Physics of Functional Materials and Devices
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Lecture – 49, Week 12
Scanning and Transmission Electron Microscopy

Welcome to the third lecture of week 12. In this week, we are focusing on characterization tools which are used to investigate the properties and response characteristics of functional materials and devices. Let us continue with that in today's lecture also. In today's lecture, I will focus on scanning and transmission electron microscopy. You will see that these are two techniques which are extensively used to understand the morphology of the particle. that is the shape the size of the particle.

It is used to understand the elements which are constituting a given particle also what is the nature of lattice planes in these particles. are the particles which are forming the overall material of uniform shape or you have inhomogeneities. That means, if you go from one region to the other you have different sized particles. Homogeneous distribution of particles is critical for having the reproducible results.

These techniques are also used to understand sometimes the nature of transitions which can occur in a material if you go from low temperature to high temperature. Is there melting taking place or is there any kind of modifications taking place in solids or alloys. So, they are extensively used till few decades back. The problem was that the instruments were so costly compared to the funds available that these techniques were not routinely available to most of the research institutes. But now you will find that the access to these instruments has become quite easy and therefore, they are being routinely used.

So, we will start with scanning electron microscope. What is the principle behind? This you should understand because that will give you an understanding about the nature of particles or materials which can be investigated using this technique. It is not that you can use all types of materials and then investigate under an SEM. Then we will talk about the instrumentation, the applications of SEM before we move to TEM and finally, we will wind up by talking the applications of TEM. What are we talking about in this week? we have been talking about the characterization techniques for materials.

We already talked about XRD, I mentioned in the previous lecture when and where we use neutron diffraction and electron diffraction. We have also talked about FTIR, we have talked about UV-visible and when we were talking about the thermal properties of materials, I had talked to you about the TGA, DTA and DSC measurements and if you talk

about the expansion properties in solids then that is measured using dynamometer. that is also discussed in one of the lectures. So, let us now shift our focus and look into few of the microscopic techniques which are used to understand the properties of materials. So, those would be SEM and TEM.

If you look into the major difference between an optical microscope and an electron microscope, you will get an idea why this technique is becoming important. If you have an optical microscope, you use the light source for imaging. you have a specimen and you can just put it under an optical microscope and you can scan the surface of the sample quite easily. You can operate the optical microscope in air, you do not need vacuum conditions. The optical glass is used as the lens that magnifies the picture of the specimen.

You can look into the image by eyepiece or you can get it coupled with CCD camera and you can directly see it on the screen. The maximum magnification is nearly 2000 times. In comparison, the electron microscope you do not use the optical beam as the name suggest you use the beam of electrons. The samples which you are going to investigate under an SEM are to be placed in a vacuum chamber. Otherwise, if you have a beam going through air they will get scattered by the particles of air and you will never have an electron beam.

So, you have to place this sample in a vacuum chamber. So, you cannot put any sample which is very loose in the sense that they can be sucked out of the sample holder if you have the vacuum pump switched on and you are talking about very high vacuum conditions. So, you are going to very low pressures. So, you are going to have the diffusion pumps operating. So, the samples can not be left loose or you cannot have samples which would be giving out volatile components or moisture content because once you have very high vacuum suction then you what you are doing these things can come out when you are putting the sample in the vacuum chamber and they will contaminate the column.

And then slowly the electron call beam column would get contaminated and you would have to have serious cleaning and refurbishing process undertaken before the system can be reused. The lenses are replaced by a series of coil shaped electromagnets. So, that you use the E beam and the B component to modulate the path of the electrons. The image is formed on a photographic plate and it is called as electron micrograph. It can be observed on a screen of a TV or it can be printed directly through an output and the magnification is sometimes 100,000 times or more.

If you look into the scanning electron microscope, it basically tells you that you are going to scan that is where the term scanning comes. Scans the surface of the specimen using focused beam of electrons. These electrons will do what? They will interact with the atoms or molecules of the sample, but which are on the surface and produce the signals that contain information about the sample topography and composition. the resolution of the

modern SEMs are of the order of few nanometers. So, they can go to really very low dimensions and they have very high resolution.

So, you can go up to few nanometers and scan the surface and find out what is there in the specimen. In comparison to what approximately 1 micrometer for a conventional optical microscope. So, 10 raise to the minus 6 meter is micrometer, 10 raise to the minus 9 meter is nanometer. So, you can clearly see you can scan to very low dimensions and understand the properties of the sample. basic components of the scanning electron microscope would then become you must have a source of electron that is given out by the electron gun.

Then you must have the focusing lenses. What type of lenses would those be? Basically those would be the lenses where electric field or magnetic field based lenses which can modulate the path of the electron beam. So, these EM lenses are the condenser lens and the objective lens. Then you need to have scan coils which will allow you to scan the surface. All these things have to be kept in a vacuum chamber otherwise you will not have the electron beam going directly down and hitting the sample the electrons will get scattered by the particles of the air if you are doing the same experiment in air.

You are also talking about very high voltages. So, you have to ensure that the whole system is properly sealed and not exposed to the user. You will have detectors which will receive the signal and then finally, the processing unit that will collect that signal which are sent by the detectors either the pack scattered detector or the Hartley-Thornley detectors which analyze the secondary electrons. Now, you have electron which are generated and they are hitting the target. Once this beam hits the target in this case the specimen what can happen? You can have two types of electrons which are ejected those can be backscattered or secondary electrons.

So, two types 1 and 2 that is backscattered electrons or secondary electrons. The detectors will collect these electrons and give you certain set of information which we will discuss in coming slides. but you can see that there are two types of electrons. That means, you will have two types of detectors connected to these SEM. Backscatter electrons are the one which are coming out with very high energy and secondary electrons are the ones which are coming out with low energy.

So, if you have the incident beam what all things can happen? you can have the backscattered electrons, the secondary electrons, the Auger electrons, you can have the absorbed electrons, transmitted electrons or cathodoluminescence. Each of them gives you a technique to characterize the sample. Why? Because the nature of the electron that is backscattered or secondary or adsorbed will depend upon the materials property and therefore, you will have different techniques by which you can analyze the samples. In SEM, we will mostly focus on secondary and backscattered electrons. These backscattered

electrons are high energy electrons which are scattered backwards at an angle greater than 90 degrees.

That means, you have the beam if it is coming down the back scattered electrons are also going back towards the same direction. So, you have the primary electron beam and then the back scattered electron. these electrons have energies ranging from a few electron volts to energies which are comparable to the incident primary electrons. Now, what will happen? The interaction between the incident electron with the sample will lead to different processes. You can have elastic scattering or inelastic scattering.

The backscattered electron primarily results from elastic scattering that means, you do not lose too much of energy, where the incident electron will be colliding in the sample and coming backwards while it is conserving the energy and momentum. Now, suppose you have a detector in the path of the backscattered electron, collect the backscattered electrons and this will give you information about the atomic number of the elements in the sample and what is the energy by which these electrons are coming back. In comparison these secondary electrons are low energy electrons. that are ejected or emitted from the surface of the sample. These secondary electrons are typically generated through inelastic scattering that means, you lose certain amount of energy.

So, you have backscatter electrons and secondary electrons. Obviously, the secondary electrons will have much lower energy. So, the incident beam which comes and hits the sample it ejects the electrons from the upper orbitals and you have electrons which then actually push out some more electrons while it is coming out of the orbitals and then you have electrons coming out, but with much lower energies. So, these secondary electrons have energies to few electron volts to maybe 100 electron volts or so on. They are emitted from the top most atomic layers of the sample surface and provide information about the surface morphology and topography.

So, the shape and the size of the particles are analyzed using the secondary electrons. they are sensitive towards the surface and therefore, they become useful for surface features determination. They can also be quite sensitive towards the surface height and materials composition. This means that if you look into the sample. So, you can have samples of different shapes and sizes.

So, the secondary electrons are coming out from this sample, from this place, from this place, from this place. So, you will find that these electrons which come out they are also interacting with the sample having different profiles on the surface and hence they will have slightly different energies. And therefore, these secondary electrons are very sensitive towards surface height and the composition of the material. The image you get is by detecting and mapping the secondary electrons and having a high resolution profiling of the samples surface. These are often referred to as secondary electron images.

You also have a mechanism by which you can actually have different emission from different regions of the sample. if you have areas with higher electron emission you will see slightly brighter images. While if you have regions with lower emission they will appear darker in comparison to other region. This contrast can reveal what? It can reveal the details about the surface topography the texture or even it can give you information about composition variation. The characteristic information from a SEM therefore, becomes what? You can have information about the topography that is how it looks and its texture, morphology that is the shape and the size of the particles and composition that is the elements and the compounds that the object is composed of. It is extremely important to carry out these determination Suppose you have a sample in which you thought that you have 20 percent calcium, 40 percent titanium and 10 percent of lead. When you analyze the samples and then you get the data which says no you do not have 20 percent of calcium you have 70 percent of calcium and only 10 percent of lead. because during synthesis something happened and you were not able to incorporate the elements in the desired stoichiometry. Obviously, the response characteristic of these materials would be very different.

So, it is essential that you get the nominal compositions using these measurements also which are consistent with what you had proposed during the synthesis of the material. If you have information about the particle morphology for example, if you have spherical particle or you have rod like particles or you have any other shape of particle. then what will happen? You will clearly see that there would be difference in the reaction at the surface of these particles. You will have different reactivities and obviously, the shape of the particle would then become very critical. Now, suppose you have very large size particles and then you have small size particles of the same material.

For example, this is also barium titanate, this is also barium titanate, but the size of the particles which are there that constitutes the overall material are very different. Will the properties be same? Will you have the same surface to volume ratio? no you will have very different values and therefore, their performances would be very different. Hence, you must know what is the size, the shape of the particle and that information also will come out while you perform the scanning electron microscopy measurement. So, this is a typical SEM schematic. So, you have the electron gun, the condenser gun, you have the objective lens, then you have the scan coils, you have the funnel aperture through which the electron beam comes and hits the specimen, then you have the detector which is connected to an amplifier if required and that amplifier amplifies the signal which is received by the detector.

You can then have the cathodic tubes or the signal analyzers. As I mentioned you have two detectors, you have the backscattered electron detectors and then you have the detector for secondary electrons. You see that there is a mesh on top of these Eberhard Thornley detectors. This mesh structure actually allows you to pass the electrons which are moving

towards this detector which is positively biased. So, that when the secondary electron comes out of the sample, they find a positive bias and then they move towards this mesh and when you suppose you have a solid structure and you have a instead of mesh you have the solid structure.

what will happen? Then you will see the electrons which are coming through will not be able to go and hit the scintillator material and then you will never be able to analyze these. So, you must have a mesh like structure which allows the electrons to pass through and then hit the material which is being used in the detector. So, you can have the secondary electron detectors, you can have backscattered electron detectors or you can have the EDS analyzer which is used for energy dispersive spectrometer analysis. They have very high resolutions for typical SEM you have the probe size which can go up to 1 to 3 nanometers and there you have to have very high energy electron beams coming out and impinging the sample. So, you have to have very high voltages which are there.

If you look into the SEM, you will find that the surface of this sample is actually scanned and you can have either a b scan that means, horizontal or you can have a cross-b scan. Now, if you have the two-dimensionally scanned specimen surface, you will find that the image which will come on the screen of the display unit will be magnified. When the size of this monitor screen is let us say 10 centimeter and the scan width of the electron probe is 1 millimeter, the magnification would then become 100 times. So, you can find out that you have the specimen which is being scanned from different regions and magnification is then given by d by small d. So, what are you having if the electron probe is 1 millimeter.

So, you are scanning the 1 millimeter region and this overall region which you have defined in which the image will come out is let us say 10 centimeter, then the magnification is what is 100 times. So, if you go to let us say instead of 1 millimeter you go to 1 micrometer. then it will become what another improvement by another 1000 times. So, you will have a magnification which is around 10,000 times. You go even less you go to nanometers then it will improve by another 1000 times.

So, therefore, if you have a larger screen and a very small scan width then the magnifications go on improving. These are the typical examples of SEM pictures which we had seen in some of the slides during the lectures. For example, these are particles which are having a bowl like shape and they are carbon particles. So, generally you believe that carbon particles would be spherical. and solid, but here you see no they are not solid, but they have a bowl like structure and a clear cavity in the middle you can see that this region is much darker than the region where there are particles and the size of these particles are quite small.

Then you can have capped carbons. very different they are also carbons exactly made by using the same raw materials, but for different time they have been treated. You see that

there is a cap on top of the carbon particles. So, they are called as capped carbon. Now, if you go from carbon to any other structures we have talked about V_2O_5 some metal oxides. You see they are like sheet like particles they are nano sheets you are already in the nanometer scale.

So, these widths of these sheets are already let us say around 100 nanometers or so on. Then you can see you have hollow spherical particles or you have nano rod type particles and you can also have porous particles. Clearly by naked eye or by optical microscope you will not be able to differentiate between these particles as most of them would be of same color. and you will not be able to say that there will be a difference between these particles and their properties. But once you take a high resolution picture you can clearly say that these particles are very different and therefore, their performance would also be very different and that is where the whole trick lies that you must understand the shape, the size and the topography of the particles so that you can predict its behavior.

Let us now spend some time in understanding the transmission electron microscope. In comparison to SEM as the name suggest here you will be analyzing the transmitted electrons. So, if you have a sample and the beam is coming from the top and you have to analyze the sample which are transmitted. What will you require? If you have very thick sample the electron beam will not be able to go through it and you will not get any signal. Therefore, you need to have thin specimen with which these electrons will interact.

After you collect the transmitted electrons, you will again get certain set of information. Let us see what information can we get. So, now, we are going to talk about the transmitted electrons. The schematic of TEM is slightly more detailed and the whole design is more complicated. but the principle remains the same that you will have the focusing lenses, you will have the specimen and because you are looking into the transmitted beam again you will use a series of lenses by which you can have the image which is formed on the phosphor plate or the photographic plate. So, this is what the whole design is looking at. You have two modes of operation for TEM that is bright field image and a dark field image. In bright field image which is most commonly used you will find that some the area of the sample certain area of the sample are going to absorb or scatter electrons and appear darker. While other areas that transmit the electrons will be brighter. So, you will have certain regions which would scatter the beam and you will not have any signal after the sample and therefore, you will see that region as the dark image.

In the bright field image, the unscattered transmitted electron beam is selected with the aperture. So, you unscattered beam while the scattered electrons are blocked. Since the unscattered beam is selected what will happen? The areas with crystalline or high mass materials will appear darker. If you see the bright field and then move to dark field imaging what you are doing? Here you are going to now analyze the scattered electrons and then

analyze it. The areas where there are no electrons scattering will be black while the areas where the material is scattering will appear bright.

So, here you are allowing the scattered electrons to go through. This technique can be used to enhance the contrast when the bright field image is not clear enough. it is commonly used to study the crystal lattice, the crystal defects, the stacking faults, the dislocation and the size of the particle or the grains. So, if you look into let us say the bright field or the dark field images using TEM, you can clearly see that you can improve the contrast significantly by using the dark field mode of the same sample area. So, keeping the sample area same you can change the modes and you will find that the contrast is much higher in the case of dark field modes. So, TEM is used to have high magnification images of the internal structure of a sample.

You can find information about the crystal structure of the materials and you can even get information about the lattice defects. The surface features shape size and structure can be easily investigated. Typical SEM or field emission SEM that is FE SEMs you can go and get information to about 20 nanometers or so. But when you use TEM you can go up to few nanometers let us say up to 2 or 3 nanometers and investigate the properties of the materials easily. You can have the energy dispersive spectroscopy and that will give you information about the elemental composition of the materials.

So, if you compare the SEM and TEM images you can see these are the SEM images here you were just thinking that the particles are agglomerating, but when you take a high resolution, you will see that they are quite separate out. from here the SEM images of the Fe_2O_3 sample looks as if they are solid and just having porosity, but when you look under TEM you will find they are like hollow spheres, but here you do not see any cavities. that when you go to very high resolutions and low dimensions you will find that the structures are hollow. You can see the places where the particles are found are darker than the inner area where you see the brightness is quite different. Similarly, you can have the copper oxide particles and you can find out the nature of cavities in these systems.

And you can see from the scale you are talking about very low dimensions, you are talking about 200 nanometers, 100 nanometers or so or even 50 nanometers. If you compare the two techniques mostly SEM you are talking about scattered electrons back scattered or secondary electrons, TEM you are talking mostly about transmitted electrons. For SEM you can have slightly bigger samples or thicker samples whereas, for TEM you have to have thin samples which have to be supported on a TEM grid. you can get the pictures on TV monitor in a SEM and in TEM generally a fluorescent scheme is required. If you go on to go to very high resolutions and want to investigate the internal structure of the samples you will have to utilize TEM.

And, if you talk in terms of resolutions let us say 1 nanometer to slightly less than that is the real resolution limit of SEM whereas, the resolution limit for TEM is 1 angstrom or slightly less than that. You can have around 2 million times magnification in SEM whereas, in TEM you can go up to 50 million time magnification. You can have high resolution TEM which can give you even more information and you can talk at the level of atomic arrangements in the samples. So, clearly SEM and TEM are two most commonly techniques in today's research activities and industries which are focusing on materials and devices which are quite small as they give information about the shape, the size, the defects, the nanoscale features of these materials and devices. To get more information about these techniques you can go through these books which have explained these topics quite in detail.

So, I thank you for attending the third lecture of this week. With this we complete the discussion on characterization tools and in the final lecture of this course I will give you a summary of the whole course which was covered and then you will find out that whatever we have been discussing is a logical way forward from one to the other. Thank you very much.