Techniques of Material Characterization
Prof. Shibayan Roy
Department of Materials Science Center
Indian Institute of Technology – Kharagpur

Lecture – 28
Signal generation in SEM Continued

Welcome everyone to this NPTEL online course on techniques of materials characterization and we are now in 6th week module 6 we are discussing about scanning electron microscopy and we will be continuing our lecture on signal generation in SEM. So, in the previous two lectures we have discussed about little introduction of scanning electron microscope then we discussed about the history of scanning electron microscope.

And we try to highlight some of the differences between scanning electron microscope, the transmission electron microscopes, some of the similarities between the two techniques and so on and then we also discussed about the versatility of scanning electron microscope and then in one of the key points in that versatility is that various different type of signals that generates when electrons hit any specimen.

Various type of inelastic scattering events happen and those inelastic scattering events usually are the main basis of signal generation in case of scanning electron microscope. So, we have seen how different signals generated like phonon scattering like through Plasmon scattering, single valance shell electron, but we also said that none of these events, none of these inelastic scattering events are useful signals for scanning electron microscopes.

There are various reasons to that. Number one like one reason is the energy detection the amount of energy which is lost in those processes for example phonon scattering it is very less and that kind of to collect a signal or to identify an event where the energy loss is of that order around one electron volt is extremely difficult to detect and also the occurrence probability of such events phonon scattering or single valance electrons is also very, very less.

And that is why the mean free path is very large and it is very difficult to collect or difficult to identify the events from those signals or those changes in energy in the primary electron beam if we try to detect we will not be able to capture much of the information about the material. Plasmon scattering is definitely another one where it was possible the energy lost is quite high and the occurrence is also quite large.

But there the problem was mostly that this events Plasmon scattering events could not be related to the material identity or chemical identity because of which this is happening. So, more or less all these signals are not that useful for any imaging purpose or for chemical identification purpose in scanning electron microscope.

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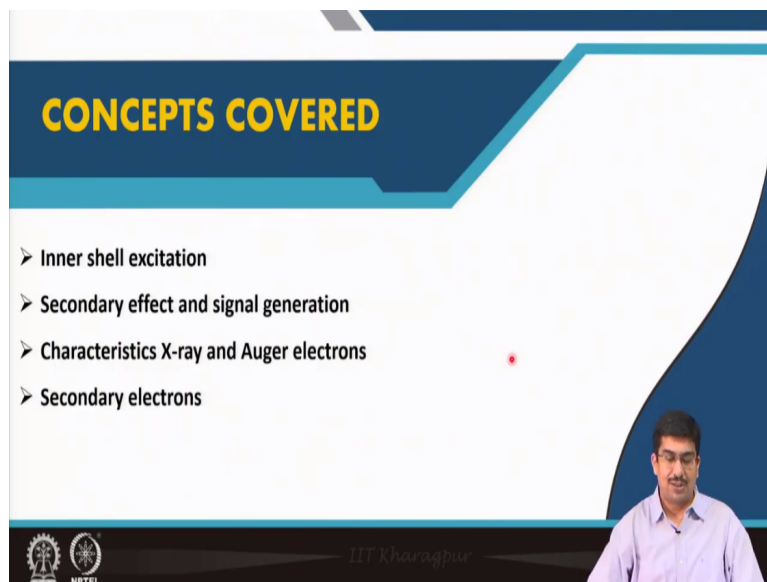
From there we will be discussing today about some of the signals which are useful for scanning electron microscope which we can detect and most of the scanning electron microscope basically uses these signals. So, first of all is inner shell excitation this is another type of inelastic scattering and this produces some secondary effects which we will discuss out of the secondary effect most important is the characteristics x-ray and Auger electrons and finally we will try to discuss about secondary electrons as well.

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Inner shell excitation

- A rare but valuable form of inelastic scattering is the knocking out of an inner shell electron.
- Because the binding energy of K and L shell electrons are high, the energy lost by the primary electron can be quite large in this process.
- It takes 283 eV to remove a carbon K electron, 69508 eV to knock out a tungsten K and 1100 eV to excite a copper L electron.
- The mean free path for this type of inelastic scattering is quite large (in micron range), so the process occurs much less frequently than, say, plasmon scattering.
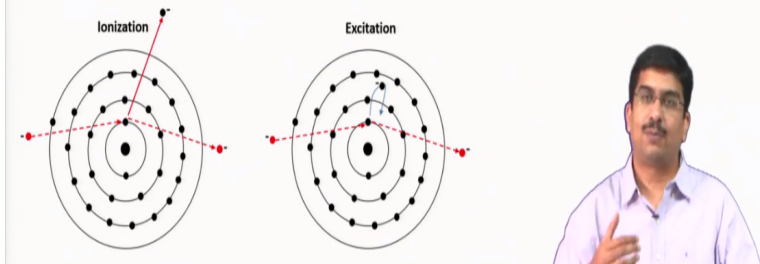
So, inner shell excitation is just like single valance electron excitation. This happens not with the outer electrons present in the valance band or in the conduction band not with like Plasmon scattering or single valance electron excitation, but this one involves an inner shell electron. So, here what happens is it is a rare event it is occurring probability is less, but in this case what happens the primary electron beam basically knocks out an inner shell electron from the specimen atom.

The primary electron beam comes and it knocks out a inner shell electron may be in the K shell may be from L shell and so on and so forth and what happens in the result definitely there will be a vacancy created in that material, in that atom and this atom will go to an ionized state or in a high energy state and then there will be some secondary effects which we will discuss in later.

But the important point here is that the binding energy for this inner shell electrons like for K shell or L shell electrons these are typically very high and therefore the energy that is lost in this case by the primary electrons which is also quite loss. So, if we capture the primary electron before and after this inner shell electrons we can see a lot of change in energy and that change in energy is again very, very characteristics of the specimen atom itself because K shell, L shell we already discussed these are localized electron states and very well defined energies are there.

So, primary electron which encounters these atoms and knocks out an electron from any of these inner shell that is that amount of energy change involved is very, very well defined. So, we can basically identify the nature of the specimen or chemical nature of the specimen atom from this inner shell excitation just if we check the primary electron before and after this. There are secondary effects and there are other signals which is generated that is the separate thing.

But if we compare from something like a Plasmon scattering this one is or rather from a phonon scattering or single valance electron excitation this one has a signature this event inner shell excitation events inner shell electron excitation event has a signature of the specimen with which or specimen atom with which the primary electron in interacting so that is the first thing.

And what type of energy change we are talking about here. So, for example if you take a carbon K electron to remove it the binding energy of a carbon K electron is 283 electron volt and as the atomic number increases of course we are talking about heavier nuclear and definitely then the binding energy also will increase. So, it will take around 60,000, 70,000 electron volt to knock out at tungsten K electron.

And around 1,100 electron volt to excite a copper L electron. So, this is we are talking about a very high amount of energy change much higher than even Plasmon scattering or anything and the mean free path of course because as I said that this high energy changes involves that is why the occurrence probability of this inner shell excitation is not much so it will not be very frequently happening like for example of phonon scattering.

So, this process occurs less frequently then like Plasmon scattering which is much Plasmon scattering which happens by let us say for example it is in the conduction band event so that probability is much higher than this inner shell excitation probability. So, mean free path for inner shell excitation is quite large most often in the micron range and that has its implications which we will discuss in later.

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Inner shell excitation

- The secondary effects produced when the excited atom relaxes are almost ideal for analysis.
- The interaction cross-section for inner shell excitation, in common with that for most scattering processes, drops as the primary electron energy increases.
- It is also lower for elements of higher atomic number Z, since E_C (the critical energy to excite a secondary effect e.g. characteristic X-ray) increases with Z.

Ionization   Excitation
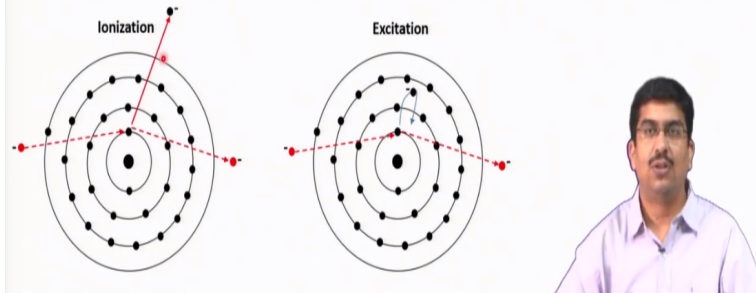
So, inner shell electrons as I said we can measure the energy change, but more easily what we can do we can measure the secondary effects which we will discuss in a couple of minutes from now. So, this secondary effects are produced when this excited atom comes back to the relaxed state. So, when it comes back to the relax state there is again an energy. So, when it goes to that energy this high energy state; so that amount of energy has to be supplied.

So, if we want to remove K electron just now we saw around we have to remove around 283 electron volt from carbon K to remove a carbon K electron. So, that much energy is gone to the specimen atom in the process. So, it takes that much energy from primary electron beam and this one electron is knocked out from K shell for example and now this entire atom is in the ionized state with that much of energy present.

So, that energy that atom has to somehow relax somehow it has to get rid of this much of energy and in the process what happens it generate some kind of a secondary signal this inner shell excitation generate some secondary signal which are very much characteristics which are very related to the chemical identity of the specimen atomic structure it is very related to that.

So, from there these secondary effects are very ideal for chemical analysis number one. Also the interaction cross section for inner shell excitation it strongly depends on the primary electron energy that is involved. So, if the primary electron energy is very high meaning that

acceleration voltage if the acceleration voltage is very, very high then it is those primary beam electrons are not suitable to cause this inner shell excitation.

That means what happens is that we know most of the atomic place we can imagine that within the atom the positive charge is only contained within this nucleus in a very small place and electron clouds are filling the rest of the place. So, most of the places is vacant. So, primary electrons can straight away pass through this vacant places without causing any interaction.

Any inner shell excitation if the accelerating voltage is very high means the electron kinetic energy is very, very high. So, this effect to take place inner shell excitation effect to take place the primary electron beam energy also has to be within a certain range first of all. So, this is again this is very much specific. So, what type of specimen atom I have and then what amount of energy is required for generating for removing one K shell electron or L shell electron or M shell electron.

This accelerating voltage is related to that and accordingly you have to choose the accelerating voltage in order to produce any one type of inner shell excitation event. So, that is the relationship that is the first thing. Next thing is that it is related this inner shell excitation event is also related to the atomic number of the specimen and that is already we discussed.

That it is because every inner shell electron has a specific amount of energy which is characteristics of that particular atom. So, we have seen how it varies between carbon and tungsten and copper and if we go for iron and then aluminum and it is even it is distinctly different between the L of say if we compare K of different K shell of different atom, L shell of different atom it is completely different.

So, it is very much related or characteristics to that particular chemical species. So, definitely then what will happen is that the probability of this inner shell excitation will be lower for elements of higher atomic number. So, as the atomic number increases it will be more and

more difficult for the primary electron beam to knock an inner shell electron to cause this kind of inelastic scattering event.

This is basically the critical energy to excite any of the secondary effect like a characteristic x-ray emission and all which we will discuss to cause any of these events it will be very difficult, the amount of energy will increase with atomic number because now this positively charged nucleus will contain much more it is a much more number of protons the charge is higher.

And thus therefore it can bind or it can hold this electron inner shell electrons with a much or tightly energy is correspondingly higher. So, these are the two dependence of inner shell excitation event with atomic number and acceleration voltage.

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So, secondary effects as we said that secondary effect are happened when this specimen atom from its ionized high energy state when it comes back to the relaxed condition then this amount of energy, the extra energy that is contained or that is supplied from the primary beam to this atom of the specimen that energy needs to be relaxed and that is what causes the secondary effects.

Now secondary effects not only it is related to the relaxation of energy, but since we are talking about an opaque sample we are talking about a detection here. So, this secondary

effect there is also another clause that these secondary whatever secondary effect that happens because of this inner shell excitation caused by the primary beam whatever secondary effects or secondary signal is generated that needs to be detected out of the specimen that is also is very important.

So, the secondary this inner shell excitation effect if it produce a secondary effect, but that is contained within the specimen. So, we are talking mostly here about a opaque solid specimen and you have seen that interaction volume and so on. So, if that signal does not come at all outside the specimen and cannot be detected then we cannot identify that secondary effect. So, secondary effect here has two parts.

Number one, it is produced from inner shell excitation that is one and second thing the secondary effect must be detected by the detector outside the specimen then only this can be called as secondary effect. So, secondary effect in this case in case of at least in scanning electron microscope in that perspective the secondary effects can either be electrons or some kind of an electromagnetic radiation.

And this we can discussed it can be x-ray electromagnetic radiation means either it can be an x-ray or it can be a light. So, we know that everything is electromagnetic radiation whether it is light or whether it is x-ray or gamma ray (14:27) everything is electromagnetic radiation just the wave length range is different for them. So, it is another way of saying that either or even for that matter electron is also an electromagnetic wave we can consider that.

So, it basically depends on what is a wavelength of the secondary effect that is finally produced. So, depending on that what different type of inner shell excitation at different type of this relaxation process, different type of electromagnetic wave is generated with different amount of or different value of wavelength.

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Relaxation of excited atoms

- If an inner shell localized electron is knocked out of an atom, the atom is in an excited, high energy state.
- At some later time, the empty electron state will be filled and the atom will relax giving off the excess energy as a secondary effect.
- If the vacant electron state is an outer state, then the energy to be given off will be small and is commonly emitted in the form of a photon which may be in the visible range.
- This effect is known as cathodoluminescence.
- If the vacant state is an inner state, the amount of energy to be released is larger.
- There are two main possibilities: a characteristic X-ray or a characteristic (Auger) electron may be emitted.
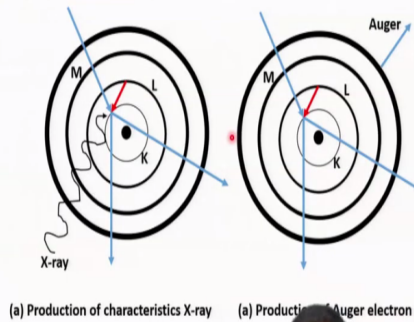
(a) Production of characteristics X-ray   (a) Production of Auger electron

So, let us see how it happens as we already discussed that okay first a primary electron beam comes it hits let us say K shell electron or L shell electron it hits and that inner shell electron is knocked out of the atom and then it goes to an higher energy state and from there when it comes back to the relax from that high energy state when it comes back to the relaxed condition it has to remove that amount of excess energy.

Now how this excess energy can be removed? So, that process we can imagine that there is three different situation that can happen. First of all that this vacant electron state. So, in order to fulfill so there is an electron vacancy that is created in the inner shell so there is no doubt about that primary electron beam comes and it causes and electron vacancy in the inner electron shell.

What happens is that in order to remove this energy this excess energy. So, there is the empty electron state invariably will be filled by some electrons jumping down to that inner electron shell. So, that is how the most often or most probable situation is that some electron from some other outer electron state somewhere this there will be an electronic jump. So, from higher energy state let us say I have this K electron K electron energy state is having an electron vacancy.

Now from higher anywhere L, M or anywhere from any other electron energy state there will be an electron jumping in and filling out that this vacancy, but in the process there will be

vacancy created in other electron states as well. What happens is that if this vacant electron state so after this electronic jump electronic state the vacant electron state is happening in the outer states meaning that it is not K, L or M all those shells.

Now the electronic jump is happening in the outer electron state from there some electron comes out to the inner shell. So, from outer let us say from conduction band or valance band from there one electron jumps from there all the way up to the K shell the inner shell. In that case what happens is that the energy because those electrons the outer shell electrons have very less binding energy what will happen?

So, the energy change in this process when it happens between an outer shell and the inner shell. The energy change here will be very, very small and since the energy change is very small the energy or the electromagnetic radiation that will be emitted in the process due to this electronic transition and that electronic transition is always the amount of energy is a difference of energy between this electronic state.

So, that amount of energy change is very, very less and as a result the electron or the electromagnetic wave that is produced is in the or the wavelength of that electromagnetic radiation is within the visible range or other way round we can say that in this case the secondary effect or secondary signal that is produced by this relaxation effect is a light signal and that effect is called the cathodoluminescence.

Again this process the energy difference is again very, very related to the chemical identity of the specimen. So, if we are able to capture that light signal we can find out, we can correlate that with the chemical identify of the specimen atom which is producing this. So, this is another way of identifying the chemical nature of the specimen atom with a very high accuracy in fact cathodoluminescence.

Obviously this has its own implication, this has its own drawback, the detector that is needed or the kind of vacuum that is needed because the cathodoluminescence signal that is produced is very minimal. So, there are lots of issues of detection and production and detection of these signal and we will try not to go into the cathodoluminescence part so much, but basically this

much you can remember the cathodoluminescence in that case the secondary signal which is produced due to this inner shell excitation process is a visible light signal that is it.

Now, if the vacant state if the state from which this electron jumps back to the inner shell that is also an inner shell. So, that means the electronic transition now happens if I have a K shell vacancy the electronic transition happens from L, M and all of these inner shell only the electron jumps back to there. For example now I can imagine that there was a vacancy in the K shell due to the primary beam and electron jumps from L shell to this one.

Now what there will be two different situation again so cathodoluminescence is basically an electronic transition between the outer shell electron and inner shell electron and now I am talking about another type of relaxation effect where this is an inner shell to inner shell electron transition. So, this inner shell to inner shell electron transition and relaxation by the inner shell electron transition this can generate two different type of signals.

One is characteristics x-ray signal and other one is a characteristics electron. So, characteristic means it is related to the chemical identity of the specimen atom which is producing the signal. So, this x-ray signal or electron signal which is produced carries the information about the chemical identity of this specimen atom so that is why they called characteristic that is there.

So, characteristic x-ray so we get one x-ray signal which is called characteristic x-ray or we can get one electron which is called Auger electron so r is silent here so it is called Auger electron. So, these two types of signals can be produced in this case.

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Characteristics X-ray emission

- An X-ray is to be emitted when a single outer electron jumps into the inner shell vacancy.
- The energy of the X-ray is the difference between the energies of the two excited states and this is characteristic of the particular atomic species.
- If a K shell electron has been knocked out of a Mo atom, and replaced by the 'jumping in' of an L electron, the energy difference, ΔE is 17400 eV, which is emitted as K_α X-ray of Mo.
- Wavelength of K_α X-ray of Mo is 0.071 nm.

Now, let us see that what is the difference how these two types of signals can be produced in this entire method? So, first of all let us understand the characteristic x-ray emission that it is easier to understand. I have this inner shell the primary incident electron beam comes, it hits the electron beam or it hits and knock out this K shell electron this is ejected here and now what happens there is an electronic transition from L shell to K shell.

And whatever the energy difference between the K shell and L shell the binding energy of K shell is much higher than L shell. So, whatever this energy difference between these two shells that much of energy will be emitted as an x-ray photon. So, an x-ray photon will be emitted in this L to K shell electronic transition and that will carry the energy which is equal to the energy difference between the K and L shell that is it.
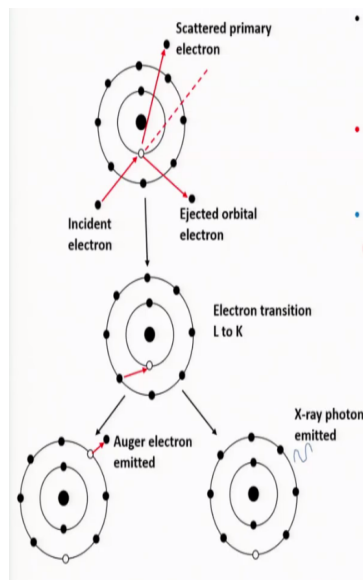
And we know that energy of an electromagnetic radiation is directly related to its wavelength. So, that means the x-ray photon which is emitted will have a particular amount of energy and will have a very certain value of the wavelength and these two are again related to the energy difference between L and K shell and that means it is again related to the atomic or chemical identity of the specimen atom.

So, now if we take couple of specific example then we can understand this process. So, K shell electron let us say from a molybdenum. So, let us take a very high heavy metal in this case. So a K shell electron is first knocked out by this primary electron beam and it is

replaced by an L shell electron jumps from L shell to K shell let us imagine. So, in this process the energy difference between these two electronic states is around 17,400 electron volt.

And as a result we get an x-ray emission which is called the K alpha x-ray we will discuss about characteristics x-ray more when we discuss about the x-ray part within couple of weeks we will discuss about x-ray production of x-ray and so on and there we will discuss more about this. So, basically now this K alpha x-ray of molybdenum wavelength of this K alpha x-ray of molybdenum is again as I said is very, very it is very fixed 0.071 nanometer.

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Now, if you take another example that let us say not from L shell so this electronic transition is again K shell vacancy is there, but this electronic transition is not happening from L shell now it is happening from M shell then the energy difference will be even greater because K shell remains K shell so its energy is fixed M shell is having lower binding energy. So, the difference between these two will be much higher.

And therefore the electron now the electron or the x-ray signal that is produced from here will have also correspondingly a smaller wavelength because energy and wavelength is inversely related. So, it will have larger energy difference or larger energy and smaller wavelength and this characteristic x-ray will now be called molybdenum K beta characteristic x-ray. So, this

is the way different type of characteristic x-rays will be emitted which carries the signature of not only the chemical identity of this material.

But also the about information about how this electronic transition basically happens. So, you can imagine this difference between this process inner shell excitation and secondary effect generation with something like Plasmon scattering there the information the inelastic scattering that happens is not related to the chemical identity of the specimen. So, it was not revealing any specific information about the specimen atom.

But in this case it is really directly related to the chemical identity of the specimen atom. So, if we now measure this energy and wavelength for this x-ray signals which are generated we can easily determine that which elements are present in the specimen and this exactly what forms the basis of analytical electron microscopy by these two methods which we will discuss EDS and WDS energy dispersive spectroscopy and wavelength dispersive spectroscopy.

And there is another method not a regular SEM, but a little specialized SEM form of SEM called electron probe microanalysis EPMA. We will try to discuss this also after we discuss about scanning electron microscope and image formation, but this the base of those techniques is basically this characteristic x-ray emission.

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The other way this can happen is called Auger electron emission. So, what is Auger electron emission? Now same process up to here it is the same the primary electron comes, it knocks out a K shell electron and then there is a electron vacancy in K shell and the atoms goes to higher energy state and when it comes back, when it jumps back that time it produces this electromagnetic radiation like x-ray most often.

But sometimes what can happen is that the L shell electron now jumps back to K shell. So, an electronic transition happens there also, but that electronic transition instead of producing an x-ray photon what it can do is that it can produce an energy again that amount of energy, the energy difference that amount of energy difference will cause a higher shell electron an outer shell electron will be knocked out.

So, that energy difference will be sufficient or that will provide the binding energy for an outer electron outer shell electron so that will be removed from this specimen atom and it will carry the kinetic energy. So, the kinetic energy of that outer shell electron or the electron which is removed from the specimen atom in this process will be exactly same as the difference of energy between this L shell and K shell.

So, just instead of an x-ray emission now we have an electron emission from the outer shell and that electron that is produced in this case is called the Auger electron. So, the Auger electron emission involves three different type of electron. First there is incident electron which knocks out a K shell electron creating a K shell vacancy then an outer shell means L shell electron let us assume L shell electron that jumps into that vacancy.

And then whatever the energy difference that will be supplied to an outer shell electron and that electron that will be enough for as a binding energy is enough to surpass the binding energy of that electron outer shell electron and it will leave the atom and that excess energy will now convert it to the kinetic energy of this electron. So, this process is Auger emission and just like characteristic x-ray Auger electrons the energy of the Auger electron, the wavelength of this Auger electron is also created or also carries signature of this electronic transition which originally happens so relaxation process itself.

And in turn it is also related to the chemical identity of the specimen. So, if we can capture the Auger electrons again just like characteristic x-ray we can get an idea about the chemical nature or chemical identification of the elements present in a specimen is possible in the Auger electrons and that forms the basis of another characterization techniques just like cathodoluminescence there is another characteristic techniques of chemical identity measurement that is called Auger electron microscopy.

Again it is a very specialized method we will not go and discuss about it and like the problems associated with Auger electron spectroscopy the advantage of it and all those things we will discuss not within this lecture, but maybe in the next lecture. So, now the Auger electron one thing you must remember is that Auger electron and characteristic x-ray emissions are alternates because their origin is the same.

The genesis of Auger electrons and the characteristics x-ray emission is exactly the same. So, up to here up to this process still this inner shell excitation and the jumping of inner shell electron to the vacancy state vacant electron state up to there is exactly the same thing after which whether the specimen atom will remove an x-ray photon or an Auger electron that depends on the atomic number basically.

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So, these two processes simultaneously can happen. So, whether it removes and characteristic x-ray emission will be emitted, x-ray photon will be emitted or Auger electron will be emitted

that depends on the atomic number that is it, but it is equally probable in general terms for any materials. Of course, what happens is now with atomic number the x-ray fluorescence yield.

The amount of x-ray emission, amount of this primary fraction of this out of the total fraction Auger electron and characteristics x-ray the secondary effect. Out of the total secondary effect the fraction of x-ray signal emission that is called fluorescence yield. So, this is related to the atomic number in this way w equals z raise to the power 4 / Z raise to the power 4 + C. Now here z is obviously the atomic number.

And this constant c this has a value of around 10 raise to the power 6 for atoms whose K shells are excited and similarly c has different, different values for L and M shell if there is a vacancy at K shell it is 10 raise to the power 6. If it is a vacancy in L shell or M shell the value is completely different and the yield of Auger as I said either it can be a characteristics x-ray or can be Auger.

So, the yield of Auger electrons is 1 − w. Now what happens is that for a heavy electron like for a higher atomic number material element there this w will be much higher than the Auger that means characteristics x-ray emission will be much higher chances of characteristic x-ray emission is much higher than the Auger electrons and but on the other hand the chances of Auger electron emission will be much higher for lower atomic number or lower elements with lower atomic number.

So, if we take an example again if we compare something like carbon with tungsten Auger electron emission probability will be much higher for carbon than tungsten which will possibly have much higher probability for characteristics x-ray emission. So, this is how these two process is related and that is why Auger electron spectroscopy or to identify the chemical nature of light element Auger electrons are much better than the characteristics x-ray.

So, characteristics x-ray emissions are not that better or that large in number from elements of lower atomic number for them the chemical identity determination with EDS signal or with

x-ray signal is very, very difficult and then the problem with Auger electron again is that the most of the materials, most of the general materials that we see other than this low atomic number materials for most of the other elements the emission of Auger electrons is very less.

So, if we can see here this is the amount of two other emissions, two other electron emissions which are possible which we will discuss like secondary electron emission and backscattered electron emission compared to that the Auger electron emission is very less in number. So, in the y axis it is basically the number and x axis it is basically the electron energy. So, Auger electrons are having very identify their energy level is very, very fixed which is characteristics of that particular element or the number is very less for a general elements above carbon, nitrogen and all.

So, Auger electron for most of the metals and all number of Auger electron generation is very, very less. So, that is the problem of doing Auger electron spectroscopy for this kind of material. So, we will discuss more about these aspects and about other electron signals in the next class. Good bye.