Indian Institute of Technology Kanpur

National Programme on Technology Enhanced Learning (NPTEL)

Course title
Manufacturing Process Technology - Part-1
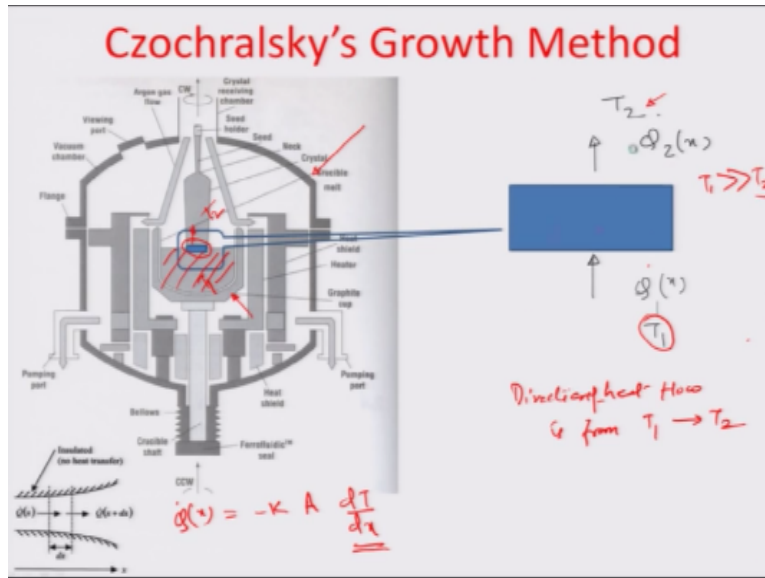
Module – 06

by
Prof. Shantanu Bhattacharya

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Hello and welcome to this manufacturing process technology part 1 Mmodule 6.

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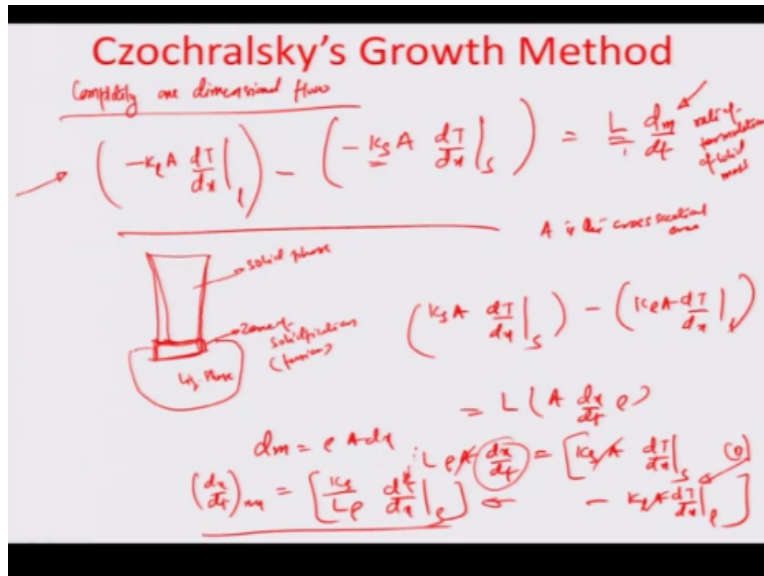
Czochralsky's Growth Method

We are talking about Czochralsky's growth method for getting single crystal line silicon. And we have mentioned about one dimensional heat transfer case which is analyzed right here. You can see here that there is a crucible, there is a vacuum chamber which is filled with, first of all evacuated and filled with organ gas. And then there is crucible which is heated from the walls, then there is poly silicon or poly which is actually 99.99% pure present here and the core of the hearth, and hearth is heated up, so that there is a liquid silicon.

And then, there is a controlled lowering of seed crystal with is chemically polished and which would give and provide the direction and then as the vacuum chamber rotates and the crucible rotates, and also the opposite direction the seed rotates. You basically change the rotations for both and try to make a larger or smaller bowl of silicon which is obtained by pulling out the seed, so that it goes suddenly into a solidification zone.

And so this is the zone of fusion or zone of solidification that you may refer to where there is heat transfer taking place at a certain rate from the temperature T1 which is much higher value then the temperature T2, which is the ambient this is T2 and this right here is T1.

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Czochralsky's Growth Method

Completely one dimensional flow

$$\left(-k_\ell A \left.\frac{dT}{dx}\right|_\ell\right) - \left(-k_s A \left.\frac{dT}{dx}\right|_s\right) = \frac{L}{i}\frac{dm}{dt}$$

A is the cross sectional area

$$\left(k_s A \left.\frac{dT}{dx}\right|_s\right) - \left(k_\ell A \left.\frac{dT}{dx}\right|_\ell\right)$$

$$= L \left(A \frac{dx}{dt}\rho\right)$$

$$dm = \rho A dx$$

$$L\rho A\left(\frac{dx}{dt}\right) = \left[k_s A \left.\frac{dT}{dx}\right|_s - k_\ell A \left.\frac{dT}{dx}\right|_\ell\right]$$

$$\left(\frac{dx}{dt}\right)_{ms} = \left[\frac{k_s}{L\rho}\left.\frac{dT}{dx}\right|_s\right]$$

And so, basically there is again a heat out flow $\acute{Q}_2(x)$ which takes place across this other boundary here. And based on that we had actually formulated, these heat rates we had taken this from the Fourier law of cooling or heat transfer which talks about the proportionately of the heat rate to the negative temperature gradient. And also the thermal conductivity of the medium which is in question.

So here from one side the thermal conductivity property that would be utilized would be that of the melt or the liquid because the heat is mandating from the liquid side into the zone of fusion. And on the other side the heat maintaining out, so basically the case that of the solid silicon which is formulated. So this part is solid silicon as you can see the solid phase this is zone of solidification this is liquid phase.

So this is really $\acute{Q}_1(x)$ and this is really $\acute{Q}_2(x)$, so obviously the Fourier's law can be written in term of thermal conductivity of the liquid, times of area of interface, times of the temperature gradient across the liquid phase to through zone of fusion, and for subsequently for the solid phase. So this heat which is released in the form of heat conduction across the liquid to solid transition also accounts for the bond formulation process.

Because obviously more heat will be pumped from this side into the zone of fusion, but less heat would be pumped out. So the total amount of heat accumulated in the zone of fusion is really the difference of the heat inflow minus the heat outflow, and that heat is converted into the bound energy because there is formulation of the solid.
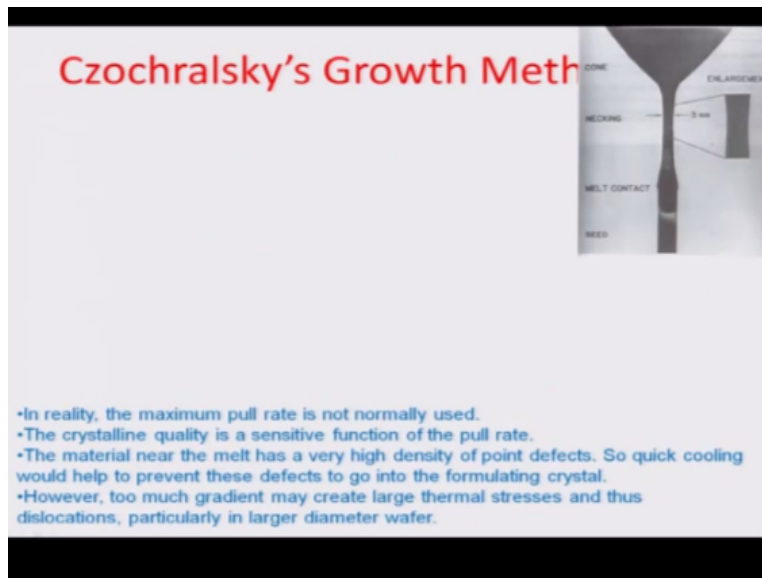
And let us say the rate of which the formulation of the solid mass takes place if we consider that to be dm/dt, then $L.dm/dt$ where L is the latent heat permanent mass is basically the heat rate that is getting lost into the zone of fusion by virtue of the solid bounding formulating because of change in temperature. So then it is left to a very reasonable approximation where we can convert this dm/dt as basically the area of interface times of the density times of the upward pull rate dx/dt of this particular seed crystals.

So it moving by dx/dt. So that is the only variation in time which is happening we assume the interfacial area the zone of constant and the density also does not vary much. So therefore from the zone of fusion into the solid zone. So therefore, if we just solve the equation it comes to have

a form $L\rho\dfrac{dx}{dt}=k_s\dfrac{dt}{dx}$ the solid phase minus $k_l\dfrac{dt}{dx}$ in the liquid phase area gets cancelled off.

And obviously the maximum pull rate that can be obtained is a condition where mathematically this part of the right hand side goes to zero. So if we assume that the total amount of latent heat that is lost within the system is heat that is extracted it out. And so, you can write down this maximum pull rate dx/dt as ks/Lρ dt/dxS okay. So let us just rewrite this here as v max, the

maximum pull velocity of the seed crystal dx/dt which you can now write as ks/ρL dt/dx of the solid side.

So obviously the maximum pull out rate of dx/dt therefore is proportional to be dt/dx of the solid meaning there by the increase the temperate gradient in the zone of fusion to solid transition, obviously more is this gradient the more would be the pull rate or in the order to for the heat balance, or for the heat optimum balance to take place to pull out can be increased with the temperature gradient.

But in reality the maximum pull rate is really not the one which is used normally and one of the reason is the crystalline quality which is a sensitive function of the pull rate okay. So one hand if the material is near the melt it has a very high density of point defects. And if supposing if we are quickly cooling the material, then it will really prevent these defects go into formulating the crystal.

However too much gradient on the other hand may create the problem of thermal warping, or thermal stresses, large thermal stresses within in the crystal material. So on one hand we are trying to make the pull rate little faster, so that the point defects may not be enable to get into the system on one hand, we are saying that if the pull rate which depends on dt/dx, the dt/dx is very high, then they are going to be thermal stresses.

So they are going to be dislocation, or defects just by virtue of thermal stresses. So it is a trade off you know. So you have to really have an optimum balance where without including the point of defects, in the silicon melt to go into the crystal, you should also be able to ensure that the thermal stress are by enlarge, neutralized, or they not present and gradient is not too much over shoot. So that is the trade the silicon industries have to play in order to get the single crystalline silicon.

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Single Crystalline silicon formulation (Float zone method)

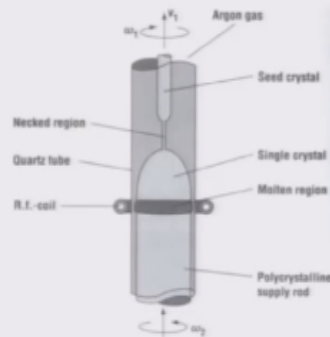•This method is used for extremely high purity silicon growth.

•A rod of high purity polycrystalline material is held in a chuck while a metal coil driven by a high power radio frequency signal is slowly passed along its length.

•Alternatively, a focussed e-beam can also be used for heating the rod.

•The field setup by the RF power leads to eddy currents and joule heating and the material is melted.

• To enhance the growth along the preferred crystal orientation a seed crystal is injected into the top of the molten rod.

•In this technique a thin neck of 3mm diameter and 10-20mm long is pulled and the pull rate and the temperature lowered to shoulder the crystal out to a larger diameter.

In other method that is very commonly used is float zone which is used normally for a smaller wafer and here the method is little different, because here the rod of high purities polycrystalline material held in chuck while a metal coil driven by a high power radio frequency signal is slowly passed along its length. So it basically a non contact mode of heating and there are not many thermal stresses or thermal gradients by enlarge because of eddy current material heats uniformly.

And so alternatively you can also reduce this to focused e beam also, that can also do the job of heating the rod. But the idea is that the crystal is lowered from this end from the top end as you can see here and this crystal is the one which causes the growth to happen, and so whatever the liquid is created in this area because of heating and the rod has been fed inside, so the liquid would ooze out from here and fill up this and this would be a melt and the seed crystal what is coming out in this particular area you are pulling out.

So that the same constitution is of the quality only thing is the heating here is not a wall mediated heating but uniform heating of the material, so in this technique the thin neck of 3mm diameter and out 10 to 20 mm long is pulled and the pull rate and the temperature lowered to shoulder the crystal out to a larger diameter. So that is how you can actually get this kind of a larger diameter constitution even though the oozing out only through a small orifice small cavity.

So you cannot go really for the big size here there would be issues related to incomplete supply of the fluid or extremely slow pull rate which would determine the overall size of the crystal etc. So that is another way of growing single crystal line silicon.

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So I would now come to the crystal imperfections and as you probably, as you are aware of some of the properties of the crystalline solid, that really depend on the crystal structure on thus that should be vary a lot , based in imperfection in such structure. So the study of crystal imperfection and effects on the property of the material is a really a very, very wide domain of research or study where various properties including.

Let us say the mechanical properties, electrical properties so on so forth depend on these defects and I am just showing you a small table here which talks about what are the properties which are depended on the basic crystal structure vice versa what is property dependent on the crystal imperfection. So on one hand it is the structure which is determinant on other hand it is defect of the imperfection which is determinant.

So for example, property like density would depend on the crystal structure in specific heat, quotient of thermal expansion, melting point, plastic constant, hardness and ductility these are something which are structurally dependent. On the other hand if you look out properties like electric conductivity they are definitely going to be dependent on crystal imperfection. Think about it you are having doping material like group 3, or group 5 material into the silicon and

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changes the properties, electrical properties of the silicon, makes n type in one case if it is group 5 makes p types in other case if it is group 3 okay.

So a small amount of imperfection of this material may change the electrical property considerably. Illustrate for example, creep, fracture strength, semi conductivity, work hardening, fatigue strength, these are some of the properties which are utilized by you know change in the crystal imperfection.

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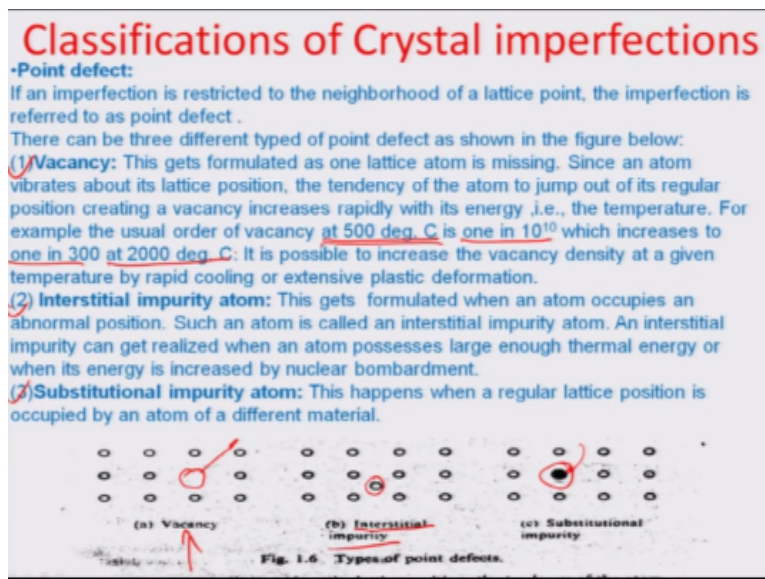
So if you look at how and what kind of classification we can give to the crystal imperfection really there are three different kind of defects which are important. One of them is called the point defect, whereas the name suggest the defect of the imperfection is about single point, there

can be line defect, where we are talking about several such arrays of points together to formulate a whole line.

And then there can be a surface defect, where across the whole surface, it is some kind of the complete movement of the surface, from the regular orientation within the crystal which may change the nature of the crystal. So let us look at theses individual defects in a more classified manner. So points defects for example, they can also be sub classified into the different point defects one is, where the atom can mess, the regular sight.

And another is where the atom can be of a different constituent of occupying the normal atom, of a particular sight, and the third is where let us say within the interstitial phases, where there was suppose to know about atoms in the regular arrangement of the crystal, there is impurity which gets plugged in okay. So based on this the point defects is classified into vacancies, obviously the name suggests that vacancy is a sight which is created because in otherwise regular atom has been moved out you can see this particular figure here.

There was an atom which was supposed to there, but it was moved out and so this creates a vacancy. The other is interstitial impurity where the interstitial that is the sight where the atom is not supposed to be present, there is some kind of the atom of the same kind or of a different kind present in such an interests, which actually relates to the bulging out of crystal you change in shape and size of crystal.

And that can be a very pertinent cause of the mechanical, change in mechanical properties, because of the induction of such a defect in the crystal that is basically made the crystal to already we pre trust from its regular orientation. And then there is substitution impurity which means that any regular sight of the atom is replaced by different material all together. It is not the same atom that is substituting, but different atom which is substituting, regular sight locations.
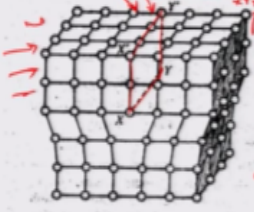
So that is how you classify the defects, as vacancies, the point defects is vacancies, interstitial impurities and substitution impurities, how they formulate what is the usual order, of the vacancy. So at about 500 degree of Celsius, for example, it can be about 10^{10} and it increases to 1 and 300, and about 2000°C, if we talk about above a certain particular lattice. So it is possible to increase the vacancy density at a given temperature, by rapid cooling or extensive plastic deformation okay.
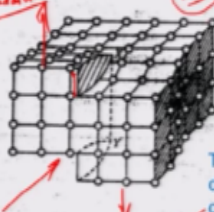
So that is how you create the point defects, then there are line defects, now as the name suggest, there are more than one points which are in an array and like a line and that moves. So here you can see an example a two different kind of such a line defects, edge dislocation and screw dislocation. For example, there is a complete line across many such point together which comes up, and there is because of this line, and additional plane.

So if you look at this particular lattice varying from here to here, there is an extra plane X dash, y dash, XY and additional plane which has come up here for having edge dislocation. So whenever there is mechanical work which is done on the particular lattice, there is movement of this extra plane which leads to probably a quicker, response of a crystal to a mechanical deformation, this is called a edge dislocation.

So the dislocations can also be that instead of pumping and additional plane of atom if I really tried to sheer apart or tear apart by few phases, by few atomic units the crystal can look

something like this which is called screw dislocation, you can seen that one part of the crystal, this part has been short of in shear with respect to the other part, and there is one plane movement okay, of one part with respect to other based on that, so that is the screw dislocation okay.

So the dislocation density is something is very important term here, so you can say that it is the total length of all, dislocation lines per unit volume and so in this particular case, if I had let say 15 nano meter, line defects about 15 numbers, and in about may be 1 centimeter cube of the material. So you can think of how would be this dislocation, density so you have about 25 hundred nano meters 10^{-9} per cm^3 which makes $10^{-6}\,m^3$ and 100 cm.

So therefore, you can think of the dislocation density by virtue of only 50 nanometer lines in $1cm^3$ volume of the crystal, to be high as 2.5 per meter square. So that is how you can calculate the dislocation density.

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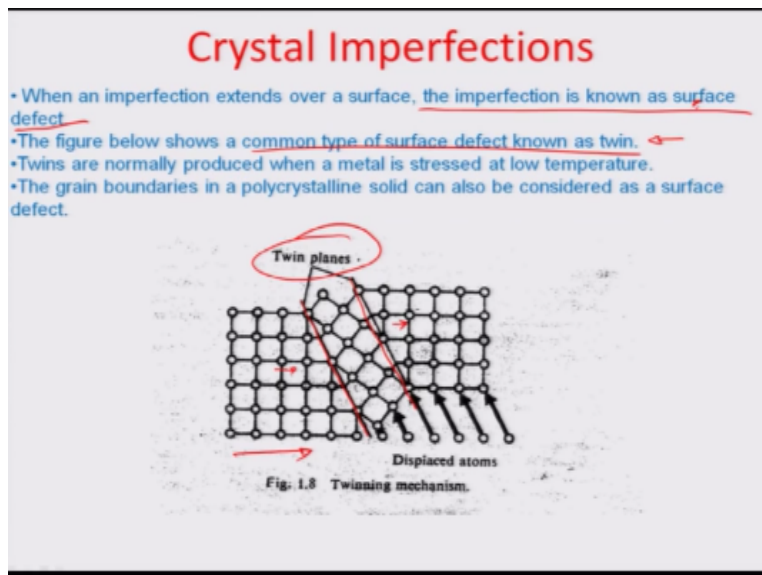
So typically in a crystal the minimum attainable dislocation density of the order of about 100 to 1000 per cm square would be in the range of 2.5 times of 10^4 cm^2, so that is $2.5*10^{-4}$ per cm^2. So you can think of it that the actual tenable dislocation density is the order of 100 to 1000 which is about the 10^6 this value. So they are definitely maximum most of the lattice which is basically pre stressed because of the all these conditions.

And that really gives a very wonderful insight into why such dislocation are what is going to be the effect on the overall mechanical properties of the material. So it so happens when I going to now do may be in next two slides that the actual modules of the elasticity of the actual shear modulus, if you modulate from a lattice view point, and then if you try to see what happens because of dislocations, you will see that the modulus are quite far apart probably 2 or 3 hundreds magnitude apart.
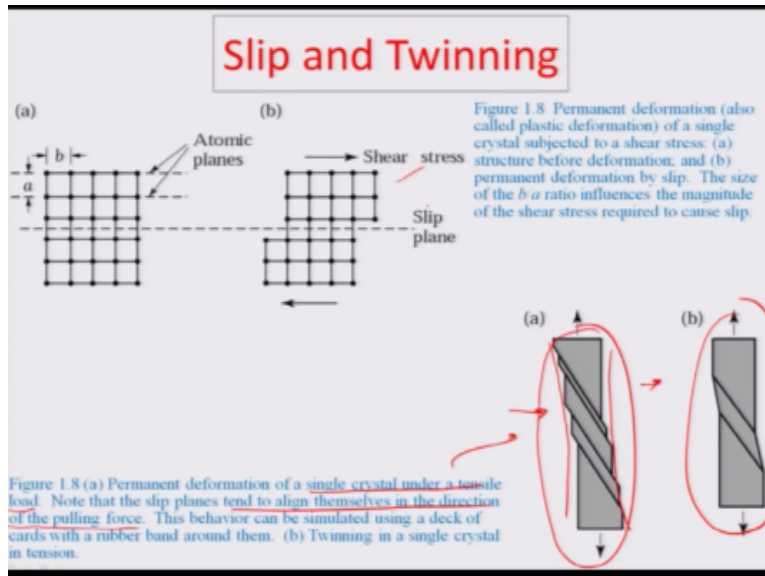
And one of the reasons is that when you doing a pre trust lattice and trying to sheer it or stress it obviously the dislocation are going to help you out ok to do that. So having said that let us see the third different kind of imperfection which extends over a surface, so imperfection is known as a surface defect for example you can see here the lattice was moving in this direction, and suddenly because of the stress to this letters as can be applied from, you can seen by this arrows here.

The plane has changed into an all together different direction. And so, basically these results in the formulation of these two parallel discontinuities between the regular direction of the crystal either way and these are known twin plains, and this imperfection is known as a surface defects. So the figure shows a common type of surface defects known as a twin which are normally produced when the metal is stressed at low temperature.

And you can see that the grain boundaries in a polycrystalline solid can be also considered as a sort of surface defects, because here is where there is discontinuity in the direction of the crystal ahead already I mentioned that the polycrystalline grain you have one direction in this particular manner, you crystal growing in this direction another direction may be, on another grain may be in different randomized direction.

And so, between those direction there are the discontinuities which exists which are called grain boundaries, so this grain boundaries are similar to the twin planes that is how you can probably an vision it.
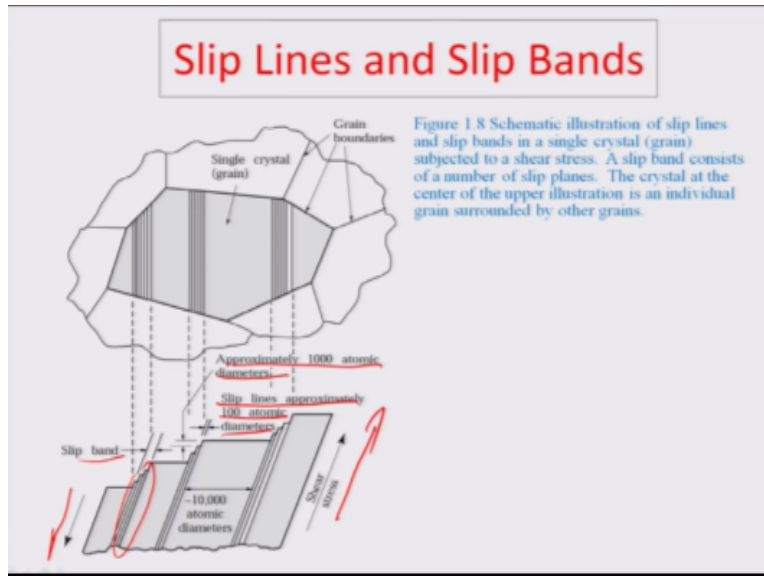
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Figure 1.8 Permanent deformation (also called plastic deformation) of a single crystal subjected to a shear stress: (a) structure before deformation; and (b) permanent deformation by slip. The size of the *b a* ratio influences the magnitude of the shear stress required to cause slip.

Figure 1.8 (a) Permanent deformation of a single crystal under a tensile load. Note that the slip planes tend to align themselves in the direction of the pulling force. This behavior can be simulated using a deck of cards with a rubber band around them. (b) Twinning in a single crystal in tension.

And know the difference that you can see from a external point of view that lets say a object is stressed longitudinally.

And so, the way that twinning would happen would be represented here, where permanent deformation of the single crystal under a tensile load acts or looks like this. The slip planes tent to align themselves in the direction of the pulling force, so that is generally a reduction in the cross sectional area, as you pull the specimen okay. So that is how you can envision that how twinning helps in sort of overall longitudinal extension process. Whereas, this is a pure shear stress from which the atomic plains are dislocated with respect to each other.

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Slip Lines and Slip Bands

Figure 1.8 Schematic illustration of slip lines and slip bands in a single crystal (grain) subjected to a shear stress. A slip band consists of a number of slip planes. The crystal at the center of the upper illustration is an individual grain surrounded by other grains.

So here we are talking about the formation of a slightly different zone with a different orientation of the crystal itself between those carded planes which would try to angularly try to shift like a pack of cards and try to reduce the cross section of the material as you can here right in the example. So that how slip and twinning can be defined. So in a general polycrystalline material you can have several of these slip, surface slips which are happening.

And you can see that here for example you have a band of such slips which are together so, these are all then different bands you can see how it has deformed in a particular direction, because of a shear stress which is applied to this crystal in two parallel, twenty parallel directions on both sides. And so, you can see that the sort of slip lines that are generated here are about 100 atomic diameters in our regular polycrystalline material.

And approximately the quantum of the slip in the shear direction that is happened is about 1000 atomic diameters. So that is how you can generate the slip lines and slip bands. So a sequence of such slip lines in a poly crystal, as you can see here is normally know as a slip band. So with this I would like to finish this module, and the next module you will see how numerically the values can be calculated with the keeping the whole crystal structure in view and then trying to pile dislocation to see what are the actual values.

And we will see what is quantum of the difference between the modulus of the rigidity may be as the presumptions shift to dislocation driven as supposed to be an polycrystalline. So I am going to do that topic in the next module as of now, good bye.

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