

**Advanced Material Characterization by Atom Probe Tomography and
Electron Microscopy
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Week-12
Lecture-36**

So, welcome to the second class of this microscopy course. Here, in the last class, we dealt with some basics related to the lens system and also how the electrons are produced by using the filaments, and these are accelerated by the Lorentz force, which is provided by using the electromagnetic lenses. Now, these electrons, for example, interact with the specimen, and depending upon the thickness of the specimen, different types of signals can be produced and can be used for the several imaging purposes or spectroscopy purposes.

So, in this diagram, what I am showing is the interaction of an electron beam with a sample that is thin enough so that these electrons will interact with the sample to produce secondary electrons. They can produce backscattered electrons. These secondary electrons and the backscattered electrons can be used in SEM for imaging purposes. Then, they also release Auger electrons, which we will discuss later, and they also produce X-rays, which are very important for elemental composition analysis.

These are energy-dispersive spectroscopy, and these X-rays have a characteristic wavelength corresponding to the element present in the sample. So, you can get the quantification or the composition of that particular sample. If the sample is thin enough, then there will be a transmission of this electron beam across the sample, and if you place a screen here, a fluorescent screen, what we can get is these transmitted electrons can be collected

and out of these transmitted there will be certain electrons that are elastically scattered and certain electrons that are inelastically scattered. Based on the elastically scattered electrons or the inelastically scattered electrons, you have different types of Elastic scattering means that there is no energy loss. In elastic scattering, where there is an

energy loss. So, it means that during the interaction of the electron beam with the sample, there will be a certain energy loss

and that loss in energy can be converted into certain other secondary radiations. We will discuss these radiations in detail in the subsequent slides. Now, the first thing to understand is some basic terms related to the interaction. The two basic terms we usually deal with are the cross section and also the mean free path. So, when the primary electrons enter the specimen, the same or different electrons leave again to form an image. Okay, different electrons mean these primary electrons will knock out the electrons from the sample surface, and those different electrons can be used for imaging purposes.

So, usually these are used for secondary electron imaging. These interactions of primary electrons with the atoms in the specimen. So, with the interaction of these electrons, you will produce images, diffraction patterns, and also other radiations which are used for analytical spectrums. For example, compositional analysis.

So, there are important terminologies, one of which is called cross section. What is cross section? This is the area which scatters the particle. In the sample, it appears to present for the electrons. Okay?

It means that this cross-section or this area is present for the electrons to be scattered. Okay? So this is the cross-section. Okay? If you consider there are n particles per unit volume of the sample with the cross-section σ for a particular scattering event, the probability of a single electron

being scattered in its passage through a thickness of dx —remember, we are talking about area, so there is a thickness dx —then that can be given as $n \sigma dx$, okay? n is the number of particles per unit volume of the sample, σ is the cross-sectional area, and Δx is the thickness across which the beam has traveled. Okay. Alternatively, we can actually calculate the mean free path for the scattering as the inverse of $n \sigma$, which is called λ . Okay.

So, they have an inverse relationship. So, what is lambda? From the formula, what we can see is, this is the average distance an electron will travel before being scattered. Okay. So these are the two terms we usually use for the scattering events.

So, a little bit more about mean free path. It is different for both TEM and SEM specimens. In TEM specimens, for many scattering processes, the mean free path is similar to the thickness of the specimen because TEM samples are electron transparent, and the thickness ranges from 20 nanometers to 80 nanometers. So, these are very thin samples.

So, usually, the mean free path is similar to the thickness of the specimen. But in SEM samples, which are bulk samples with a few hundred microns of thickness, it might occur that the electron can be single-scattered, plural-scattered, or multiple-scattered. So, what is single scattering? It scatters only once during the interaction with the sample.

There are several scatterings or many scattering, multiple scattering events in the sample. So, the probability of an incident electron suffering n scattering events while traveling a distance x across the sample. It can be given by Poisson's equation where P_n equals 1 by n factorial x by lambda raised to the power n exponential x by lambda. X , remember, it is the thickness through which the electron has traveled. Now, similarly, if you have two scattering events.

I told you about plural scattering; then, this can be given by n can be replaced by 2, but We can use this Poisson's equation to estimate somewhat accurately for some scattering events. But if there are many scattering events, usually the Poisson's equation is not useful due to scattering by different mechanisms. For that use Monte Carlo methods are used. So, this is just to introduce the definition of mean free path and how it is different in the TEM sample and the SEM samples

and based on the thickness these probability of incident electrons to be scattered the end scattering events can be calculated. Now, little bit details will go to the scattering. As I told you, when an electron interacts with the specimen, it either elastically scatter or it will be inelastically scattered. First, we will talk about the elastic scattering. Elastic

scattering, it means that there is no change in the energy of the incoming electron after scattering event.

Direction might change. For example, this is a typical atom. There is a nucleus and there is an electron cloud around the nucleus. If an incident electron comes and scatters, it can be scattered at the nucleus.

It can be there is no change in energy but there is a change in the direction. Some of the incident electrons they may be scattered through the electron cloud and they may not with an angle θ with a larger angle and some of the electrons they can scatter with a very small angle. So these are called scattered electrons if there is no change in energy then these are called elastically scattered electrons. So, elastic scattering usually occurs by Coulombic interactions, meaning electrostatic charges.

So, you know that the electron is negatively charged, and the nucleus is positively charged, so based on this, you will have a Coulombic interaction. So, between the primary electron and both the nucleus and all the electrons around it. So, this scattering event is between the electron, both the nucleus, and the electrons around it. So, this particular scattering is called Rutherford scattering.

So, it is nothing but the strong forward peak distribution of electrons. And here, if there is an E_0 , which is the energy of a primary electron, then the probability of it being scattered through an angle θ is given by this particular equation where the probability at an angle θ is proportional to the inverse of E_0 squared and sine raised to the power of 4 θ . It means that the higher the energy of the primary electron, the lower the probability of scattering because it moves very fast. It is accelerated toward the sample very fast.

So, the probability of scattering, as there is a term called $\sin^4 \theta$ here, so for small-angle electrons, the probability of scattering is much higher compared to large-angle scattering. So, if θ is more, then your probability reduces, but for any angle, it decreases with the increase in electron energy. Fine, so this is the probability of scattering. Now, how important is the mean free path? The mean free path depends actually strongly on the atomic number of the scattering atom.

Atomic number of the scattering atom. For example, if there is a 100 kV of electrons which are accelerated with a 100 kV potential, then the mean free path—remember, the mean free path is the distance at which the electron can scatter. So for the gold sample, you can see that the mean free path is very small, meaning the scattering tendency will be very high. For carbon, the mean free path is very high, okay?

And this elastic scattering of the electrons is the main contribution to the diffraction patterns, which are very important in TEM. This will come later in the class, and the strength of scattering depends on the atomic number, as I mentioned before and this is described by the atomic scattering factor, which is F . So the amplitude of scattering from the atom divided by that from a single atom. So this is the definition of the atomic scattering factor, which is the amplitude of scattering from an atom divided by that from a single electron.

So now, I hope that you understand what elastic scattering is. So remember, elastic scattering contributes to the diffraction patterns. And the probability of elastic scattering is inversely related to the energy of the primary electron and also the angle of scattering. Now, we will move on to inelastic scattering. Fine?

Inelastic scattering—what does it mean? If there is a detectable change in the energy of the primary electron B , it means that whatever energy the primary electron has, the E_0 , when it interacts with the sample, what will happen is it loses some of its energy. Depending upon the amount of energy lost, different types of scattering can be divided or different types of radiations can be produced. Usually, if the energy lost is greater than 0.1 electron volt, we call it inelastic scattering.

This is due to the interaction process. Here, we describe the energy lost by the primary electron and transferred to the electrons or atoms of the specimen. Whatever energy is lost is usually transferred to the electrons and atoms of the specimen, resulting in the release of certain radiations and different types of energies. This inelastic scattering is also responsible for

the stopping of an electron by a solid. When the electron enters the sample and interacts, inelastic scattering occurs, meaning it loses energy until it is eventually stopped within

the solid. Here, almost all the kinetic energy carried by the primary electron ends up as heat in the specimen. This production of heat releases certain amounts of energy, which we will now discuss. A small proportion of the energy escapes as X-rays, which are used for spectroscopy, light, or secondary electrons used for imaging and analysis.

These are the results of inelastic scattering. This is the result of the loss of certain energy from the primary beam to the specimen or to the electrons or atoms of the specimen. Now, based on the amount of energy which is absorbed by the specimen or which is lost from the primary beam, you will have different types of energies that can be released. These energies are either phonon scattering, plasmon scattering, single valence electron excitation, inner shell excitation, and inelastic scattering and absorption.

So, this order corresponds to the energy loss. It means that a very small amount of energy loss can lead to phonon scattering or plasmon scattering. For higher energy loss, you will have single valence electron excitation and inner shell excitation, and here there is complete absorption. First, we will cover phonon scattering. What is phonon scattering?

Usually, when an electron interacts with the sample, it will induce atomic vibrations in the solid. So, phonon scattering is a result of this, and the level of loss is less than 1 electron volt. Remember, in TEM and SEM, we are dealing with 30 kilo-electron volts or, in TEM, up to 300 kilo-electron volts. 300 kV. So, you can see the figure here.

If less than 1 electron volt is lost, that corresponds to the atomic vibrations, which are related to phonon scattering, and the whatever the lost—less than 1 electron volt—it contributes to the heat or the atomic vibrations in the solid. So, a primary electron loses energy less than 1 electron volt by exciting a phonon, effectively heating the solid. The mean free path for the high-energy electron is very large, a few microns in this case.

So, all the electrons which remain in the solid are likely to excite phonons. After they lose larger amounts of energy. And this is how the solid is heated by the electron beam. So, whatever radiation comes after heating the sample, we call this phonon scattering. The scattered electron is deflected by large angles, more than 10 degrees.

And it can be used for image contrast. Usually, phonon scattering is very important for heat transfer, spin relaxation, thermal expansion, okay. So, phonon scattering can be termed as the quanta of elastic waves, which are generated during and result in atomic vibrations in the solid, effectively heating the solid, okay.

Now, the next is the plasmon scattering. So, if your energy—if your beam—remember, the beam energy, if you are talking about the transmission electron microscope, it is 300 kilo electron volts, sorry. For SEM, it is 30 kilo electron volt. For TEM, it is 300 kilo electron volt.

Now if the primary electron beam loses energy between 5 to 30 electron volt, then it excites a plasmon. So, what is a plasmon? It is defined as the it is a wave in the sea of electrons in the conduction band of a metal. So, it is what we call it is a waves in a sea of electrons. So, here the mean free path the lambda is very short and it is only few hundred nanometers.

This frequent occurrence in all electron solid interactions and usually it is dominated by the energy loss spectrum. Energy loss spectrum there is another method which in the TM what we use is EELS. electron energy loss spectrum okay. So with this we are using so we can actually based on the energy loss we can identify the chemical species or the composition of that particular sample correct. So this is dominate the energy loss spectrum which is called a plasmon scattering and it is nothing but the waves in the sea of electrons.

Usually the plasmon scattering is to study the surface plasmons in microscope using EELS and this also a large application in nano antennas, then sensors, optical detectors etc. So this is a plasmon scattering. Now we will see that first we discussed about the phonon scattering which is a less than 1 electron volt. Now, we talked about this phonon. Now, we talked about the plasmon, which is a 5 to 30 electron volt loss of energy.

Now, the next is the single valence electron excitation, okay? And usually, the primary beam here—what will happen is that the primary beam, the primary beam which has an energy of E_0 , transfers energy to the single valence electron. It transfers energy to the single What are the valence electrons? You can see that if any orbital is there, if any atom

is there, the outermost shell—the valence shell—whatever the electron, these are called valence electrons.

And these valence electrons get energy from the primary beam. So, the primary electron transfers some energy to a single valence electron rather than a sea of electrons. Here, the mean free path is very large. It is a few micrometers. The scattering angle is also very small, and this is not very useful in electron microscopy.

Fine, this is a type of single valence electron excitation. Now, next comes the inner shell excitation. So, if you see an atom, it has a nucleus and certain shells, okay. You will have a K shell, L shell, M shell—K, L, M shell—and depending upon these shells, the electrons are present in them, and they have a definite energy. So, these all shells have a definite energy.

So, this but inner shell excitant means the primary electron, the primary electron beam will travel and it will knock out the inner shell electron out. Either K or either L shell. This is L shell, this is K shell. But you can see that the K shell is much closer to the nucleus.

So what will happen? Your binding energy with the nucleus of that K electron is much higher than the L electrons. So the binding energies are very high for K and L shells. The energy lost by the primary electron is very high. So it will be more than few hundred electron volts.

For example, for a carbon K electron, you will have to... 283 electron volt to remove a carbon k electron. But if it is a tungsten k electron then you need a very high energy loss which is around 69508 electron volts to knock out the k electrons. In this case the mean free path is very large few micrometers and in this case the inertial excitation the secondary effects are very useful. Remember, these are inelastically scattered, so whatever the energy loss is there, that is absorbed by this particular electron

which is present at a particular shell depending upon which shell it is, and by taking up that energy, these electrons can be knocked out. So, the cross-section for this inelastic

excitation drops as the primary electron energy increases. So, typically this is given by $\sigma = \sigma_0 \frac{Z^2}{E^2}$ where σ_0 is a constant, Z is the atomic number, and E is the primary beam energy. Correct?

And the critical energy to excite an X-ray increases with Z because with increasing Z , the number of electrons and protons also increases. So, your binding energy also increases with the increase in Z . These are called inner-shell electrons. Now, we come to inelastic scattering and absorption. What is this? So here, in solids, when the primary electron interacts with the sample, many scattering events will occur until the electron is stopped or leaves the surface.

Stopped means it is completely absorbed. onto the sample. So, the trajectories of a few electrons are simulated with Monte Carlo methods, which introduce many scattering angle probabilities. So, the majority are brought to a halt within the solid, but a few are backscattered and leave the specimen. So, the volume where 95% of primary electrons are brought to rest.

It means they are getting absorbed into the sample, and it is referred to as the interaction volume. So, you can see that this is the Monte Carlo simulation of aluminum. With an interaction of the electron beam, you can see that the electron travels, scatters, loses energy, and travels until it stops at a certain position. So, each electron will stop at a certain position, and joining these points of the distance where they stop corresponds to your interaction volume. So, for thin specimens, the absorbed means not detected in the experiment, and these are scattered through an angle greater than θ .

So, here there is an equation called the Lambert-Beer law, where I/I_0 is the fractional intensity which remains after absorption in a thickness x , and n is the number of scattering atoms per unit volume. And this N can be given by $N = N_A \rho / A$, where N_A is the Avogadro number, ρ is the density, and A is the atomic mass. So, this way we can estimate the fractional intensity which remains after absorption in a thickness X . Now, we will talk a little bit about the secondary effects. As I told you, when an electron beam interacts with the sample, it loses energy

especially in knocking out electrons from the inner shell, which generates secondary effects. First, we will describe the interaction of the electron beam with the sample. Now

here, you can see that most of the secondary effects can be written as either secondary electrons or backscattered electrons. What are the secondary electrons? The secondary effects are caused by the primary beam, which can be detected outside the specimen.

So, when the electrons hit the sample, what will happen? They knock out the valence electrons of the surface atoms. If they knock out the valence, knock out the valence electrons from the surface atoms. These electrons will escape from the specimen with energies below 50 electron volts. Remember, for SEM, we are using 30 kilo electron volts.

So, if these energies are less than 50 electron volts, the valence electrons will escape and the yield is high. And abundant, and these are used for imaging the surface atoms of the sample surface, okay. Then there is another type of interaction, which is backscattered electrons. What are backscattered electrons? The primary electrons leave the surface before giving up all their energy.

So, here the primary electron will go into the sample, and before losing all its energy, it gets back scattered again from the sample surface, and those primary electrons which are backscattered are detected. So, it has information related to the inside of the sample, backscattered, and they are not as numerous as secondary electrons but carry high energy. These particular BSE electrons are used for imaging and diffraction in SEM.

Diffraction in SEM means it is used for EBSD, electron backscattered diffraction. So these are the primary and secondary effects. Now, there are other secondary effects which are very important to understand, and these are caused when the primary beam can be detected outside the specimen, okay. So, the first type, there are three types of the interaction here, secondary effects. relaxation of excited atoms what does it mean if an electron has been knocked out of an atom in the specimen the atom is in the excited state

okay but it is in the unstable state it is in the excited state or we can call it is a high energy state remember the electron has been knocked out of the of the atom in the specimen the empty electron state Means the electron has been knocked out. So the space, it has created a space. The empty electron state will be filled and the atom get relaxed due to which it will give off the excess energy as secondary effect.

Based on which type of electron is getting knocked out, based on that different types of different excess energies can be released as a secondary effect. The first type is cathodoluminescence. What is cathodoluminescence? When the vacant electron state is an outer state it means that if you have a valence electron, valence shell if the electron hits to the electron on the valence shell

and this particular electron gets knocked out. If the vacant electron state is an outer state, then the energy to be given off will be very small. And the electrons which are in the conduction band, usually those electrons will occupy these vacant sites of the valence. So, these conduction electrons Those occupy the vacant sites of the valence electron.

And these are commonly emitted in the form of a photon, which may be in the visible range. So, these are called cathodoluminescence. And cathodoluminescence is used mainly to understand resonance effects, bandgap defects, It is also used for light transport, electronic structure, and especially in semiconductors. Remember cathodoluminescence: it is the energy released when the electrons in the conduction band occupy the vacant electron state

in the outer shell, which is knocked out by the electron beam. So, this is one type of relaxation of excited atoms. Another type of excited atoms occurs when an electron knocks out the inner-shell electrons. So, now you have a nucleus and shells. If an electron comes and knocks out the inner-shell electrons, this may release two types of energies.

So, here the vacant electron state is an inner state. Then the energy to be given off will be very large because, in the vacant states, the electrons are bound toward the nucleus. So, they need higher energy to knock out. So, whenever an electron is knocked out from the inner shell, if the outer-shell electrons occupy these inner-shell states, they will produce X-rays. And these X-rays are characteristic, depending upon the energy—whether from the M shell to the K shell or the L shell to the K shell—the X-rays have different wavelengths.

And these are characteristic of every element. And these X-rays are used to quantify the composition analysis. So, what are the X-rays here? A single outer electron. Jumps into

the inner shell vacancy, which is created by knocking out an electron from the electron beam.

And the energy is the difference between the energies of the two excited states. So here, the lambda is given by hc by Δe . These are the generation of X-rays. Now, there is a second type of excited state when the inner electron is knocked out: the Auger electrons. These are called Auger electrons. What are Auger electrons?

These are alternatives to X-rays. What happens is that when an inner electron is knocked out from the atom, then what will happen? There will be a vacancy. There will be a first vacancy, correct? Then the outer electron jumps into the vacancy, and another outer electron leaves, carrying the energy.

It means that when an electron is knocked out from the inner shell, what will happen? The outer electron will jump into the inner shell electron, And whatever energy is released during that time, that energy will be used by the other outer electron that leaves, carrying the energy. And these electrons, the outer electrons which leave carrying energy, are called Auger electrons. And these are usually used for surface studies.

Sometimes chemical and compositional analysis. Fine. So with this, we will end this class now. So I have given you a brief explanation of the electron's interaction with the sample and what type of signals we produce and Depending upon elastic and inelastic scattering, you can get different types of secondary effects.

Elastic scattering mostly produces diffraction patterns, which are very useful for crystallography information in TEM. And inelastic scattering, based on the energy loss, releases different types of radiations, which can be used for specific purposes. So with this, I will end this class now, and we will meet in the next class. Thank you.