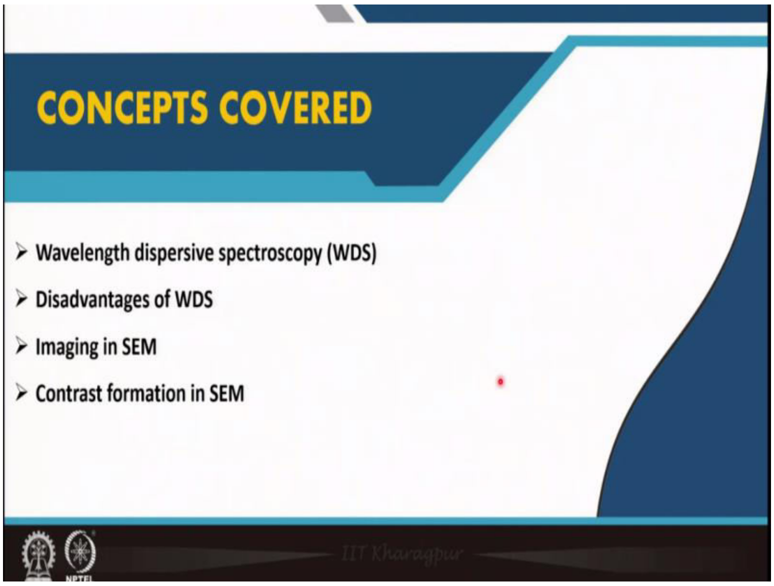
Techniques of Material Characterization
Prof. Shibayan Roy
Department of Materials Science Center
Indian Institute of Technology – Kharagpur

Lecture – 37
Analytical (WDS) Detector and Contrast Formation in SEM

Welcome everyone to this NPTEL online certification course on techniques of materials characterization. We are in 8th week we are continuing with scanning electron microscopy and this is going to be the second lecture. In the first lecture, we discussed about the energy dispersive spectroscopy which is meant for chemical analysis of specimen, elemental concentration determination.

So, we will continue with that. We have one more detector to finish for analytical or chemical analysis of specimen and we will also try to discuss and start with SEM imaging part and the first topic we will discuss is contrast formation.

(Refer Slide Time: 01:10)

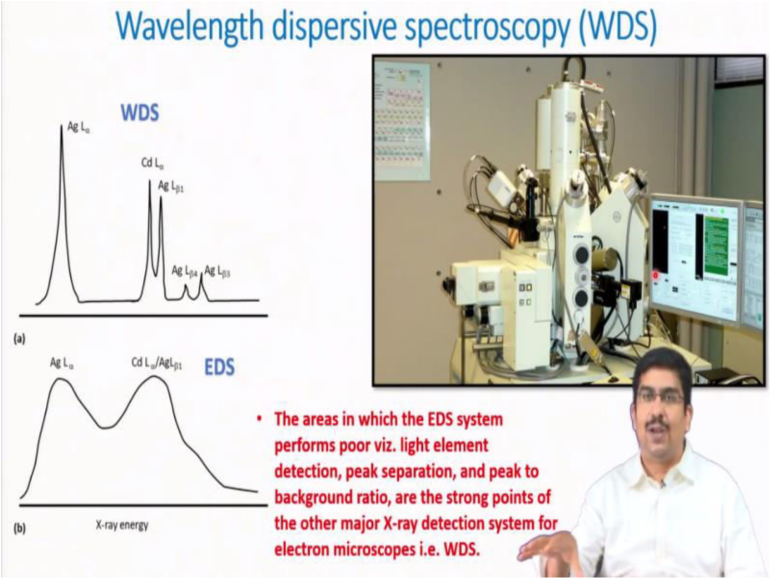


CONCEPTS COVERED

- Wavelength dispersive spectroscopy (WDS)
- Disadvantages of WDS
- Imaging in SEM
- Contrast formation in SEM

So, here are the topics for today and first as I said we will be discussing about WDS, wavelength dispersive spectroscopy detector and then we will see some disadvantages of WDS and some application of WDS of course advantages and disadvantages it should be. And then we will see about imaging in SEM in general and about contrast formation how the contrast appears in an SEM image.

(Refer Slide Time: 01:38)



Wavelength dispersive spectroscopy (WDS)

- The areas in which the EDS system performs poor viz. light element detection, peak separation, and peak to background ratio, are the strong points of the other major X-ray detection system for electron microscopes i.e. WDS.

So, the first thing is again WDS wavelength dispersive spectroscopy and as we discussed in the last class and before that the chemical analysis in scanning electron microscopic can be brought in two different ways either for qualitative. We can either measure the energy of the incoming x-ray. So, it is all about measuring the characteristic x-ray which is generated as a secondary effect from an inner shell excitation when an electron beam hits a specimen.

And inelastic scattering happens in the form of secondary signal generation and we have seen how the characteristic x-rays are related to the atomic structure of a material so that their wavelength or the energy of those characteristics x-rays are very much well defined. So, in EDS detector we have seen that how that energy of the electrons or energy of this characteristics x-ray signal which is coming from the specimen how that is determined.

So, we have seen that semiconductor silicon detector is used and then the incoming x-ray photons are creating electron hole pair and this process of electron hole pair creation is also an energy so certain energy or certain very fixed amount of energy is expanded there. And then from that we can calculate basically we can calculate that how many electron hole pairs are generated from the incoming x-ray signal by measuring the current and so on.

And from there we can determine the energy of the incoming x-ray signal and we match it with a library function using an MCA multichannel analyzer and we find out that, okay fine what this x-ray signal belongs to this element. So, that is what we did in EDS, pretty much the same thing we can do with WDS detector as well, but in this case WDS measures as the name suggest wavelength.

Instead of energy of the incoming x-ray signal we measure the wavelength of x-ray signal and this offer certain advantages so far over EDS system basically the areas in which EDS system is not good, it is poor those areas are WDS has ace over the EDS detector. So, those areas let us discuss that. First one is light element detection so here we discussed about how EDS is not good because of the presence of this beryllium or polymer window the EDS detector.

And most of the incoming x-ray signals are basically absorbed from light element if we go down anywhere below sodium then the energy of the incoming x-ray signal is so low that most of them is getting absorbed by the beryllium which is very close to those light elements like Boron like nitrogen and all. So, we cannot detect such elements in using EDS. So, light element detection is definitely problem with EDS.

Of course, we have discussed about other ways like windowless detector and how the good vacuum and use of liquid nitrogen all of these things can improve the detection ability all the way up to Boron with EDS, but definitely WDS is much better because here there is no such limitation of like beryllium window or other things. There is no limitation. So, for light element detection WDS detector is far better or for superior still now compared to EDS detector which we will see.

Then peak separation and peak to background ratio, these two things are pretty much related. So, if you look at this EDS spectra and the corresponding WDS spectra for the same specimen this is taken and this is for some material which contains; it is a multiphase material, multi element materials so it contains silver at the same time it contains some cadmium.

Now, what happens is that if you take the EDS spectra then you will see that you are seeing a broad hump here and then another broad hump here. Now, this broad hump basically belongs to silver L alpha and this, another broad hump can belong to both cadmium L alpha and silver L beta 1. So, you cannot really identify these elements with great precision in this case. If you use an EDS the peaks are so broadened and the background noise is so high that it is really difficult to measure these peaks.

And this is inherently because the characteristics here the energy is measured through that electron hole pair creation and finally the current. So, this entire process has lots of uncertainty. So, it depends a lot on the ability of the detector to find out or the electron hole pair and then the silicon detector has lot of issues then there are contamination issues as well the electrons whatever you do if you use a window then there can be contamination.

If you use windowless detector even further difficulty we have discussed all of these that how you need to have a good vacuum and so on. Altogether what it does is that the noises in the signal are pretty high here and that is why the peak measurement identification of peak is very much its precision is in question always. So, peak separation if you have a multiphase material peak separation is always an issue.

And particularly when you are having something like higher wavelength. So, this like or lower energy that means in L lines, K lines are still okay which are higher energy of course detecting L lines which are lower energy is always questionable. Now, if you go to WDS you can see that the peaks are much sharper here and the background is pretty less in this in between.

So, you can very clearly identify this silver L line from cadmium L line and even for cadmium L and silver L beta 1, sliver L beta 2, beta 3 all of these you can very clearly identify which are here these all lines are overlap all of these peaks are overlap and they joined to make a broad hump. So, the peak detection efficiency of WDS detector is much better is way better than the EDS detector.

And that is related to the way this chemical nature of any element is detected in WDS we will come into that, but that is much more efficient than EDS detector. So, these two main advantages that the WDS detector has it can be used very efficiently for light element detection and it can be used for chemical identification of any element with a much better resolution much better precision than an EDS detector.

So, altogether WDS detector has become very, very popular and this is the kind of one machine is shown and this is WDS detector let me go to the pointer here. I think that was the pointer anyway. So, this laser pointer is here so this is the WDS detector. Basically this one this is the WDS detector here. And usually in one SEM there are multiple WDS detectors are used so we will come what exactly it mean.

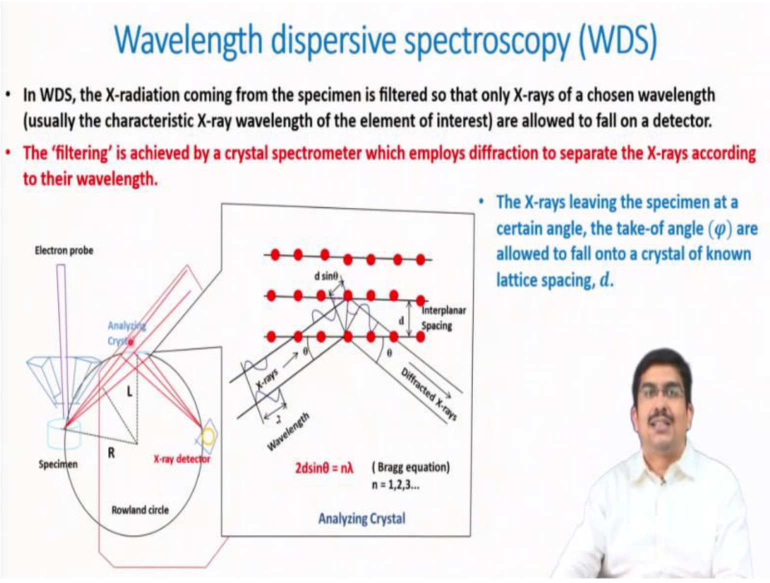
So, you have this one detector, two detectors and then what you are able to see there is possibly a third detector in the back side. So, there can be till now there can be maximum 5 detectors in WDS yet to be developed 5 different detectors yet to be developed in WDS. And all of them have a range basically the detectors have a range like certain detectors are meant for low element low atomic number element light element.

And that has a range like for example Boron to aluminum or something like that. Certain other WDS detector is meant for higher atomic number elements or transition metals and something like that. So, all 5 detectors basically collectively they cover the entire range or nearly the entire range of elements. And so depending on the; kind of specimen that you will be encountering in your daily routine.

You can either have one single WDS detector or if you think that you will always working with the light elements and you can go for one detector or max two detectors if you think that you will be encountering all possible elements in the periodic table better to have more detectors in your machine. So, these are the EDS detectors, WDS detector and most often or at least whatever machine I have seen they usually have a EDS detector as well because EDS detector is not that costly. WDS detectors are pretty costly.

So, EDS detector people anyway like to have and then on top of that generally you tend to have a WDS detector and the way normally the machines are operated is first you do an EDS scanning rough EDS scanning get an idea about various elements present and where they are. And then you go for this WDS scans or WDS spot analysis whatever and for a finer analysis and for chemical identification with a much better resolution. So, that is how typically these kind of chemical analysis is done using WDS detector.

(Refer Slide Time: 11:00)



Wavelength dispersive spectroscopy (WDS)

- In WDS, the X-radiation coming from the specimen is filtered so that only X-rays of a chosen wavelength (usually the characteristic X-ray wavelength of the element of interest) are allowed to fall on a detector.
- The 'filtering' is achieved by a crystal spectrometer which employs diffraction to separate the X-rays according to their wavelength.
- The X-rays leaving the specimen at a certain angle, the take-of angle (φ) are allowed to fall onto a crystal of known lattice spacing, d.

Now the working principle of this WDS detector what happens here. So, in WDS the x-ray radiation from the specimen that is x-ray radiation. So, when the electron probe is encountering the specimen it generates an x-ray. Let us say it is a multiphase element and all of these elements are generating its own characteristics x-ray. So, ultimately I am getting an electron beam which has different x-ray which contains different x-ray beam with or different x-ray photon with different wavelength.

So, it is an x-ray beam with multiple wavelength unlike a normal x-ray diffraction so that is the different. In normal x-ray diffraction what we do is that we use an x-ray beam with a fixed lambda as fixed as possible as monochromatic as possible. Here by default if it is a multiphase material then or even if it is a multiphase material then you will have a mixture of this x-ray photon.

And if it is a single phase then also you then you can possibly expect to have monochromatic x-ray characteristics, x-ray beam whatever it is. So, you have this x-ray beam let us say with a mixture of lambda or a fixed lambda. Now, what happens is x-ray radiation coming from the specimen this is filtered out in this WDS detector. So, WDS detector has two different parts basically one detector and then there is an intermediate crystal is there.

So, it has two different parts altogether we will come into that. So, all of these x-ray beam which is coming from the specimen it first falls on this crystals and then it is basically gets filtered. So, only x-rays of a particular wavelength usually the characteristics x-ray wavelength of any element of interes,t this is allowed to fall on a detector. So, a detector is kept somewhere over here.

So, there is a crystal here in the middle first the x-ray encounters in a crystal then the crystal basically filters out the x-ray signal of a particular wavelength and that makes fall on the x-ray detector where you basically measure you can do all sorts of things, you can measure this x-ray detector the wavelength of the incoming x-ray signal number of x-ray photons and so on, energy of that x-ray whatever that can be a simple EDS.

Even that can be an EDS detector just similar like a semiconductor silicon detector as well which can measure the energy of this electron, but basically the point is this crystal what it does is this crystal make sure that only x-ray of a given wavelength is falling on the x-ray detector that is all. And this process this filtering process is achieved typically by this crystal spectrometer and the way it works is related to the diffraction effect here.

This crystal is usually of a known d value known d spacing. So, this is typically a single crystal and not only a single crystal it is single crystal of known d value that is what you use. Now, when it is of a known d value what happens first is the detector is kept at a particular angle to the specimen. And there the criterions are pretty same as the EDS detector you want maximum amount of x-ray signal coming from this specimen should enter and fall on this crystal should enter the detector and fall on the crystal.

So, you want to keep it as close as this specimen as possible and at a particular angle which is known as the take of angle. So, this x-ray beams coming with a particular take of angle usually psi that is what it is called. So, take of it is coming and falling on this crystal of known lattice spacing d value. Now what happens? We apply the Braggs's law in this case. Now if the angle of incident, angle of this incident x-ray is known.

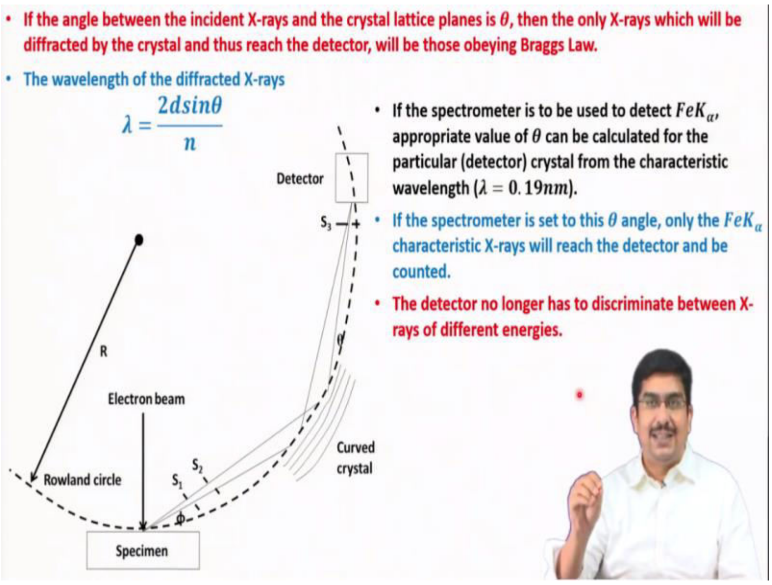
So, basically what we get it here this x-ray is falling here with a particular theta value. The crystal is placed in such a way that this x-ray beam with certain let us say it is a mixed one. Let us say it is a multiphase multi different elements are there and this x-ray beam is a mixed one. So, this x-ray beam is falling on a particular theta angle here the x-ray crystal is the crystal is kept in such a way that it is falling with the particular theta angle.

And we know the d value here. Now what will happen is that the x-rays only those x-rays will be diffracted from here which are satisfying the Bragg's condition. What does it mean? So, this incoming x-ray is coming with a certain lambda value let us say with our mixture of lambda value or certain lambda value whatever. I have a d known here if I apply this Bragg's law here I know the d is there.

The lambda is also let us say it is coming with a particular lambda and this detector this crystal is kept at an angle that it is making certain theta angle with this. So, the entire lambda value this, incident x-ray whichever lambda value is satisfying this Bragg's condition here will be diffracted by this crystal. The rest of the x-ray beam will just be passing through. They will not be diffracted because they are not satisfying the Bragg's law in the first place.

So, that is what is shown here out of this entire x-ray beam certain parts is getting transmitted because they are not satisfying for this particular position of the crystal. They are not satisfying the Bragg's condition and the crystal have a fixed d value and kept at a fixed theta angle. So, for conditions only a part of the incoming x-ray beam is basically satisfying the Bragg's law and that is getting diffracted from here.

(Refer Slide Time: 16:57)



- If the angle between the incident X-rays and the crystal lattice planes is θ, then the only X-rays which will be diffracted by the crystal and thus reach the detector, will be those obeying Braggs Law.
- The wavelength of the diffracted X-rays

$$\lambda = \frac{2dsin\theta}{n}$$

- If the spectrometer is to be used to detect FeK_{α}, appropriate value of θ can be calculated for the particular (detector) crystal from the characteristic wavelength ($\lambda = 0.19nm$).
- If the spectrometer is set to this θ angle, only the FeK_{α} characteristic X-rays will reach the detector and be counted.
- The detector no longer has to discriminate between X-rays of different energies.

So, ultimately what is happening the wavelength of the diffracted x-ray you can very easily measure from again the Bragg's law only that lambda. So, the diffracted x-ray beam from this crystal you can image that it is kind of reflection this is getting and you have this x-ray this crystal here, the incoming beam is hitting there it has different lambda values x-ray photon of different lambda value and out of the entire beam only that x-ray photon will get diffracted which has the specific lambda which is satisfying the Bragg’s law.

And that lambda value will be the diffracted beam will have a lambda value of 2 d sin theta / n. So, we can find it out from here. Now, if you take a specific example this will be very clear. Let us say we setup this element that we want to determine is Fe and we are interested in measuring the Fe K alpha iron K alpha x-ray signal which has a characteristics wavelength of lambda equals 0.19 nanometer.

So, I know lambda here I know d the crystal with the curved crystal which is here. So, I know the d value of this crystal I know the lambda what lambda I am interested on so after diffraction what lambda it is going to be. What I can calculate from here is the sin theta and then I can keep this crystal at such a way with this take of angle. So, obviously the take of angle has to be considered here.

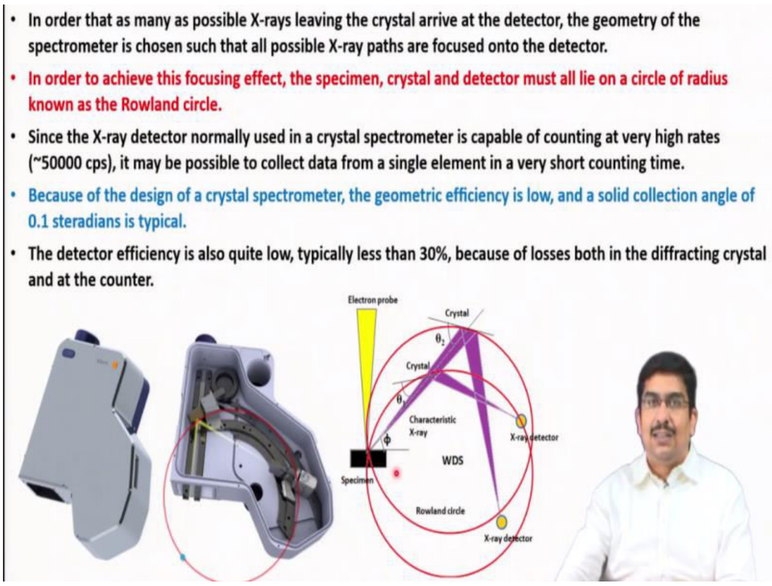
So, I keep this curved crystal in such a way with respect to the specimen with respect to this incoming x-ray signal that only those beam which F e K alpha or out of the entire x-ray beam only the Fe K alpha x-ray photons are satisfying the Bragg’s condition here. And then only those x-ray beam which belongs to Fe K alpha with a characteristics wavelength of this they are falling on the detector.

So, that is how I am finally basically filtering out from this entire x-ray beam only for Fe K alpha it does not the detector no longer has to identify all the x-rays of different energies unlike an EDS detector. So, that is a problem with the EDS detector. If a complete x-ray beam with different wavelength and different energy it hits the detector the detector has to find out that which beam it is.

So, if it is not very suitable the EDS detector the signal mixing is a big problem. So, that is what also reduces the resolution of EDS detector. Here by default it is kept in such a way that it is just identifying or just filtering out that particular wavelength. And that is why this signal mixing happens in EDS detector very easily, but the signals are completely unmixed in case of WDS detector.

The possibility of signal mixing is very, very less particularly for multiphase material in WDS. So, this is inherently one advantage of WDS detector because it works on this principle of Bragg's diffraction. Here it is a slightly different than x-ray diffraction when we discuss about x-ray diffraction we will understand this difference better.

(Refer Slide Time: 20:18)



- In order that as many as possible X-rays leaving the crystal arrive at the detector, the geometry of the spectrometer is chosen such that all possible X-ray paths are focused onto the detector.
- In order to achieve this focusing effect, the specimen, crystal and detector must all lie on a circle of radius known as the Rowland circle.
- Since the X-ray detector normally used in a crystal spectrometer is capable of counting at very high rates (~50000 cps), it may be possible to collect data from a single element in a very short counting time.
- Because of the design of a crystal spectrometer, the geometric efficiency is low, and a solid collection angle of 0.1 steradians is typical.
- The detector efficiency is also quite low, typically less than 30%, because of losses both in the diffracting crystal and at the counter.

Now, in order that as many possible x-rays that is generated in the specimen that arise in the detector finally in this detectors the geometry of this entire the spectrometer is such that all possible x-rays which are entering into the detector are finally falling or finally this they are focused on the detector. So, every x-ray beam which is coming inside the detector the crystal is placed in a way that finally everything is getting focused on the detector here.

So, as I said the entire WDS detector this is how a WDS detector looks like. So, the entire WDS detector contains two parts. One is this crystal of known d value and another one is simply an x-ray detector which is pretty much similar as EDS detector just measures the energy and from there it can identify now even better way that which element it is and in which number that also it can determine here.

Now in order to achieve this focusing effect basically the specimen the x-ray beam which is coming from here it gets diffracted by this crystal and finally getting focused on an x-ray detector in order to do this entire process the specimen the crystal and the detector must lie on a circle and that circle is basically called Rowland circle here. So, this specimen this crystal and this x-ray detector all of these should lie over a particular circle.

And now if you just now I told that there are multiple different type of detectors and different type of detectors with different d value. So, basically the difference between different detectors which I was showing here that 1, 2, 3 like that in WDS detector the difference is the crystal here the crystal has a different d values that is why they are able to detect or able to work for different, different elements because different elements has a different characteristics x-ray.

So, depending on that lambda value the crystal here this so if you look at this Bragg's law. There are two different two independent variables. So, lambda is fixed either I can change d or I can change sin theta in order to make the crystal work for certain lambda. Changing the sin theta is very difficult because that means I have to rotate the crystal through the entire circle.

So that is very difficult it has a limitation how much angle what sin theta angle it can do. What I can do basically it has I mean it can be changed the sin theta also can be changed the way the detectors are made, but it is much easier it has a limit after that is saturate and then I have to go for another crystal with a different d value so that works for another set of elements.

So, that is how the different WDS detectors are used for different range of elements here. So, if you use any one such detector again that detector must lie specimen that detector an x-ray detector and that crystal should also lie along another circle which is Rowland circle again called Rowland circle and that is why the WDS detectors if you look at here looks like they are like a part of the circle.

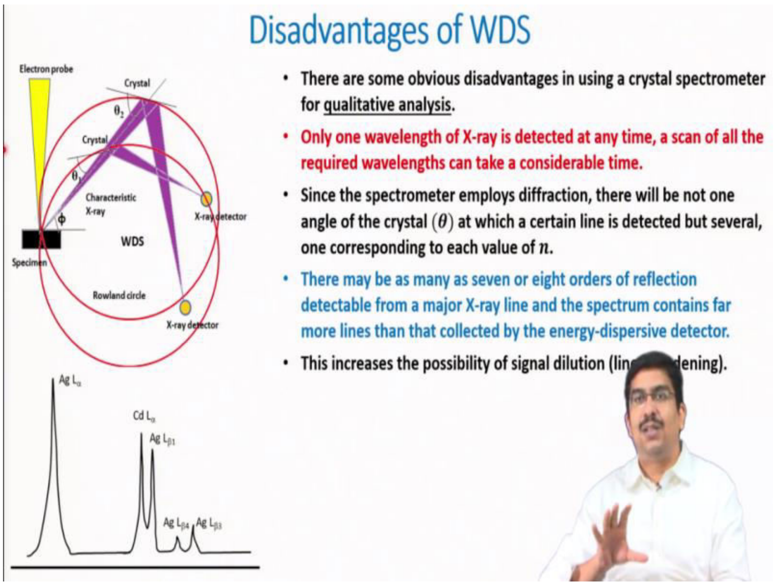
So, these detectors are actually covering a small part of this bigger circle physically. The rest of the part the rest of the circle is not there, but only this part is physically is representing one circle along with this specimen. So, this is how the WDS detector basically works. Again the WDS detectors are pretty much usually very fast and because if this detector is just like an EDS detectors.

So, its response time is very fast and for one single element it is possible to collect data in a very high speed like 50,000 cps and usually that too this is quite focused this x-ray beam is quite focused. The problem is that in this detector because it lies over this large this entire it is a very small part of this entire Rowland circle here the geometry efficiency of this detector is very low.

That means the solid angle of collection the x-ray signal is generated all over here only a very less amount of x-ray signal is finally going into this crystal and falling on the crystal and finally getting detected by the x-ray signal. So, this solid angle of collection for this crystal is very low that is one and second problem is the detector efficiency is also quite low and it is like only hardly 30% of the x-ray beam that is falling on the detector is getting detected because of the losses in both the diffracting crystal and at this x-ray detector.

So, the entire detector is basically efficiency is not that good although the response time is very good for single element detection.

(Refer Slide Time: 25:22)



Disadvantages of WDS

- There are some obvious disadvantages in using a crystal spectrometer for qualitative analysis.
- Only one wavelength of X-ray is detected at any time, a scan of all the required wavelengths can take a considerable time.
- Since the spectrometer employs diffraction, there will be not one angle of the crystal (θ) at which a certain line is detected but several, one corresponding to each value of n.
- There may be as many as seven or eight orders of reflection detectable from a major X-ray line and the spectrum contains far more lines than that collected by the energy-dispersive detector.
- This increases the possibility of signal dilution (lin dening).

Now the disadvantages of WDS detector obviously the first disadvantage is that it is meant for qualitative if you use this for qualitative analysis then only one wavelength of x-ray is detected at any given point of time. So, it is very accurate, but it takes considerable time if you have a multi element system. So, for all of different element you have to scan it with like at different and certain times it happens that more than one WDS detector has to be employed.

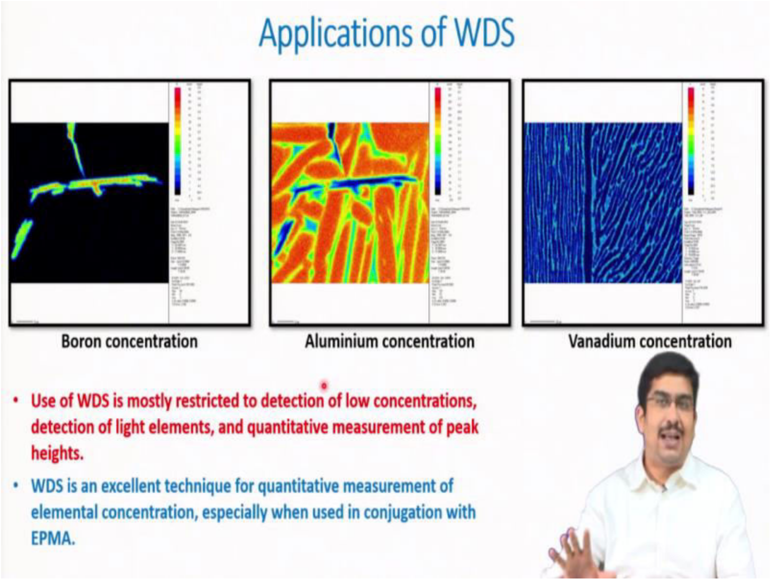
You have a multiphase material with a multi element system then more than one detector has to be work in any given point of time and that will take a considerable amount of time for the entire scan to happen. The second problem that happens is that the crystal because of this order of diffraction. So, it works on the diffraction principle n lambda equals 2d sin theta. So, this n value the order of diffraction because for this the WDS detector can collect different lines more than one lines because you cannot ensure that it is always collecting or the diffraction is always the first order diffraction.

There can be higher order diffraction also possible and the detectors those diffracted beams also can be collected by the detector for certain element. So, ultimately what will happen is that there will again be a signal mixing because the first order let us say you have two different elements. And the first order diffraction from one characteristics x-ray beam will be mixing with let us say higher order diffracted beam with another element.

So, there will be always a chance of signal mixing and signal dilution and this will finally produce a line broadening. Though, it is not as severe as EDS detectors, but still you have a chance of line broadening because of this signal dilution due to higher order different order of diffraction here. The application of WDS these are pretty much the two different or two disadvantages of WDS you can still have signal dilution.

And second thing is you can have the scan time it usually very large here compared to EDS detector which is very fast, but with a less resolution WDS detector of course give you higher resolution, higher precision, but with a much higher response time and multiple detectors need to be used at times here.

(Refer Slide Time: 27:56)



Applications of WDS

Boron concentration

Aluminium concentration

Vanadium concentration

- Use of WDS is mostly restricted to detection of low concentrations, detection of light elements, and quantitative measurement of peak heights.
- WDS is an excellent technique for quantitative measurement of elemental concentration, especially when used in conjugation with EPMA.

Of course, application of WDS is mostly restricted still now for detection of low concentration. So, WDS detectors are very good for quantitative measurement EDS detectors the resolution for quantitative measurement is not that good because of this signal mixing and because of many other problems associated with it which we are not going, but WDS detector the signal identification.

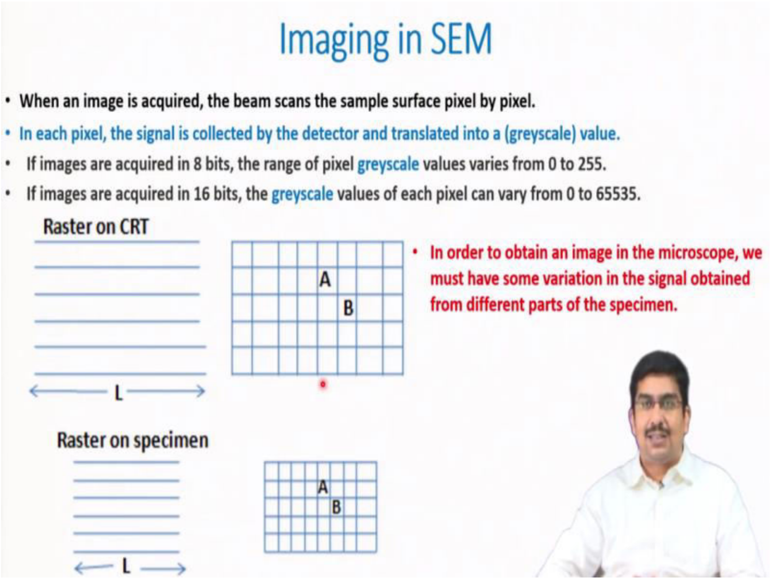
So, identification of individual elements itself is very high and from there it can be the quantitative measurement can be done very easily if proper calibration is meant. So, the use of WDS is mostly restricted to detection of low concentration elements and detection of light elements also quantitative measurement of peak height and so on. So, some examples are given from my own research like you can determine the Boron concentration as low as Boron concentration very efficiently you can determine that.

And with a quantitative measurements which is very close to the bulk concentration that you measure from some other spectroscopic techniques. It can very well match to that level of accuracy almost on the ppb level you can measure the concentration for very light elements like Boron very easily and then you can always have this advantage of very high spatial resolution which the other spectroscopic techniques cannot provide.

So, with all of these you can have these WDS detectors measuring low concentration, light elements very efficiently as it is shown here and it is an excellent technique for quantitative measurement of elemental concentration with spatial resolution particularly when it is used in conjunction with EPMA that is electron probe microanalysis. EPMA is basically you have a larger probe size so signal strength is higher and so on.

So, this is how the WDS detectors works and WDS detector can be used for elemental concentration.

(Refer Slide Time: 29:56)



Imaging in SEM

- When an image is acquired, the beam scans the sample surface pixel by pixel.
- In each pixel, the signal is collected by the detector and translated into a (greyscale) value.
  - If images are acquired in 8 bits, the range of pixel greyscale values varies from 0 to 255.
  - If images are acquired in 16 bits, the greyscale values of each pixel can vary from 0 to 65535.
- In order to obtain an image in the microscope, we must have some variation in the signal obtained from different parts of the specimen.

So, we will be starting that imaging in SEM in the next class and we will not be going through this and we will discuss it in the next class with other imaging modes in SEM. Thank you.