Non - Metallic Materials

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Module - 09

Characterization of structure, composition, and microstructure of non-metallic materials

Lecture - 49

X-ray photoelectron spectroscopy

Welcome to my course Non-metallic Materials and today, we are in module number 9, Characterization of structure, composition and microstructure of non-metallic materials. This is lecture number 49, where I will be taking X-ray photoelectron spectroscopy.

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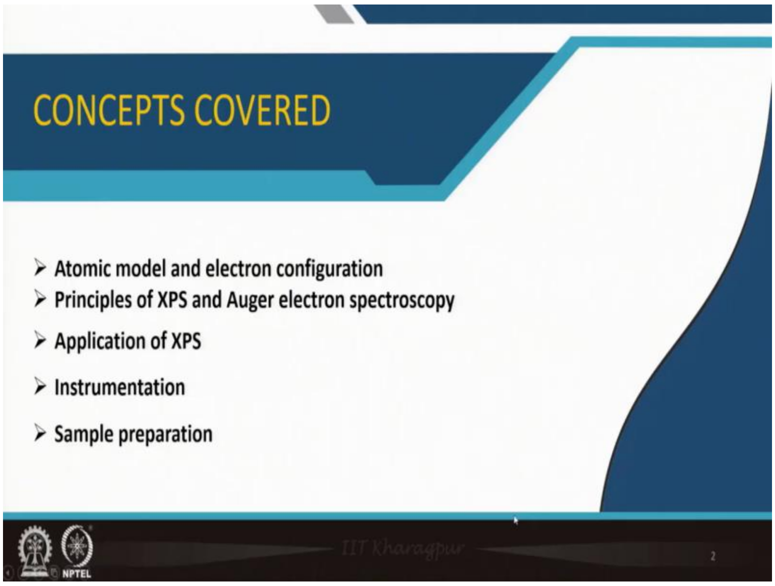

CONCEPTS COVERED

- Atomic model and electron configuration
- Principles of XPS and Auger electron spectroscopy
- Application of XPS
- Instrumentation
- Sample preparation

So, we will first introduce or rather re-brush the general idea about atomic model and electron configuration in them. Then we will discuss about the principle of XPS and Auger electron spectroscopy; then certain applications of XPS will be highlighted and a very brief details about the instrumentation will be taken followed by the sample preparation for doing this X-ray photoelectron spectroscopy measurements.

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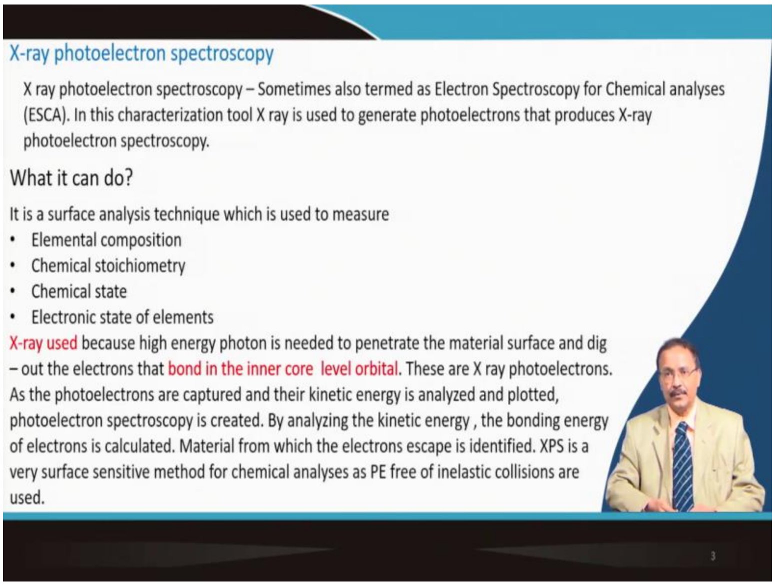

X-ray photoelectron spectroscopy

X ray photoelectron spectroscopy – Sometimes also termed as Electron Spectroscopy for Chemical analyses (ESCA). In this characterization tool X ray is used to generate photoelectrons that produces X-ray photoelectron spectroscopy.

What it can do?

It is a surface analysis technique which is used to measure

- Elemental composition
- Chemical stoichiometry
- Chemical state
- Electronic state of elements

X-ray used because high energy photon is needed to penetrate the material surface and dig – out the electrons that bond in the inner core level orbital. These are X ray photoelectrons. As the photoelectrons are captured and their kinetic energy is analyzed and plotted, photoelectron spectroscopy is created. By analyzing the kinetic energy , the bonding energy of electrons is calculated. Material from which the electrons escape is identified. XPS is a very surface sensitive method for chemical analyses as PE free of inelastic collisions are used.

Now, this X-ray photoelectron spectroscopy sometimes we also term it this as electron spectroscopy for chemical analysis and it is abbreviated as a ESCA. In this particular characterization, X-ray is used to generate photoelectrons and that eventually produces the photoelectron spectroscopy.

So, X-ray basically knocks out core electrons and we analyse the energy of the emitted electrons to have this X-ray photoelectron spectroscopy. It is basically a surface analysis technique and this is used to measure primarily elemental composition, chemical stoichiometry of a compound. It also can analyse the chemical state of a particular element and also electronic state of the elements.

Generally, X-ray is used because it is of high energy proton and that is needed to penetrate the material surface and in fact, knock out the electrons that is in the inner core level orbital of the corresponding atom. These are X-ray photo electrons and this photo electrons are captured and basically their kinetic energy is analysed and plotted and eventually this photoelectron spectroscopy is generated.

So, we analyse the kinetic energy once we analyse the kinetic energy we can have the idea about bonding energy of the electrons and that is also eventually calculated. The material where from this electrons escape is identified and this is as I told is a surface sensitive method and chemical analysis of the photo electrons are basically inelastic collisions they are used. So, therefore, it is limited to the surface of the material, which is being identified.

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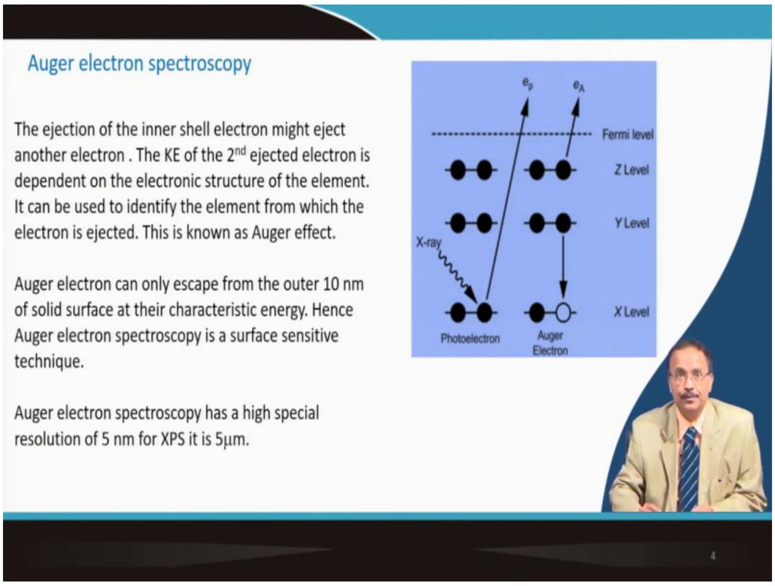

Auger electron spectroscopy

The ejection of the inner shell electron might eject another electron . The KE of the 2^{nd} ejected electron is dependent on the electronic structure of the element. It can be used to identify the element from which the electron is ejected. This is known as Auger effect.

Auger electron can only escape from the outer 10 nm of solid surface at their characteristic energy. Hence Auger electron spectroscopy is a surface sensitive technique.

Auger electron spectroscopy has a high special resolution of 5 nm for XPS it is 5μm.

So, as I told that X-ray basically knocks out the core electron and it is also possible, which is slightly variable from the photoelectron spectroscopy, something similar where another electron falls down to the vacant space and this energy whatever is emitted that can knock out another electron.

So, in the second case we term this as Auger electron and the effect is known as Auger effect. And usually this Auger electron they are escaped from the outermost surface layer and therefore, it is used to characterize the surface of a particular material.

So, Auger is also a surface sensitive technique. Now, if you compare between Auger and X-ray electron spectroscopy, you will find that the Auger electron spectroscopy is having a higher resolution about 5 micron as compared to only 5 nanometre in case of XPS, X-ray photoelectron spectroscopy.

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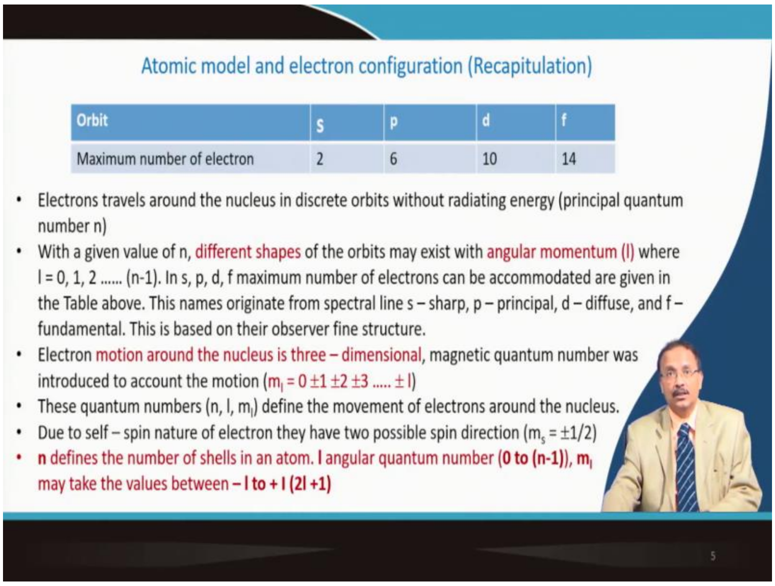

Atomic model and electron configuration (Recapitulation)

Orbit	s	p	d	f
Maximum number of electron	2	6	10	14

- Electrons travels around the nucleus in discrete orbits without radiating energy (principal quantum number n)
- With a given value of n, different shapes of the orbits may exist with angular momentum (l) where l = 0, 1, 2 ...... (n-1). In s, p, d, f maximum number of electrons can be accommodated are given in the Table above. This names originate from spectral line s – sharp, p – principal, d – diffuse, and f – fundamental. This is based on their observer fine structure.
- Electron motion around the nucleus is three – dimensional, magnetic quantum number was introduced to account the motion ($m_l = 0 \pm 1 \pm 2 \pm 3 ..... \pm l$)
- These quantum numbers (n, l, m_l) define the movement of electrons around the nucleus.
- Due to self – spin nature of electron they have two possible spin direction ($m_s = \pm 1/2$)
- n defines the number of shells in an atom. l angular quantum number **(0 to (n-1))**, **m_l** may take the values between **– l to + l (2l +1)**

Now, I will take you to the basic atomic model. So, as you know the electron travels around the nucleus in discrete orbits without radiating the energy and in that respect we can define the principal quantum number which is actually stated as n.

So, if you know for a given value of n, different shapes of orbits that may exist and with its specific angular momentum which is defined as l. l can take the value up to n minus 1 starting from 0 and this angular momentum. This is actually designated as s, p, d, f etcetera.

So, this s for example, you can take 2 electron, p can take 6 electron, d can take 10 electrons, f can take 14 electron maximum. So, that is shown in the this particular table. So, the name this s, p etcetera that has been originated from the name like s stands for sharp, p for principle, d for diffuse and f for fundamental and this is based on the fine structure observation.

So, the electron motion around the nucleus is in 3-dimensional. So, one can define magnetic quantum number and magnetic quantum number can take the value including 0 and plus minus 1, 2, 3, up to plus minus l. So, this three sets of quantum number n, l and m we abbreviated as m l that basically, define the movements of electron around the nucleus and you know the electron is having itself spin nature.

So, it can have also two spin state plus minus 1. So, spin quantum number is also defined as plus minus half. So, basically n defines the number of shell energy shell in an atom; l defines the angular quantum number it takes the value from 0 to n minus n, m, l may take any values from minus l to plus l. So, total number is 12 plus 1. So, this is known to most of you.

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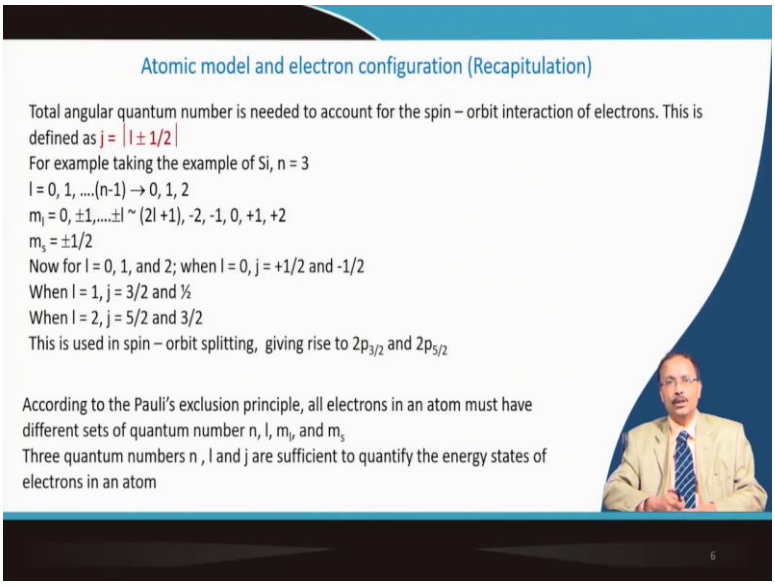

Atomic model and electron configuration (Recapitulation)

Total angular quantum number is needed to account for the spin – orbit interaction of electrons. This is defined as $j = |l \pm 1/2|$

For example taking the example of Si, n = 3

$l = 0, 1, ...(n-1) \rightarrow 0, 1, 2$

$m_l = 0, \pm 1, ... \pm l \sim (2l + 1), -2, -1, 0, +1, +2$

$m_s = \pm 1/2$

Now for l = 0, 1, and 2; when l = 0, j = +1/2 and -1/2

When l = 1, j = 3/2 and ½

When l = 2, j = 5/2 and 3/2

This is used in spin – orbit splitting, giving rise to $2p_{3/2}$ and $2p_{5/2}$

According to the Pauli's exclusion principle, all electrons in an atom must have different sets of quantum number n, l, m_l, and m_s

Three quantum numbers n , l and j are sufficient to quantify the energy states of electrons in an atom

Now, the total angular quantum number is needed because you will have to account for both the orbital motion of the electron as well as it is spin motion and there is a spin orbital interaction of electron. And, this is basically defined as this small j, which is the magnitude of l plus minus half and this stands for the speed and l value is the other quantum number.

So, if you take the example of silicon which is having three electrons so, l can assume the value of 0, 1 and 2, so that up to n minus 1 it can take the value of m l that can be 0 plus minus 1, plus minus 2 and so on. So, it can take basically for if n equal to 3, it is having 12 plus 1 value. So, total you have minus 2, minus 1, 0, plus 1, plus 2.

And, m s is plus minus half. So, if you consider l equal to 0, 1 and 2, then if l equal to 0 then after the spin orbital coupling j can have the value either plus half and minus half. When l equal to 1, then it can take one plus half and one minus half; that means, 3 by 2 and half, similarly when l equal to 2 it can take 5 by 2 and 3 by 2. So, this is used in spin - orbital splitting and that give rise to 2p 3 by 2, 2p 5 by 2 and stuff like that.

So, according to the Pauli's exclusion principle all electrons in an atom must have different sets of quantum number n, l, m l and m s. Now, basically three quantum number since this spin orbital coupling is there so, basically three quantum number n, l and j. They are sufficient to quantify the energy states of electron in an atoms.

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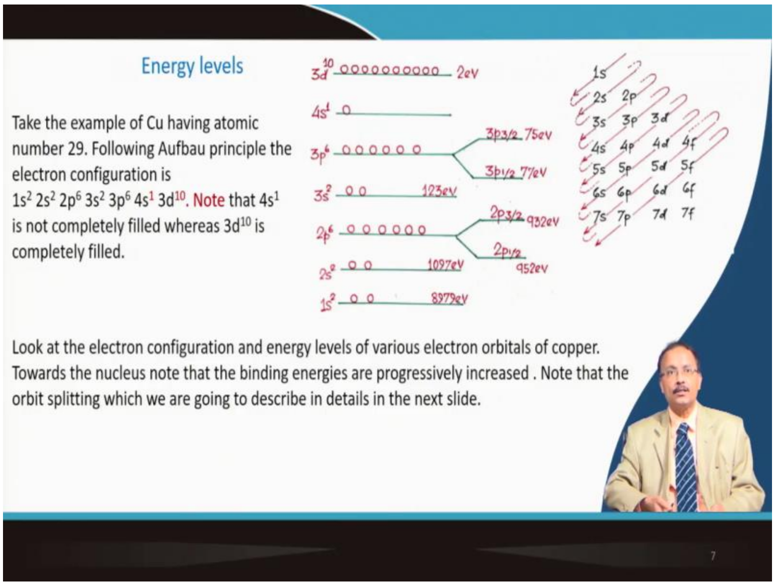

Energy levels

Take the example of Cu having atomic number 29. Following Aufbau principle the electron configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$. Note that $4s^1$ is not completely filled whereas $3d^{10}$ is completely filled.

Look at the electron configuration and energy levels of various electron orbitals of copper. Towards the nucleus note that the binding energies are progressively increased . Note that the orbit splitting which we are going to describe in details in the next slide.

So, you can take the example of copper which is slightly different if you follow the Aufbau principle the atomic number here is 29 and if you follow the Aufbau principle then you can fill it up as 1s 2 2s 2 2p 6 3s 2 3p 6 instead of 4s 2 it takes 4s 1 and 3d orbital are completely filled.

So, that has been shown here based on the estimation of Aufbau principle to fill up the electron level. So, here 4s 1 is the 4s orbital is not completely filled, but this 3d orbital is completely filled instead, it should have been 9. So, you just look at the electron configuration and the energy level of various electron orbital’s particularly for copper.

So, towards the nucleus that the binding energy are progressively increased as you can see here and due to this orbital splitting, which we are going to describe in detail in the forthcoming slides you can see that this 2p orbital and also 3p orbital they are split in terms of 2p half and 2p 3 by 2, which have different energy level and similarly 3p half and 3p 3 by 2.

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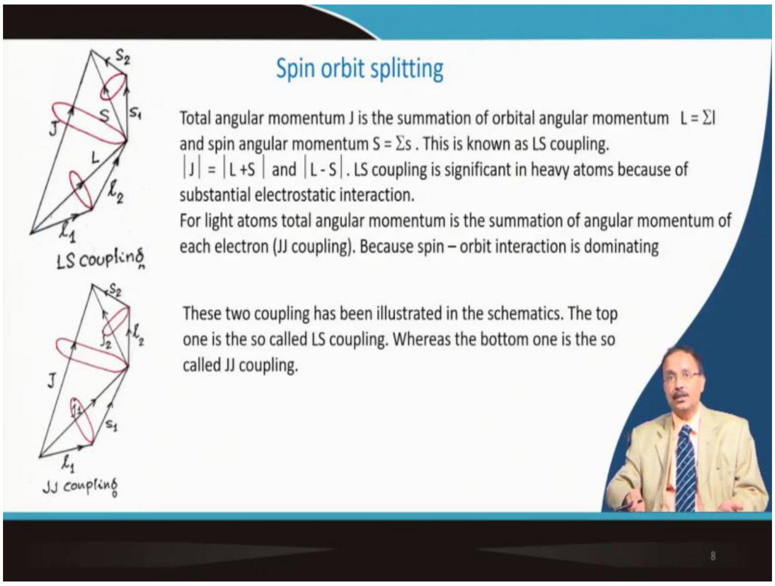

Spin orbit splitting

Total angular momentum J is the summation of orbital angular momentum $L = \Sigma l$ and spin angular momentum $S = \Sigma s$. This is known as LS coupling.
$|J| = |L+S|$ and $|L-S|$. LS coupling is significant in heavy atoms because of substantial electrostatic interaction.
For light atoms total angular momentum is the summation of angular momentum of each electron (JJ coupling). Because spin – orbit interaction is dominating

These two coupling has been illustrated in the schematics. The top one is the so called LS coupling. Whereas the bottom one is the so called JJ coupling.

So, this spin orbital splitting just now, I mentioned that is important total angular momentum that J is basically the summation of all orbital angular momentum because in a particular element I am not considering one single electron, there are number of electrons. So, this capital L is basically the summation of the small l, which just I described and the spin angular momentum this capital X S is also summation of small s.

So, this is known as LS coupling. So, the J modulus of J is nothing, but L plus S and L minus S. So, this LS kind of coupling that is significant in heavy atom because of substantial electrostatic interaction. For lighter atoms the total angular momentum is a summation of angular momentum of each electron. So, we call this is a JJ coupling and here spin orbit interaction is dominating.

This has been demonstrated in this two schematic. So, in case of LS coupling you can see that L and L that gives rise to this L vector and similarly S and S different S that gives to this that is a summation of this small spin and then this is a LS coupling that gives rise to J. In case of JJ coupling, it is L and S that gives you J here. And similarly, this l 2 and s 2 that also gives J 2 and then basically you get from this vector and this vector this. So, called JJ coupling that is achieved.

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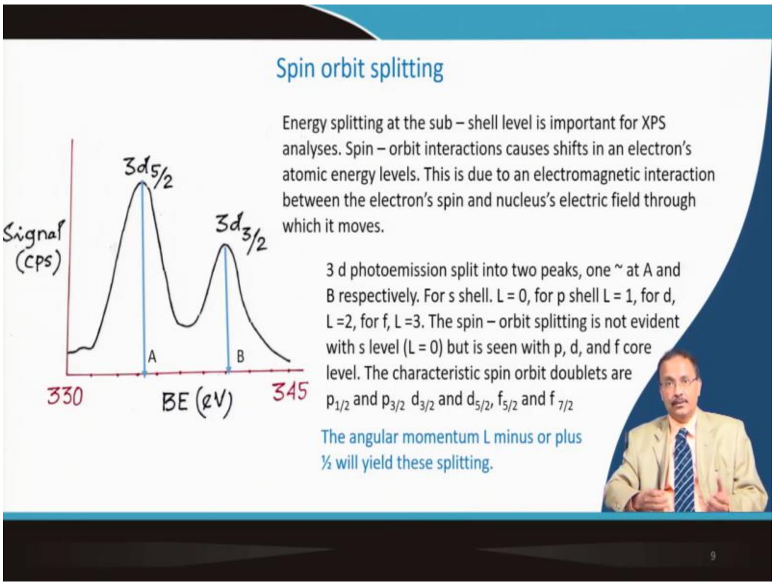

Spin orbit splitting

Energy splitting at the sub – shell level is important for XPS analyses. Spin – orbit interactions causes shifts in an electron's atomic energy levels. This is due to an electromagnetic interaction between the electron's spin and nucleus's electric field through which it moves.

3 d photoemission split into two peaks, one ~ at A and B respectively. For s shell. L = 0, for p shell L = 1, for d, L =2, for f, L =3. The spin – orbit splitting is not evident with s level (L = 0) but is seen with p, d, and f core level. The characteristic spin orbit doublets are $p_{1/2}$ and $p_{3/2}$ $d_{3/2}$ and $d_{5/2}$, $f_{5/2}$ and $f_{7/2}$

The angular momentum L minus or plus ½ will yield these splitting.

Now, the energy splitting at the sub shell is very important in case of XPS analysis. So, this spin orbital interaction that causes a shift in an electron atomic energy level and basically this is due to the electromagnetic interaction between the electron spin. And the nucleus electric field through which it moves across this nucleus.

So, for example, the 3D photoemission split into two peaks as you have seen that one is at a position of binding energy A and another one is binding energy B. So, for s shell we can take L equal to 0 and p shell L equal to 1, for d shell L equal to 2, f shell L equal to 3.

So, the spin orbital splitting is not evident with the s level where L equal to 0, but with p, d, f that core level the characteristic spin orbital doublet is observed in terms of p half and p 3 by 2 as I have shown d 3 by 2, d 5 by 2, then f f by 2, f 7 by 2 and so on. So, the angular momentum L minus or plus half that is due to spin that will lead to this kind of splitting.

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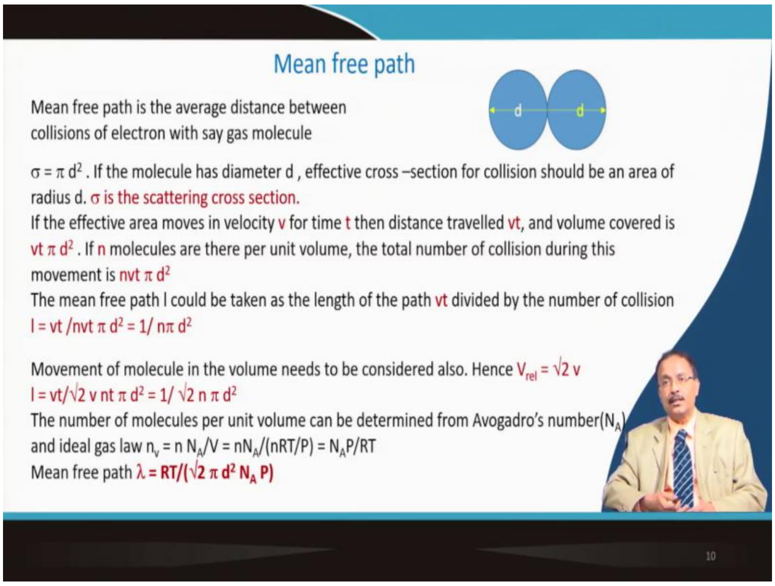

Mean free path

Mean free path is the average distance between collisions of electron with say gas molecule

$\sigma = \pi d^2$. If the molecule has diameter d , effective cross –section for collision should be an area of radius d. σ is the scattering cross section.
If the effective area moves in velocity v for time t then distance travelled vt, and volume covered is $vt \pi d^2$. If n molecules are there per unit volume, the total number of collision during this movement is $nvt \pi d^2$
The mean free path l could be taken as the length of the path vt divided by the number of collision
$l = vt / nvt \pi d^2 = 1/ n\pi d^2$

Movement of molecule in the volume needs to be considered also. Hence $V_{rel} = \sqrt{2}\, v$
$l = vt/\sqrt{2}\, v\, nt \pi d^2 = 1/ \sqrt{2}\, n \pi d^2$
The number of molecules per unit volume can be determined from Avogadro's number(N_A) and ideal gas law $n_v = n N_A/V = nN_A/(nRT/P) = N_A P/RT$
Mean free path $\lambda = RT/(\sqrt{2}\, \pi d^2 N_A P)$

Now, we should also consider the mean free path and which is the average distance between the collisions of the electron say with the gas molecule. It is important for XPS analysis because you are keeping the sample in an evacuated chamber I will describe it and then finally, you are getting this photo electron emitted.

So, there is a possibility for the photoelectron to get scattered by the gas molecule, which may be still there in the vacuum chamber. So, mean free path calculation is important here we are trying to give you some idea about how to estimate really the mean free path. So, here two arbitrary molecule that you can consider which is having a diameter d. So, you can define a scattering cross-section, which is basically defined as sigma which is pi d square.

So, this effective area that moves say in a velocity of v for time t, so, the distance that it will travel is vt and the volume that it will cover is distance into area. So, vt into pi d square. So, now you assume n molecules are there per unit volume. So, the total number of collision during the movement could be just the product of this n with this scattering volume vt pi d square.

So, the mean free path which is defined as l initially that could be taken as a length of the path vt the distance divided by the number of collision. So, this l value is vt divided by n vt pi d square. So, that eventually comes to 1 by n pi d square. Now, we did not consider here that the gas molecule will also move. So, there should be a relative velocity for the gas molecule and we can take it as root over of this v that we considered.

So, if you put back this value with the mean free path expression, then you will get 1 by root 2 n pi d square. So, the number of molecules per unit volume that can be determined from the Avogadro number I am applying the well known ideal gas law. So, that we have done. So, this is the number of atom this is into Avogadro number by the volume.

So, the volume you can apply in ideal gas equation PV equals nRT. So, replace by this. So, basically you are getting this expression Avogadro number into pressure by RT. So, the mean free path that will be RT divided by root over of pi d square N A into P.

So, if the P is reduced, then the mean free path will suddenly be increased; temperature if it is increased there will be more collision so, the lambda will be reduced. So, this expression is useful for analysing the XPS spectra.

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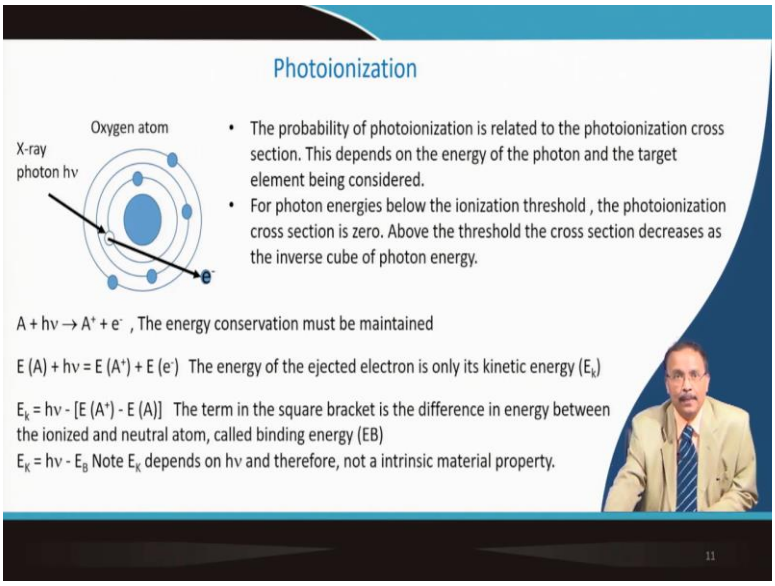

Photoionization

- The probability of photoionization is related to the photoionization cross section. This depends on the energy of the photon and the target element being considered.
- For photon energies below the ionization threshold , the photoionization cross section is zero. Above the threshold the cross section decreases as the inverse cube of photon energy.

$A + h\nu \rightarrow A^+ + e^-$, The energy conservation must be maintained

$E(A) + h\nu = E(A^+) + E(e^-)$ The energy of the ejected electron is only its kinetic energy (E_k)

$E_k = h\nu - [E(A^+) - E(A)]$ The term in the square bracket is the difference in energy between the ionized and neutral atom, called binding energy (EB)

$E_K = h\nu - E_B$ Note E_K depends on hν and therefore, not a intrinsic material property.

Then what actually is happening? This is called photo ionization. So, in the photo ionization as I mentioned that X-ray they knock out one of the core electrons. So, the probability of this photo ionization is related to the photo ionization cross-section and this basically depends on the energy of the photon and the target element where it is hitting.

So, that is important. Energy of the photon and the target element that is being considered what binding energy is there at this particular energy level. So, if the photon energy is below the ionization threshold then the photo ionization cross-section is considered to be 0. But above the threshold the cross-section decreases roughly as the inverse cube of the photon energy.

So, that you can consider that leads to the probability for the generation of this photo ionization this photo electron. So, during the process the energy conservation must be maintained. So, if I consider A is one atom and it is being struck by this energy h nu. So, electron is going out so, it is getting ionized and ionized atom will be there and the electron this photo electron will be generated.

In terms of the energy conservation, energy of E A plus the energy that you were putting that is equal to energy of this ionized atom plus the kinetic energy of the electron. The electron energy is only kinetic energy; we have termed it as E K. Now, you can get the value of E K is equal to the energy that you are putting this X-ray energy minus the energy of the ionized atom minus E A.

So, the term in the square bracket is the difference in the energy between the ionized and neutral atom and this is called the binding energy. So, the kinetic energy of electron is nothing, but the energy of the X-ray minus binding energy. So, this kinetic energy E K it depends on the X-ray energy h nu and therefore, this is not an intrinsic material property. We change the X-ray energy, so, that will also change the binding energy will also change.

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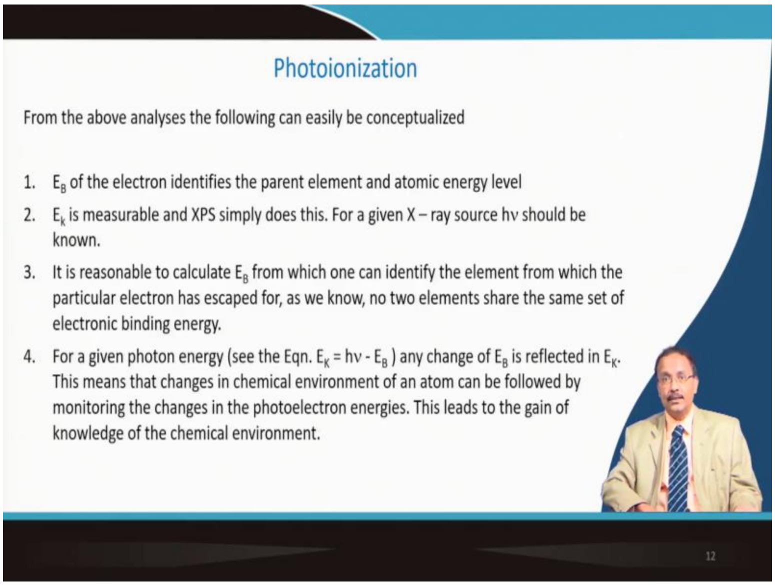

Photoionization

From the above analyses the following can easily be conceptualized

1. E_B of the electron identifies the parent element and atomic energy level
2. E_k is measurable and XPS simply does this. For a given X – ray source hν should be known.
3. It is reasonable to calculate E_B from which one can identify the element from which the particular electron has escaped for, as we know, no two elements share the same set of electronic binding energy.
4. For a given photon energy (see the Eqn. $E_K = h\nu - E_B$) any change of E_B is reflected in E_K. This means that changes in chemical environment of an atom can be followed by monitoring the changes in the photoelectron energies. This leads to the gain of knowledge of the chemical environment.

So, this above analysis we can tell that, E B the binding energy of electron that can be used to identify the parent element and atomic energy level where the electrons are situated, E K is basically miserable XPS does only that. For a given X-ray source the h nu should be known, right in order to calculate the value of E K.

So, it is reasonable to calculate E B from which one can identify the element from which the particular electron has been escaped as we know that no two elements share the same set of same electron binding energy. So, for a given photon energy just recall the equation E K is equal to h nu minus E B.

Any change in E B is reflected in E K this means that the change in the chemical environment of an atom can be followed by monitoring the changes of the photoelectron energy. This leads to the gain of knowledge of the chemical environment. So, that is the principle of XPS analysis.

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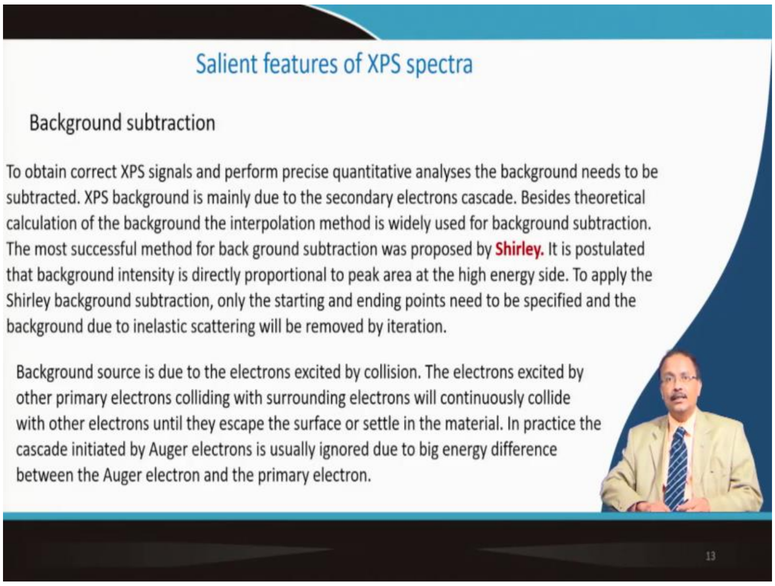

Salient features of XPS spectra

Background subtraction

To obtain correct XPS signals and perform precise quantitative analyses the background needs to be subtracted. XPS background is mainly due to the secondary electrons cascade. Besides theoretical calculation of the background the interpolation method is widely used for background subtraction. The most successful method for back ground subtraction was proposed by **Shirley.** It is postulated that background intensity is directly proportional to peak area at the high energy side. To apply the Shirley background subtraction, only the starting and ending points need to be specified and the background due to inelastic scattering will be removed by iteration.

Background source is due to the electrons excited by collision. The electrons excited by other primary electrons colliding with surrounding electrons will continuously collide with other electrons until they escape the surface or settle in the material. In practice the cascade initiated by Auger electrons is usually ignored due to big energy difference between the Auger electron and the primary electron.

So, there are certain salient features of the XPS spectra: To obtain the correct XPS signal and perform a precise quantitative analysis you must remove the background. So, this XPS background that basically due to the secondary electron cascade. So, beside theoretical calculation of the background, the interpolation method that has been widely used for this background subtraction and most successful method to subtract the X-ray background is given by Shirley.

And, nowadays software’s are available if you just call your XPS spectra according to this Shirley method, it can very nicely remove the background. So, during this Shirley postulate that the background intensity is directly proportional to the peak area particularly at the high energy side.

So, apply the Shirley background subtraction, only the starting and ending point needs to be specified and the background due to inelastic scattering will be removed by iteration. So, then the background will be removed. So, the background source is due to the electrons excited by collision.

So, electrons are excited by the primary electrons. They also collide will surrounding electrons and will keep colliding with other electrons and finally, escape the surface or it can settle in the material as well. So, in practice the cascade initiated by Auger electron is usually ignored because of a very big energy difference between the Auger electron and the primary electron.

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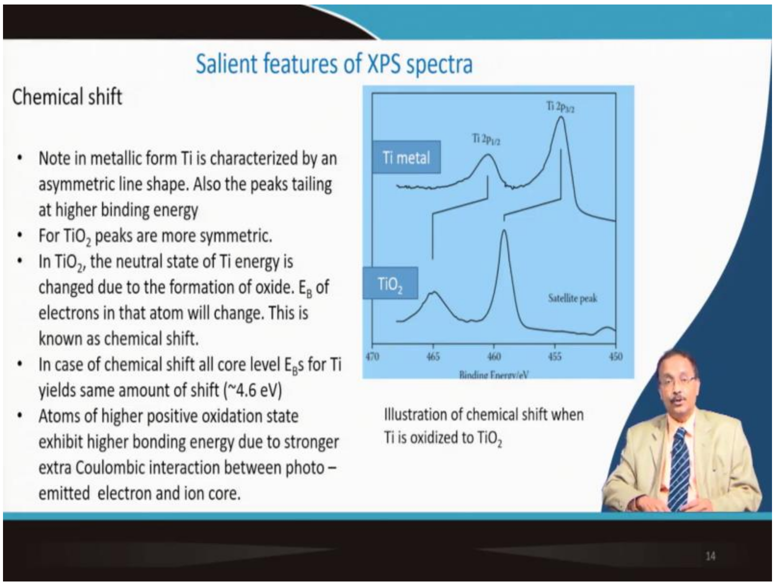

Salient features of XPS spectra

Chemical shift

- Note in metallic form Ti is characterized by an asymmetric line shape. Also the peaks tailing at higher binding energy
- For TiO_2 peaks are more symmetric.
- In TiO_2, the neutral state of Ti energy is changed due to the formation of oxide. E_B of electrons in that atom will change. This is known as chemical shift.
- In case of chemical shift all core level E_Bs for Ti yields same amount of shift (~4.6 eV)
- Atoms of higher positive oxidation state exhibit higher bonding energy due to stronger extra Coulombic interaction between photo – emitted electron and ion core.

Illustration of chemical shift when Ti is oxidized to TiO_2

So, you can get the chemical shift you I have shown two examples, one is the metallic form of titanium. This is basically characterized by an asymmetric XPS peak and also the tail of the peak is towards the higher binding energy. When the oxide forms the peak as you can see they are more symmetric in titanium oxide.

So, the neutral state of titanium energy is changed due to the formation of the oxide. So, the binding energy of the electron in the atom will change and this is known as chemical shift you can see the it is T titanium 2p half is shifted here and 3 by 2 is also shifted here. So, the chemical shift for both the peaks they are actually same.

So, in case of the chemical shift for core level the binding energy is for titanium in the same amount of shift; in this case it is about 4.6 electron volt. So, atoms of higher positive oxidation state exhibits higher bonding energy due to stronger existing Coulombic interaction between the photo-emitted electron and the ion cores. So, this thing you can estimate.

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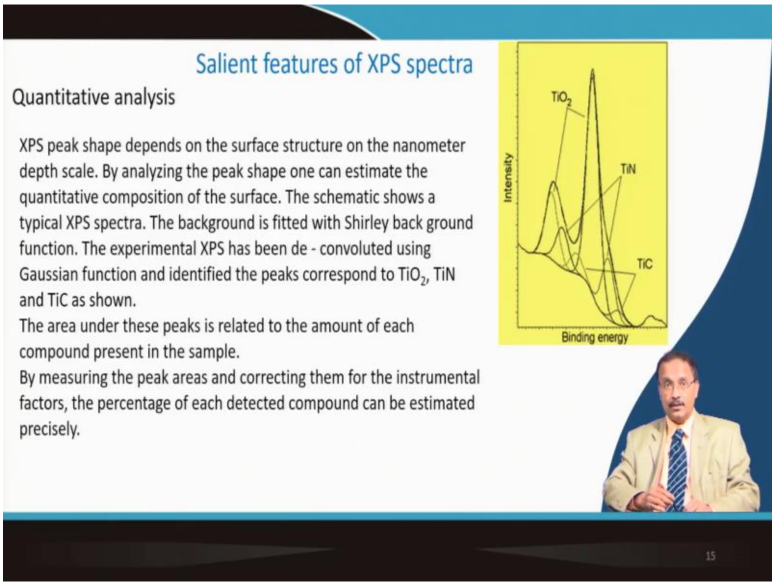

Salient features of XPS spectra

Quantitative analysis

XPS peak shape depends on the surface structure on the nanometer depth scale. By analyzing the peak shape one can estimate the quantitative composition of the surface. The schematic shows a typical XPS spectra. The background is fitted with Shirley back ground function. The experimental XPS has been de - convoluted using Gaussian function and identified the peaks correspond to TiO_2, TiN and TiC as shown.

The area under these peaks is related to the amount of each compound present in the sample.

By measuring the peak areas and correcting them for the instrumental factors, the percentage of each detected compound can be estimated precisely.

Second one is you can do quantitative analysis. So, XPS peak shape is dependent on the structure on the nanometre depth scale. So, you analyze the peak shape one can actually estimate quantitative composition of the surface, surface of the material.

So, a schematic is shown a typical XPS spectra where you can see the original spectra has been de-convoluted using mainly a Gaussian function because it is quite symmetric when it is not metallic form, but it is oxide or other compound form.

So, one can identify the peak correspond to TiO_2, TiN, titanium carbide in this material. So, area under the peak that is related to amount of the each compound, present in the sample. So, that give you some idea about what is the composition of the material particularly at the surface.

So, if I measure the peak areas and of course, some correcting factors are involved that is called instrumental correction factor and nowadays, the software takes care of it, then percentage of each detected compound can be very precisely estimated by this technique.

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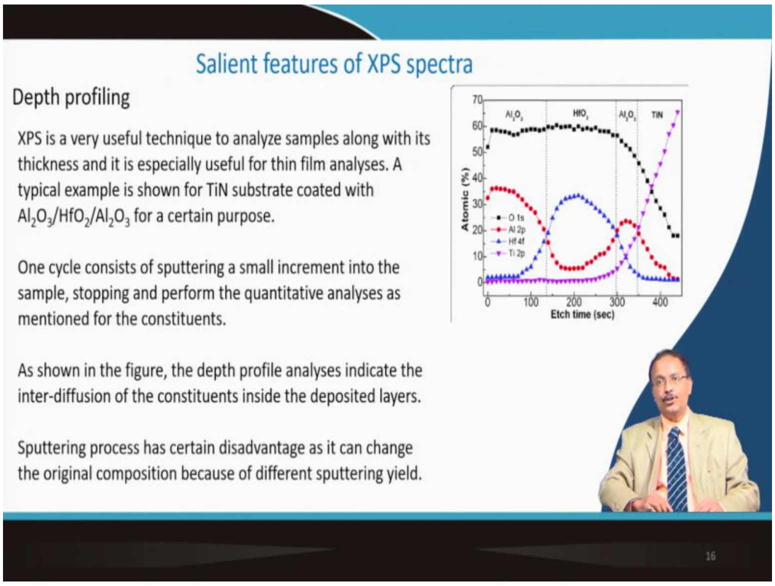

Salient features of XPS spectra

Depth profiling

XPS is a very useful technique to analyze samples along with its thickness and it is especially useful for thin film analyses. A typical example is shown for TiN substrate coated with $Al_2O_3/HfO_2/Al_2O_3$ for a certain purpose.

One cycle consists of sputtering a small increment into the sample, stopping and perform the quantitative analyses as mentioned for the constituents.

As shown in the figure, the depth profile analyses indicate the inter-diffusion of the constituents inside the deposited layers.

Sputtering process has certain disadvantage as it can change the original composition because of different sputtering yield.

Another thing that you can do is called depth profiling. So, XPS is very useful technique to analyse sample along with this thickness. So, what you do you sputter part of the material and then keep taking the XPS spectra as a function of depth and then analyze the constituents in terms of it is composition.

And, here is a typical plot where I have shown that on titanium nitride initially aluminium oxide film is there, then Hafnium film is there, then aluminium oxide film is there. So, for across the depth starting from the surface towards the substrate you can basically get the composition of each elements from their different XPS spectra and you can plot it. We call this is a depth profile.

And, this kind of plot is very important for you to identify that along with the depth – how this type of elemental composition changes, whether you have a very sharp boundary or you have a diffused boundary or whether substrate is eventually coming into inside the film. Here you see the titanium has been diffused in the first layer, but that is not that prominent in the outermost layer.

But, sputtering is having a problem you know that in case of sputtering each of this element is having different sputtering yield. So, during sputtering also it is possible for you to change the composition. So, one must be cautious that sputtering may not be that much effective in very precisely knowing the composition across the film thickness. So, this is another way of doing it.

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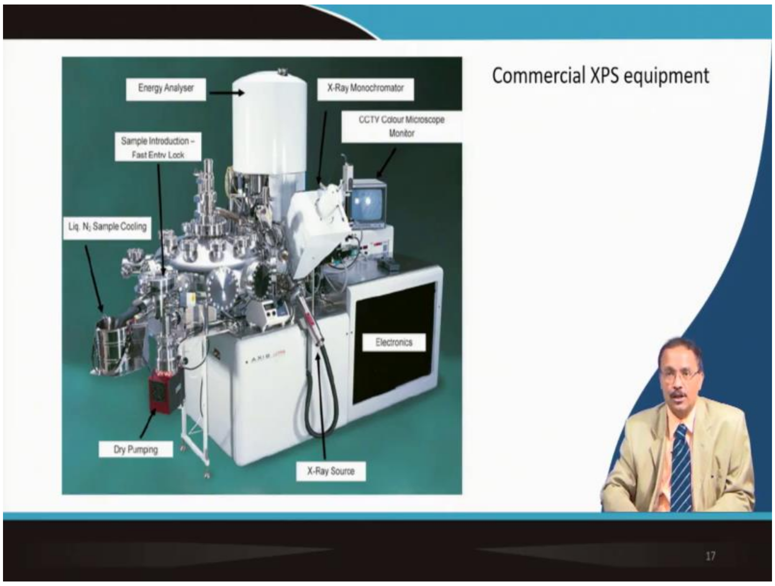
Commercial XPS equipment

The actual XPS equipment that is quite complicated, but you know that there should be an X-ray source. There should be a CCTV to image the sample inside the chamber, the sample sits somewhere here; then to make X-ray monochromatic one monochromator is there.

So, an energy analyser is there which basically analyse the electron energy which is coming out the photoelectron that is coming out, the kinetic energy is analysed and in on the basis of having the value of h nu of the X-ray you can estimate the binding energy.

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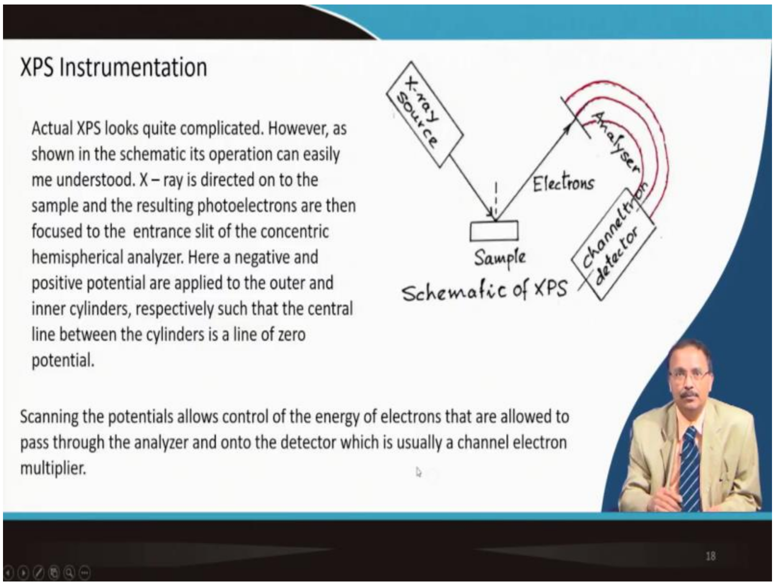
XPS Instrumentation

Actual XPS looks quite complicated. However, as shown in the schematic its operation can easily me understood. X – ray is directed on to the sample and the resulting photoelectrons are then focused to the entrance slit of the concentric hemispherical analyzer. Here a negative and positive potential are applied to the outer and inner cylinders, respectively such that the central line between the cylinders is a line of zero potential.

Scanning the potentials allows control of the energy of electrons that are allowed to pass through the analyzer and onto the detector which is usually a channel electron multiplier.

So, it is it looks quite complicated, but it is not that complicated I mean in principle they are quite simple you need an X-ray source. And, this is directed on the sample and the resulting photoelectron are focused in an entrance slit of a concentric hemispherical analyser.

So, here a negative potential is applied at the outer surface and the inner surface it is having a positive potential so that the central line between the cylinders is a line of zero potential. And, scanning the potential allows to control of the energy of electron that are allowed to pass through the analyser. And finally, to the detective which is termed as a channel detector multiplier to know the kinetic energy of the electron which is emitted because of the X-ray bombardment.

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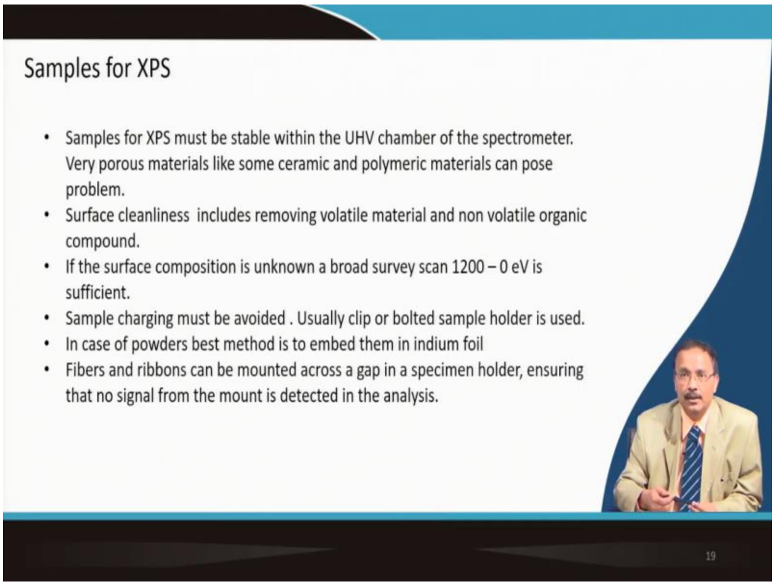

Samples for XPS

- Samples for XPS must be stable within the UHV chamber of the spectrometer. Very porous materials like some ceramic and polymeric materials can pose problem.
- Surface cleanliness includes removing volatile material and non volatile organic compound.
- If the surface composition is unknown a broad survey scan 1200 – 0 eV is sufficient.
- Sample charging must be avoided . Usually clip or bolted sample holder is used.
- In case of powders best method is to embed them in indium foil
- Fibers and ribbons can be mounted across a gap in a specimen holder, ensuring that no signal from the mount is detected in the analysis.

The sample of XPS must be stable; one should not use a porous sample. It is difficult to hold it. It can pose problem particularly when you are maintaining a very high rate of vacuum because of the mean free path criteria, which I described earlier. Surface cleanliness that is also important to remove the volatile material and non-volatile organic compound it is important.

One advantage is that you cannot get rid of the carbonaceous residue in fact to calibrate the XPS we use the carbon peak position to know the instrumental shift. So, in what in one way it is good to have carbonaceous residue on the surface which is almost unavoidable and if the surface composition is unknown then a broad scan initially is done in a range of 0 to 1200 electron volt. And, then whatever area you are interested in you can have a short scan to identify the particular 2 p or 3 d peaks to analyse your spectra.

Sample charging usually must be avoided and usually the samples are either clipped or bolted firmly inside the chamber. Powder sample it is difficult to do XPS. So, sometimes it is embedded in indium foil to get the XPS spectra. In case of fibre or ribbons they must be mounted across a gap specimen holder, but it must be ensured that the signal is detected only from the tiny sample, but not from the sample holder for the analysis.

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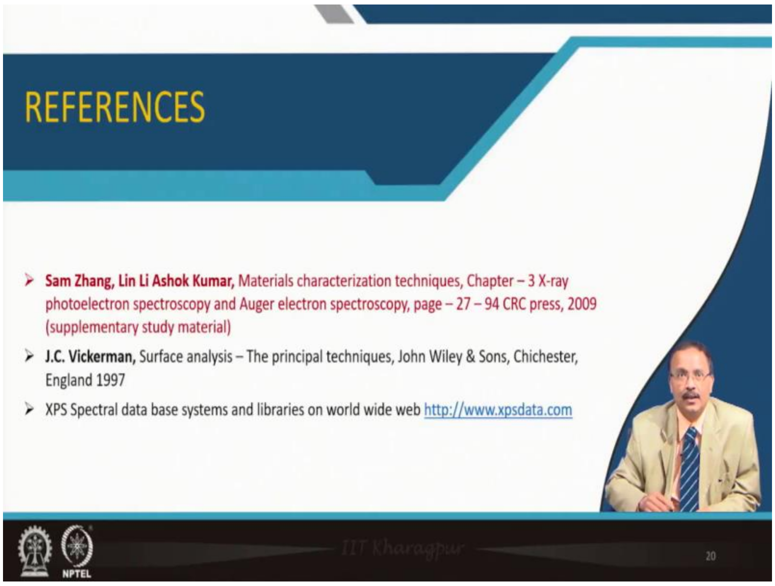

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- **Sam Zhang, Lin Li Ashok Kumar,** Materials characterization techniques, Chapter – 3 X-ray photoelectron spectroscopy and Auger electron spectroscopy, page – 27 – 94 CRC press, 2009 (supplementary study material)
- **J.C. Vickerman,** Surface analysis – The principal techniques, John Wiley & Sons, Chichester, England 1997
- XPS Spectral data base systems and libraries on world wide web http://www.xpsdata.com

So, the book by Zhang Materials characterization technique, Chapter 3 is the study material; other than that the book by J. C. Vickerman, Surface analysis is also a good source. And XPS Spectral data base they are available in the website to get the idea of various XPS spectra in a single space.

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CONCLUSION

- Atomic model and electron configuration
- Energy levels
- Spin – orbit splitting
- Mean free path
- Principle of XPS
- Application of XPS
- XPS instrumentation
- Sample preparation

So, in this particular lecture we talked about atomic model and electronic configuration, then the energy levels, then spin-orbital’s splitting, then the concept of mean free path and why they are important, then principle of XPS, as well as Auger analysis – analysis part of Auger I have not covered in this particular lecture. Then various applications of XPS has been highlighted.

And then finally, a brief look at the XPS instrumentation followed by that the precaution that you will take in sample preparation.

Thank you for your attention.