overall degeneracy can be to the order of something like this, we can get half we get half 3 by 2 1 by 2. So, we can see that there is some degeneracy which is basically occurring out here, when we have overall degeneracies 2 j minus 1. Then overall degeneracies coming out it is basically, we are seeing the split in this over p orbital, so we have this 2 p 1 by 2 2 p 3 by 2. So, we are seeing some splitting out here because of the total angular momentum which is being given by the combination of l plus s.

So, this overall degeneracy gives rise to the splitting of the peaks and again the magnitude of spin orbit it increase with the atomic number or it also decreases with the distance from the nucleus. As the electron is much farther from the nucleus, then there is much more, it is much more the distance the magnitude of splitting will decrease because it is very far from the nucleus. So, there is increased decreased nucleus shielding from the nucleus it is actually will be it will decrease because the electron is very far from the nucleus. It will be basically, decreased nucleus shielding and again the magnitude of spin orbital splitting will increase with the atomic number. And that is what is defined by the total angular momentum we can see the overall shift out here.

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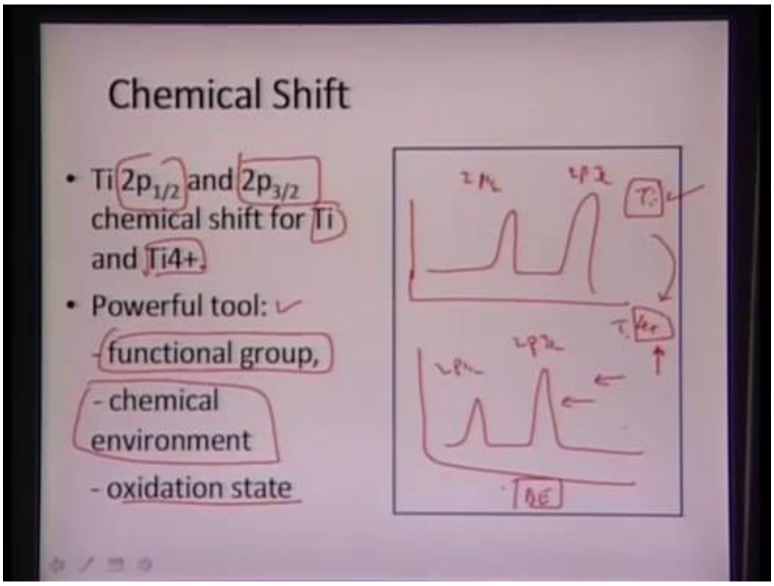
Chemical Shift

- Ti $2p_{1/2}$ and $2p_{3/2}$ chemical shift for Ti and Ti4+
- Powerful tool:
  - functional group,
  - chemical environment
  - oxidation state

And in the second case, we can also see some chemical shift we can also observe a chemical shift in this particular material, like we have titanium 2 p 1 by 2 and 2 p 3 by 2. So, the chemical shift will be different for titanium and titanium 4 plus. So, that part can be easily seen out here like, if we had a peak for p 1 by 2 and p 3 by 2 and then it will be very different once we have say titanium. And then in other case, if we had titanium 4 plus we can see there is some shift in the peaks.

So, for the same peaks p 1 by 2 say it was 2 p 1 by 2, 2 p 1 by 2, 2 p 3 by 2 and 2 p 3 by 2. So, in this case we have titanium 4 plus since, titanium is easy it is easy to basically, give out electrons. We can see that the binding energy will decrease because now, we have one more electronegative material which is associated with it. So, titanium can easily give out electrons, so its overall peaks will shift in the left direction, we can see that particular part that titanium will have certain binding energy. Whereas, titanium 4 plus will have this binding energies shifted to lower values. So, that what is basically can be easily achieved even can be easily seen via XPS .

So therefore, it becomes a powerful tool in terms of being able to detect the functional groups or being able to decide, what is the chemical environment and where the species is associated and also the oxidation state. So, as we can see here the titanium it was neutral and then in this case we had certain binding energy. Whereas, as far as become 4 plus we see a shift of the binding energy out here.

So, that is what is telling that we can chemically detect what is happening with the material. So, it becomes a very powerful tool in terms of detecting any functional group, which is associated with a particular chain or deciding the chemical environment. If there is any oxidation is happening with the particular material. So, these are some important aspects of characterizing via XPS.

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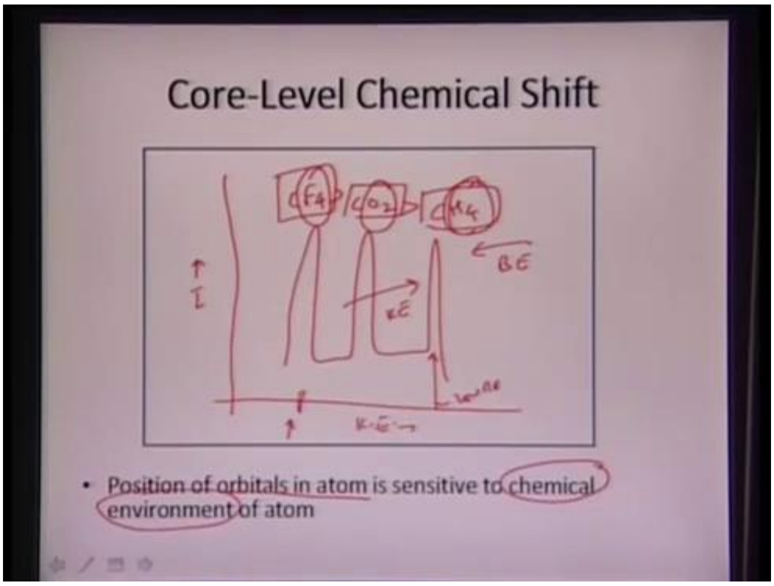

Core-Level Chemical Shift

- Position of orbitals in atom is sensitive to chemical environment of atom

And also there can be some core level shifts like in case we have a carbon and then carbon basically is interacting with certain materials. So, that can be say calcium tetra fluorine or it can be carbon dioxide it can be CH 4. So, if we see that what is the overall binding energy or maybe say let us this will be the kinetic energy in this direction and we have intensity in this direction. In this particular case, we see that the kinetic energy is increasing in this particular direction. So, we have kinetic energy in this direction, so obviously the binding energy is increasing in this direction.

So, we can directly say that the CF 4 is bonded very much strongly as compared to CO 2 and then CO 2 is much more strongly bound as compared to the CH 4. So, we see CF 4 will have the lowest kinetic energy or it means it has the highest binding energy and CH 4 is showing the highest kinetic energy. It means, it has the lowest binding energy. So, it also depends on the electro negativity of the material in this case, we had hydrogen in this case we had oxygen and in this case, we had fluorine.

So, that is also very important that position of orbitals in the atom is sensitive to the chemical environment. So, that is what we said earlier that shifts are very much dependent on the chemical environment of the material as well. So, that is what we are able to see in particular spectrum that once a particular element is bounding much more strongly to some another element. So, the binding energy will be very high and therefore, we will have very low kinetic energy for those particular bonds. So, we can easily decipher the shifts which are arising due to the chemical nature of the material.

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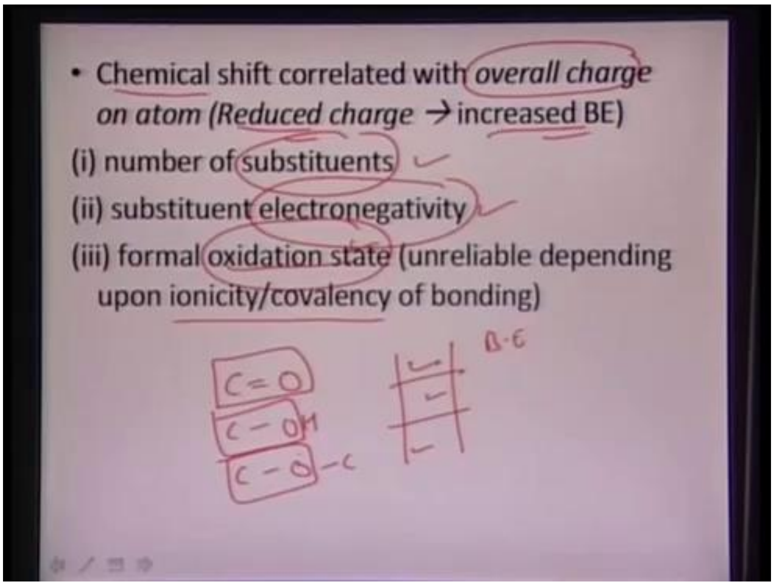

- Chemical shift correlated with *overall charge on atom (Reduced charge* → increased BE)

(i) number of substituents

(ii) substituent electronegativity

(iii) formal oxidation state (unreliable depending upon ionicity/covalency of bonding)

Going to the next and therefore, chemical shift is correlated with the overall charge of an atom and as we have reduced charge, we will see increased binding energy. And it also depends on the number of substituents, it depends on the substituent electro negativity it also depends on the oxidation state. So, again depending on the ionicity or covalency it can be little unreliable, but that is what it depends on, it depends on the oxidation electro negativity and number of substituents. So, that is all is also being defined by the particular chemical shifts.

Coming back to it we will see difference say, if we have a particular bonding C double bond O or CO bond H or C bond OC something like this. They will have different binding energies may be marginally different, but they will again be little different they will have different kind of bonding's. In all the cases, we have seen bounding with O, but still will have very different binding energy. So, typical binding energy of oxygen with certain carbon it again will be little different.

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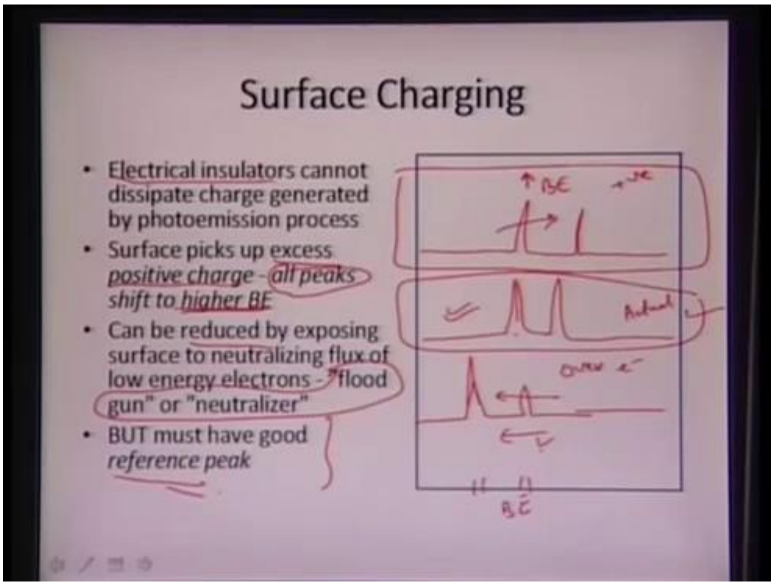

Surface Charging

- Electrical insulators cannot dissipate charge generated by photoemission process
- Surface picks up excess *positive charge* - all peaks shift to higher BE
- Can be reduced by exposing surface to neutralizing flux of low energy electrons - "flood gun" or "neutralizer"
- BUT must have good *reference peak*

And coming to the surface charging since, what happens in case of electrical insulators they cannot dissipate the charges. We are incidenting the surface with photons and then we are basically releasing those electrons from the surface. So, overall the material is getting deficient of any electrons, so once the material is deficient of any electrons. Now, it is very hard for a particular material to again emit much more number of electrons. So, we see there is some when the surface charging occurs, we have excess positive charge which basically comes out on the surface and it shifts all the peaks to higher binding energies.

So, say if we had certain spectra and then basically, once we are once it is it is certain charge developing on it. So, we see that the overall binding energy peaks will all shift to the higher binding energy level. So, we have because now it has some positive charge and now it is very difficult for the charge to go and escape the surface. So, what we do we tend to reduce the particular charge by inducing a flux of electrons via flood gun or neutralizer?

So, we need to always neutralize this was the actual and once it is becoming positive it shifts on this direction. And we need to supply a flood gun to remain to maintain it at the actual value, but we over saturate. In case we over saturate it then again the binding energy will shift to the left because now in this case we have over saturated with electrons. So, we have oversaturated with electrons and then binding energy will go little lower value because now electrons for electrons it is much more easier to escape.

Since, they are any way having excess surface charges of negative electrons on the surface. So, it is much easier for the electron to go away and therefore, the binding energy is very, very less in this particular case. So, that is what we really see in the in the particular spectrum, that we had the binding energy and this is for the actual case. And if we have a charge developing on the surface we have some positive charge developed on the surface. So, it becomes harder for electrons to move, so it basically is increasing the binding energy.

And if we supply a flood gun, so we are if we are able to maintain it at very low flood level. So, that it is maintaining the standard level, then we can get the charges at certain binding energy at certain location, but if we oversaturated we can see the shifting of those peaks to a lower binding energy level. So, that is what can also be observed. So, we should also have a good reference peak to supply the neutralizing gun or the flood gun to neutralize the surface charge which is being developed. So, we need to take care of these things as well in this particular thing.

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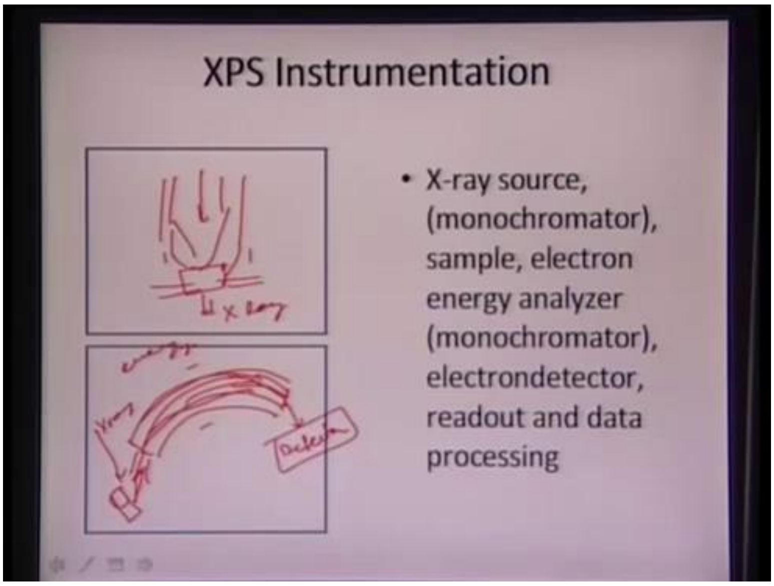

XPS Instrumentation

- X-ray source, (monochromator), sample, electron energy analyzer (monochromator), electrondetector, readout and data processing

Coming to the experimentation part obviously, we need to have a monochromatic x-ray source, so that can be basically generated via using monochromatic source. We can have anode and filaments and then water supply to basically, generate a x-ray with certain window level to generate the monochromatic x-ray. And secondly, we also need some sort of a detector or analyzer and then detector to be able to differentiate the energies which are being achieved by the electrons. So, we apply certain bias to certain voltage or certain bias to this analyzer and it allows only a certain energy electrons, to pass from one end to the other end and then get detected at this particular location.

So, we had this energy analyzer this allows only certain levels of energy to flow through it, without touching the electrodes and then basically we tap it as electrode. So, we have the sample we generate the x-rays we excite the sample and then the photoelectron, which are being emitted they pass through this analyzer. And then they come out at the detector level and that is basically, goes out for the data processing.

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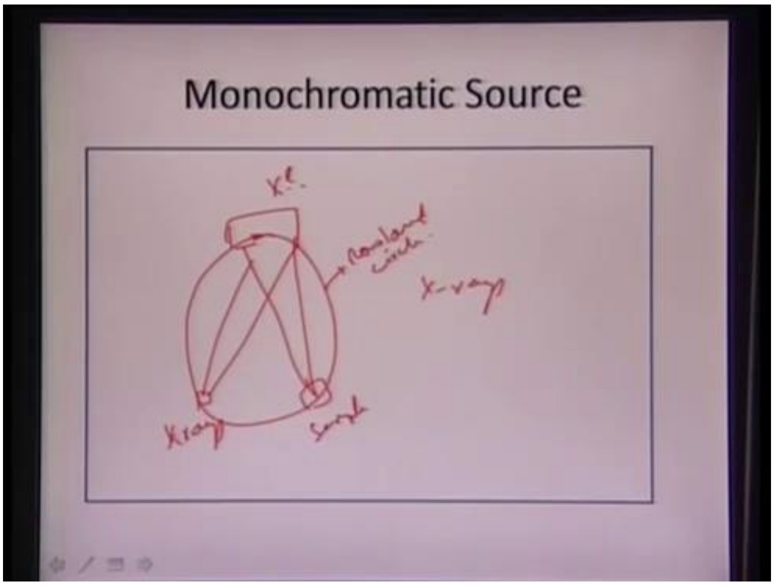

Monochromatic Source

And monochromatic source as we know that we have x-ray source and they sit on the role and circle, we have a crystal and that is basically generating the x-ray. And there we have the sample, it falls on the sample and that is basically that is how we can generate a monochromatic source for this particular x-rays. So, we have this crystal here and that is generating the x-ray source and now, because it is falling on the crystal we can get a monochromatic source and that basically falls on the sample. And all this set is in the on the role and circle, so that is how we can get a monochromatic source.

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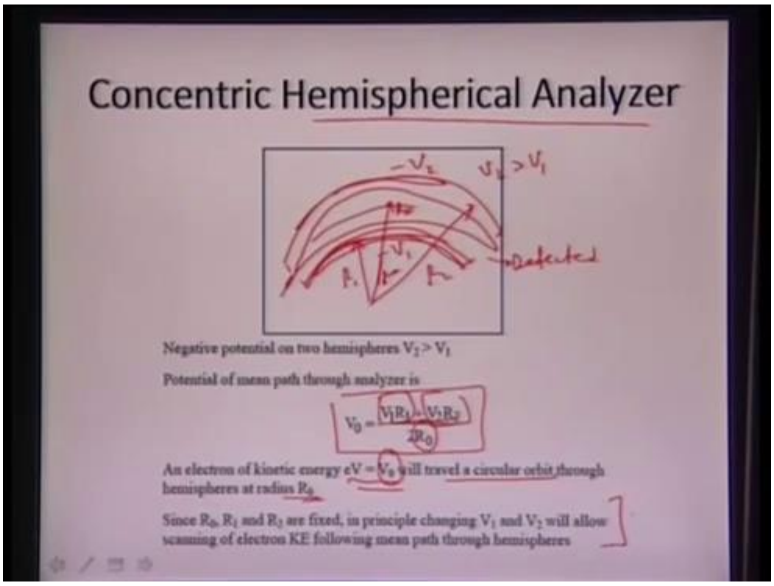

Concentric Hemispherical Analyzer

Negative potential on two hemispheres $V_2 > V_1$

Potential of mean path through analyzer is

$$\boxed{V_0 = \frac{V_1R_1 - V_2R_2}{2R_0}}$$

An electron of kinetic energy $eV = V_0$ will travel a circular orbit through hemispheres at radius R_0

Since R_0, R_1 and R_2 are fixed, in principle changing V_1 and V_2 will allow scanning of electron KE following mean path through hemispheres

And the analyzer what we talked about is something called concentric hemispherical analyzer. And in this case, we have 2 electrons on the surface and we set apply certain voltage to it minus v 1 minus v 2. And if electron is basically, if it is touching any of the surfaces it is basically absorbed and v 2 is basically greater than v 1. So, v at certain location we supply electron, the overall energies and those electrons travel and they come out on the other side something like this. And then this particular thing is getting detected.

And when once we apply certain negative potential and the mean free and the mean path of the analyzer is given by v naught and we have certain radiuses like, we have r 1 then this is r 0 and this is r 2. So, we get v 1 r 1 which is being dependent on the lower side electrode v 1 r 1 plus v 2 r 2, which on the top side electrode divided by the 2 r naught r naught is the mean radius of the path. The mean radius which is nothing but r naught, so 2 times r naught will gives the overall potential. And if electron is the kinetic energy which is approximately equal to the v 0, will travel a circular orbit with at a radius of r 0.

And by changing the v 1 and v 2 we can allow only a certain range of energy values to pass through this particular analyzer. So, by changing the biases at the v 1 and v 2 we can alter how which particular electrons will cross through and which one will not. And once we have certain energy of electron which comes out we can detect those electrons by using photomultiplier tubes and dynodes and to basically, give a particular count for the particular material.

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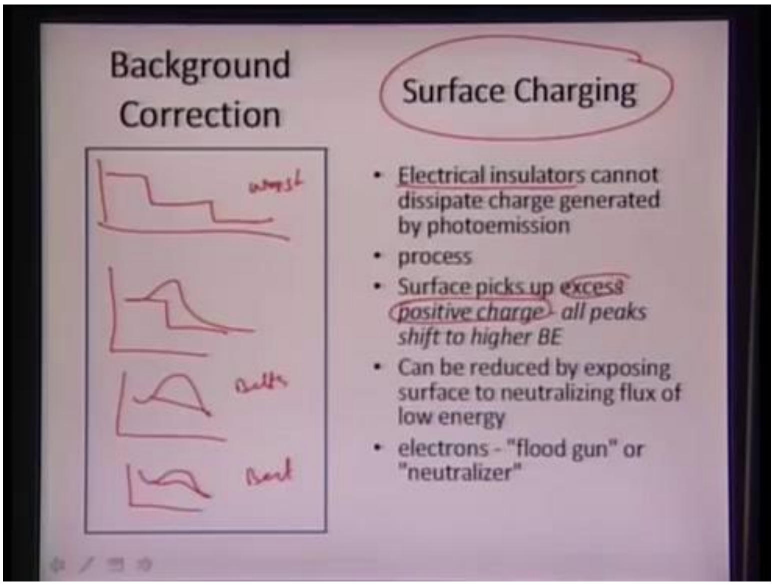

Background Correction

Surface Charging

- Electrical insulators cannot dissipate charge generated by photoemission
- process
- Surface picks up excess positive charge - *all peaks shift to higher BE*
- Can be reduced by exposing surface to neutralizing flux of low energy
- electrons - "flood gun" or "neutralizer"

Now, here background correction is also one of the very important part and, so we once we have a background which is because the spectrum shows a stepped background, we always need a good correction. So, this one is the worst case, but if we can start correcting it so because we had spectrum originally like this. And then if we are able to correct it like this it is a little better approximation, but if we are there can be another way of correcting is via joining the straight line that is little better, but the best will be if we can have a similar kind of a modulation in the background as well.

So, this is basically the best kind of background which can be corrected out here, again there can be surface charging which generates from a surface. So, basically electrical insulators cannot be dissipate charge via photoemission and surfaces basically, picking up all the excess charges. And excess positive charge since, the insulators not being able to dissipate the charge it will develop some positive charges onto it nor it will become very hard for the electron to escape.

So, all the peaks will get shifted to a higher binding energy, higher binding energy levels. And again we need can reduce the surface charge by exposing it through a neutralizing flux or low energy electron gun, which is also called the flood gun so that is what thing is all about.

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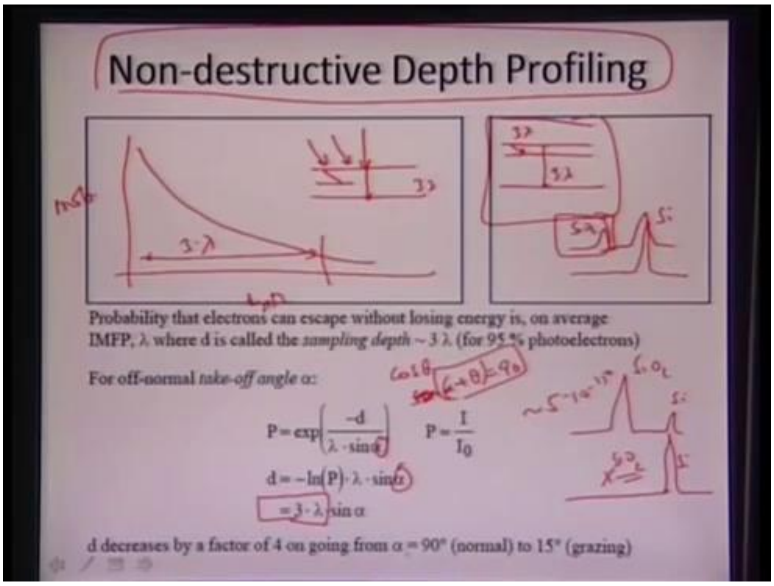

Non-destructive Depth Profiling

Probability that electrons can escape without losing energy is, on average IMFP, λ where d is called the *sampling depth* ~ 3 λ (for 95 % photoelectrons)

For off-normal *take-off angle* α:

$$P = \exp\left(\frac{-d}{\lambda \cdot \sin\alpha}\right) \qquad P = \frac{I}{I_0}$$

$$d = -\ln(P)\cdot\lambda\cdot\sin\alpha$$

$$\boxed{= 3\cdot\lambda}\,\sin\alpha$$

d decreases by a factor of 4 on going from α = 90° (normal) to 15° (grazing)

And as we realized earlier that the electron which is being emitting, which is coming out from the surface. It will the probability of electron to come out from the surface will be the probability of electron, which is coming out from the surface will decrease with the depth. So, at around 95 percent of electrons are coming from a depth of around see if this is the depth they come out from a region of around 3 times lambda. And what is advantage of this particular thing is, we can alter the angle at which the beam is being incident on the material. And we can detect what is happening at the surface of the material.

So, if we had a coating like this and we start incidenting the beam at certain 90 degree and keep starting inclining the particular beam. So, 95 percent of the depth will be around this much and this case it might go up to here, this is say 3 times lambda, but in this case this is 3 times lambda. So, we can easily correlate what is the overall depth of a particular layer. So, say if we had a particular depth and then say normally say if this was 3 lambda at certain angle, we can say this one is around 3 times lambda.

And the intensity which is coming out from there from that we can eventually say what is the overall depth profile of a particular material. So, what is on the surface and what is on the beneath the sample. So, in case in one case if we are getting certain peak for say silicon in a material and then at certain inclination, we start seeing some peaks of SiO 2 so we SiO 2 and then after inclining, we able to see SiO 2. It means there is SiO 2 is predominant on the surface and say if we incline it to a extent then we can easily see very high peak of SiO 2 at inclination angles of 5 to 10 to 15 degrees. Whereas, 90 degree normal to it will show much higher Si peak and no SiO 2.

So, this particular technique can be utilized to find the non-destructive depth profiling of a particular material. And as we had defined it earlier via using cos theta, so in this case it is sin alpha so we have sin alpha. So, we have alpha plus theta is equal to 90 degree, so that is what we have been defining here. So, alpha plus theta is 90 degree in this case we have grazing angle of alpha so that is the grazing angle.

Whereas, the theta was the overall incident angle, so that is what we able to see difference out here. So, overall depth is dependent on 3 times lambda and again it depends from 90 degree to 15 degree. So, grazing to normal angle we can basically say how much information is coming from how much depth. So, overall we in this particular technique we realize what is x-ray photoelectron spectroscopy.

So, we learned about what is x-ray photoelectron? And how it is different from an auger electron because photoelectron will depend, the energy of the photoelectron will depend on the incident energy as well. Whereas, auger electron the kinetic energy of auger electron will not depend on the incident energy which is exciting it. And then we realize, what is the kind of splitting which can occur because of the orbital splitting and the spin of an electro? So, we did see that how splitting can occur in the orbital.

Whereas, in S it is the splitting is not present whereas, in PD and other shells we do see some splitting and that particular lambda which is the mean free path the overall interaction depth of photoelectron, extends to the order of 3 times lambda. So, we can also perform a non-destructive depth profile via utilizing some grazing angles and that will provide us the chemical composition of the surface. So, with that basically I end my lecture.

Thank you.