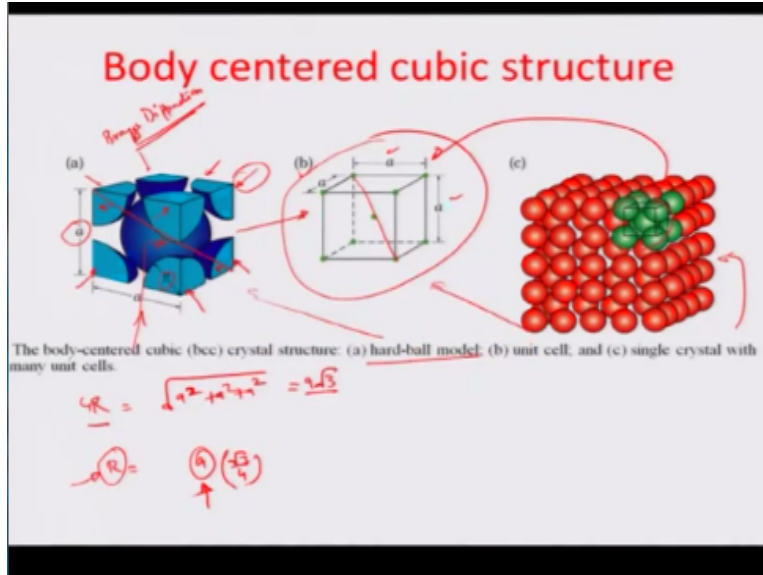Hello and welcome to this manufacturing process technology on module 5.
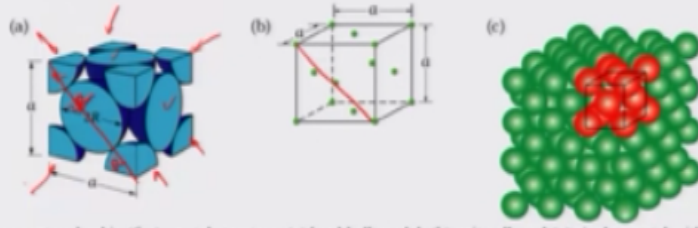
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We are discussing about the various crystal structures and started with the body centered crystal structure, here in this particular case we obtained that you have a unit cell which would be able to predict based on latest constantly, radius.

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Face centered cubic structure

The face-centered cubic (fcc) crystal structure: (a) hard-ball model; (b) unit cell; and (c) single crystal with many unit cells. *Source:* W. G. Moffatt, et al., *The Structure and Properties of Materials*, Vol. 1, John Wiley & Sons, 1976.
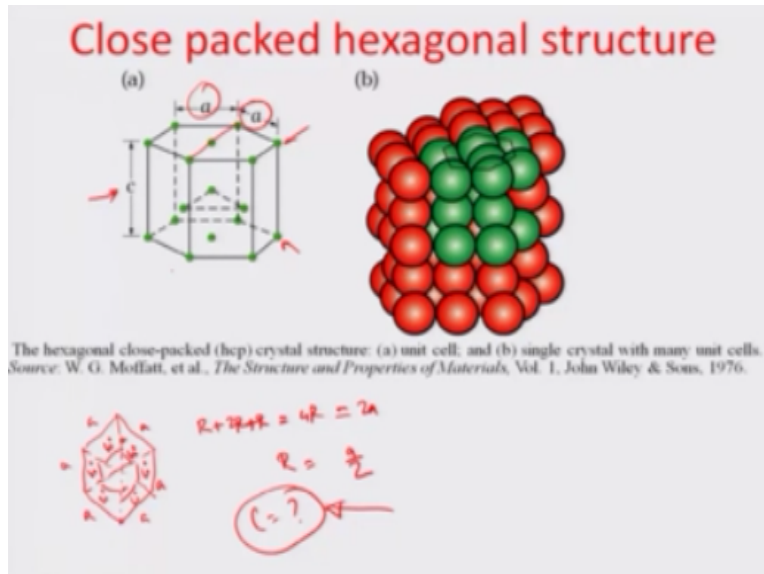
$$4R = \sqrt{a^2 + a^2}$$
$$= a\sqrt{2}$$
$$R = \left(\frac{a}{2\sqrt{2}}\right)$$

Let us do this similar kind of the thing for the face centered cubic structure as well which is represented here. In the face centered cubic structure you have half contributions of the atoms at all the six faces of the cube. And then there are these one eighth contributions of the atoms with the corner which results in the building of this unit cell recorded us face centered cubic structure. So here as you can see the diagonal length of one of the faces is composed of R+2R+R=4R, and this results, this actually can be recorded as the face diagonal of a cube of size a which is nothing but a $\sqrt{2}$. And so R can be correlated to the latest constant a by just dividing the a by 2 $\sqrt{2}$.

So that is how you can constitute the face centered cubic structure or similar behaviour can be obtained for the hexagonal close packed structure.

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Close packed hexagonal structure

The hexagonal close-packed (hcp) crystal structure: (a) unit cell; and (b) single crystal with many unit cells. Source: W. G. Moffatt, et al., *The Structure and Properties of Materials*, Vol. 1, John Wiley & Sons, 1976.

So here each plane of the hexagon would have six atoms and would be the central atom which is in the particular plane. So if I just look at one of these hexagonal faces build up here let say, and these are faces of a regular hexagon. And when we were talking about just interconnected vertices of such hexagon. So obviously because it is a regular hexagon the angles that these triangles would formulate are all 60° and they would be lateral triangles and each of them has a unit cell size A as can be recorded here in the closed packed hexagon structure.

And so obviously the total amount of distance that you would have between this and this atoms is basically R+2R+R=4R, and this results in because it is a lateral triangles all sides are equal and this is equal to 2a, so obviously the R becomes a/2, similarly I would like you guys to find out what is c value, which is between this different planes of the materials for this atoms.

So having said that you have looked at the hexagonal close packed structure and you have also looked at the face centered cubic and the body centered cubic structure, and how the atomic radius can map to respect to the latest spacing.

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4

Crystal structures of some common metals

Let us look at some of the materials commonly available which can be classified into the various structures we have discussed for example material, chromium, tungsten, vanadium, molybdenum, iron, there is obviously one temperature range of iron in which it formulates the bcc. Similarly, in the temperature range in a different temperature range, it can result in the formulation of a face centered cubic.

Some other materials are aluminum, copper, lead, nickel, silver which are actually unit cell is like face centered cubic, iron of course within this range 910-1400°C is formulate of face centered cubic structures whereas any other temperature range it is actually more like a BCC or a body centered cubic. So such materials do exits well there are more multiple lines states and particularly in case of iron it is more temperature it is specific that the FCC state gets formulated in a certain temperature range with the iron can be kept.

So those materials are known as allotropes where you have more than one such crystalline states which are possible. There are many other materials which can again classified into the third close packed hexagonal structure like titanium, zinc, zirconium, magnesium, cobalt so on so forth. And so with this you get to feel of what are the different classifications of the commonly available engineering materials in terms of the crystal structures.

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Crystal Structure

- When a liquid metal solidifies by cooling, the atoms arrange themselves in regular space lattices, forming a crystal.
- The crystallization starts simultaneously at various places within the liquid mass.
- As shown in the following figure the growth of crystal grains and the ultimate formation of the polycrystalline structure with inbetween grain boundaries get formulated.

Fig. 1.5   Formation of grains and grain boundaries during solidification.

- Most metals have only one crystal structure. A few metals can however possess more than one crystal structure. Such metals are known as allotropic metals.
- A number of material properties are dependent on the crystal structure. Like BCC metals are usually harder, FCC are usually ductile. In CPH structures the ductility is low.

So having said that now let us look at little more into the aspect of what this crystal structure is at having an issue and how it gets started or formulated. So the atom is always as in a flow able state and there is a liquid metal with the atoms are very less bondage, because of the high thermal energy or the high kinetic energy of the atoms with respect to each other.

So as the liquid metal solidifies by cooling the atoms arrange themselves and regular space lattices formulating the crystals as you can see here, the crystals are just about starting to take place. So such centers are known as nucleation centers where this nucleation center is basically the start of the activity of solidification and regularizing of the unit cells and these centers are many across the whole liquid stream whenever there is a temperature which comes to the solidification point and that can be any were within the liquid matrix there are development of the small centers of the small crystal growth.

Unfortunately, the crystals are growing, because of the randomness of such nucleation sites of centers in all possible directions. And therefore, there are definitely some point of time the crystals would go against each other. For example, in this case, the crystal is growing in a different directions as you can see from this nucleation side and the crystal from the nucleation side is going in a different directions.
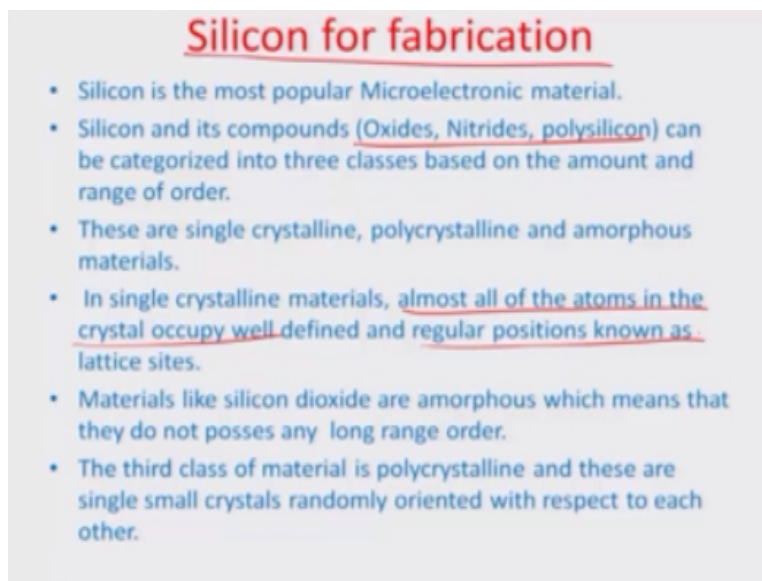
And they are going to sorted of face each other and not be allowed any more to expand in the regular direction. And so therefore, you formulate limited growth long range order areas which are also known as the grains and the boundaries where these because of the randomness of the

directions of this arrangement, the boundaries are really of those points were growth is no further possible, because of the limitation of the other boundary which has come very close.

And that point is really were you have the grains and grain boundary just as in a poly crystalline material. So I have already discussed that most metals have only one crystal structures, but a few have can however have more than one, so those are known as allotropic materials. So the reason again why we are trying to study this different kinds and units cell arrangement of crystal structures, because the material strength are some of the other material properties be at electronic and mechanical they would heavily depend on the overall crystal structure.

So let us study one system of materials which is very commonly used in microelectronic fabrication and they are like silicon.

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Silicon for fabrication

- Silicon is the most popular Microelectronic material.
- Silicon and its compounds (Oxides, Nitrides, polysilicon) can be categorized into three classes based on the amount and range of order.
- These are single crystalline, polycrystalline and amorphous materials.
- In single crystalline materials, almost all of the atoms in the crystal occupy well defined and regular positions known as lattice sites.
- Materials like silicon dioxide are amorphous which means that they do not posses any long range order.
- The third class of material is polycrystalline and these are single small crystals randomly oriented with respect to each other.

As you know that the silicon is very, very widely used material most of the silicon and its compounds like lead oxides, nitrides, polysilicon and they have variety of different layouts

including spanning from crystalline, single crystalline, to poly crystalline to amorphous range and they can formulate very suitable material for the electronics industry.

So you have again some of the materials like lead oxides of silicon, etc., which are completely amorphous state where there is no long range order at all or the single crystalline or poly crystalline silicon also commonly known as poly are again two different structures were one there is a reputation of a BCC body centered cubic cell and the other the poly crystalline structure is for particularly deposited silicon etc., through LCVD or PCVD processes.

And I am going to touch upon these things later on when we try to cover some of the microelectronic material, but the idea is that this is a system which is very commonly available in all the three different forms of crystal structures. And in single crystalline materials almost all the atoms in the crystal would occupy regular positions as we talked about lattices. And because of that the silicon becomes very useful materials particularly for the microelectronic applications.

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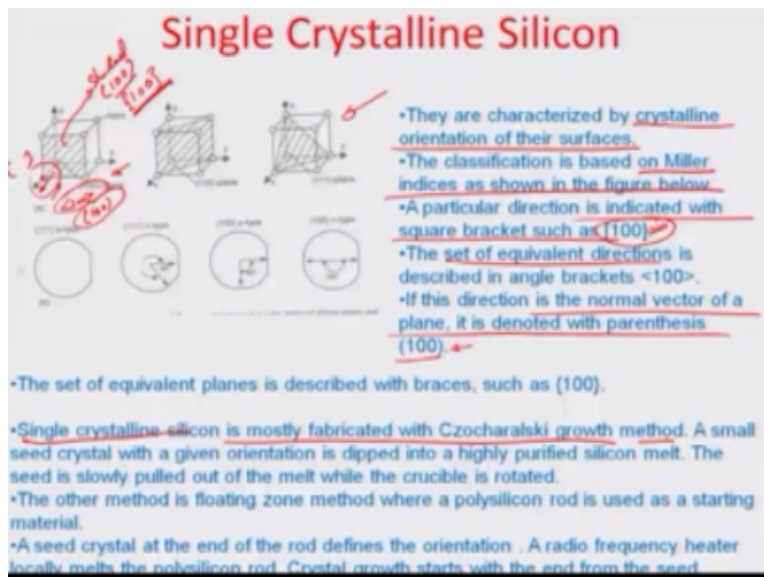
So if we talk about crystalline orientation of silicon and its surfaces, typically the classification would be based on something called Miller indices as shown in the figure here right in this corner. And in the Miller indices if you want to represent the crystal direction particular direction would be indicated in the square bracket like [100] for example in this particular plane the 100 directions would be one along the x axis, 0 along the y axis, and 0 along the z axis.

So this direction right here in this particular direction the x direction is called 100. So you have to represent that by a square bracket. If you wanted to represent a set of equivalent directions it is described by an angular brackets again in a crystal, you have many such unit cells or lattices and you have to describe commonly what is the 100 directions. So you would actually make a angled bracket in order to represent that and if this directions is normal vector of a plane that is the noted by the parenthesis is 0.

The (100) so direction represented by []square brackets, set of directions represented by {} angular brackets and if you wanted to represent the plane that is perpendicular to the direction 100, so the plane that is perpendicular to the direction 100 the shaded plane represented here right. So that is the plane perpendicular to the 100 direction. And so this plane is now recorded as circular bracket (100).

And all such kinds of planes would be then represented by these braces (100) that is the representation in which the planes and the directions and the group of directions and the group of planes are represented respectively. The single crystalline silicon is mostly fabricated with Czocharalski's growth method and I am going to touch upon this method in trying to do some may be thermal module to illustrate that what are the operational parameters which need to come out particularly while growing such a matrix highly purified silicon material.

So the other method is obviously the float zone method which may be discussed later on when there is a polysilicon broad which is heated and converted into a single crystalline materials, but then we start with the Czocharalski's growth.

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Single Crystalline silicon formulation (Czochralski's growth method)

- Single crystal silicon is formulated with Czochralski growth method.
- A small seed crystal with a given orientation is dipped into a highly purified silicon melt.
- The seed is slowly pulled out of the melt while the crucible containing the melt is rotated.
- The material is polycrystalline silicon and is 99.9999% pure.
- The poly is loaded into a fused silica crucible that is contained in an evacuated chamber.
- The chamber is back filled with inert gas and the crucible is heated to 1500 deg. C.
- The seed crystal is a small chemically etched crystal lowered into contact with the melt. This must be carefully oriented since it will serve as the template for growth of the much larger crystal.
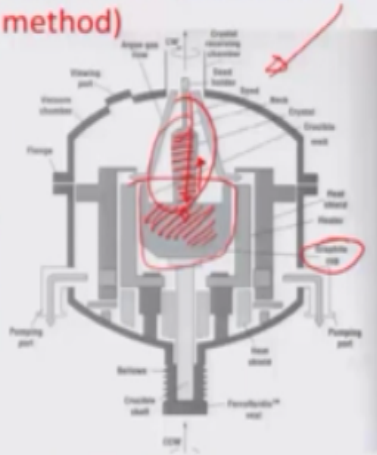
So the Czocharalski's crucible is represented here in the particular figure which is really a vacuum chamber where first of all you evacuate and then you flow inner gas, so that there are no reactive constituents available in the crucible. The crucible here is right about in this particular place is really a graphite cup and it is loaded with polysilicon materials. And you have to heat the walls of these cups. So that the silicon which is the poly silicon which is here gets converted into liquid melt okay.

And what happens step by step is the following that a small seed crystal with the given orientation is dipped into a highly purified silicon melt, you can see the seed is dripped in this direction and the seed was probably somewhere here which started this all activity of the crystal and what really happens is that the seed is slowly pulled out of the melt while the crucible containing the melt is rotated.

So the crucible is rotated and the seed which is being pulled out in perpendicular direction to the rotation plane of the particular crucible. So what is going to happen is that depending on the relative velocity between the direction of rotation of the crucible and let us say the rotation of the seed. There is going to be difference in the way that the melt would adhere to the surface of the seed.

So therefore when the foreign object is now a solid object is emerged in this liquid obviously there is going to be forces of cohesion and forces of addition. The forces of addition are going to

be between the melt and the seed and the forces of cohesion are between the melt molecules as such, and therefore, if we can utilize this clean to the surface phenomena based on the various speed of rotation of the dwell times, because on one hand you are pulling the seed out.

So you are trying to bring it to a lower temperature, so solidification would start happening and in one hand you are actually trying to limit the amount of dwell time by increasing the rotation speed of the crucible. So there is a behavior of this material to formulate different diameters as a result of this process delay as suppose to the rate at which the seed is being pulled out. And so, therefore there can be various diameters of solidified materials and the solidification has been initiated by the central seed crystal which already have a certain direction.

So this process therefore converts the polycrystalline silicon which is actually 99.999% pure very very highly pure polycrystalline silicon into the direction which the seed has the crystal direction that the seed has. So therefore, that brings you a bowl of the material here the material is evacuated you can see the moment it comes out it becomes solidify. So this particular material is actually the solidified.

They are all grown in the direction same as the seed crystal, and so there is a single crystalline growth within this particular bowl. So the seed crystal is obviously small chemical crystal load into the contact with the melt and this is always suppose to give direction. And this must be carefully oriented since it will survive the template of the growth of the much larger crystal. So therefore it is slight misalignment of the orientation the result in the different direction of the growth one has to be very, very careful about this Czocharalski growth process.

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Czochralsky's Growth Method
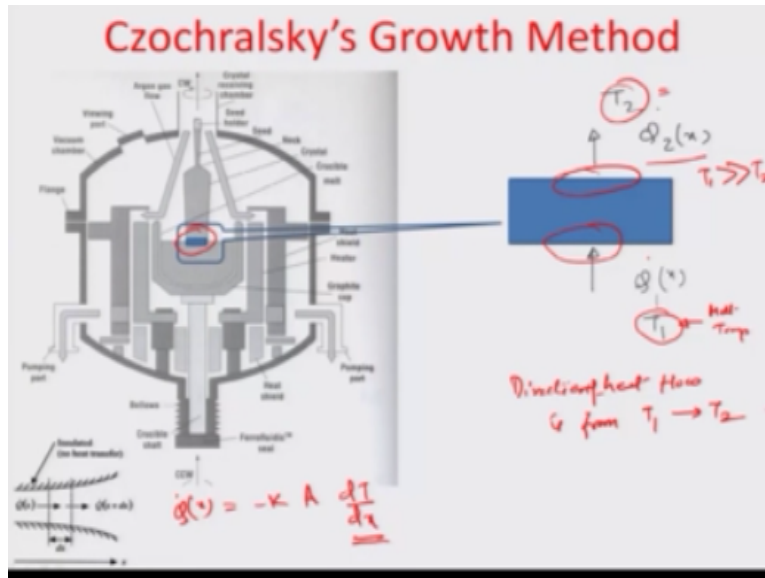
So if I looked at the one dimensional thermal transport in this such a system, we would like to look at the particularly this zone which is semi solid, semi liquid and then let us assume that the temperature below this particular zone is the temperature of the melt T1, so I will just say melt temperature and T2 which is outside atmospheric temperature which is much lower than the melt temperature.

So T1 obviously is much much higher than T2 in the particular case and therefore because of this temperature gradient there is going to be a heat flow across this particular boundary from liquid into the fusion zone into the solidification zone and then there is a heat outflow from the solidification zone into the solid metal which is Q2. So there is a rate at which heat is flowing in to this zone of you can call zone of fusion or zone of solidification.

And there is a rate at which the heat is flowing out from the other boundary here which is from the zone of fusion into the solid material. So obviously the amount of heat transport Q(x) would depend on the thermal conductivity of the material the area of the interface and also the gradient dt/dx of the material. And obviously the direction of the heat flow in this particular case would be from higher temperature, direction of heat flow is from T1 boundary to T2 boundary okay.
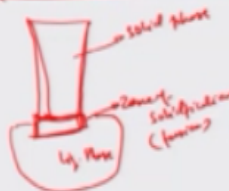
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$$Q(x) = -kA\, dt/dx$$

Czochralsky's Growth Method

So having said that let us assume completely one dimensional flow and you can actually record the heat flow to be $-k_l A \, dt/dx$ of the liquid side which is actually the heat flow because of liquid into the zone of fusion this particular boundary and thermal conductivity here is the thermal conductivity of the liquid on this particular side. And this minus the heat transport across the other face from the zone of solidification to the solid side were the thermal conductivity determinant of heat flow would be that of the solid $-k_s A \, dt/dx$ which excess in the solid side.

And this really would be determining the amount of heat which is trapped in order to built the solid material which is also known as the latent heat of solidification in the particular case times of dm/dt, which is actually equal to the rate of the formulation of solid mass. So you can see that this is the really the thermal balance which is created across the zone of fusion. And we can just indicate this here just the small section as the zone of fusion, the liquid face zone of solidification or melting as you look at it and then you have solid face.

So better known as the zone of fusion actually, so A is the area of cross section which we can assume to be equal in all this cases, so A is the cross sectional area we assume that this is quite uniform this particular area. So A is the area is the cross sectional area, and so as the zone of fusion and therefore the equation can be further modified as

$$\left(k_s A\, dt/dx\right)_s - \left(k_l A \frac{dt}{dx}\right)_l = L\, A\rho\, dx/dt$$ becomes equal to L times of area times of rate at which you are pulling that is the way that the volume is emerging.

So this is the rate of volume of solid mass, time, density which keeps the grade of mass which comes out of the solid face. So basically representing the $dm = A\rho\, dx$ and that brings you to a point where the LPA obviously $LA\rho\left(dx/dt\right) = \left(k_s A\, dt/dx\right)_s - \left(k_l A \frac{dt}{dx}\right)_l$ and further the A can be taken off I can say that the maximum pull rate here can only be if liquid side this conductivity, this value becomes numerically 0.

And so the maximum pull rate $\left(dx/dt\right)_{max} = \frac{k_s}{L\rho}\left(\frac{dt}{dx}\right)_s$. And I am going to talk about this in the next module interest of the time I am going to close this particular module. And in the next module we will discuss about t
he pros and cons of what happens because of this formulation, and how you know the maximum pull rate will be really depend on the temperature gradient.

But on the one hand it is temperature gradient and on the another hand it is how much temperature gradient you can maintain, because otherwise there may be thermal warping and all sort of changes in the crystal. So we are going to discuss this topic in the next module as of now let us close this module, thank you.

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