Physics of Renewable Energy Systems
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Lecture – 48
SEM, TEM and XPS

Welcome to the final lecture of this course. In this week and the previous week, we have discussed quite a few characterization tools that are used to characterize nanomaterials, or devices that have been discussed in this course.

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And in today's lecture, I will talk to you about scanning electron microscope, transmission electron microscope, and XPS techniques, which are extensively used to characterize nanomaterials. Today, we will see what do we understand by the concept of microscopy. What is the difference between an optical microscope and an electron microscope?

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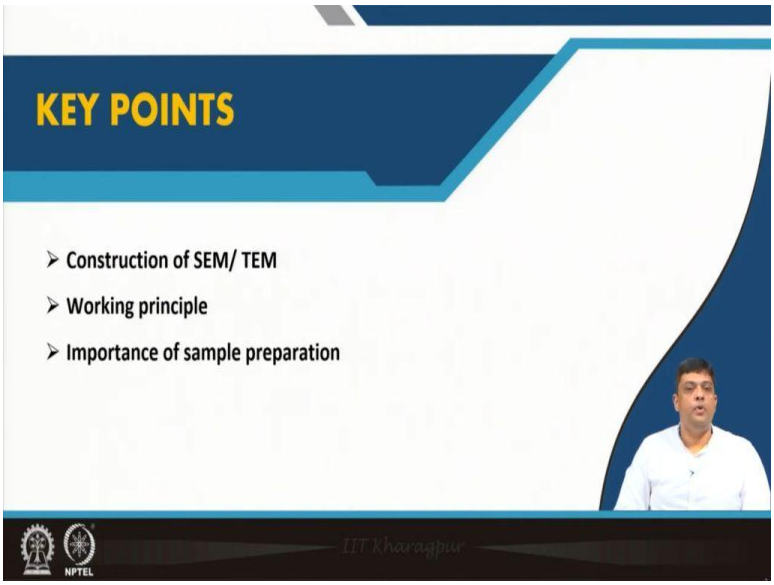

Very briefly, we will discuss the construction of this high-end electron microscope; be it be scanning electron microscope or transmission electron microscope. TEM means Transmission Electron Microscope, SEM means Scanning Electron Microscope. After you have understood the construction of these two kinds of microscopes you will also be able to understand the working principle of SEM and TEM. And you will very clearly understand that sample preparation is a critical step to obtain the proper results using SEM or TM studies.

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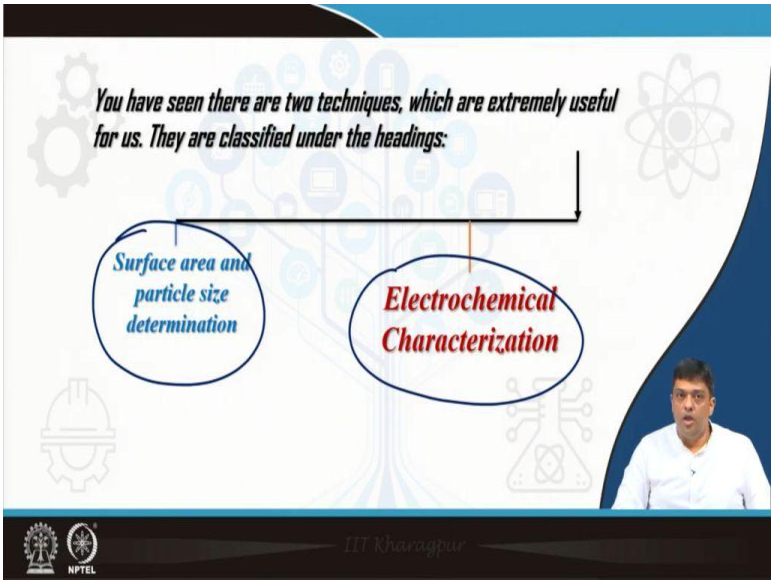

So, till now we have seen what we have seen, surface area and particle size determination techniques. We have talked about electrochemical and techniques, such as CB and CD and EIS techniques to investigate the electrochemical properties of devices.

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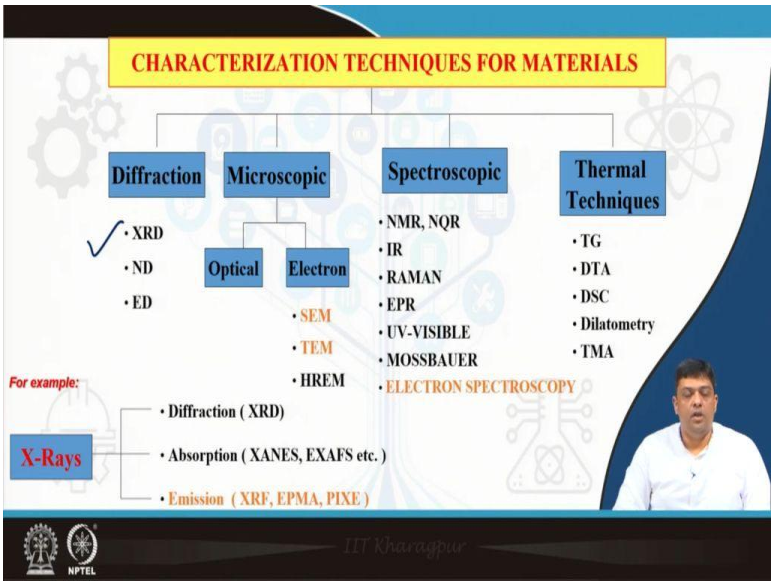

In the previous week, we saw techniques like XRD. We had also discussed with you the techniques such as Raman, IR and UV visible.

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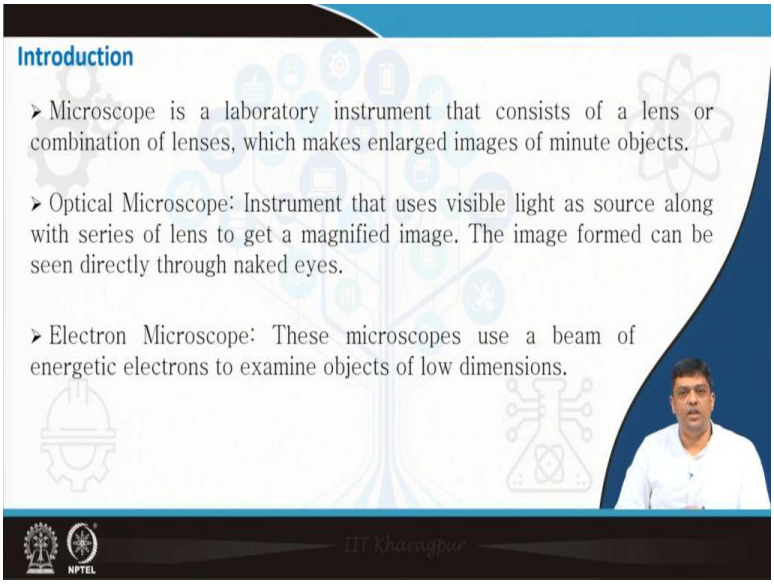

Today, let us take a technique which is in the classification of optical microscopy or microscopy. What is a microscope? As you have studied from school days, a microscope is a laboratory instrument, which is made using a combination of lens or lenses. And the whole idea of making a microscope is to get an enlarged image of an object; so, you want to have an enlarged image.

What is optical microscope? Optical microscope, you are primarily using a visible light as the source; then what would be the electron microscope. Obviously, these kinds of microscopes would be using electrons as the incident beam to investigate the objects.

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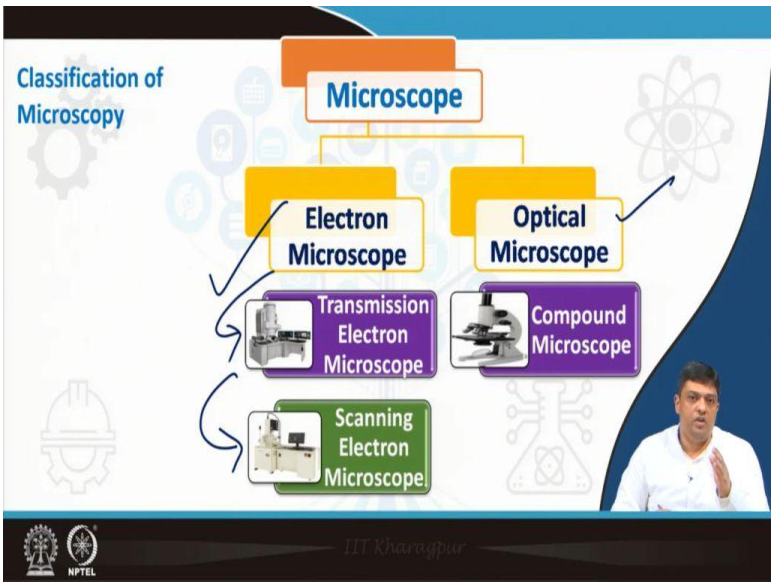

So, classification of microscope can be made. You can have optical microscopes, or you can have electron microscopes. Under electron microscopes, you can have transmission electron microscope or scanning electron microscopes. Scanning electron microscope, sometimes you also here FESEM that is field emission scanning electron microscope, is just the target of FESEM is changed; the target from where the electron beam is actually coming out. So, that is the major difference between SEM and FESEM.

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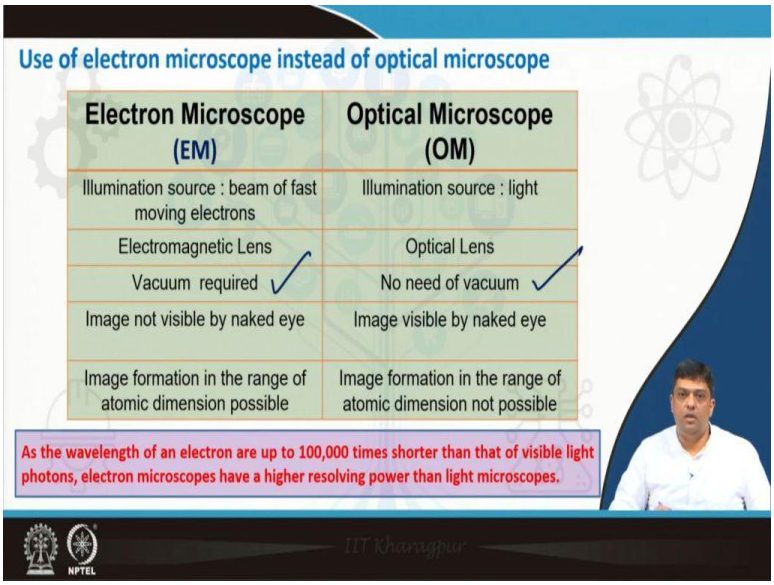

If you compare the two microscopes, then in electron microscope, you are using electrons as the fast-moving beam; whereas in optical microscope you use light as the illumination source. You can focus electrons using electromagnetic lenses; but for optical microscopes, you are using optical lenses. In the case when you have optical microscopes, you do not need vacuum.

But, because you are having charged particles moving through then if you allow them to get scattered in the way; then you will lose the intensity, or you will have scattered scattering, which will change the characteristics of the incident beam. So, you need to have vacuum in the chamber, and then only you can switch on the generation unit, from where you are going to get the electron beam.

Electron Microscope can give you images, which are not visible to the naked eye; and optical microscope can actually enlarge the image, which may be visible to the naked eye. You can go up to let us say around 20 nanometers, using electron microscope SEM or FESEM. If you are using transmission electron microscope, then you can go below 20 meters to sizes, let say 2 nanometers or more. But in optical microscope, you are mostly talking in terms of micron level particles; which are then enlarged and the images can be analyzed.

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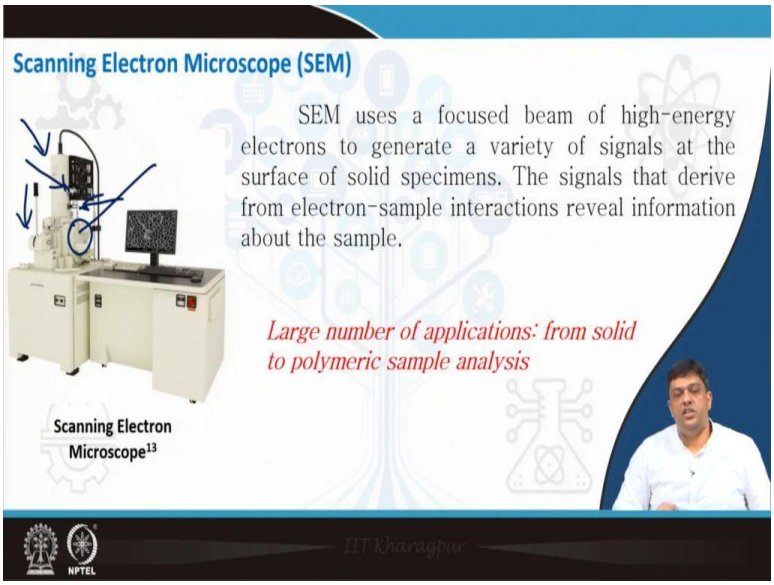

So, this is a typical scanning electron microscope, which uses the focused beam of high energy electrons; and you have the chamber, electron is generated. Then, you have these sample changers in which you will have the sample. And then you have the connections, where you will have vacuum; or you can have any kind of lens combinations which you will be using. So, you can have aperture controls, and you can have the lens combinations for focusing the signal, and various kinds of materials can be investigated using SEM.

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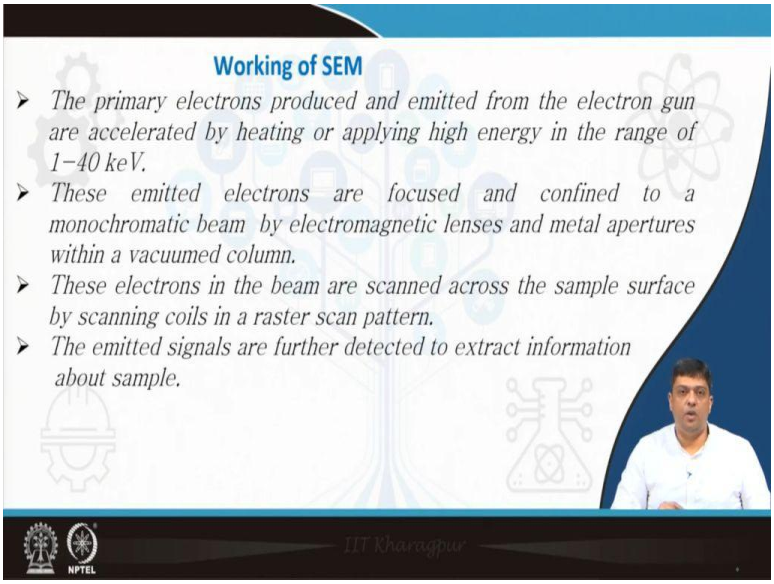

In SEM, you have the emission of electrons, either from electron gun which are accelerated, or by heating or by applying high energy in the range of 1 to 40 kilo electron volt. These emitted electrons are focused and then confined in a monochromatic beam of electromagnetic lens, and metal apertures within the vacuum column.

So, using the electromagnetic lens you can focus the beam, and then you choose the monochromatic beam; so that you have the electrons with similar energy going down the stream and hitting the sample. Once the electron beams reach the sample, they are scanned in a raster scan pattern; so, you have both x-y scan, which is performed. And that leads to emission of signals. You can have backscattered signal, or emission of secondary electrons. Both are analyzed, and they give you different kinds of information about the sample.

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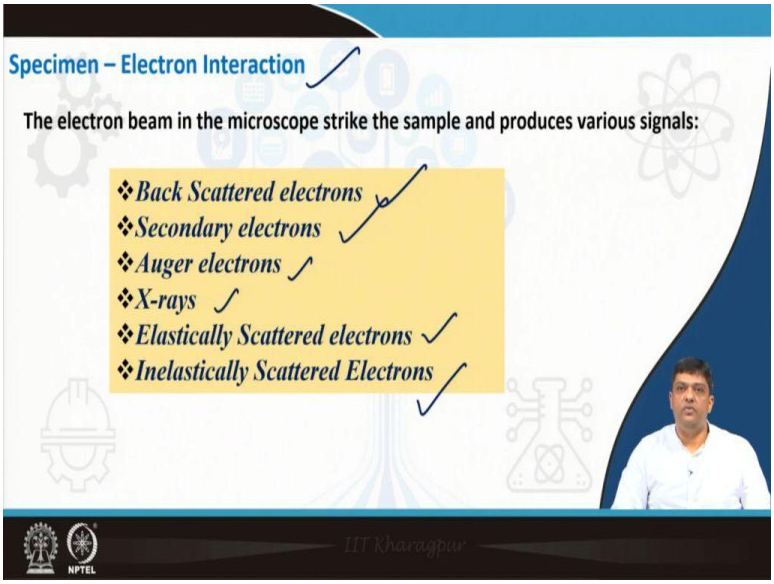

So, you can have back scattered electrons or secondary electrons, which are the two most used outputs of the specimen electron interaction. But there are other signals which can be obtained and analyze, you can get the auger electrons. You can get X-rays, you can get elastically scattered electrons, and inelastically scattered electrons. And then you will get auger spectroscopy or you will get excerpts on different kind of instruments are there, where you analyze these kinds of signals.

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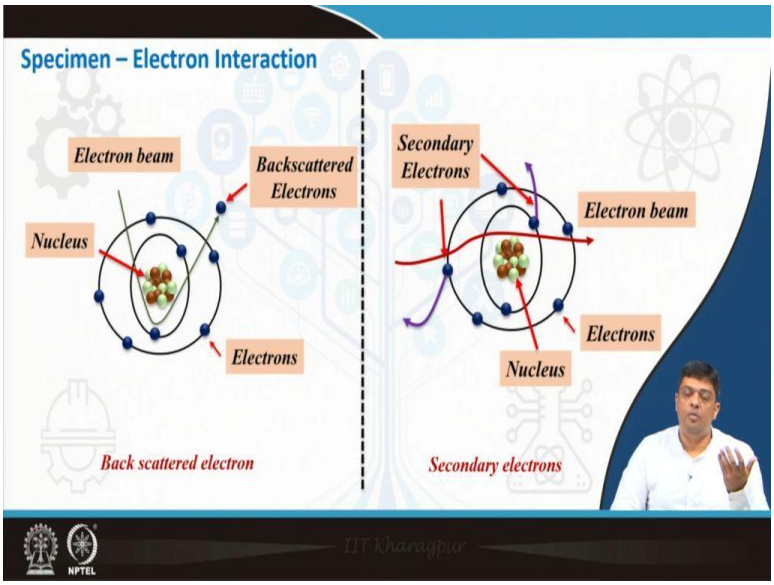

So, back scattered, the backscattered electrons have energies very similar to those of the incident beam whereas the secondary electrons are the energies which are coming out, because of the excitation or emission of the electrons from the surface of the electron, of the specimen. So, these secondary electrons give you information about the surface morphology, whereas the back scattered electrons give information about the elements which may be present in the sample.

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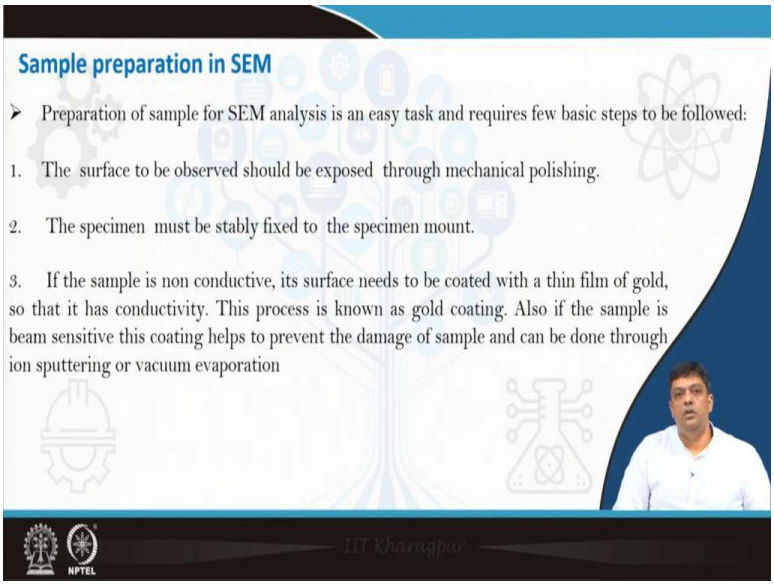

The sample preparation step in SEM is very critical; you must ensure that the samples are properly deposited on the sample grid. Otherwise, during vacuum they can be sucked inside the vacuum chamber, and you can get the column getting damaged or you will lose the sample. So, if you have solid sample then if you want to get the information about the surface, then you must remove the contaminations which may be available on the surface.

Then, you must polish the samples properly before you scan in the SEM, and they must be fixed properly on the specimen mount. If the sample is non-conducting, then you need to code these samples with thin film of gold or any kind of conducting material; so that you do not develop any charge on the insulating samples, and they can diffuse and go to the earth. So, that is critical. You can scan both powdered samples, or you can scan pellet or any other kind of samples.

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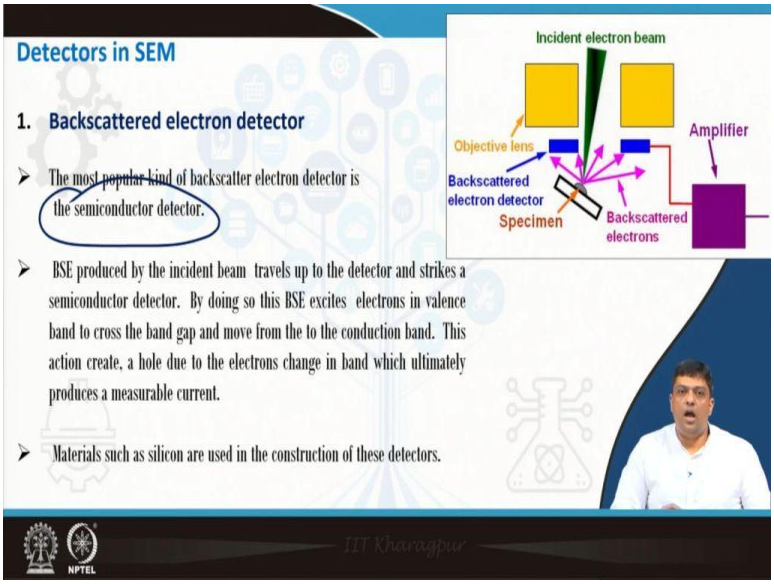

As we said, we in the back scattered mode you are understanding the elements above of the sample. So, you have various kinds of detectors, which are used in the back scattered electron mode; you have the detector, which is mostly a semiconductor-based detector. And in this, what happens when the electrons are received, then the electrons excite the valence electrons to the conduction electron.

And this creates a hole in the balance band, and you can measure the kind of energy generated or obtained from the incident electron on these detectors. And from there you can back calculate,

what was the energy coming out from the sample, or the element. And materials such as silicon are used for the construction of these semiconductor-based detectors.

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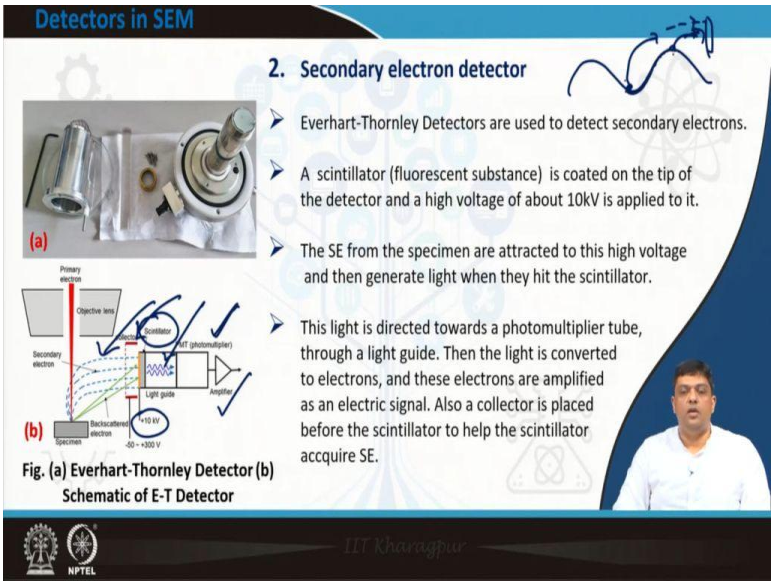

For(semi) secondary electrons you have a slightly different detector that is the Everhart-Thornley detector. This is a very simple design; the concepts are very similar. So, you have emission of low energy electrons, so then you have the potential which is able to attract these electrons which are emitted. Then you use a mesh, so you see that there is a mesh in the front of this detector. This mesh allows the secondary electrons to go through the opening.

Once the electrons are hitting the scintillator detector, then they lead to the emission of signals will be photon or a light signal. That is then passed through a photomultiplier tube, you get an amplified signal; and by back calculating, you can find what was the energy. As well as you can see by the variation of the energy profile, you will find out what was the shape of the sample. So, if you have shape like this, then electrons are reaching the detector.

So, they will have different energy, then this will have a different energy; and you can then back calculate by finding out what is the energy, and you can trace out the surface structure.

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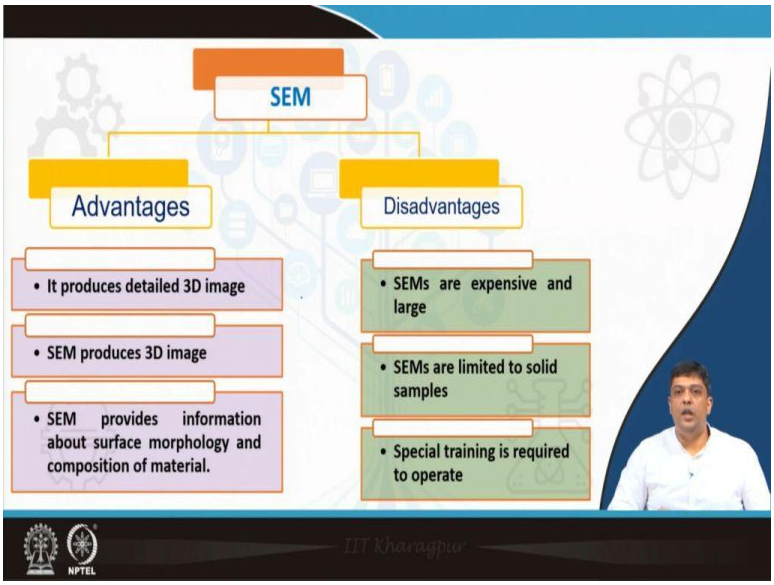

There are advantages and disadvantages associated with SEM; SEM will give you 3D images. They will give you information about surface morphology, and the composition of the sample; but the major disadvantage it is expensive, requires a lot of space. And you need specialized trained men manpower to operate these instruments, and mostly SEMs are limited to the use of solid samples.

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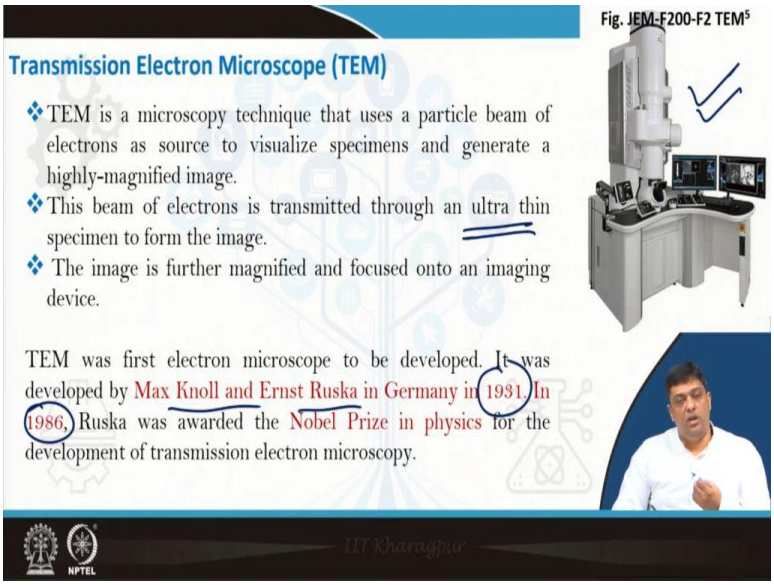

In addition, SEMs are able to give you, reasonable micrographs in the range of 40 nanometers or above. If you want to go to dimensions less than that, then you use FESEM's, which can give you reasonably acceptable quality micrographs in the range of 20 nanometers, plus/minus. But, if you want to go below that, then you need to go to transmission electron microscope. And this is a typical instrument of a transmission electron microscope.

As the name suggests, you are going to analyze the data, where you are seeing the transmitted beam; so, electron beam interacting with the sample, and then you analyze the transmitted P. If you have to have transmitted beam, what will you require? You need 10 samples; so that the beam can actually cross through, and interact with the sample and also cross.

TEM was developed in 1931 by Knoll and Ruska, and the Nobel Prize in physics was given to Ruska in 1986 for the development of TEM; because this technique has led to extensive improvement in the knowledge we have about nanomaterials.

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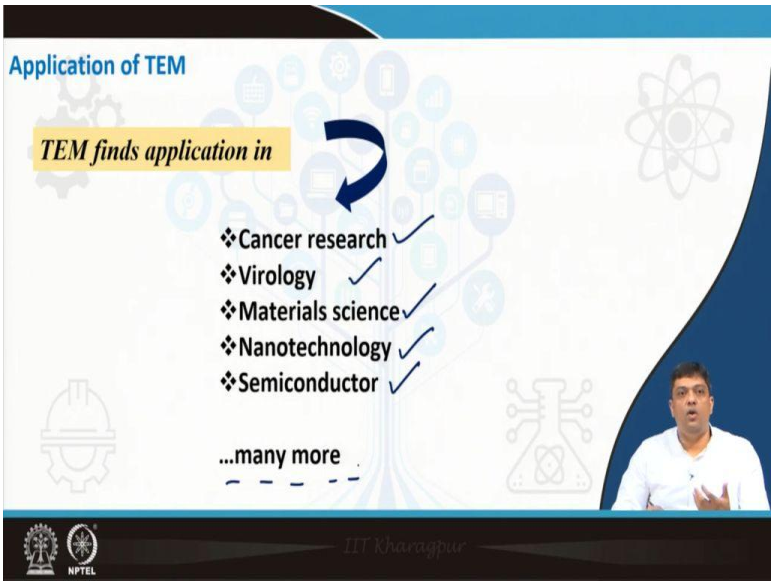

It is used in cancer research, medical material science, nanotechnology, semiconductors and many many more. So, you can just go on adding the applications of TEM.

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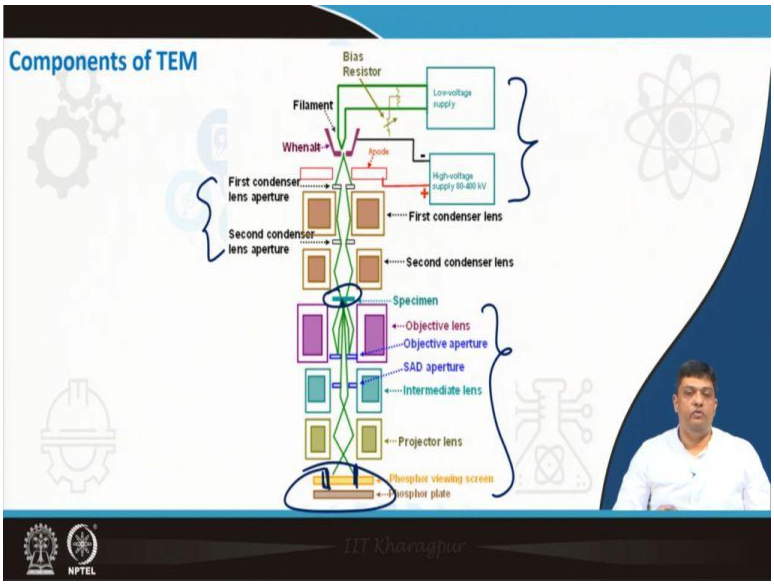

This is a typical TEM which is explained in schematic. So, what do you have? You have the generation of electron, you have the generation unit, then you have the focusing unit. You use the sample in the middle, and then you use the combination of various lenses to actually get the picture at the bottom. And you can see, you have started with a small region, but the image which you get is much more enlarged.

So, you can get enlarged image of the sample by using proper lens combination, which focuses the transmitted beam in a way that by the time they reach the screen. You have the enlarged image of the sample area, which was scanned by the electron beam.

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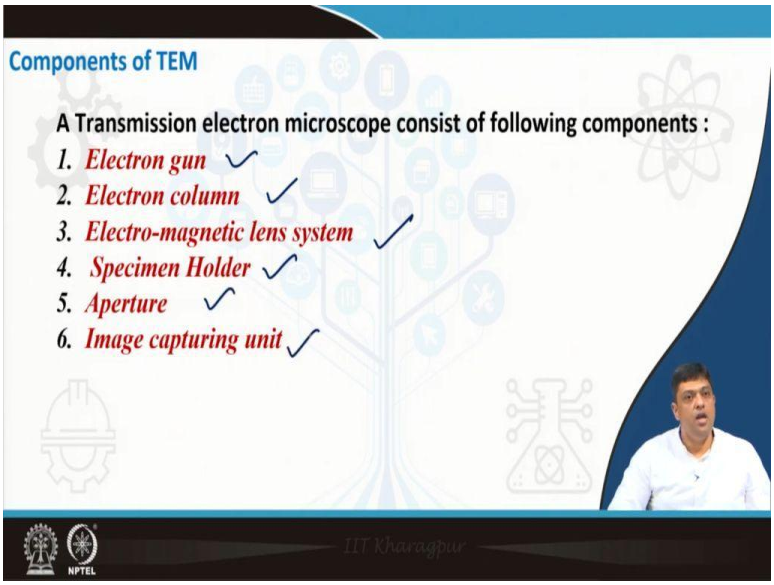

So, the transmission electron microscope has electron gun electron column, the combination of electromagnetic lenses, the specimen holder, the apertures and image capturing unit.

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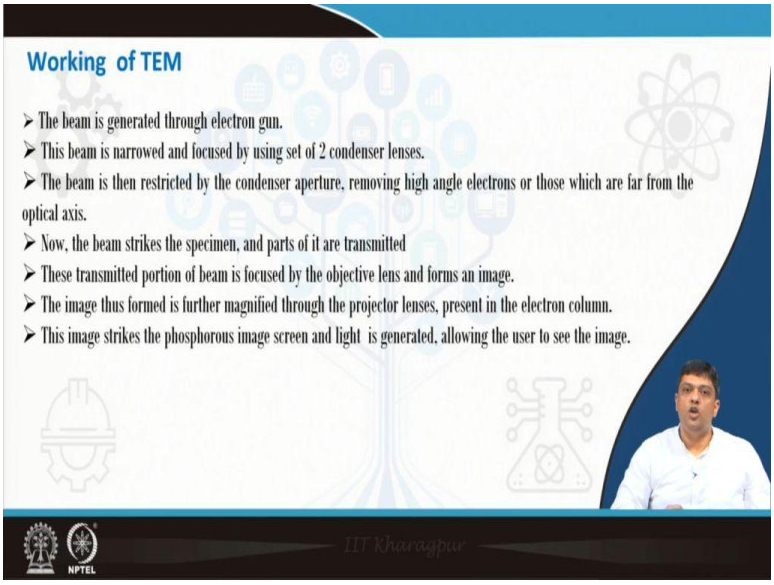

Very similar to what we had seen in SEM, you have the generation then the focusing. But, here the major difference is that once the sample is finding the electrons falling on them, the sample must allow the beam to go through. Or, you will must have signal in the transmitted region, and that signal is mostly analyzed to get the image.

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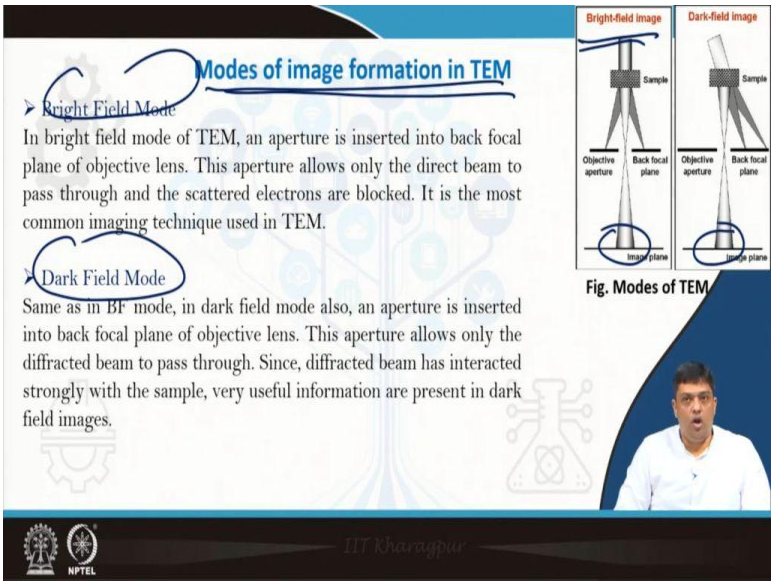

You can have various modes of operation of TEM, the bright field or the dark field; so, it depends on what type of beam you are using. So, whether you are using the direct beam to pass through and scattered electrons are blocked, or they are not blocked. So, depending upon what type of field or image you are constructing, you will have the two modes, and right field image mode is mostly used. And you at this moment, that is good enough for you to understand.

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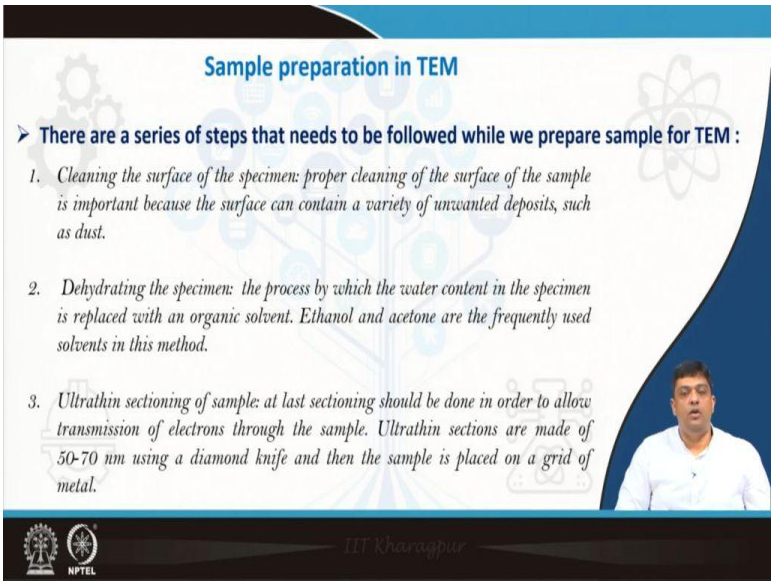

For making TEM samples, you must again clean the surface, you must have thin samples. You must not have samples which contain water, which can get evaporated in the column. If you have very large samples, then you must make it into three sections; and then that is done using the technique of (microtome). That is cutting of thin slices from a sample using diamond cutters, and that is called as (microtome); and this involves a trained manpower, because this is a non-trivial exercise.

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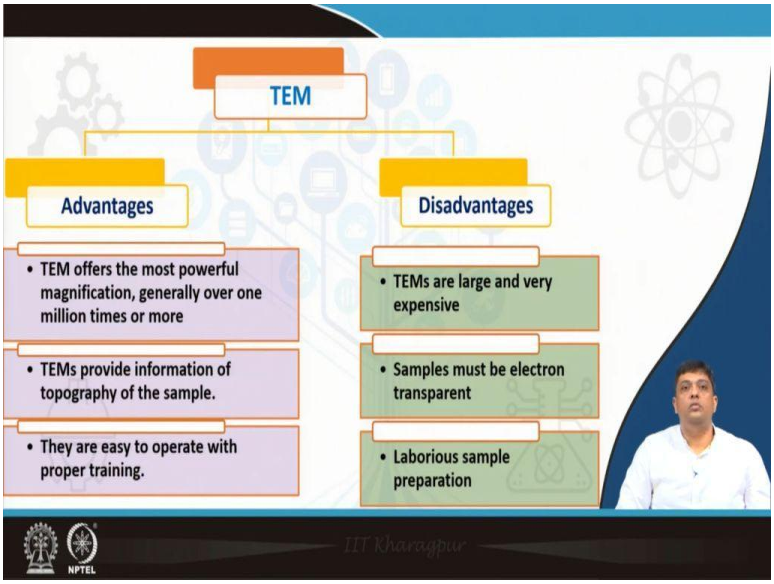

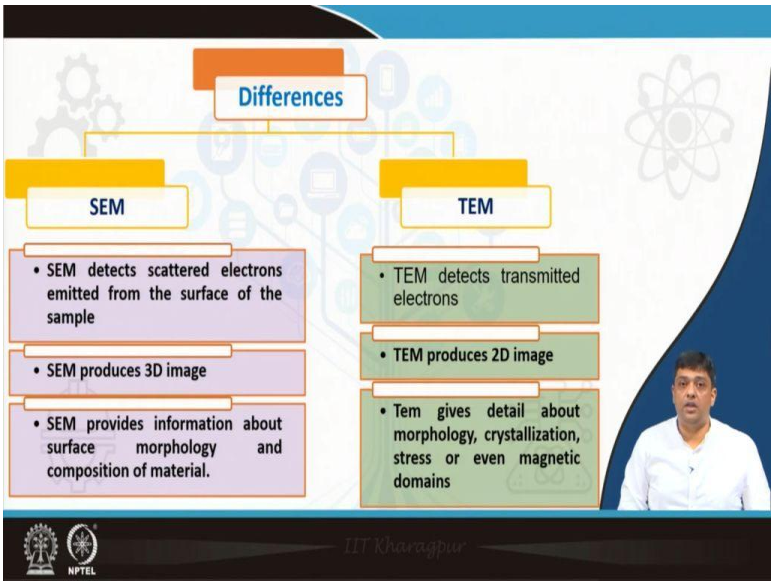

Again, TEM have certain advantages and disadvantages. It is a powerful technique gives you high resolution pictures; you can go to very low dimensions and see the morphologies, as well as the crystal lattices, but again expensive. The samples which have to be used must be electron transparent, and it is not easy to make sample, which are used in TEM.

The difference between SEM and TEM would be scanning electron; you are actually seeing and analyzing these scattered electrons, where in TEM you are analyzing the transmitted beam. In SEM, you are getting a 3-dimensional image; in TEM you are getting a 2-dimensional image. SEM will provide information about the morphology and the composition; whereas TEM gives details about morphology, crystallization, stress, or even magnetic domains.

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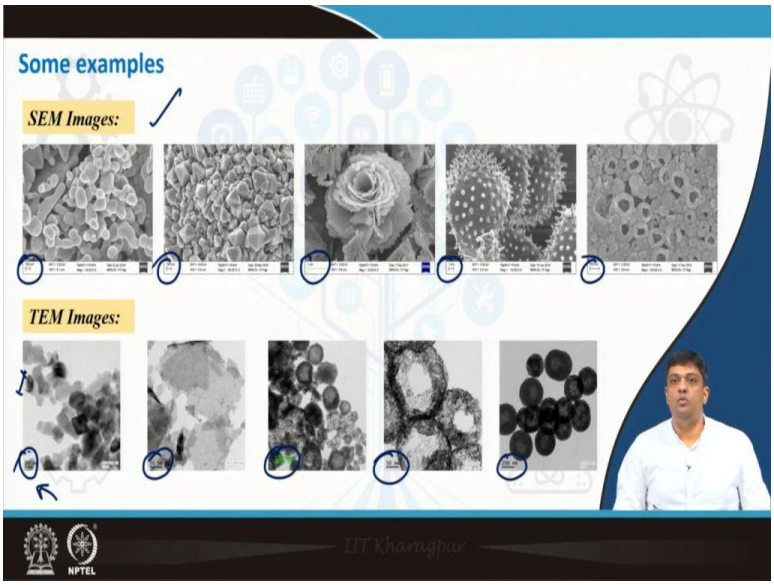

So, if you compare the two micrographs, you have SEM pictures on the top; you can see that the scales which are given are 200 nanometers, wine micrometers or so. But, the scales which you are seeing at the bottom are 20 nanometers, 50 nanometers, 100 nanometers are much smaller. So, you can go to very small size particle and analyze them; whereas in SEM, you cannot reach such levels. And so, if you have very small size particles, then they have to be analyzed using SEM. But if you want surface morphology determination, then SEM is mostly used.

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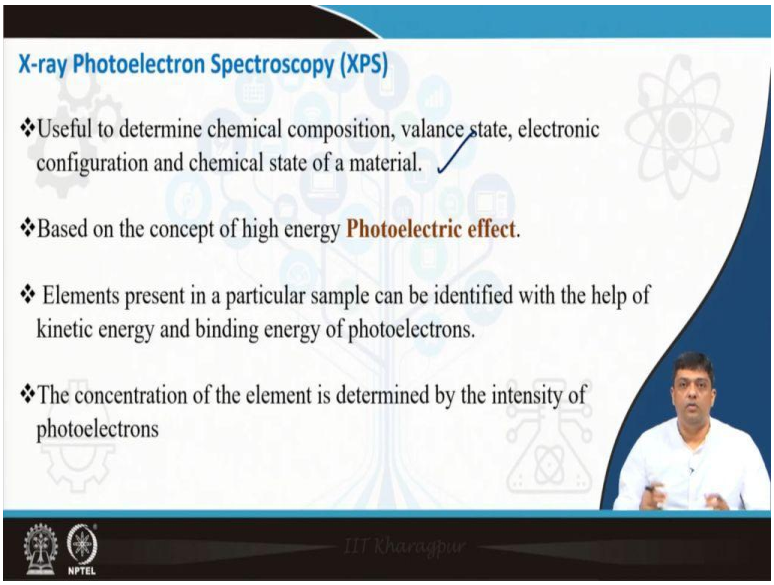

The final technique, which we have been using to understand the properties of nanomaterials, and I have mentioned earlier is XPS. This technique is basically high energy photoelectric effect-based technique. You can determine the elements which are present in the sample, you can find the chemical composition, you can find the valance state, you can find the electronic configurations, and you can also find the nature of interaction between the elements.

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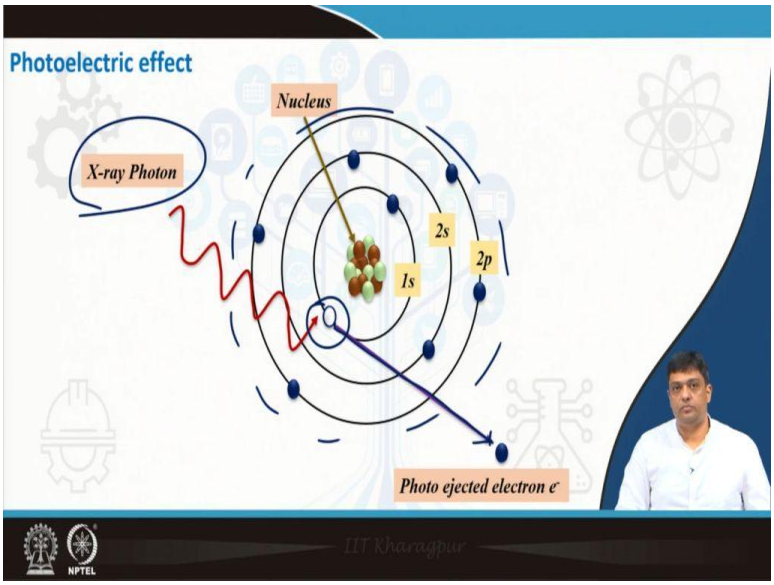

So, what do you have? You have the photoelectric effect. What happens, you have the X-ray photon incident on the sample; you have the nucleus surrounded by electrons. And because it is high energy X-ray photon, that is able to knock off the electron from the inner most shells or inner shells; so, you get information about the elements.

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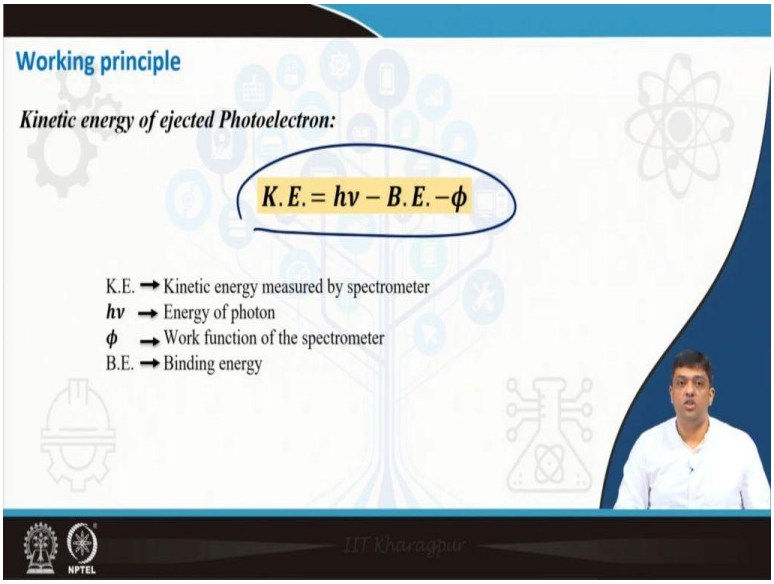

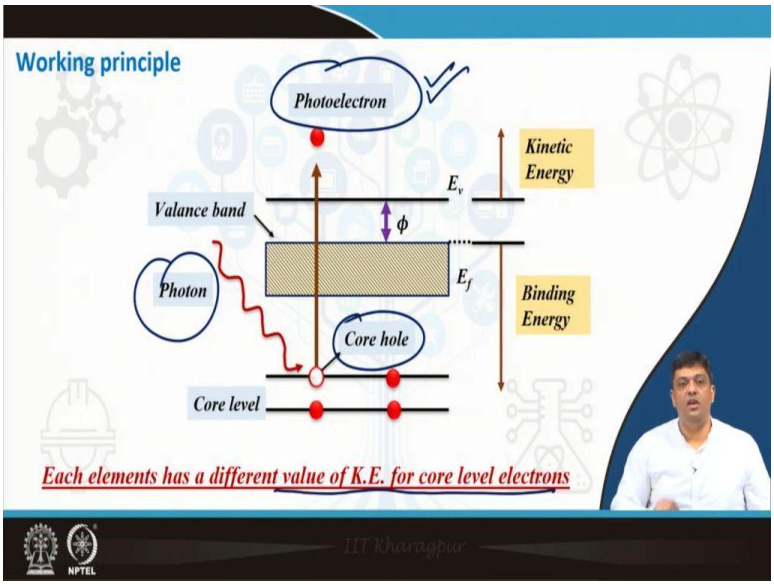

Working principle; again, just like photo electron or the photoelectric effect; you have the energy, which is given by hν minus the binding energy minus the work function of the spectrometer. If

you want to see in terms of energy levels, what you see; you have the photon which is incident is able to knock out photoelectrons.

And by the energy, you have of these photoelectrons, you can estimate what type of element you are analyzing, or what type of elements are present in the sample. Because each element has a different value of kinetic energy for the core level electrons and this is well known.

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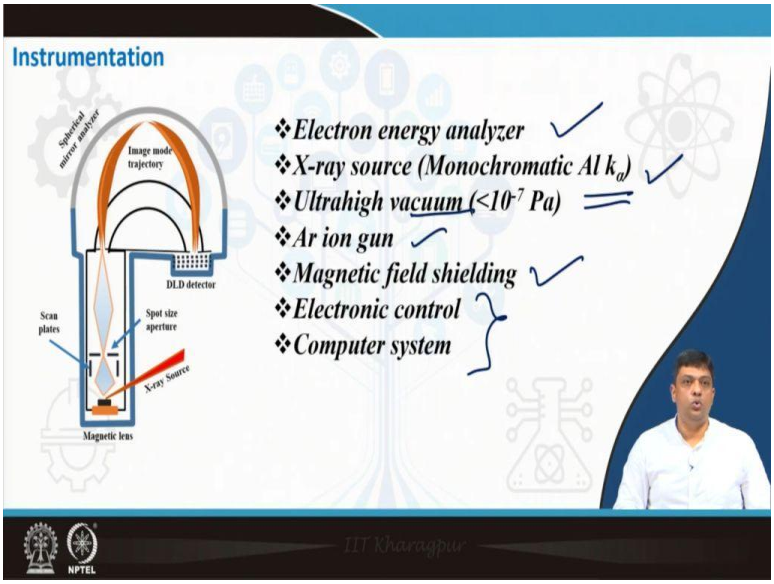

A typical XPS instrument has the electron energy analyzer. The source, mostly aluminum k alpha is used. Why aluminum source? Because it is a monochromatic source; so, you have one wavelength hitting the sample, then you need to have ultrahigh vacuum. You have the Argon iron gun, you have the shillings, and then the control units; this is what you do and you get. It is a very simple technique, but then you can find out the details about the sample.

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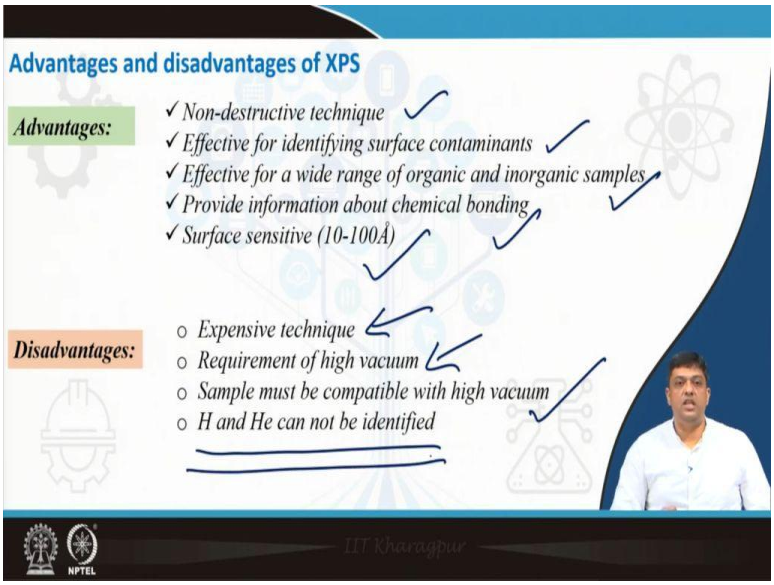

It is a non-destructive technique. It can be used to actually identify contaminants on the surface of a sample; large number of organic as well as inorganic samples can be investigated. It can give you information about the chemical bonding; and it is able to give you information about the surface. Again, with the techniques like XPS or the ones which we have discussed earlier today that is SEM and TEM. One factor gets associated, and that is they are quite expensive.

You need high vacuum, sample must be stable under high vacuum conditions; and elements like hydrogen and helium cannot be identified.

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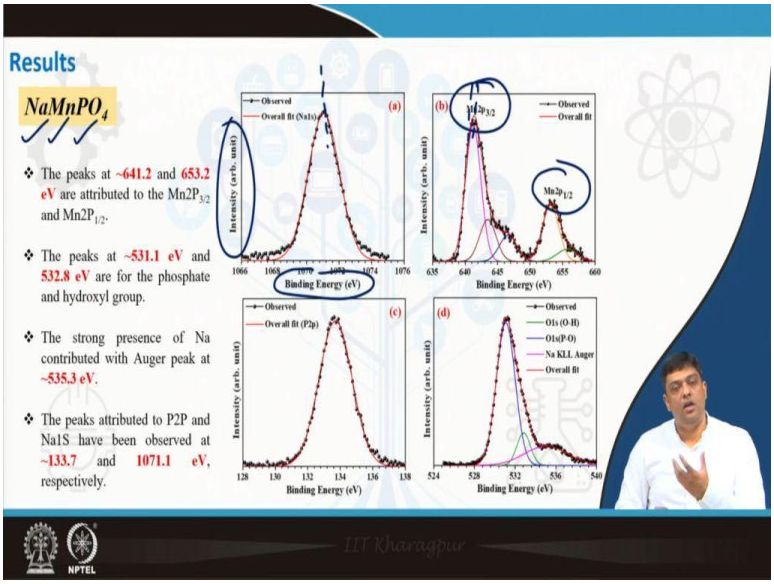

So, this is what a typical XPS micrograph looks like. So, I plot the intensity as a function of binding energy; so, this is basically the binding energy which is going to play the important role. For each element I know where the binding energy will lie. And then I can back calculate the element, which will be giving that binding energy.

So, for example, in this sample where you have sodium manganese and phosphates, then you will find; you can have emissions because of oxygen, emission because of the manganese, you because of sodium. So, you can have various kinds of peaks, and from there you can find out the energy levels which are giving the output.

And then you can find out the nature of sample or you can find the chemical composition of the sample, if you are able to analyze the sample carefully, over the whole spectral range.

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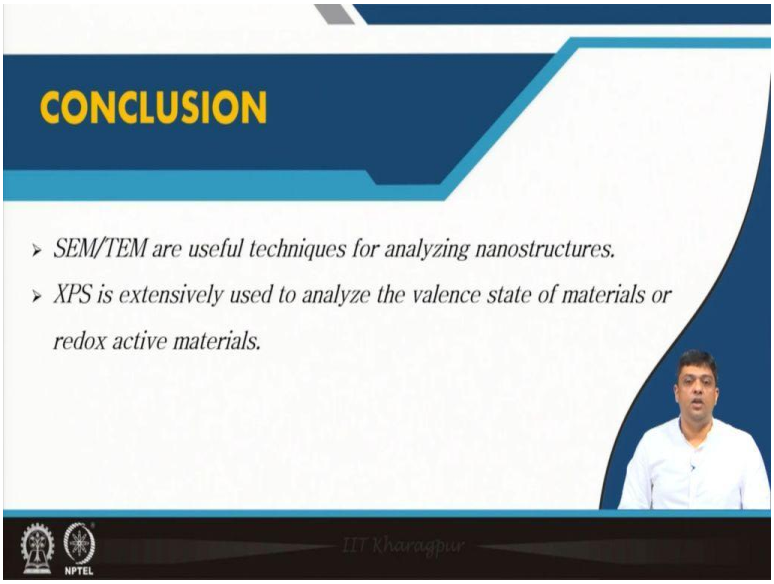

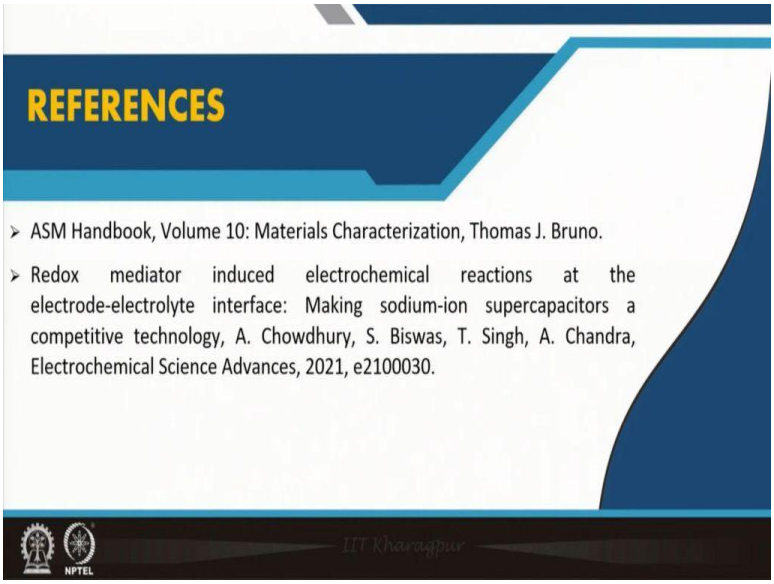

So, I hope it is clear to you, as to why we use SEM and TEM in the field of nanomaterials and nanotechnology, because we need to see the morphology of the particles at low dimensions. XPS is another technique which is routinely used to analyze different types of materials. XPS is not necessarily used for nanomaterials; it can be used for bulk size materials also.

But the materials which we have discussed in this course, XPS is also extensively used to determine their state; so that you can predict their redox activity or stability to various conditions, or the possibility of presence of vacancies, or any other contaminants. These are the references from where you can read and get more information about SEM, TEM and XPS.

And I thank you for attending the course on physics of renewable energy systems, and I hope you enjoyed the course. Thank you very much.