Nanostructres and Nano Materials: Charecterization and properties
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Lecture - 39
Auger Electron Spectroscopy

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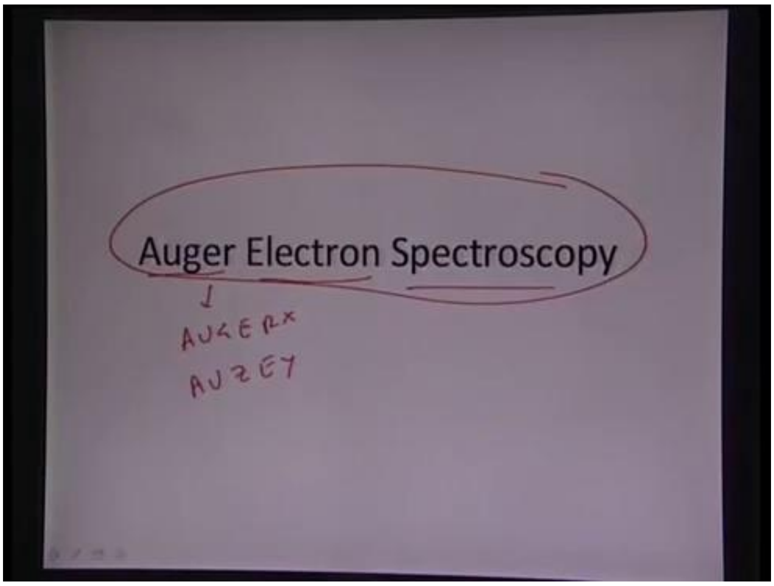

Auger Electron Spectroscopy

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AUZEY

In this lecture we learn about Auger electron spectroscopy. Here, we say, but o u g g e r it is not pronounced as oogar, but it is pronounced as o j a u z e y. so, pronunciation is more like Auger electron spectroscopy and that we utilize Auger electrons for the for achieving a particular spectrum, so that is the reason we use Auger electron spectroscopy.

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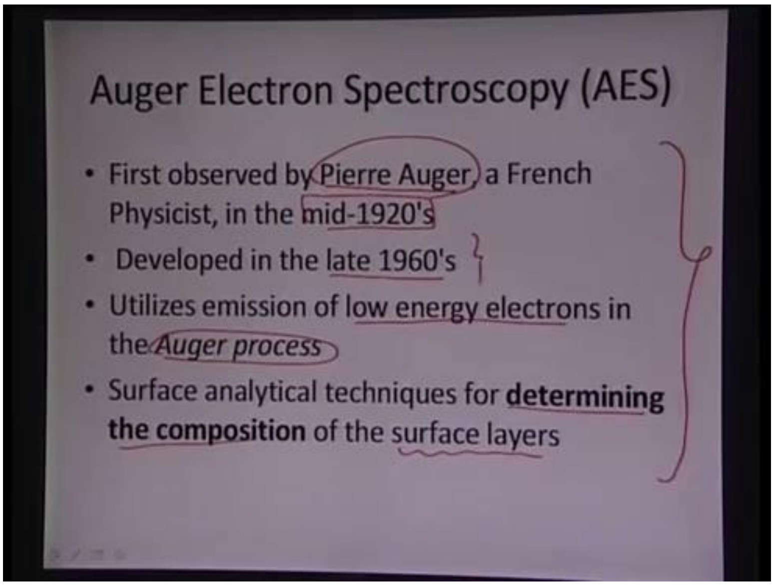

Auger Electron Spectroscopy (AES)

- First observed by Pierre Auger, a French Physicist, in the mid-1920's
- Developed in the late 1960's
- Utilizes emission of low energy electrons in the *Auger process*
- Surface analytical techniques for **determining the composition** of the surface layers

Auger electron spectroscopy, the Auger effect was initially observed by Pierre Auger a French physicist in mid 1920 s and this process have developed only in the late 1960 s. This particular process utilizes emission of low energy electrons which are generated by the Auger process. What is this Auger process, we will see we will understand that later on, but it is a surface analytical technique for determining the composition of the surface layer. So, it is highly surface sensitive technique and that is what we will see in this particular lecture.

So, this Auger electron it was discovered by Pierre Auger on which this particular spectroscopic technique is named on. It was later on developed only in 1960 s, which utilizes a low energy electron which is a Auger electron to achieve a chemical composition mainly of the surface, it is highly surface sensitive technique.

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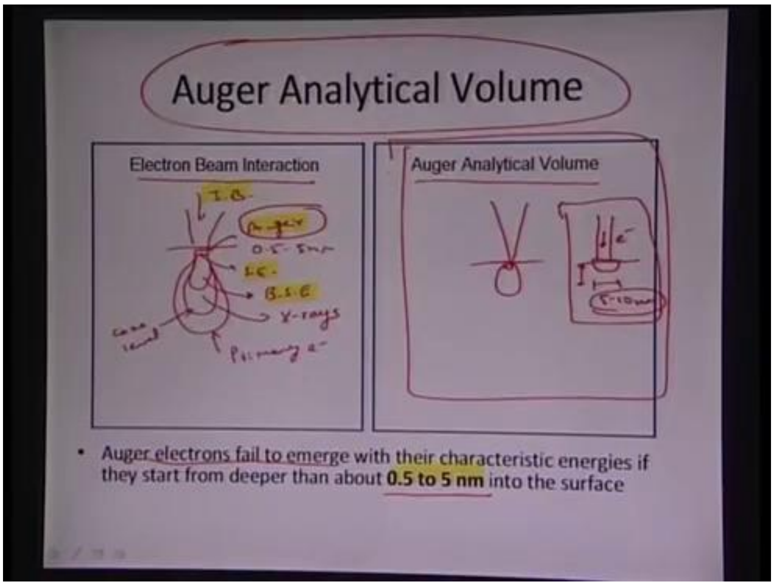

Auger Analytical Volume

Electron Beam Interaction

Auger Analytical Volume

- Auger electrons fail to emerge with their characteristic energies if they start from deeper than about **0.5 to 5 nm** into the surface

Once we initiate a electron beam how does this particular process emerges, we will see initially the how the electron beam interact with the material. So, we have this electron beam which comes and interacts with the material, so there is there are certain interactions which are which keep occurring. It forms overall interaction is contribute certain region for the depth of a material, so we certain regimes which are more like this that we see only a very surface depth of 0.5 to 5 nanometer, which generate something called Auger electrons. This is nothing but the incident beam which is tracking on to the surface of a material and we need the surface we will have some interactions from which comes out of the secondary electron.

Then, we have some elastically scattered electron some regime of back scattered electron then we have something, which is corresponding to the regime of interaction with electron beam to produce x rays. Then, this is regime of primary electrons and this regime is coming out from the core level ionization, so we see that the Auger how the electron beam is interacting with the material we see that the incident beam. The incident beam actually which is out here like this is the incident beam, it is interacting with the material and the surface layer generates Auger electrons and Auger electrons are characteristic within a certain regime of around 0.5 to 5 nanometers.

Beneath that, we have some electrons which are emerging which are called secondary electron these are again elastically scattered electrons. Then, we have some elastic scattering with the material, which result back scattered electrons and in this particular lecture we are more interested in what is happening at the surface layer. So, we are more interested in the Auger process for this particular case and the Auger analytical volume it means how much volume is being interacted when the electron beam is interacting with the material to generate some Auger electrons. So, we see that once the electron beam is being indenting on to the material it is interacting only in very small amount which is corresponding to around 0.5 to 5 nanometer.

This particular analytical volume this is the overall interaction volume and then if we consider this is an electron beam which is indenting onto the material only a very low level of volume. It may be limited to may be couple of nanometers 5 to 10 nanometersis really interacting with the material to result Auger electrons and as we say that this is highly surface sensitive because all the interactions, they are they are being coming to the detector only within a surface regime of 5 to 10 nanometers. It does not mean that the Auger electrons are not being generated in any other location, it just mean that only the surface electrons surface Auger electrons which are generated they are able to escape the surface of the material or the sample to reach the detector.

So, Auger electrons are being generated even inside the material once the beam is interacting with the material. So, we see in this particular process though electrons are Auger electrons are being generated they do not acquire sufficient energy to come back to the to leave the sample surface and that is what we see that the that the interaction volume is limited to around 5 to 10 of nanometers. So, basically that is what the characteristic of Auger electron is that Auger electron fail to emerge with their characteristic energies, if they are deeper than about point five to five nanometer from the surface.

So, that is what is all about the Auger analytical volume, so we see how the beam is interacting with the material and the Auger electrons are being generated only from the surface. Though, they generated throughout the material like till where the electron beam is interacting with the material, all the Auger electrons cannot escape out, so that is what leads to the Auger analytical volume which is which makes it highly surface sensitive.

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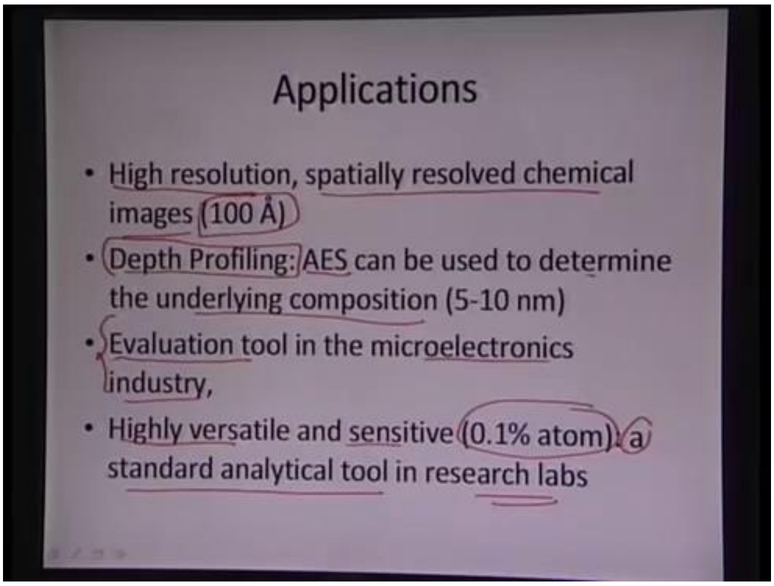

Applications

- High resolution, spatially resolved chemical images (100 Å)
- Depth Profiling: AES can be used to determine the underlying composition (5-10 nm)
- Evaluation tool in the microelectronics industry,
- Highly versatile and sensitive (0.1% atom): a standard analytical tool in research labs

Since it is highly surface sensitive and it is coming out from a very narrow regime, it basically has very high resolution and it can spatially resolve chemical images, which are approximately to the order of 100 angstroms or 10 nanometers. Additionally, Auger electronic spectroscopy can also be utilized for performing depth profiling and it basically we remove the surface layers, we see what is on a surface and we startutilizing some iron etching. We can start removing the surface layer and see what the composition on the top surface is beneath the material, so we can have and it might be an oxide of for a particular material.

Then, we start etching out using certain iron guns and then once we etch out the material we see what is the composition beneath that particular layer and that is called depth profiling. Auger electron spectroscopy can be utilized to determine the underlying compositions, so that is what so nice about it and it is a one of the very essential evaluation tool in the microelectronic industry. We want to see what are the basic interconnects or what is there any oxide forming on the surface or there are very certain connectors or the goal coatings, which are basically plated on to microelectronic devices.

So, AES becomes a very essential tool in terms of analyzing or in terms of confirming whether the proper connection is achieved or what is the overall, the surface is very clean enough to have the conduction at particular level. So, that is what it has become an essential tool and it is highly versatile and sensitive as it can detect up to 0.1 atom present for a particular composition.

Therefore, it has become a standard analytical tool also in the research lab, so that tells its applicability of how Auger electron spectroscopy can be utilized because it has very high resolution in terms of 10 nanometers. Then, it can it is highly sensitive in terms of being able to detect up to 0.1 atom present concentration for a particular sample and that makes it very useful in research as well as proper analysis of certain materials.

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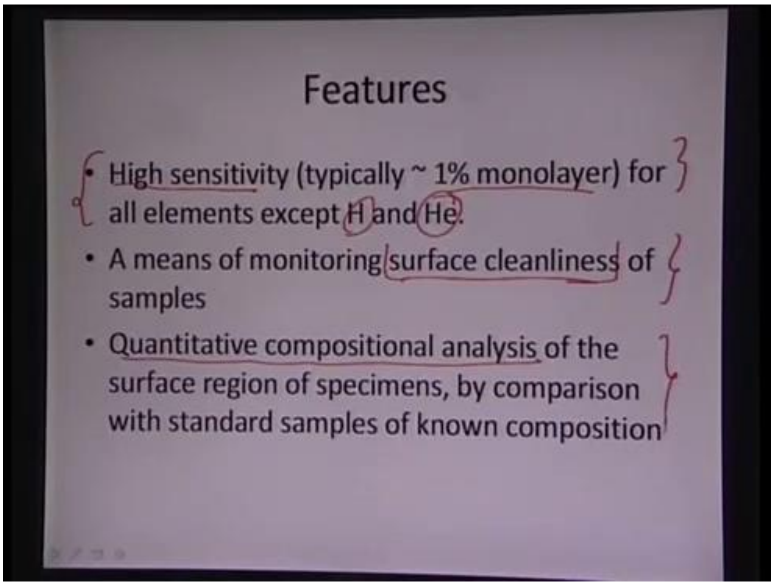

Features

- High sensitivity (typically ~ 1% monolayer) for all elements except H and He.
- A means of monitoring surface cleanliness of samples
- Quantitative compositional analysis of the surface region of specimens, by comparison with standard samples of known composition

Though it is highly sensitive, it can detect up to one monolayer which is lying on the surface so that tells its capability in terms of detecting a particular composition, which is even a single or a monolayer. It can detect all the elements except hydrogen and helium why these things cannot be detected, we will come back as we learn about the Auger process. It needs a minimum of three electrons in the process the Auger process and since hydrogen and helium they only have one two electrons in the outer shell.

It cannot yield an Auger electron and since it is highly sensitive it can also be used for monitoring the surface cleanliness of samples. Since the process is highly surface dependent like what is our surface composition it is highly surface sensitive that is the reason we can also detect or monitor what is the cleanliness of a particular sample. Again, it can also do some quantitative compositional analysis of surface regimes by comparing it with some standard sample. So, basically you come to that it can detect even single monolayer, it can also monitor the overall surface cleanliness. Also, it becomes a essential tool in terms of quantitative composition analysis only once when we have some standard sample also available for its comparison.

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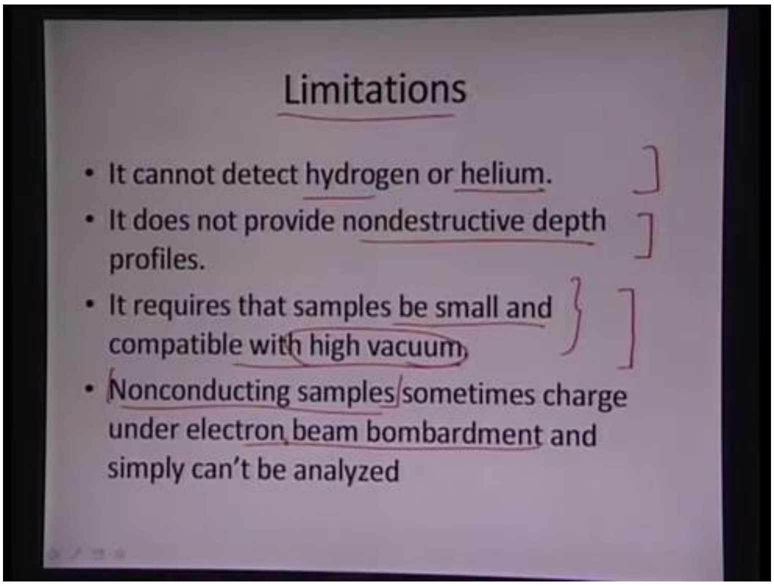

Limitations

- It cannot detect hydrogen or helium.
- It does not provide nondestructive depth profiles.
- It requires that samples be small and compatible with high vacuum.
- Nonconducting samples sometimes charge under electron beam bombardment and simply can't be analyzed

As we said earlier, the limitations extend to that it cannot detect hydrogen and helium just because Auger process itself requires a minimum of three electrons in its outermost shell. That is the reason hydrogen and helium are eliminated from promotes detection and at the same time it will not provide a nondestructive depth profile. So, if you want to see what is beneath the surface, we obviously need to cut it we need to remove, so that is the reason Auger electron, Auger electron spectroscopy.

It can provide depth analysis only once the surface layers are removed it is unlike the x ray diffraction, but x ray can penetrate much more depth in many microns to be able to detect the information from the bulk. But, AES Auger electron spectroscopy cannot do that because it is highly surface sensitive it can penetrate only a depth of around 5 to 10 nanometers not more and it is also required that samples be small and compatible with high vacuum. This is because that Auger electron they were low energy electron and since if the electron has to come out of the surface, it has to come out without any interaction.

It should be able to come out without any collisions with the atmospheric atoms if it is colliding with the atmospheric atoms it means it is losing the information. That is the reason that the samples they have to be compatible with the high vacuum and most of the time sometimes that non conducting samples also become a problem because we are always bombarding the sample with certain electrons. Once you are bombarding the sample with the electrons that charge also has to be removed, it has to be grounded if sample itself is non conducting in nature.

Basically, the charge is not going away it is not getting earthed, so for this particular Auger electron spectroscopy need the sample to be conductive and because to avoid any charge development on the surface. So, in this particular case the non conducting samples, they develop charge and it becomes impossible to really analyze them because of the electron beam bombardment. So, that is the particular one more limitation of it that hydrogen and helium cannot be detected, it cannot provide nondestructive depth profile and it requires the sample be compatible to that of for high vacuum.

It becomes little bit problem in certain biological sample or polymer samples, where the samples themselves cannot take much of vacuum as they start as the mic start decomposing. So, this is one of the major limitation that it cannot be used for detecting certain biological samples, so and again it also cannot have it cannot take the non conducting samples as well, so that makes it certain limitations of the Auger electron spectroscopy.

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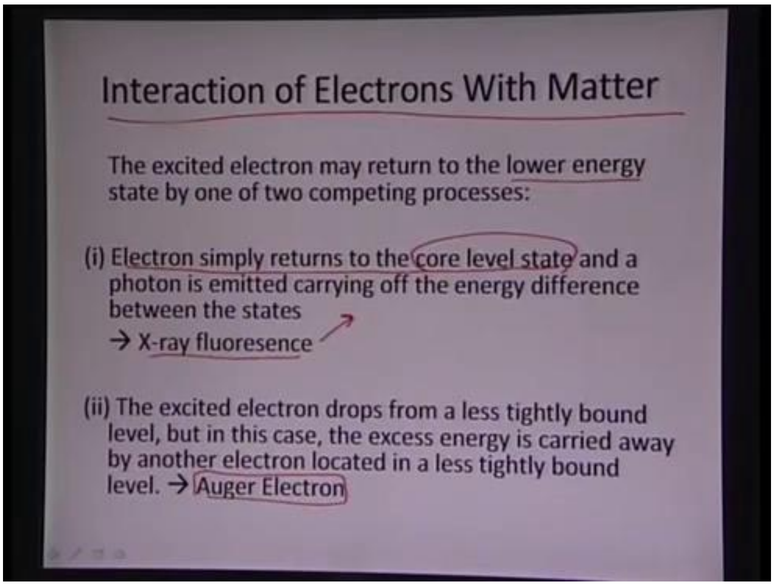

Interaction of Electrons With Matter

The excited electron may return to the lower energy state by one of two competing processes:

(i) Electron simply returns to the core level state and a photon is emitted carrying off the energy difference between the states
→ X-ray fluoresence

(ii) The excited electron drops from a less tightly bound level, but in this case, the excess energy is carried away by another electron located in a less tightly bound level. → Auger Electron

Once the electrons are interacting with the matter, so the basically the excited electrons it can return to its lower energy state because if sample is interacting with the with an electron beam, it can excite the electron and the excited electron can come back. It can relax in certain different processes, so there are two competing processes, one is that the electron is simply return to the core level state. So, once we had excited electron it has gone out one electron is knocked out from the core shell and then one electron will come back to its core level state, which was earlier knocked off and the differential energy will yield to some x ray fluorescence.

So, we have certain knocked off electron that knocked off electron core shell is being occupied by electron from higher energy shell and that basically the differential energy is left as a x ray fluorescence. Secondly, it can also happen that the when the knocked off shell is it is gone when electron is knocked off, one electron can jump from higher energy to the lower energy straight or from a higher shell to a lower shell. Once it has happened, that particular energy can be acquired by a second electron, which basically leaves the particular sample surface as Auger electron.

So, instead of going out as a photon with certain with certain x ray, x ray photon that energy can be absorbed by a secondary electron which is in a little higher shell. Then, it can have acquire certain energy as well and that is called a Auger electron to provide a picturesque explanation of this one.

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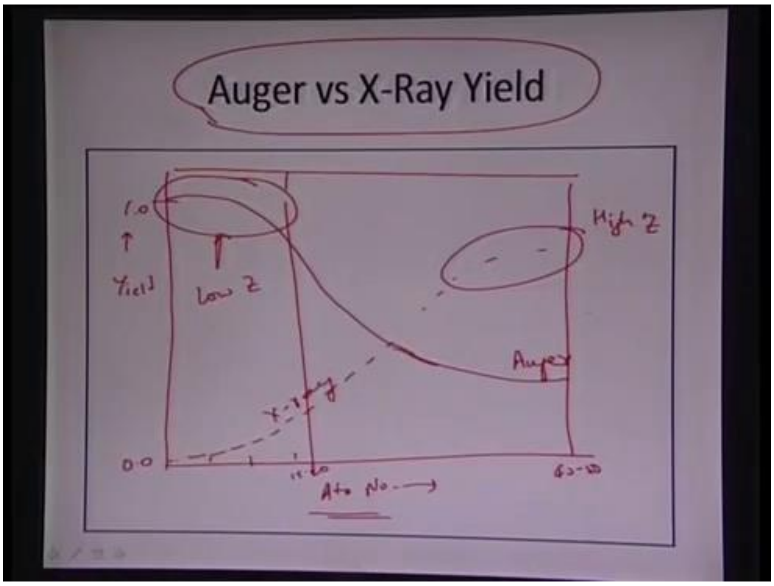

Auger vs X-Ray Yield

How the particular things really work out, but before that it just makes that Auger and the x ray they are more complementary in nature. So, whatever we have like we have some atomic number out here, so we write atomic number atomic number in this particular axis x axis and say we have yield of either x ray or Auger. So, we will realize that the lower atomic number the lower atomic number elements will have very high Auger and it will drop down with atomic number.

So, Auger is typically very higher for say up to 15 to 20 atomic number, whereas x ray yield is complementary to it. So, it will start building up from here and then the total will always be 1, so x ray plus Auger will yield a total yield of 1. So, if say this was 1.0, this one will be 0.0 and generally the Auger yield is very high for lower atomic number elements. So, it is very high for lower atomic number that elements, whereas x ray yield is typically very higher for higher atomic number and the Auger yield is typically very low for higher atomic number.

So, this Auger electron spectroscopy is generally utilized for low atomic number elements since the yield is very higher so the detection becomes very easier. So, the overall explanation of overall yield which is which combines Auger and x ray, so this is what the overall chart tells you about that the Auger yield will drop down with increasing atomic number, whereas, x ray yield will keep increasing for higher atomic number.

We keep Auger limited to like up to 15 then I will come to the transitions, but it can be detected up to like 40 or 45 atomic number, we can have a considerable Auger yield. Until there, we can utilize the Auger electron spectroscopy because after that x ray yield is so high that it becomes much easier to go with x ray and the nit might give a very high background for higher atomic number elements.

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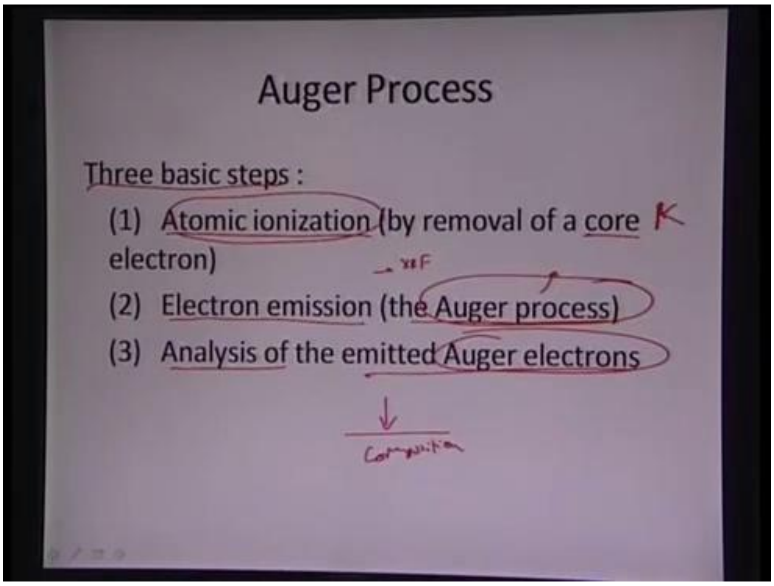

Auger Process

Three basic steps :

(1) Atomic ionization (by removal of a core K electron)

→ XRF

(2) Electron emission (the Auger process)

(3) Analysis of the emitted Auger electrons

↓

Composition

So, Auger process how it is to be defined it is defined by three basic steps, so as we saythat we bombard the surface with very high energy high energy beam and that basically leaves leads to atomic ionization. Atomic ionization means that we are removing an electron of from a core shell or K shell, so the first step is that a electron is removed from the K shell of the material. Now, the material or the sample is in higher energy state now that higher energy state has to go out either via x ray fluorescence or via electron emission, which leads to the Auger process.

Third step is once the Auger electron has released from the surface it is the characteristic of a particular material and then we analyze that emitted Auger electron and that basically completes the process of Auger spectroscopy. So, initially we have atomic ionization relaxation by the emission of Auger electrons and then detecting that particular Auger electron to get the overall composition of a material. So, that basically completes the Auger process and how exactly what is happening at the atomic level let us go to that particular part.

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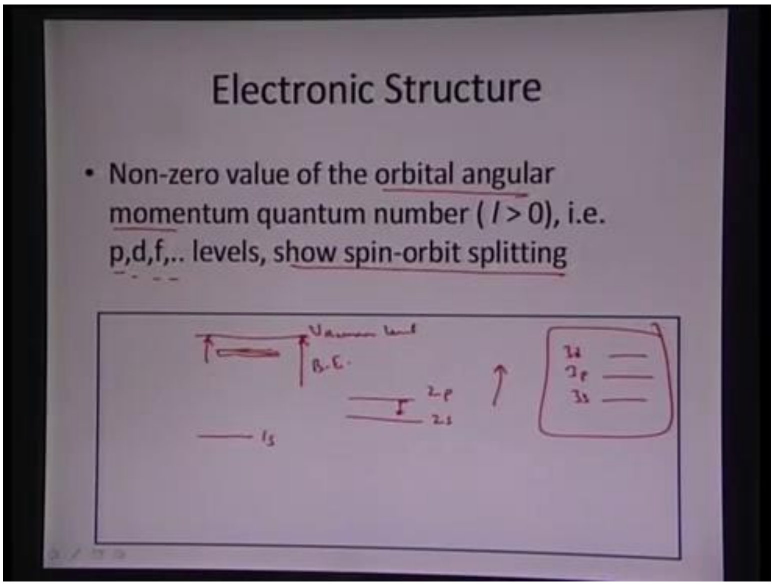

Electronic Structure

- Non-zero value of the orbital angular momentum quantum number ($l > 0$), i.e. p,d,f,.. levels, show spin-orbit splitting

First of all, the electronic structure which is being defined, it will have certain non zero value of orbital angular momentum like we have principal quantum number, we have angular quantum number. Then, we have shells like p d f level shells and all these show spin orbit splitting, because we have more than one electron in the p shell. So, like in s we have plus spin and minus spin, whereas in p we have certain shells, which lead to the splitting of the shell as we have s and p orbitals.

So, like in one s we have one level, but once it curves to 2 s and 2 p so 2 s and 2 p will show different energy levels because the overall structure of this s shell and p shell itself is different. So, it can keep going on for once we have 3 s 3 p 3 and similarly, for other levels we can see certain splitting between these particular bands.

So, these all will lead to certain splitting in the electronic structure let us not come to that right now, but again once crossing that we have a vacuum level vacuum level and then we also can have band if required out here for some conducting materials. So, the electron has to cross certain binding energy that is that is what being defined, where the electron is 1 s 2 s 2 p. So, that is overall the electronic structure, which is defined by the overall shells which the material has valence vacuum levels, where it has to overcome the barrier in terms of getting release from the surface.

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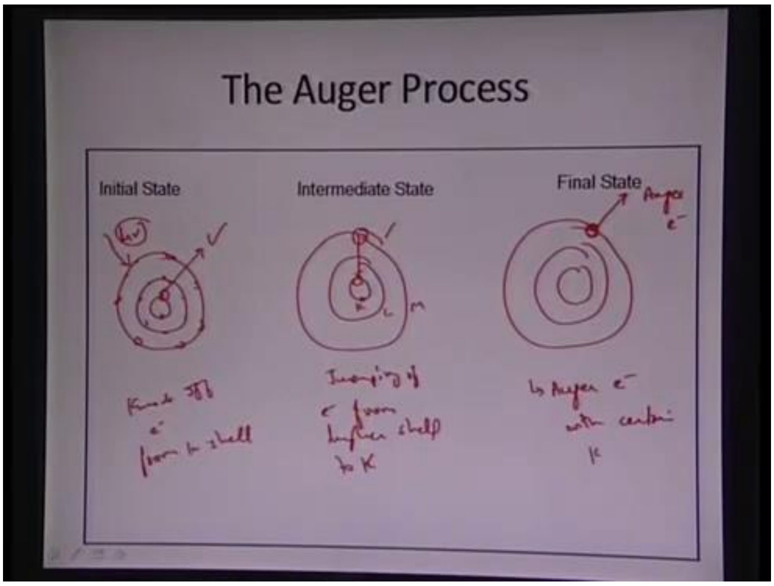

The Auger Process

Initial State

Intermediate State

Final State

So, the Auger state can be defined like this, so we have initial state, we have then intermediate state and then the final state. So, intermediate state is more like that, initially we take the material we take the particular electron, so we have particular electron and then we are supplying certain energy with h mu. So, we have electrons in the s shell K shell or L shell and then higher shells, so we have certain particular materials so because of this high energy photon, it basically will lock off a electron. So, that electron in the K shell is basically knocked off, now what will happen that the intermediate state we have we have one electron jumping from higher energy shell to a low energy shell.

So, basically what is happening is we have this K shell L shell m shell, so say an electron is jumping from m shell to K shell to basically take the position of a electron, which was knocked off or the vacancy which was created out here. So, we can lower its energy, so we have some sort of a relaxation, which is occurred by the jumping of electron from higher shell to a lower shell this is something called intermediate state, but the final state will be more like this. The additional energy which is being released by the material, it is acquired by electron in a higher shell it acquires the overall energy and then it basically leaves off as a Auger electron.

So, in the first state we had knock off electron from K shell and in the second in the intermediate state, we had jumping of electron from higher shell jumping of electron from higher shell to K shell or L shell. It can also be L shell, but coming to a core level, core level shell and then the energy is being absorbed by electron, which is in the higher shell. That basically is the Auger electron which comes out with certain kinetic energy and this kinetic energy is the typical characteristic of a particular material.

So, that is what we see that in the initial stage, we have knocking off electron from core shell and then in the intermediate state, we see a electron is jumping to the core shell and in the final state, we see the emission of a Auger electron.

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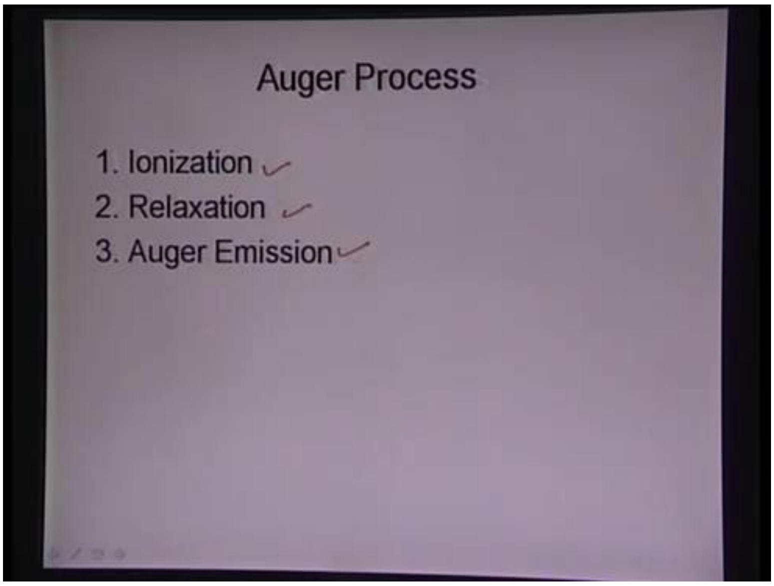

Auger Process

1. Ionization
2. Relaxation
3. Auger Emission

So, that is what is telling the Auger process and these things are classified as ionization relaxation and Auger emission, so we see that Auger process is again divided into three parts.

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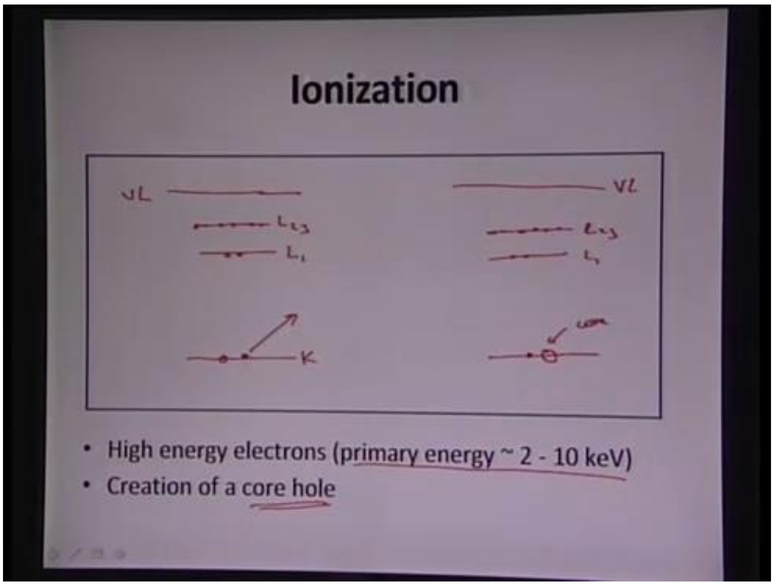

Ionization

- High energy electrons (primary energy ~ 2 - 10 keV)
- Creation of a core hole

So, coming back to the electronic structure of it, we can see that we have a vacuum level and then we have shells we can call it L 2 3 for the p orbital L 1 for the s orbital and then we have K shell which is nothing but the or 1 s orbital. So, we will have 2 electrons out here, 2 electrons out here and basically six electrons out here and then we will have a vacuum level. So, first process ionization is nothing but the removal of electron from K shell, so we have our vacuum level it remains as such and then L 2 3. It will still have six electrons L 1, it will have 2 electrons, but in K shell we have one core or the one of the electrons has been knocked off.

So, we say that this electron was knocked off, because of the high incident energy, which is being incident on the particular material and the primary energies are in the range of 2 to 10 K eV, which are nothing but the ionization energy of any material. So, we see that once we are indenting certain energy or electron beam on a certain material, it is knocking off an electron from core level shell which is the K shell. It creates a vacancy or a core in the K shell, so the first so the first step in this particular Auger processes. We see that a core is created and then we the other shell remains as such so L 1 and L 2 three remains as such and the only thing is we are creating a particular core hole in this first step.

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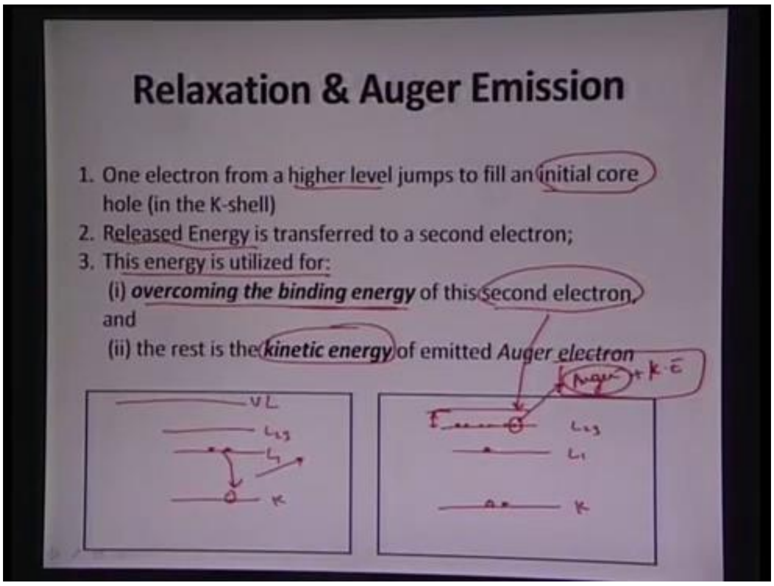

Relaxation & Auger Emission

1. One electron from a higher level jumps to fill an initial core hole (in the K-shell)
2. Released Energy is transferred to a second electron;
3. This energy is utilized for:
   (i) ***overcoming the binding energy*** of this second electron, and
   (ii) the rest is the ***kinetic energy*** of emitted *Auger electron*

Going to the second step of relaxation Auger emission, we see that that one electron from a higher level jumps to fill an initial core, so the same thing we see here that we had created a hole earlier. So, this was our vacuum level and then we had this L 2 shell, then we had L 1 shell L 2 3 and L 1 and then we had a K shell. Since we had a core an electron can jump from higher shell to a lower shell or it means from L 1 or L 2 3, any one of the electrons will jump to the lower energy shell. So, we see that one of the electrons is jumping out here from L 1 to K and then this released energy because once the electron is jumping from a higher energy shell to a lower energy shell.

Basically, there will be some additional energy which will be available with the material and that particular extra energy is now being released. So, first step was ionization in the second step we have jumping of electron from high energy shell to a low energy shell. Therefore, there is some gap or some differential energy which is being released so that is what we are seeing, so we will have certain energy release and that will again lead to.

So, that can again go back that we know our K shell is already filled and L 1 and L 2 3 if the electron had jump from L 1. So, we had only two electrons out here, now we will have only one electron out here and then we will have certain say couple of 6 electrons, but now that additional energy can be occupied by this particular electron. It can go out as Auger electron while overcoming any binding energy, so this Auger electron has to cross certain energy barrier to be able to get release from the surface.

So, we see the overall thing firstly a material is getting ionized K shell electron is getting released then there is jumping of electrons from higher energy shell like L shell, say in this case we had jumping of L 1 electron to the K shell. So, now that will release certain energy and that particular energy is being absorbed by the electron in the L 2 3 shell and that goes off as Auger electron while overcoming the binding energy barrier. So, this energy is basically being utilized for overcoming the binding energy of this second electron, so this particular second electron is this particular case and this thing.

Basically, it is coming out as Auger electron, it will have certain kinetic energy as well because the overall energy is overcoming binding energy plus acquiring certain energy which is nothing but the kinetic energy of the released electron. So, we have this energy which was attained by the jumping of electron from L shell to K shell that energy is being absorbed by an electron which overcomes which that energy it is utilized in overcoming certain binding energy.

Rest of it becomes its kinetic energy, so that is nothing but Auger electron with certain kinetic energy. So, we have this particular energy as the sum of the binding energy plus some kinetic energy, so this tells us the overall process what is the Auger electron spectroscopy.

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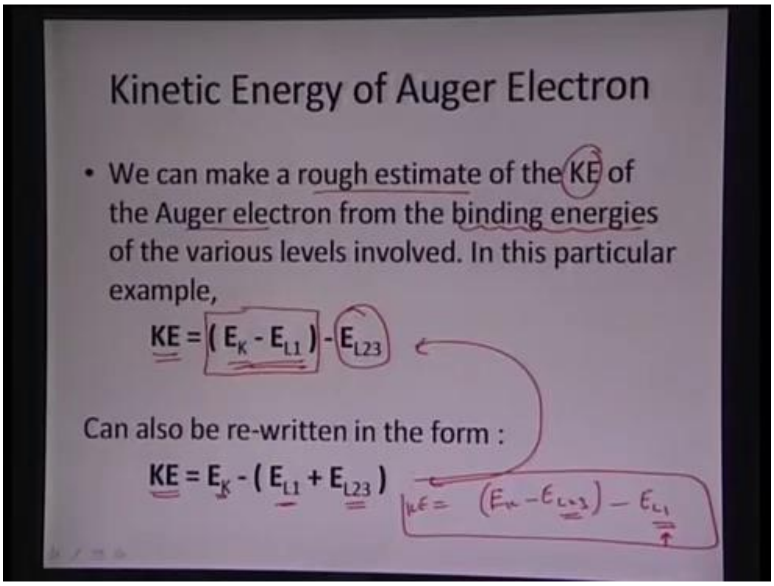

Kinetic Energy of Auger Electron

- We can make a rough estimate of the KE of the Auger electron from the binding energies of the various levels involved. In this particular example,

$$KE = \boxed{(E_K - E_{L1})} - E_{L23}$$

Can also be re-written in the form :

$$KE = E_K - (E_{L1} + E_{L23})$$

$$\boxed{KE = (E_K - E_{L23}) - E_{L1}}$$

That we can come back to it that we can make a rough estimate of the Kinetic energy of the Auger electron from the binding energy of the various levels in which the electrons are involved. In this particular case, we can see that we had the energy, which is being released is the difference between the energy levels of e K minus e L 1, because we had e L 1 electron L 1 electron had jumped to the K level electron. So, this is the overall energy which was being released and this energy is again absorbed by the L 2 3 in overcoming its binding energy.

So, we see that kinetic energy is equal to e K minus e L 1 minus e L 2 3 again if we rearrange this particular equation as below. We can make it kinetic energy of the electron the Auger electron is e K minus e L 1 and minus e L 2 3 or in the bracket L 1 plus L 2 3. If this become similar to e K minus e L 2 3 minus e L 1, it means had the electron jump from e L 2 3 and the e L 1 would have gone as Auger electron. Still, the kinetic energy of the Auger electron would not have changed, it means that all the three electrons which are participating the kinetic energy depends only on those three electron. It does not matter whether the electron had jump from L 1 or L 2 3, so these two electrons become in differentiable.

Since the latter two terms can of the energy could be interchanged without any effect because the kinetic energy is remaining the same as we saw earlier that kinetic energy is remain same whether it is e L 2 3, which is subtracted first or e L 1. This is being subtracted first, so the overall kinetic energy is just written as e K minus e L 1 plus e L 2.

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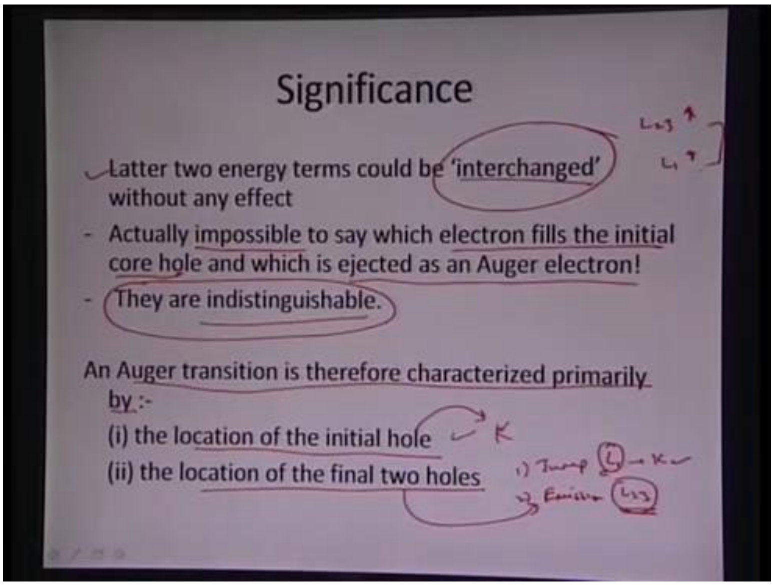

Significance

- Latter two energy terms could be 'interchanged' without any effect
- Actually impossible to say which electron fills the initial core hole and which is ejected as an Auger electron!
- They are indistinguishable.

An Auger transition is therefore characterized primarily by :-

(i) the location of the initial hole

(ii) the location of the final two holes

So, this tells that these two energy terms could be interchanged, so which makes that it is actually impossible to say which electron fills the initial core level and which electron is ejected as a Auger electron. So, that is the beauty of this particular this particular process that one electron is jumping from higher energy shell to fill the core level shell and second electron is getting emitted as Auger electron. These two electrons are indistinguishable because the energy will matter only where the initial core level electron was there and where the two electrons which have participated from a higher shell.

So, overall these two electrons are indistinguishable, the two electrons which are participating which are one is jumping which one is coming out, they are basically indistinguishable. Therefore, an Auger transition is characterized primarily by the location of the initial hole in this case it was at K level K shell and the location of final two holes one is via jumping one core is created by the jumping of electron from L shell L 1 to K shell.

Second one was emission of Auger electron from the L 2 3 shell, now we had core in L 1 and L 2 3, so this is the location of final two holes and this is the location of our initial hole. So, overall Auger process will depend what was the location of the initial hole the K shell and what is the location of the final two holes which was either jumping L 1 and L 2 3, this one will come out here. The location of initial hole was k and the location of final two holes is L 1 and L 2 3, so that is what tells that is all what governs the overall Auger process.

So, basically we can interchange whether the transition was occurring from L 2 3 2 K and then L 2 had released as Auger electron or the or vice versa. So, these two electrons are nothing but indistinguishable and energy remains same the kinetic energy remains same whether the electron is jumped from L 1 or L 2 3, so that is what the overall significance of this particular Auger process.

As we said earlier that Auger electron depends on the atomic number and we also saw that the yield is much higher in case of lower atomic just because the probability is very high that the K electron can go away or the electron can go away. They can be jumping from higher shells higher energy shells to yield this particular process, but for higher atomic number the x ray takes the predominance and the overall Auger level basically keeps going down.

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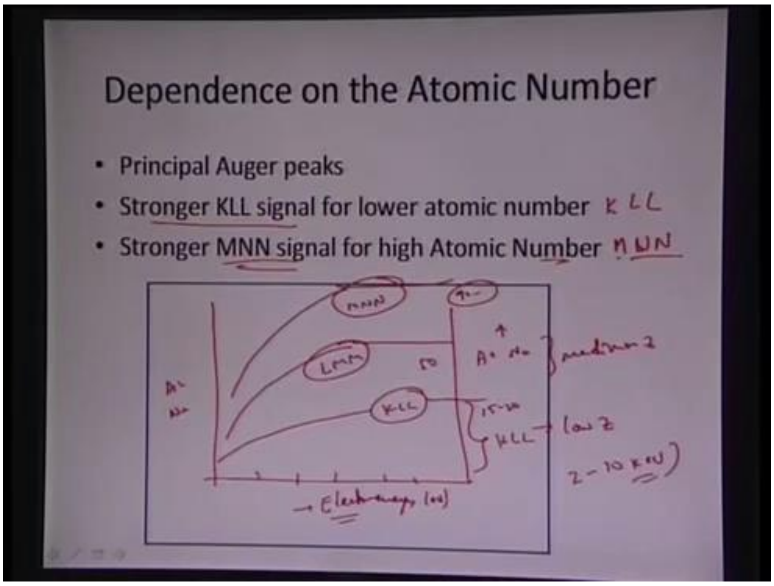

Dependence on the Atomic Number

- Principal Auger peaks
- Stronger KLL signal for lower atomic number K LL
- Stronger MNN signal for high Atomic Number M NN

Basically, we see that the there are certain Auger peaks which are which can come out, when a incident beam is applied on a material and then stronger K L l signals. It means that the location of three electrons is from K shell L shell and L shell and m n n signals are much stronger for higher atomic number. It means that the transition is occurring or creating a hole in the m shell and then n shell and n shell are participating in the jumping of electrons to m shell and then release of Auger electron from the n shell.

Generally, typically we see that the if atomic number is on this on this particular on particular abscissa your y axis, then we see that this is atomic number and in this case we have say electron energy which is being acquired electron energy. This is being supplied to the material for creating the ionization, we will see something like that this is nothing but the atomic number this case and we see that the K L l transitions are occurring something like this. Then, L l m transitions will occur more like this and m n n n transitions will occur more like this something like this.

So, we will see that K L l transitions are very predominant for certain atomic number and then we will have L m m transitions for little higher atomic numbers which are more predominant and then m n n. This is so true because if this is up to maybe say 15 to 20 atomic number, we are more K L l transitions.

Till then we do not have m shell and as soon as the m shell starts coming in, it governs that basically the L m m transitions become much more probable because it is very difficult for a particular atom. If it has the m shell n shell higher order shells, it is very difficult for electron beam to penetrate through the material and knock off a K electron because this is again surrounded by L shell m shell n shell. So, this becomes very un probable, so that is the reason this Auger process is very dominant for K L l transitions in lower atomic numbers and L n n transitions for little higher atomic number higher atomic number elements.

Then, again m n n transitions become very predominant for even higher atomic numbers so approximately up to around 50 element transitions are much more probable and again 80, 90 atomic number element transitions. They are much more probable and so we can see that the detection limit or the K L l transitions, they are very stronger for the low atomic numbers up to 50 it is medium atomic numbers. We have this element transitions which are more probable and for high atomic numbers, we have basically m n n transitions which are much more probable and we request certain level of energy to basically ionize a particular material.

Those basically run upto may be up to from maybe say couple of K e v, so we have the incident beam from running from 2 to 10 K e v to ionize the core shells. So, that is what is required in terms of ionizing a material and leading to a generation of a core hole and so that the Auger process can really occur. In this particular process, we require at least three electrons one transition to cause ionization and two more electrons to cause a jump and release of Auger electron. That is the reason we need minimum 3 electrons and hydrogen and helium cannot be detected, so minimum element which can be detected is lithium, so that is what the overall dependence of this K L l transitions and above.

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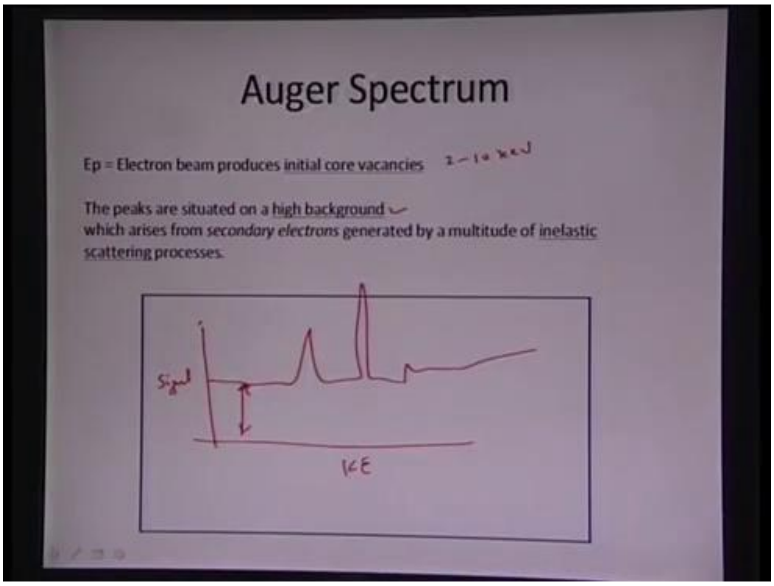

Auger Spectrum

Ep = Electron beam produces initial core vacancies

The peaks are situated on a high background which arises from *secondary electrons* generated by a multitude of inelastic scattering processes.

So, the Auger spectrum looks more like this that we have we have to supply certain electron beam which around 2 to 10 K e v to ionize a particular material and then, but these peaks are basically they generate they are on a very high background. It also undergoes an inelastic scattering processes during the Auger while achieving the Auger spectrum. So, we have certain signal and the K eV which is being detected from the particular from a particular detector, so we have signal and again it has very high background and certain peaks for certain material.

Then, it goes off, so the overall background is very higher for particular signal in the Auger process. So, basically that is not really good for detecting, it is not good for achieving a particular repeatability, so that is the reason this particular signal is differentiated with respect to the kinetic energy of a material.

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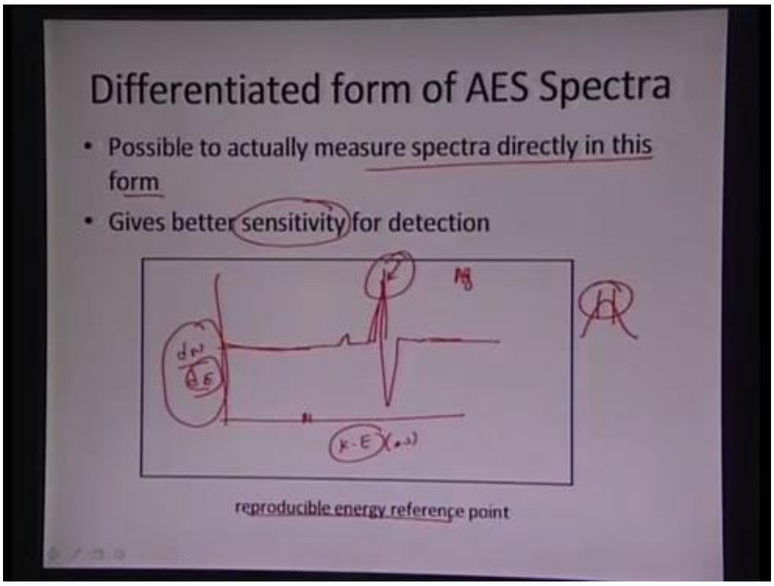

Differentiated form of AES Spectra

- Possible to actually measure spectra directly in this form
- Gives better sensitivity for detection

reproducible energy reference point

Then, basically we can achieve one more spectrum which is much more repeatable, so we have something d n with respect to d e and then we have this particular in terms of K e and electron volts. Then, we see that we achieve a very nice background with peaks very sharp peaks and very repeatable peaks, so let me draw it again. So, we have this particular peak and then we achieve certain peaks and then it goes on, so this is nothing but a kind of a zero background and we achieve certain peaks which are highly repeatable. So, it is actually possible to measure spectra directly in this particular form and, it gives very good sensitivity, because you know this peaks are more repeatable.

They are also very sensitive to particular materials, so it is again reproducible for a particular referencing. If you want to reference it, say this was peak for say silver and then the differentiated form will also give out this particular peak. Again, at the same location it would not be much with the background, it would not be more hazy like we saw in the earlier case the peaks were more hazy and they were not really very sharp. So, that is the advantage of utilizing a differentiated form which is d n by d e the number of with respect to the kinetic energy because it also consider a way of taking the probability, which was not so being defined.

In earlier case in this case we know particular, will occur at a certain energy level, so that differentiation with respect to energy makes it very sensitive and reproducible so that is the advantage of using a differentiated p. Also, the sensitivity is gone high because this particular ratio with respect to background it also increases, so that is the advantage of utilizing a differentiated form of AES that we have much more higher peak or better peak.

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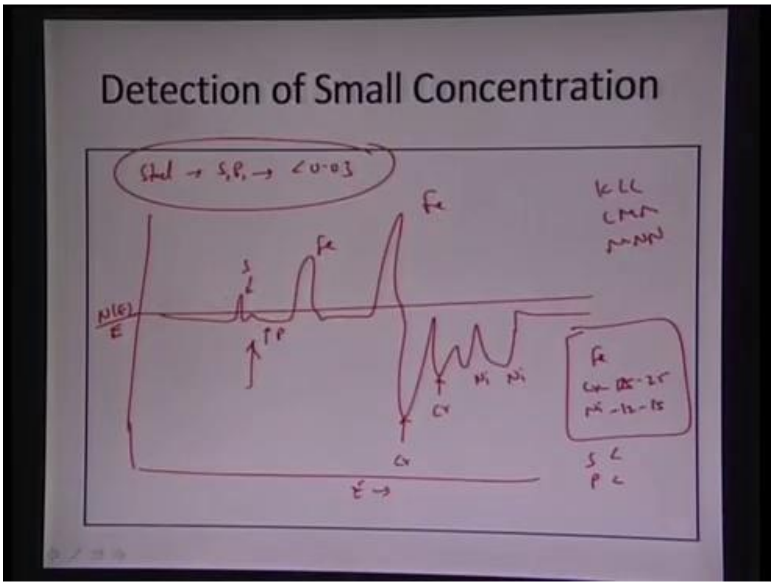

Detection of Small Concentration

Again, it can be utilized for detecting very small concentrations like we had certain spectra something like this, It can be certain spectra like this in the differentiated form. We can see that there will be certain peaks which will correspond to similar same elements because we have transitions from K L l, L m m and m n n. So, we can see that the higher energy, the higher atomic number materials they can have multitude of peaks. So, we can see certain peaks which can say belong to say chromium, then again chromium or they can also have more peaks say for something nickel or nickel.

It can also be that like in case of certain materials like in steel we have very small, very fine contributions from sulphur, phosphorous elements like that which are very which are very low concentration less than say 0.03weight percent. Still, we can see that this Auger spectra can detect, so even such a lower concentration can be defined.

Let us say sulphur or say some peaks in phosphorous, so those things can also be detected very easily in in the Auger spectra. So, we had this n in terms of energy and it can be again differentiated with respect to energy and this again the energy. So, we can detect always some peaks which are which were really not probable with concentrations of less than 0.03 weight percent. We have seen that Auger spectra can detect the major peaks which can come out either say from major peaks can be either from chromium or say nickel or even iron because that for a stainless steel the major composition will be say iron.

Then, chromium will be say around may be say 15 to 25 percent then nickel can also be from 12 to say 15, 20 percent so that those are the major peaks what you might expect to see in the Auger spectra. Then, again sulphur and phosphorous very low in quantity, but those will also be detected if utilize the Auger spectra. So, that is the beauty of this particular process that even elements with very small concentrations less than 0.03 weight percent can also be detected in the Auger process.

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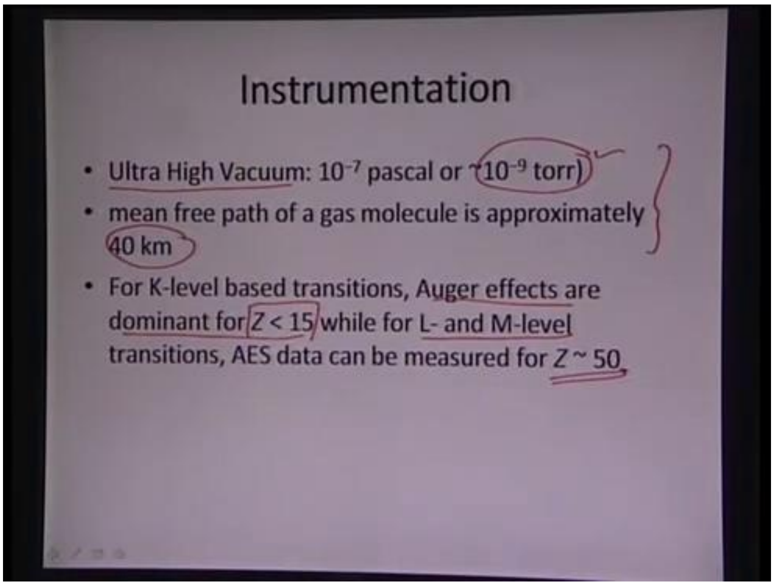

Instrumentation

- Ultra High Vacuum: 10^{-7} pascal or ~10^{-9} torr
- mean free path of a gas molecule is approximately 40 km
- For K-level based transitions, Auger effects are dominant for $Z < 15$ while for L- and M-level transitions, AES data can be measured for $Z \sim 50$

In this particular processing, we require very ultra high vacuum this is the order of 10 to power minus 9e torr, why because the Auger electrons they are very low energy electrons and once they have to leave the surface and get detected at the detector.

So, they need to undergo detection process without collision with the atmosphere if it is colliding with the atmosphere atoms then it is basically losing the energy and that will increase the background. So, this particular vacuum level will create a mean free path which is approximately 40 kilometer and as we said earlier that the Auger effects are much dominant for atomic number less than 15 and for L and m shell transitions, it can be measured up to atomic number of up to 50. So, that is the overall thing which we saw earlier because of the presence of the different shells and this is the very much requirement that it requires ultrahigh vacuum of order of 10 to the power minus 9 torr.

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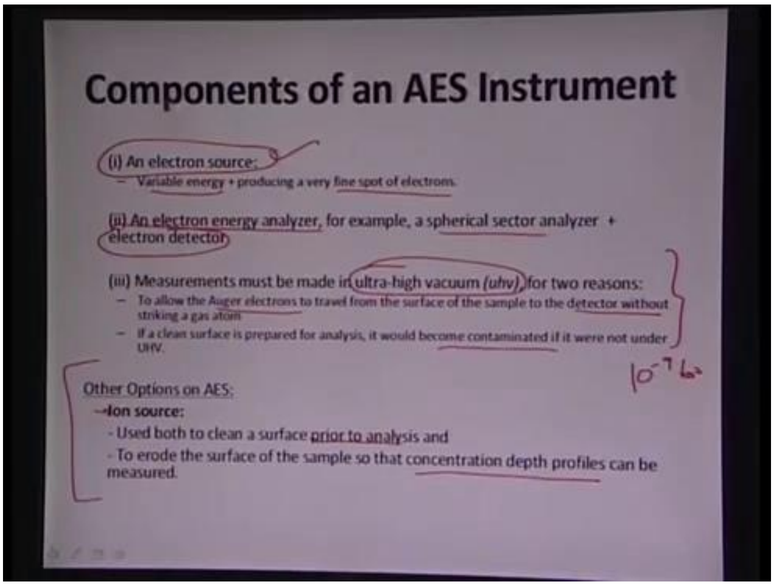

Components of an AES Instrument

(i) An electron source:
- Variable energy + producing a very fine spot of electrons.

(ii) An electron energy analyzer, for example, a spherical sector analyzer + electron detector

(iii) Measurements must be made in ultra-high vacuum *(uhv)*, for two reasons:
- To allow the Auger electrons to travel from the surface of the sample to the detector without striking a gas atom
- If a clean surface is prepared for analysis, it would become contaminated if it were not under UHV.

10^{-7} 6

Other Options on AES:

→**Ion source:**

- Used both to clean a surface prior to analysis and
- To erode the surface of the sample so that concentration depth profiles can be measured.

Coming to the components of Auger electron spectroscopy, basically we require an electron source which will have a variable energy because we want to see what the overall kinetic energy is. How it is dependent on the ionization because we are applying certain energy and it is basically knocking off K shell electron. So, we want to see how the transitions are occurring and again this particular variable source of energy is also useful in terms of describing a very fine spot of electrons. So, we should have a electron source we should have a variable energy source and then this electron has to go through a electron energy analyzer.

There are different types of analyzer which can be a spherical sector or hemispherical sector and then it has to basically pass through a electron detector. So, electron energy analyzer will separate out of the energies and those energies once it is filtered, it will basically get at electron detector, where it can basically be detected. This is an electron and then that the intensity of that particular detection will be counted at the same time the measurements have to be done in ultra high vacuum just because that the Auger electrons which can travel from surface to detector without any collision.

Secondly, the surface cleaning is also one of the very critical features out here that once as soon as we take the sample from the particular location to the Auger chamber, then it can get contaminated depending on its reactivity. So, we want to keep the sample clean and so to avoid that particular contamination, we want to use a ultra high vacuum, it is to the order 10 to the power of minus 9 torr.

There are certain other options, which can be available with Auger electron spectroscopy is something called ion source ion source can be utilized for cleaning the surface prior to the analysis. So, if we want to measure by clean surface, say if we take a sample it get oxidized you want to clean the surface to see what is the actual surface. So, we can measure its concentration depth profile and then we can measure it, so that is an accessory to the Auger electron spectroscopy.

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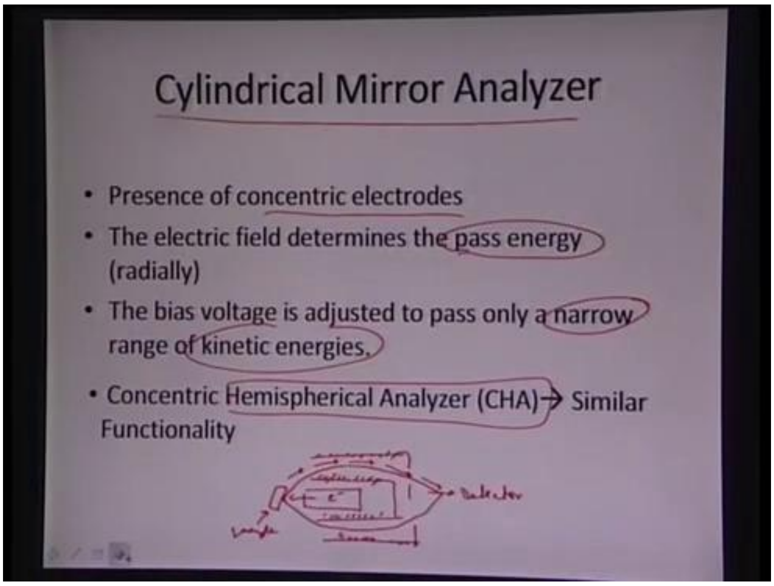

Cylindrical Mirror Analyzer

- Presence of concentric electrodes
- The electric field determines the pass energy (radially)
- The bias voltage is adjusted to pass only a narrow range of kinetic energies.
- Concentric Hemispherical Analyzer (CHA) → Similar Functionality

Coming to the analyzer part there are certain analyzers one is one of them is cylindrical mirror analyzer, it has basically some concentric electrodes and then those electrodes are basically all it is it is it is we apply certain bias to it. Then, we can allow only certain energy levels to pass through it if it is higher energy, it will be absorbed by one of the electrodes lower energy. Then, it will be absorbed by another electrodes and that those two electrodes are again, so basically certain energy gap can only travels through a particular concentric electrode set up.

So, cylindrical mirror set up, so that basically determines the pass energy and then it allows only a certain or a narrow range of kinetic energy to pass through it. Basically, the similar system also can be utilized by using a hemispherical analyzer, so how the particular analyzer looks like. Let us go back to it and let us see how the cylindrical mirror analyzer looks like, so we have this particular electron energy source, which goes and bombards a particular sample surface. Then, we have the electrodes like this and then only a certain level of energy the Auger electrons will pass through this particular electrodes set of electrodes and it will reach the detector.

If it basically coincides with one of the electrodes this electrode or this electrode, the energy level all the electron will get absorbed on to the electrodes. So, the bias on this two electrodes will basically decide how much how much the particular energy is allowed through the particular analyzer. So, we have electron energy source which interacts with the sample and then we have the Auger electrons which are emitted and they pass through the analyzer. Only certain energy is basically allowed to pass through and to reach the detector and that is all this particular cylindrical mirror analyzer really works.

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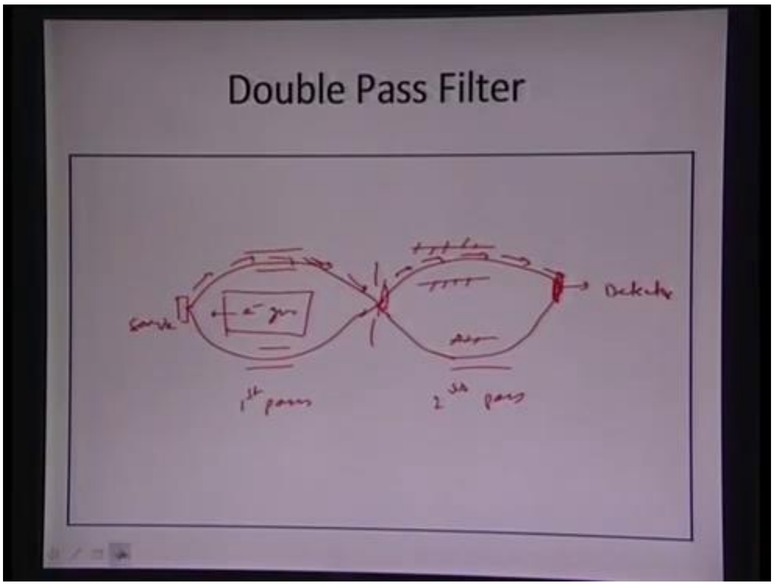

Double Pass Filter

This was a one pass filter we can also have two pass filter where we can see more like this that electron gun, it is interacting with the material and then basically it is coming out at a certain energy is coming out and to verify that. This is again the same energy level we can have one more set of electrodes out here again these electrodes will make a second pass. So, this is first pass and then again you have certain kind of opening and then you again have these two electrodes, which will again decide the overall energy and then it'll have a detector. So, this is nothing but the second pass, so we had this particular electron gun it is interacting with the sample out here and then we have Auger electrons which pass through the first.

The first becomes the second pass and then we have again electrons going out from through the analyzer like this, so we have again a detector out here and which detects the overall intensity of electrons through this particular process.

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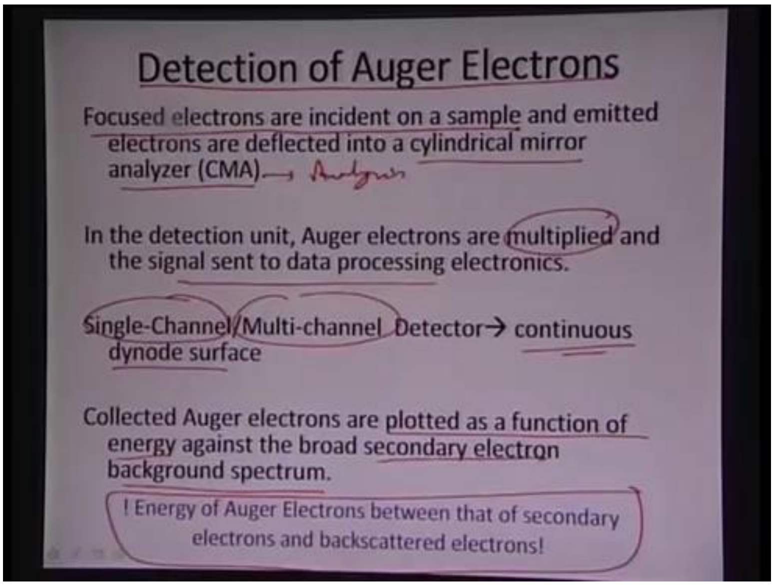

Detection of Auger Electrons

Focused electrons are incident on a sample and emitted electrons are deflected into a cylindrical mirror analyzer (CMA) → Analysis

In the detection unit, Auger electrons are multiplied and the signal sent to data processing electronics.

Single-Channel/Multi-channel Detector → continuous dynode surface

Collected Auger electrons are plotted as a function of energy against the broad secondary electron background spectrum.

! Energy of Auger Electrons between that of secondary electrons and backscattered electrons!

Now, comes the important part once it is pass through the detection pass through the analyzer. Now, we have to detect what is the overall kind of the Auger electrons, so basically we have we have to focus the electrons which were basically coming out. So, basically we have focused electrons are incident on a sample and then they are pass through the cylindrical mirror analyzer for the analysis part. Then, we have its detection where they are multiplied and signal is sent to the data processing, so we have photomultiplier tubes or the dynodes which basically take the detect the electron and multiply it.

So, again we can have single channel detector or multichannel detector depending on it can be a continuous dynode surface or a photomultiplier tube and then the collected Auger electron are basically captured. Then, they are plotted as a function of energy against the broad secondary electron background spectrum, so since it has a very huge background.

Then, again it can be again later on differentiated to achieve a very nice repeatable sensitive Auger spectrum, which is d n by d e with respect to the energy and that is what we have. We have first its analysis and then the detection part comes to the multichannel or the single channel detector or the photomultiplier tube or through continuous dynode surfaces. One more thing to mention is that the energy of Auger electrons is in between that of a secondary electron and a backscattered electron.

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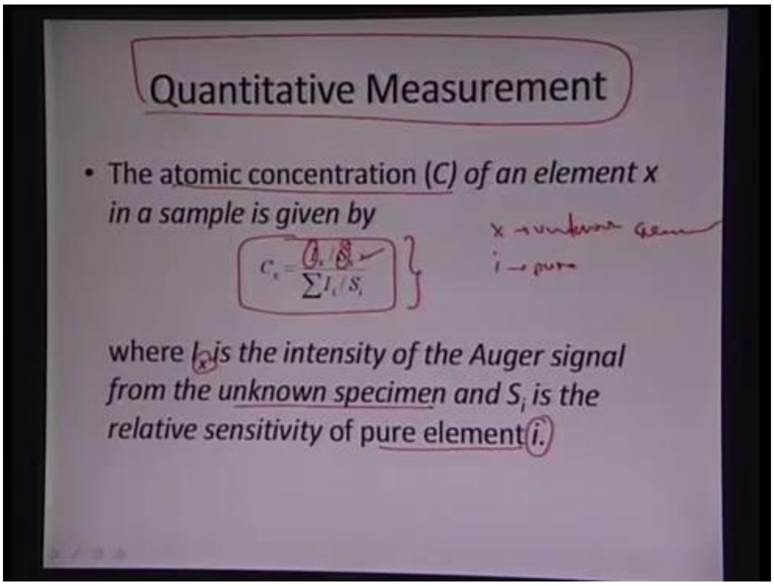

Quantitative Measurement

- The atomic concentration (*C*) *of an element x in a sample is given by*

$$\boxed{C_x = \frac{I_x/S_x}{\sum I_i/S_i}}$$

x → unknown [illegible]

i → pure

where I_x *is the intensity of the Auger signal from the unknown specimen and* S_i *is the relative sensitivity* of pure element *i.*

Again, once we have detected it we can have the quantitative measurement of a Auger composition that the atomic concentration of an element can be given by this particular equation where x is the intensity of the unknown specimen. So, x is the intensity coming out from an unknown specimen and i is the pure element, so i is the pure element and x is the unknown specimen. Then, we have i is the intensity of the Auger signal and s is coming out from the is the relative intensity.

So, by comparing in this particular manner we can see what the overall signal, which is coming out from the sample and what is overall signal which is coming out from the standard sample. So, by comparing those two we can say what is the overall concentration of x in particular sample? So, we need to have pure sample available to be able to say what the overall concentration of that particular material in the unknown sample.

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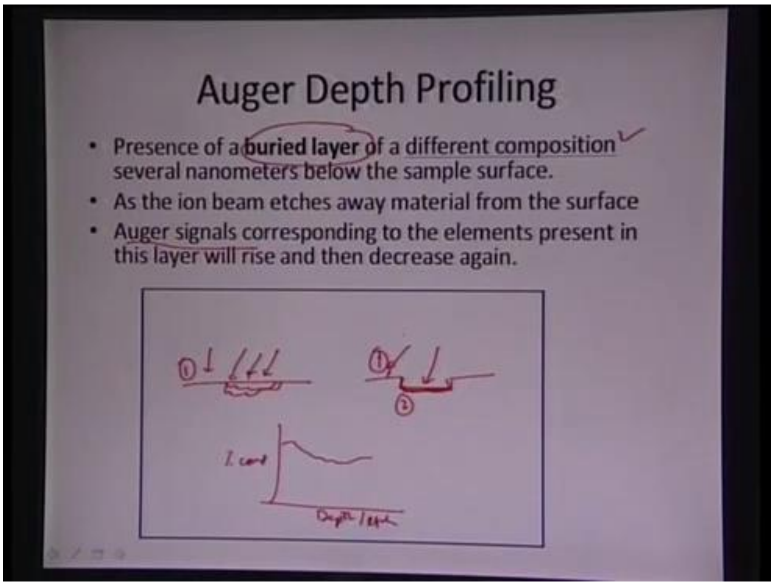

Auger Depth Profiling

- Presence of a **buried layer** of a different composition several nanometers below the sample surface.
- As the ion beam etches away material from the surface
- Auger signals corresponding to the elements present in this layer will rise and then decrease again.

Again, it can be utilized for Auger depth profiling and it can detect what is beneath the surface or the buried layer, what are the overall compositions which are basically can be attained out here. So, basically we have a surface and it is being bombarded by an ion source, so it basically starts eating the surface, now we have some surface which is beneath the original layer, the Auger process it can detect its composition from step one. It can also detect composition after it has the sample has been etched, so this can particularly provide what is the composition at level one and what is the composition at level two.

While this particular ion beam is etching, the surface it is necessary to know what the etching time is because depending on the material depending on the energy of the ion beam. The way it will eat out the material will be very different one material will be eaten away quicker second material can be eaten away little slower also depending on the current or ion beam intensity again the etching level be little different.

So, then the Auger signals which are coming out from the surface they can be correlated with the overall depth of a particular material and it can provide us information of what is the particular material concentration with respect to depth. So, this depth or the etching time can be correlated here with respect to percent composition out here so coming to just one example.

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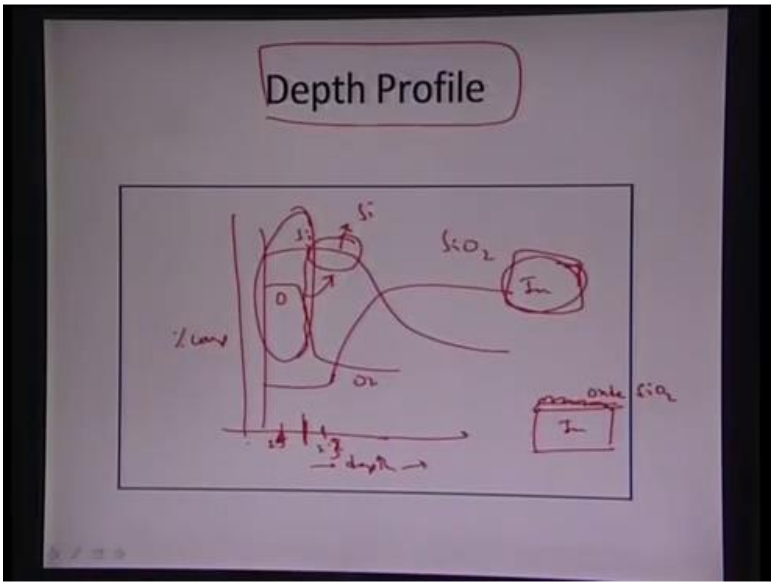

Depth Profile

So, say if we had a particular material and say we saw some things out here and then it is dying out like this, it means this particular material was sensitive only on the surface for say certain nanometer regime, say it was 2 or 3 nanometer in terms of death and in terms of percent composition. So, this particular material and then we can also see something more is something more is forming on the surface, so this was oxygen and say this one was silicon.

So, we can say there is some formation of silicon oxide on the surface, so we can say that the oxygen level will go down and then we can say that there was some higher concentration of a material say silicon. Then, again oxygen we can say silicon oxide was basically predominant at this particular on the surface, whereas say the bulk was say something like this the silicon and then oxygen.

Then, we had something like indium, so we can say the bulk of it is formed of indium whereas, it was probably coated with some silicon and which is formed oxide. So, we can say that Si O 2 is forming in an indium bulk, so that is how it will tell that what is the overall material what is the overall material, which is basically being what is really happening on the surface. How this depth profiling can help us identify what is happening beneath the surface, so by ion etching we can by this particular process we can see with the increase in depth.

We are seeing increasing concentration of indium and decreasing concentration of silicon and oxygen, so it means that there was some silicon oxide which might have formed on the surface. One more dimension can be given to it is that it can also happen that we had silicon and then it was going like this and then we had some oxygen. Then, it drops much earlier to that, so it means that that silicon oxide is forming only to a certain thickness and there is again some more regime where silicon is still intact. So, we have formation of some silicon oxide on the surface beneath that we have some silicon, and then we have some indium on which the particular silicon might have been coated, so that tells overall depth profile of a particular Auger process.

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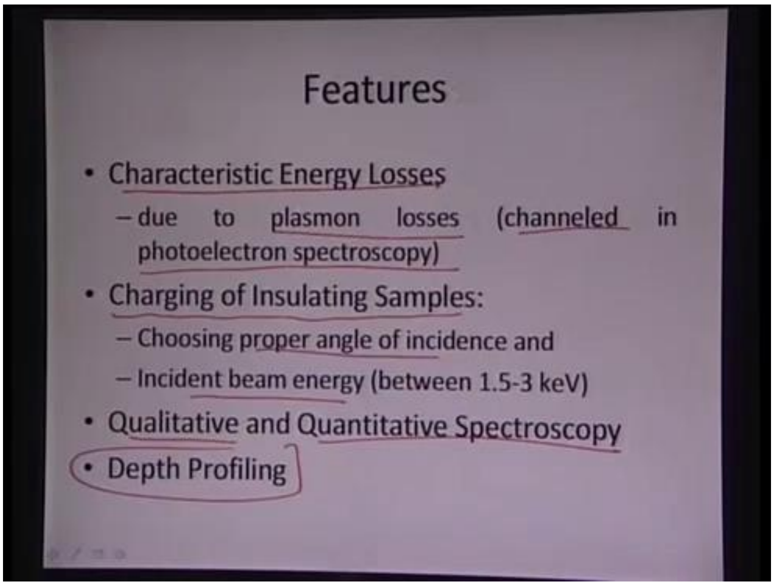

Features

- Characteristic Energy Losses
  - due to plasmon losses (channeled in photoelectron spectroscopy)
- Charging of Insulating Samples:
  - Choosing proper angle of incidence and
  - Incident beam energy (between 1.5-3 keV)
- Qualitative and Quantitative Spectroscopy
- Depth Profiling

So, now coming back to the overall features of the Auger electron spectroscopy to summarize the overall lecture that we have characteristic energy losses. They can occur because of plasmon losses or which can again be channeled through the electron photoelectron spectroscopy. So, they basically create the background and then there can be a charging of insulating samples, so by choosing proper incidence angle and by choosing proper beam energy, we can take care of that by lowering the beam energy. By inclining the surface and then Auger electron spectroscopy can also be used for qualitative and quantitative spectroscopy.

It can also be used for the depth profiling part and basically this Auger electron spectroscopy, we realize that we have basically Auger process arising from three electrons one is the core level electron, which is basically knocked off. Then, we have one electron jumping from higher energy shell to a lower energy shell and then third thing that energy is absorbed by a electron, which basically is emitted via overcoming the binding energy that is called a Auger electron.

We saw that how the overall instrumentation is also done that we have incident electron beam energy source and then we have something called analyzer that basically allows only a certain energy levels to pass through it. That allows only a certain electrons to come out with certain energy levels and that is being detected by detector, where some dynodes or photo multiplier tubes and that thing is again plotted as curve with respect to energy. So, we have signal count with respect to energy and to make it much more precise, we take a differentiated form with respect to d n by d e with respect to energy and that is much more sensitive and much more repeatable.

Then, we also saw that the Auger electron spectroscopy can also be utilized for depth profiling via doing the surface by applying certain ion beam and then etching the outer surface. Then, we will be seeing what is happening beneath the surface to comment on what is the overall composition of the overall sample which was under consideration. It can also tell you what is happening beneath the surface and so on, so basically we end our lecture here.

Thanks a lot.