

Techniques of Materials Characterization
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Lecture – 22
Electron Diffraction in TEM - Continued

Welcome everyone to this NPTEL online certification course on techniques of materials characterization. We are now in week 5, module 5. We are discussing about transmission electron microscope. And in the last class we talked about the diffraction, reciprocal lattice the interrelation mutual relation between real lattice and reciprocal lattice and diffraction pattern.

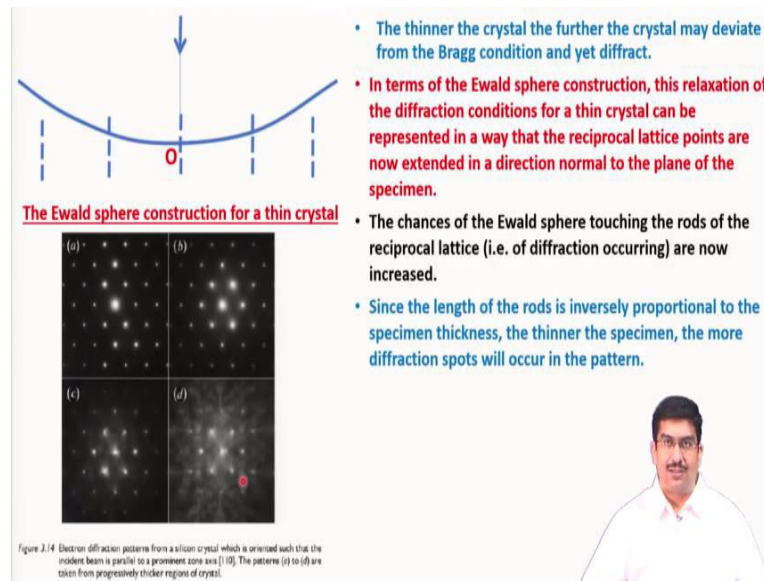
And then we discussed about Ewald sphere construction, how it is helpful, useful to understand diffraction from real finite lattice. So, we will be continuing our discussion on electron diffraction in transmission electron microscope.

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Basically, we will continue the discussion on diffraction from finite crystals. And then we will see the electron diffraction pattern, real electron diffraction pattern, how does it look like and how to understand that electron diffraction pattern. And we will see the diffraction patterns from single crystal versus polycrystals. And finally, we will discuss about selected area diffraction patterns.

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So, let us continue our discussion on this diffraction from finite crystal and what we have understood from the last class is that the distance that the intensity of any diffraction or diffracted beam, if you imagine this is the diffraction pattern, the intensity of any of the diffracted beam that is the width at half height that is related to the thickness 1 by t , inversely related to the thickness of this diffracting crystal.

So there is a relationship between these diffraction patterns, the intensity of the diffraction pattern or the width of the diffraction spots with the thickness of the specimen, real specimen and also we realized that this is happening because the Bragg's condition get relaxed. So, even if it the Ewald sphere does not really touch the reciprocal lattice point it is still satisfying the Bragg's condition and still showing some finite intensity.

So, what we can confer from this is that the thinner the crystals, that means the thickness the t , if t is small the further the crystal may deviate from the Bragg's condition and yet diffract. So, that means this s value this extension distance can be further bigger, it can be bigger. So, the reciprocal lattice the distance by which this Ewald sphere is missing the reciprocal lattice that distance will increase if the crystal is real sense in the real crystal, if it is diffracting crystal, if it is smaller.

That is that kind of relationship we can understand from our discussion in the last class. And in terms of the Ewald sphere construction this relaxation in the diffraction condition, for a thin crystal we can imagine this that the reciprocal lattice points instead

of being a point they are now getting a finite dimension. That means, they are getting extended like a rod, they are becoming like a cylinder or like a rod.

And that is why we can imagine that instead of this missing, reciprocal lattice missing and s vector and that distance by which it is missing that all those things, instead of that what we can imagine is that the reciprocal lattice vector all points itself is getting extended so that now the Ewald sphere has more possibility to touch the reciprocal lattice points so it is getting extended by that amount.

Instead of a point it is getting extended up to that that amount so that Ewald sphere can touch them and we can get those points seen in the diffraction pattern. And this extension happens in a direction which is normal to the plane of the specimen. That means if this is the beam and you can imagine the plane in the specimen is this, specimen plane means specimen surface, do not think the atomic planes.

Atomic planes are still parallel to this beam. So, in a sense, what you can understand what you can think is that this extension because if you remember the electron diffraction, the planes which are parallel to this electron beam, those planes are deflecting. So, we can still imagine those planes parallel to this incoming electron beam in the Ewald sphere also and toward that direction whatever is the direction of the planes, so this extension will happen parallel to them.

And in that effect extension will happen normal to the surface of the specimen over which this electron beam is falling that is what now since the chances for Ewald sphere to touch these rods, these rods mean in cylinder. So, in three dimension we can imagine that instead of reciprocal lattice points, those points in three dimensional in reciprocal space they are becoming like a cylinder.

And since the diffraction pattern is a section through the reciprocal lattice space normal to the to the incoming electron beam that is why we can imagine that these cylinders are now turning down to rod in the two-dimensional section. So, the chances of Ewald sphere touching those rods in the reciprocal lattice are now increased in this condition since we have relaxed the Bragg's condition.

And since the length of the rod is inversely proportional to the specimen thickness and that is coming out from the same relationship the width of the intensity, the intensity peak and the crystal thickness from that relationship what we can understand is that the length of the rods is inversely proportional to the specimen thickness. That means, the thinner the specimen, the bigger the rods.

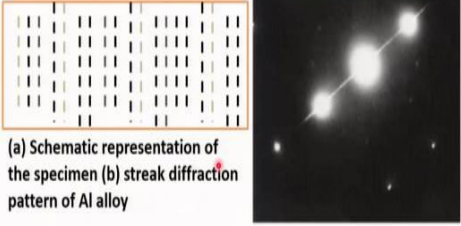
And the bigger the rods there is more possibility for the Ewald sphere to touch those rods and correspondingly the number of diffraction spots also will increase. So, not only the intensity, not only the spots will get bigger or not only they are like now a finite thickness or finite intensity or finite spread of the rods not only of the diffraction patterns. Not only that, the number of diffraction spots will also increase.

Because for thin crystal all the reciprocal lattice points are becoming like a rod and that is exactly shown here. When we take the electron diffraction pattern from a silicon crystal which is oriented such that the incident beam is parallel to zone axis 110 axis. So, the incident beam is coming along 110 zone axis and these silicon crystals is basically getting thicker and thicker. So, this is the thinnest crystal and this is the thickest crystal and these are intermediate.

So, thickness is increasing in this direction first here to here and this this here to here. So, if you can see this that the diffraction spots also it is getting much bigger corresponding to this condition when it is thickest. If the crystal is getting thicker, their number is decreasing and their intensity also getting reduced. These are the two things. This is the relationship between the thickness of the crystal in the finite crystal. Because of the finite thickness this is how the diffraction spots get modified.


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- In a thin crystal, electron diffraction can occur even if the specimen is tilted up to five degrees from the Bragg angle.
- The orientation of a crystal can only be determined with an accuracy of a few degrees from spot patterns.
- More accuracy: Convergent beam electron diffraction patterns and Kikuchi lines.



(a) Schematic representation of the specimen (b) streak diffraction pattern of Al alloy

- The idea of representing variations in electron diffraction conditions by placing a rod at each reciprocal lattice point can be generalized to deal with a crystal that is thin in any dimension.
- The diffraction condition at a reciprocal lattice point is extended in each dimension by an amount inversely proportional to the thickness of the crystal plane in that dimension.



Another source of this modification or another type of this modification is basically again from this thickness only it will come, but before that there is another important point that in case of a thin crystal the diffraction, the deviation from exact Bragg's condition because of all these things what we discussed; the Ewald sphere touching like a rod, reciprocal lattice points becoming a rod and Ewald sphere is touching them.

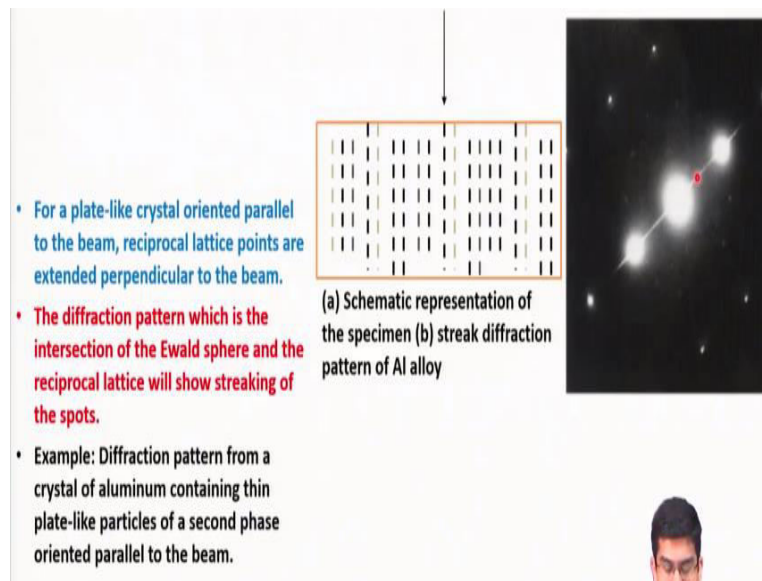
For thin crystal this deviation from Bragg's angle can be as high as 5 to 6 degrees even that kind of deviation can happen and that means that the zone axis determination will also not be very accurate that accuracy is also around 5 to 6 degrees. So that you have to remember when you do orientation measurement or zone axis measurement in case from a diffraction point or diffraction pattern, this is what we should remember the accuracy of that measurement is in question because of this relaxation of Bragg's angle.

For more accuracy of course you should go to convergent beam electron diffraction or Kikuchi patterns there is another way, we will briefly discuss about them, just very little discussion will happen in the subsequent classes. Now, also what happens is that if we imagine that the crystals that are diffracting they are thinner in only one dimension, they are not thinner in every dimension, it is not thin so we imagine that this is one crystal or this is one sample within that we have some diffracting entity.

Some crystals which are thinner only along one certain direction, then what happens is that the relationship still holds that the diffraction spots now or the reciprocal lattice points will now become rod like in a direction parallel to this plate's thinner direction.

Whichever direction is thin parallel to that the diffraction points will get extended, will become like a rod and that you can see it even in a real diffraction pattern.

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So, this basically if we know this is from a plate-like crystals, this is an example of aluminum alloy where these crystals they are really thin. They are having a very high aspect ratio and they are very thin in one dimension and thicker or longer in another direction and they are also very much crystallographic. So, for this kind of specimen where the diffracting crystals are thinner only in one dimension.

Then what happens is that corresponding to that dimension, so since they are thinner in this dimension here the diffraction spots also get or the reciprocal lattice points get elongated parallel or normal to that direction whichever direction this is thinner, these diffracting crystals are thinner parallel to that the reciprocal lattice points gets extended. That means in the diffraction point or diffraction spots also you will see that the dot diffraction spot will get extended along that direction.

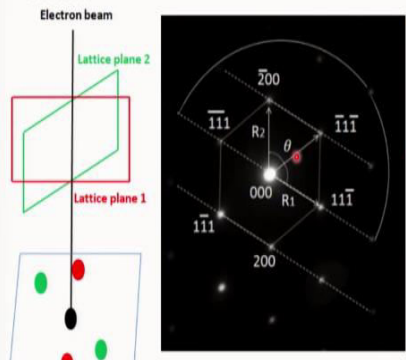
And this phenomenon is called streaking of diffraction points or diffraction spots and this happens primarily because of the thinning, because of the finite thickness or very thin crystals or very thin entities which are diffracting, atomic planes from which this diffraction phenomena is happening, this streaking pattern. So, these are the effects of finite thickness of any diffracting crystal.

And in order to understand this phenomenon in a diffraction pattern it is better to consider the Ewald sphere and reciprocal lattice. So, in order to explain these streaking points and all, we must go back to the reciprocal lattice and Ewald sphere construction, those concepts and that will help us to understand why the streaking is happening, why it is happening in along one certain direction and so only.

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Diffraction pattern from single crystals

- Depending on the size of the investigated crystallites, different types of electron diffraction patterns are observed.



- If exclusively a single crystal contributes to the diffraction pattern, reflections appear on well-defined sites of reciprocal space that are characteristic for the crystal structure and its lattice parameters.
- Each set of parallel lattice planes that occur in the investigated crystal and in the zone axis selected, give rise to two spots with a distance that is in reciprocal relation to that in real space.

The spot diffraction pattern from a single crystal along zone axis $Z = [011]$ of Al 1050 alloy



Now, let us discuss about diffraction pattern from single crystal and try to understand that why this diffraction and what is so special, how to read the diffraction pattern. So, first we will discuss only about the single crystal because it is easier to understand and then we will move to polycrystalline diffraction. Obviously depending on the size of the crystallites, we will have different types of electron diffraction patterns which we will discuss.

But basically, what happens is that we imagine that okay again the electrons are coming along the zone axis and that zone axis now will contain lattice planes and all the lattice planes will be parallel to that zone axis. So, we are just considering two different lattice planes here, lattice plane 1 and lattice plane 2, this green one and the red one. What happens is that there will be a diffraction of course.

When the incident beam will come and hit this screen, there will be this direct beam and there will be the diffracted beam corresponding to these two lattice planes which are also formed. Now, every set of lattice plane will give you two diffraction spots on either side of the origin. And we can imagine basically this is for cubic system and this is most

prominent, we are restricting mostly to cubic system, we are not going anywhere beyond cubic system.

Mostly we will confine our discussion about this electron diffraction with cubic systems and at the max we will go to tetragonal system, we will never go to orthogonal or any other low indexed systems, monoclinic, triclinic or rhombohedral such kind of system because it is very difficult to understand their diffraction patterns. We will restrict ourselves to simple cubic system FCC BCC or simple cubic that kind of a system that is enough.

So, what happens is we know because of the symmetry of the crystals, if we imagine that this is the unit cell, we can get or we can represent any point by Miller indices and just by shifting the Miller indices, we get basically two different set of points. If we imagine that if there is $1\bar{1}1$ plane, then correspondingly on the backside whatever the plane is that plane we can represent it by exactly opposite to it $\bar{1}1\bar{1}$.

So, like this every set of planes will have a corresponding plane on the opposite side or in other words what we can imagine is that if we shall consider the set of lattice planes, then we are getting two diffraction spots corresponding to diffraction beams generating from the front and backside of this planes set up that is it. That means, again the same thing, do not get confused.

If we imagine a unit cell basically these two set of planes in any family we can get these set of two planes there within the unit cell and they will be making two different two diffraction spots exactly at the same distance with it because this distance from this spot, origin to this spot and origin to this this spot is exactly the same because of the interplanar spacing. These are related to the interplanar spacing and that is why these two will be equidistant from the origin.

Same thing will happen for this green, corresponding to green plane we will be getting two different spots here. So, that is what instead of lattice planes parallel planes in the crystal, they will give two different spots and this one is showing that you can imagine that this one set of planes is basically 111 type of plane, the other one is 200 type of plane and that is why they are giving all these different set of planes.

So, from 111 family of planes I am here getting four different diffraction spots and again I am getting from 200 family of planes I am getting two different spots. If you measure this distance, this is exactly $1/d$, $1/d_{200}$. So, 200 set of planes whatever their $h k l$, whatever their $d_{h k l}$ or whatever their interplanar spacing corresponding to that I will be getting this distance here and the angular relationship of these two planes.

So, you can find out the angle between any set of planes in case of a cubic crystal, very easy to do that, that angular relationship will also be maintained here in the diffraction spot. So, diffractions pattern will be an exact replica of all the symmetry elements, all the crystal, all the relationship between different planes everything will be just represented here, but in an inverse sense the distance, at least the distance.

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Single crystal of Al 1050 alloy

Single crystal of NaCl

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Single crystal of tetragonal Ta₉₇Te₆₀

- Thus large d -values cause a set of points with a narrow distance in the diffraction pattern, whereas small d -values cause large distances.
- Diffraction pattern carries the symmetry information of the unit cell (space group)

So, since this again the relationship between or the distance between this diffracted spot and the origin here varies as inverse $1/d$ that is why what happened is that any set of atomic planes which is having large d value will now appear closest to the origin and any planes which have a farther which have a very low d value any one which is having a very low interplanar spacing that means those planes are very close together, those planes will appear farther away from the origin.

This gives a very important clue here. That means this low index planes like 100 111 110, these three usually we call it low index planes. So, this low index planes usually have largest d value. The distance between these planes say 111 100 or 110 these planes,

the planes largest have the largest d value correspondingly the points which or these diffraction spots corresponding to those low index planes will fall closest to the origin.

So, when you see a diffraction pattern and the zone axis, you know the zone axis, you need to know the zone axis so that you can make sure that this low index planes are actually diffracting or not. So, then you can know that if I know the zone axis and the zone axis is having a such a relationship with those low index planes or low index planes satisfying the diffraction condition.

Then the points which are closest to this direct beam must be from low index plane that is one the first very important information to read this diffraction patterns here. Second thing already I told that all the planar relationship, the angular relationship between various set of planes that will be obeyed in case of in the diffraction pattern. You can see whatever the angle, in the real sense you can find out the angle basically $\cos \theta$ equals this $h_1 h_2$ and so on that kind of relationship.

You find out the angle, you then take this diffraction pattern which is from a single crystal aluminium FCC. You know aluminium is FCC. So, for them again the same angular relationship that if you measure this vector and this vector, the angle will be exactly the same as you get theoretically from their Miller indices. So, it will again carry forward.

Another thing that will carry in this diffraction spot from the real lattice is the symmetry information of the unit cell that is basically the space group information. You know all crystal systems have a symmetry which is contained in their point group and space groups in which two types of symmetries are there, inversion axis, rotation axes, you must have heard all of these things. One-fold rotation, two-fold rotation, three-fold rotation, four-fold rotation, six-fold rotation and so on.

All these rotational axes, inversion symmetry, mirror symmetry or if you go for a space group then there you have the screw axis like that all of the symmetry elements will be there in case of diffraction patterns. Just a simple example I am giving here if you imagine this single crystal of aluminum which is FCC and single crystal of NaCl sodium

chloride where the structure is again still FCC, but much more complex than pure FCC aluminium.

This you can imagine as an interpenetrating FCC lattice of sodium and chlorine and I often sort of give these exercises to my students to solve them this crystallography and the diffraction patterns and sodium chloride crystal is a very preferred one for me to give it to my students for solving the single crystal for the diffraction pattern, you can try that. And this is a very good example of seeing that symmetry information from two different set of crystals.

You can imagine that sodium has its own FCC lattice and chlorine forms its own FCC lattice and in the diffraction pattern if you look you will see that there are two different, you can imagine that there are two different types of crystal lattices which are superimposed here, diffraction patterns from one set of FCC lattice is superimposed with diffraction pattern of another set of FCC lattice and that is why even though this is also FCC, this one is quite different than this other diffraction pattern from a pure FCC.

And then if you go to a single crystal of tetragonal and then you will be able to see that here the symmetry is completely different. Of course, the zone axis is, I am not sure about the zone axis, but even with that most likely this is coming around 100 of tetragonal and that it will be showing the four-fold axis here. But tetragonal obviously has some different type of symmetry to the cubic crystals that is why the diffraction pattern of the tetragonal crystals will also be quite different.

Even if you take 100 zone axis of a cubic system and 100 zone axis of a tetragonal system the diffraction pattern will be different because their symmetry along the 100 direction will be different or other atomic planes the symmetry will be different. So, that kind of information will be contained in the diffraction pattern.

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Diffraction pattern for poly-crystals

- If more than one crystal of a phase contributes to the diffraction pattern, as it is the case for polycrystalline samples, diffraction patterns of all crystals are superimposed.
- Since the d -values and thus the distances in reciprocal space are the same, the spots are then located on rings.

$d_{111} = 1.177 \text{ \AA}$
 $d_{200} = 1.230 \text{ \AA}$
 $d_{311} = 1.442 \text{ \AA}$
 $d_{400} = 2.039 \text{ \AA}$
 $d_{510} = 2.355 \text{ \AA}$

- The ring diffraction pattern from a polycrystalline pure Au film with FCC crystal structure.
- From the distances of these rings to the center of this pattern (origin of reciprocal space), d -values can be calculated.

Now, let us go to check the diffraction pattern how that form for polycrystal. So, usually in the polycrystalline material, the diffraction pattern instead of this kind of spots what do you get is these rings here, this type of ring pattern that is what we call it ring pattern from a polycrystalline sample. How it forms? Now, what we can imagine that there are many crystals, instead of one single crystal there are many single crystals here within the specimen within the polycrystal.

We can imagine that the single crystal maybe the grains which are having different orientation, but most likely they are crystallites, we call it crystallites which are much finer the grains usually. So, these crystallites basically contribute to the overall diffraction pattern. There are many number of crystallites which are present with different orientations. Now, the zone axis is the same.

So, if its zone axis is set for 111 and 200 planes just like before whatever we were showing here, the zone axis is still set such that 111 and 200 planes are diffracting, no change in that. But because of the relative orientation of the grains or crystallites, whatever the diffracting entity with the zone axis that will produce the spots, these two spots at different locations.

So, we are still getting these two spots, but because of the different orientation of these crystals, these two spots are forming at different places, but their distance from the origin is the same for all of these spots. So, if we imagine this all spots are coming from 111 plane, since the interplanar distance of 111 plane is exactly the same for all of these

grains or crystallites they will be forming at exactly the same distance from this origin point, but at different locations.

And with different orientation with respect to the direct beam because of this orientation of this crystallites or grains with respect to the incident electron beam. So, ultimately what will happen? And same thing will happen for 200 crystals here, 200 crystal same thing these spots, all the spots are corresponding to 200 planes, but they will be forming at different orientations with the same distance from the origin.

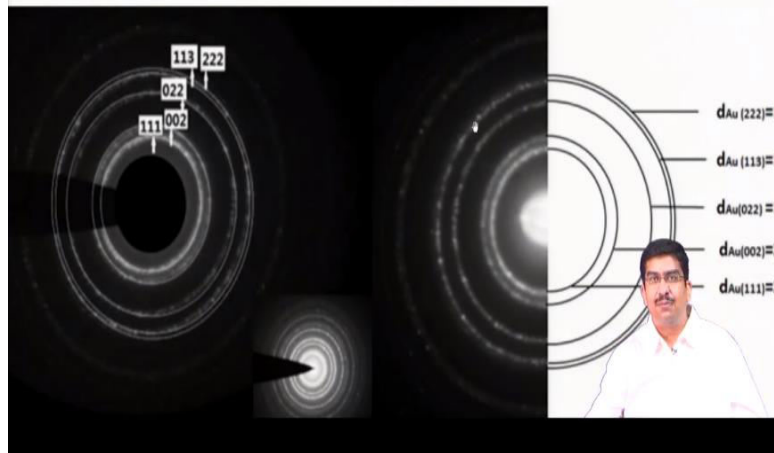
Ultimately, what will happen is that these spots if the number of this diffracting crystals are sufficiently large, then all of this diffraction spots will superimpose and form like a ring because the d values for them is exactly the same. So, that means this ring the d value of or this radius of this ring corresponds to $1/d$ in this case just like for a normal the spot pattern the distance between this spot and the origin is $1/d$.

Same way here the distance between this ring or the radius of this ring is $1/d$ and this is the ring pattern shown for a pure gold film with the FCC crystal system. So, from there again you can measure, same relationship happens that r/d equals $L\lambda$ and so on, everything remains the same, only thing here the d is or r is the radius of these rings. So, that is how also you can find out the d value from this ring patterns here.

Now, the point happens is this kind of complete ring you will get when there is this number of diffraction or diffracted entity or the number of grains of crystallite is very large and they have all possible orientation in 360 degrees with respect to the diffracting beam. If that is satisfied, then all the places these spots will form and the ring will be a complete ring. The entire ring will be complete and entire ring will have the same intensity. You have a complete ring which you are seeing here most likely.

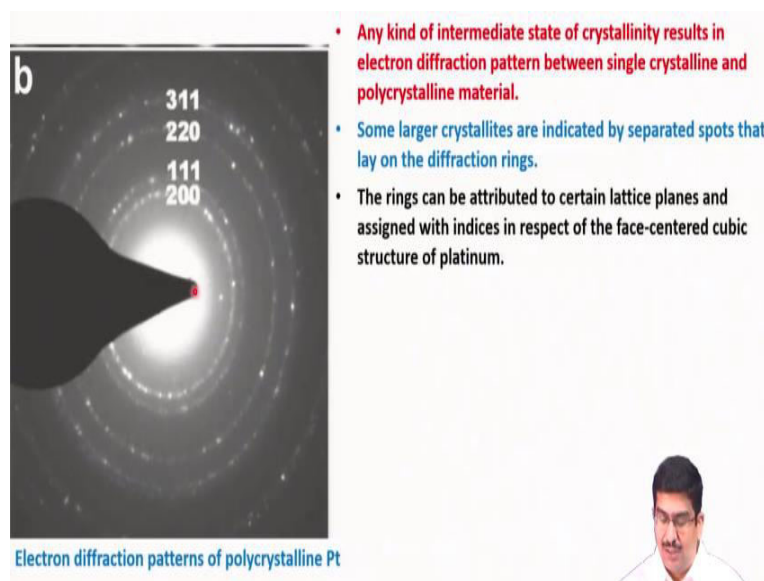
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ce the d -values and thus the distances in reciprocal space then located on rings.



If you zoom it up you can see that this ring is almost nearly completed here. You would not see a separate spot. Of course, if you zoom it out then possibly you will see that some spots are bright and some regions are much fade. But more or less these rings are quite complete.

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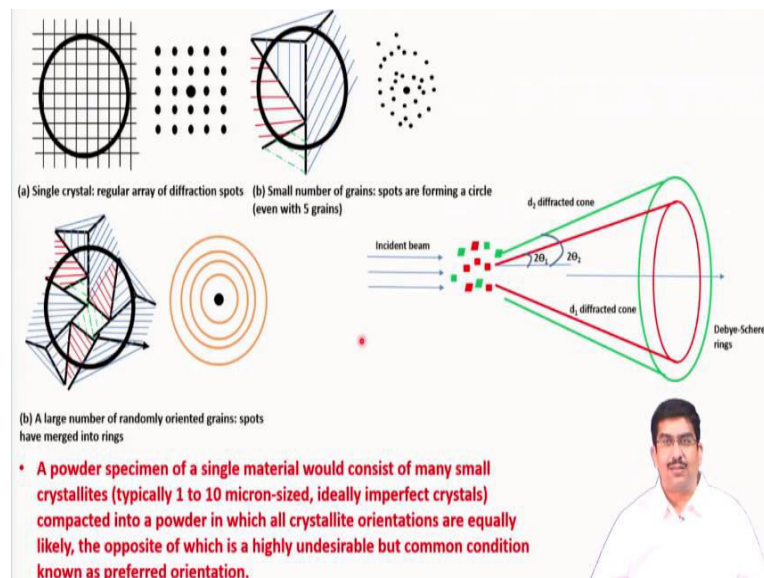


Contrary to that, if you have limited number of diffracting entity or diffracting grains, diffracting crystals in the zone, in the diffracting region there are a limited number of such crystallites or zones with different orientation with respect to your axis then these rings will be not be complete because the number of spots that is forming will not be able to cover this entire 360 degree around this zone access.

So, in this kind of cases the rings are not complete and instead of that on the ring you will have certain spots which are much brighter than the rest of the places. This kind of diffraction pattern is, again it is a polycrystalline material, but its crystallinity is somewhere in between single crystal and a real polycrystal. So, this kind of patterns are called spotty pattern.

Instead of a spot pattern or ring pattern they are called spotty patterns. And here also the same thing happens that the radius of these rings corresponds to $1/d$, so exactly the same, all the same, same theory is applicable. But here the rings are not complete rather there is a little bit of spotty pattern.

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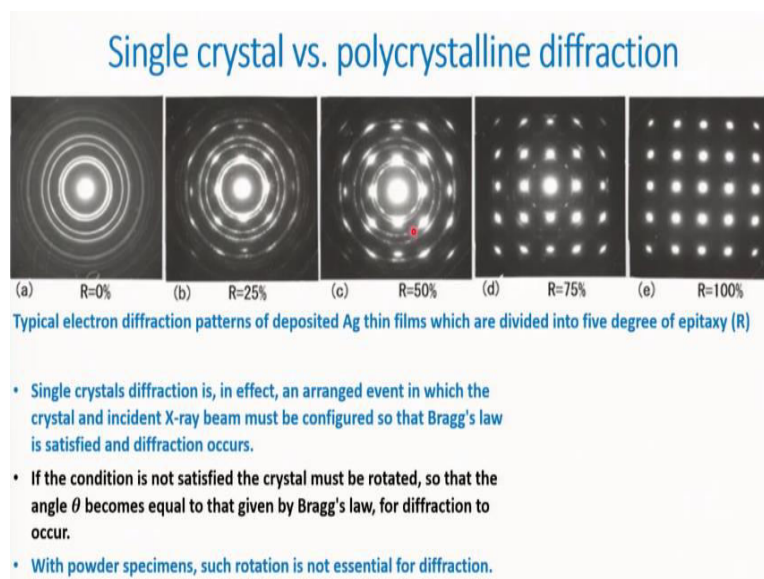
So here in schematically I have tried to show because this is always very helpful for my students to understand and to realize this when you have this. Let us say this black ring you can imagine that this black ring is your electron beam which is falling on your specimen. So, if this is the region from which the diffraction is happening or rather not the real beam, this is the region possibly from which the diffraction is happening.

If that contains single crystal that means you have a very this checkerboard type arrangement of crystals or arrangement of atomic planes which are satisfying the diffraction condition if that happens you will be getting this kind of spotty pattern, spot pattern and in the spot pattern you have definite diffraction spots corresponding to the reciprocal lattice. Then you keep your size of the beams everything the same.

Now, but from that region which is diffracting which is interacting with this electron beam that region contains a higher number of such single crystals with different orientations, then what you will get is this spotty pattern. You will be getting these spots along ring. And now when the same thing happens but with much more numbers of grains here, what will happen this spotty patterns this the rings are complete and you will be getting a ring pattern.

Basically, these rings are exactly the same phenomena as something called Debye-Scherrer rings which we will discuss when we discuss about x-ray diffraction. Just remember this and this is how the diffraction pattern basically changes between single crystal, polycrystal and even in polycrystals also when the number of diffracting grains or crystallites is more versus number of diffracting crystal or crystalline is much higher.

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Just one more example we will see which is very interesting. This is showing electron diffraction patterns from a silver thin film which is deposited and then heat treated. So, when it heat treats, there is some typical phenomena called epitaxy and epitaxy means basically the matching with the substrate. So, when the entire thin film has a very good matching with this substrate, which is again a single crystal, the substrate is single crystal, on top of that you are depositing some kind of a film.

When the thin film is exactly having the same lattice parameter that means exactly the same crystal structure, very low matching then it is called epitaxy. What it means is that if you increase the epitaxy; this r value is basically showing the increase in epitaxy, so if

that increases means this material is almost becoming like a single crystal. So, when we start with no epitaxy, it is a complete polycrystalline material, very fine grain or crystallite size, then it is a complete ring pattern.

Now, with some more epitaxy some particular regions have this started getting spotty pattern, the spots becoming more and more prominent and finally when the epitaxy is very high this becomes like a spot pattern. And the best part what we can get from here is that if we follow this transition, we can understand that what are the orientations which are growing with epitaxy what kind of orientation, what this spot is growing, if you see these are the spots which are growing.

That means those are the atomic planes that is growing or that is causing more and more, the increase in epitaxy is caused by those planes. So, that kind of study you can do just by monitoring this transition from polycrystal to single crystal and vice versa. Some other studies different definitely. There will be example where a reverse is to a single crystal is transforming to a polycrystalline material as it generally happens.

In case of deformation of material there what we get a single grain tends to divide into smaller grains or smaller orientation spread when it is deformed. So that kind of studies we can also do, we can monitor this change in diffraction pattern and we can get many more information out of that. So, we will be stopping it here and what we will be discussing in the next class is selected area diffraction pattern. Good bye.