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Structure of Materials
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Lecture - 29
Defects in Crystals

After talking about surfaces in considerable detail now, we will take up the topic of interfaces.

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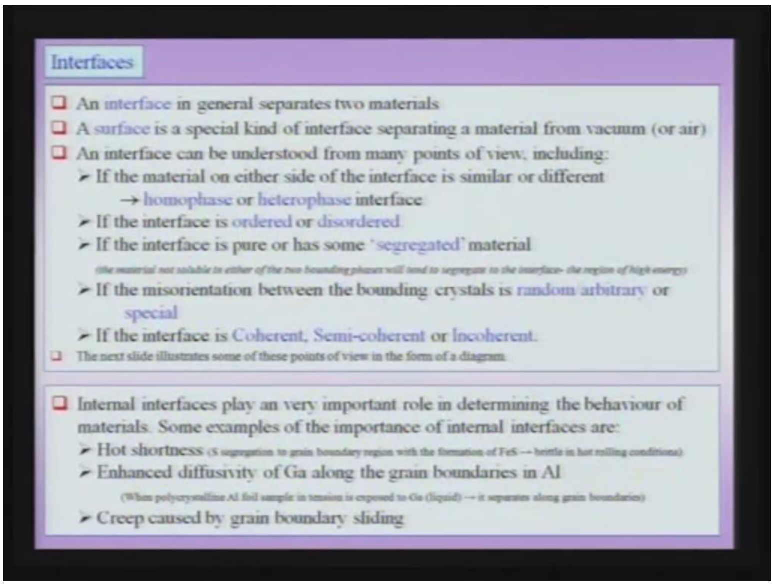

Interfaces

- ☐ An interface in general separates two materials
- ☐ A surface is a special kind of interface separating a material from vacuum (or air)
- ☐ An interface can be understood from many points of view, including:
  - ➢ If the material on either side of the interface is similar or different → homophase or heterophase interface
  - ➢ If the interface is ordered or disordered
  - ➢ If the interface is pure or has some 'segregated' material (the material not soluble in either of the two bounding phases will tend to segregate to the interface- the region of high energy)
  - ➢ If the misorientation between the bounding crystals is random arbitrary or special
  - ➢ If the interface is Coherent, Semi-coherent or Incoherent.
- ☐ The next slide illustrates some of these points of view in the form of a diagram

- ☐ Internal interfaces play an very important role in determining the behaviour of materials. Some examples of the importance of internal interfaces are:
  - ➢ Hot shortness (S segregation to grain boundary region with the formation of FeS → brittle in hot rolling conditions)
  - ➢ Enhanced diffusivity of Ga along the grain boundaries in Al (When polycrystalline Al foil sample in tension is exposed to Ga (liquid) → it separates along grain boundaries)
  - ➢ Creep caused by grain boundary sliding

Interface in general can be between a solid and a liquid solid and a vapours or between a solid. And a solid surface is nothing but a special case of an interface between a solid and or a liquid and the vapours face or the gas face interface in general separate 2 materials. And surfaces of various kinds can be understood as special cases of an interfaces, if you want to understand interface we can look at it. Through many points of view like if across an interface 2 materials are the same material or a different materials. In another word is it an homo phase interface or the hetro phase interface, we then talk about the interface in terms the order inside the interface. And now we are talking about the order in the interface and not in the crystals or the phase bounding the interface. So, interfaces can be ordered or disordered from this prospective additionally.

We could also talk about the purity of an interface that is if the interface has a material which is segregated from the bulk materials surrounding the interface. And typically it is we noticed that if a phase or a salute atom is not soluble in any of the grains or the phases separate around the interface then it will segregate to the interface. Then based on the orientation of the bounding crystals, we can talk about special or low angle interfaces or a very general kind of an interface which can be a our random mis-orientation between the 2 interfaces. We will also consider interfaces based on the terminology which is called coherent semi coherent or incoherent interfaces. So, this point will become clear when we actually take up a detail study of coherent semi coherent and incoherent interfaces. It should be noted the interfaces the once we are going to consider in this topic are going to be solid interfaces. We will not deal with liquid vapours or liquid liquid interfaces in this set of slides or in this set of topics and solid.

Solid interfaces play a very important role in determining the behavior of materials as can we highlighted some examples. Obviously, this is just illustrative examples are for example, we consider hot shortness in iron when we roll iron with some impurity of sulphur present. Then this sulphur can segregate to the grain boundary region and form the fes phase the iron sulphide phase of the grain boundary. And this can lead to what is known as brittleness during lot rolling conditions, because the fes can become a liquid phase. And the material will behave as if it is a brittle material because of the segregation. Therefore, we want to avoid sulphur impurity segregating to the interface and it is to be noted that this segregation is actually a very small quantities segregation. It is not in large amount sulphur need to be present before hot shortness is observed. Another nice striking example would be the diffusion of gallium along the grain boundaries of the aluminum if you hold an aluminum polycrystalline material as thin foil.

And you expose it to a gallium atmosphere by rubbing some gallium on it. Then this gallium would tend to diffuse very fast in along the grain boundaries and if this specimen is held in tension. Then this material would fail because gallium is liquid under room temperature of 50 60 degree Celsius. Creep is an very important phenomenon which leads to quite a bit of engineering failures at high temperatures. And grain boundary sliding is one of the important mechanisms by which creep takes place. And therefore, we can see that from these illustrative examples that interfaces play a very important role in a diverse variety of phenomena. And it as people heard of the relationship has a very important bearing coming from the grain boundary which we will study during this study on interfaces.

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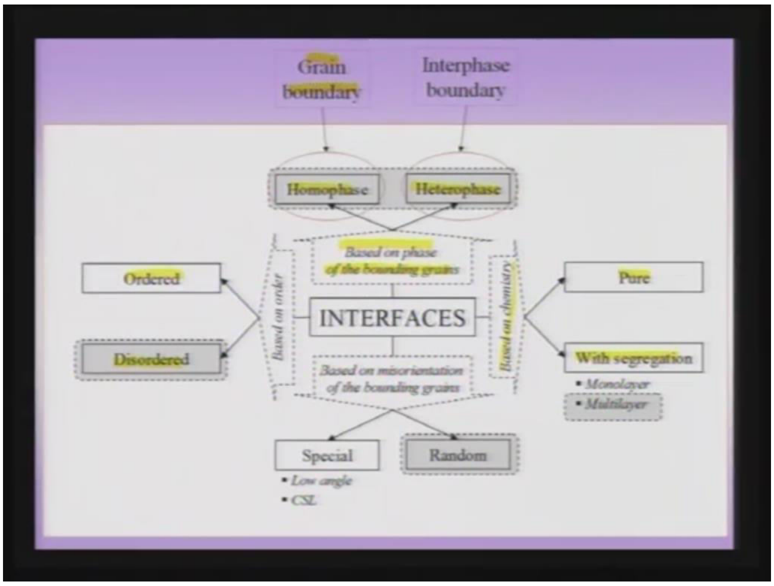

Grain boundary

Interphase boundary

Homophase

Heterophase

Based on phase of the bounding grains

Ordered

Disordered

Based on order

INTERFACES

Based on chemistry

Pure

With segregation

- Monolayer
- Multilayer

Based on misorientation of the bounding grains

Special

- Low angle
- CSL

Random

So, we had noted about various ways of classifying interfaces and we had said that based on order we can classify them as ordered or disordered based on the phase of the bounding grains. We can classify them as homophase or hetrophase interfaces. And the grain boundary being an homophase interface based on the chemistry we noted that an interface can be pure or can have a segregation. And this segregation can be a mono layer segregation or multi layer segregation based on the misorientation of the bounding grains or the bounding crystals. We can have special or random interface and special examples of special interfaces include low angle interfaces and coincidence lattice interfaces. Of course, this being an elementary course we shall not take up many of these concepts like coincidence lattices in this course.

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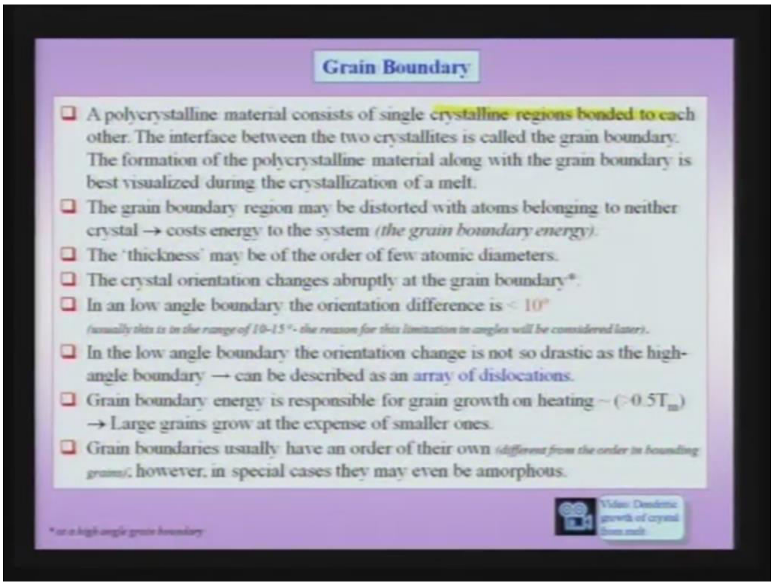

Grain Boundary

- A polycrystalline material consists of single crystalline regions bonded to each other. The interface between the two crystallites is called the grain boundary. The formation of the polycrystalline material along with the grain boundary is best visualized during the crystallization of a melt.
- The grain boundary region may be distorted with atoms belonging to neither crystal → costs energy to the system *(the grain boundary energy)*.
- The 'thickness' may be of the order of few atomic diameters.
- The crystal orientation changes abruptly at the grain boundary*.
- In an low angle boundary the orientation difference is < 10° *(usually this is in the range of 10-15° - the reason for this limitation in angles will be considered later)*.
- In the low angle boundary the orientation change is not so drastic as the high-angle boundary → can be described as an array of dislocations.
- Grain boundary energy is responsible for grain growth on heating ~ (>0.5T_m) → Large grains grow at the expense of smaller ones.
- Grain boundaries usually have an order of their own *(different from the order in bounding grains)*; however, in special cases they may even be amorphous.

*at a high angle grain boundary

Video: Dendritic growth of crystal from melt

Let us start our discussion of interfaces with the grain boundary typically if I take a piece of aluminum or a piece of wire of copper. It is a polycrystalline material this polycrystalline material has single crystalline region which is bound and bounded to one other. And the interface between this two crystallites is called grain boundary, typically a grain boundary is considered as two dimensional plain or two dimensional surface. But, of course, in reality the grain boundary region can extend a few atomic diameters into either of the bounding crystals. The best way of visualizing a formation of a grain boundary is by considering the crystallizing of a melt which we shall do now.

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Let us now consider solidification from a molten stearic acid and you can see that there is a nucleation of a crystal there are crystal which are forming in dentatic form. And when these two crystallite meet you can see that the region which were the crystalline touch would be a grain boundary. So, let us play this video again to understand how a grain boundary forms. So, these are crystallites which are growing in various regions of the melt and as pointed out a new crystallite is nucleating here and also growing in generatic fashion. And when two crystallites touch each other that region would be a region of the grain boundary atoms of the grain boundary belong to neither of the crystals. And it actually cause the system to put a grain boundary.

And therefore, grain boundary are associated with a energy which we can call the grain boundary energy. The thickness of a grain boundary can be of a odd of the few atomic diameters as I pointed out in ideal mathematical sense a grain boundary is considered as a two dimensional defect. But in general it can extend to a few atomic diameters on either side of the boundary at the grain boundary typically the orientation changes abruptly on one side. There is crystal which oriented in one way on the other side of the grain boundary there is crystal oriented different way. And therefore, the orientation changes abruptly at the grain boundary. And if you are talking about a very special class of the grain boundaries the low angle grain boundaries. Then the misorientation caused at the grain boundary may not be that abrupt.

And in fact, it will be more smaller misorientation difference across the grain boundary. And we will soon see that this low angle grain boundary have a further structure which can be understood in terms of an array of dislocations. The grain boundary energy is an important quantity and these, is responsible for the instance for the grain growth which takes place when you heat a material typically above about o.5 tm. And in during grain grow the larger grain grow at the expense of smaller grain. And you have at the end of grain grow process an average grain size which is larger than what you started with in principal you would note that grain boundaries are not having a different order then that either of the bounding grain. But, they can have an order of their own and hence grain boundaries are not amorphous. And we will see one example of how grain boundary could even be amorphous but, the important point to note in general they are not amorphous.

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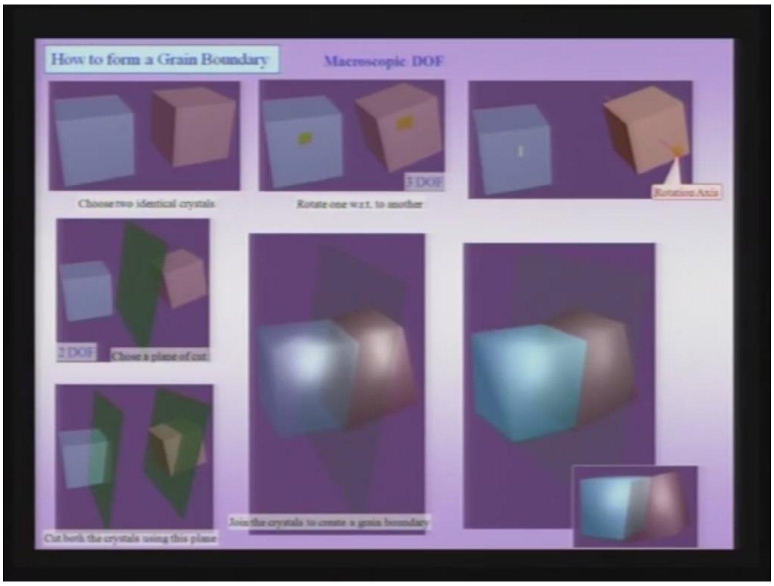

How to form a Grain Boundary

Macroscopic DOF

Let us next consider how can I form grain boundary and obviously to form a grain boundary I need 2 crystals of the same kind. And I can assume that one of these crystals is fixed crystal like the crystal in the blue color. And I can misorient as a first step the other crystal with respect to the first crystal I can do so by choosing a rotation axis. And in general these rotation axis is arbitrary. And then I can rotate one crystal with respect to the other and after doing. So, I can see that the 2 crystals are not oriented identically. And one crystal is misoriented with respect to other having done. So, then I need to chose a plain which can actually act like the grain boundary.

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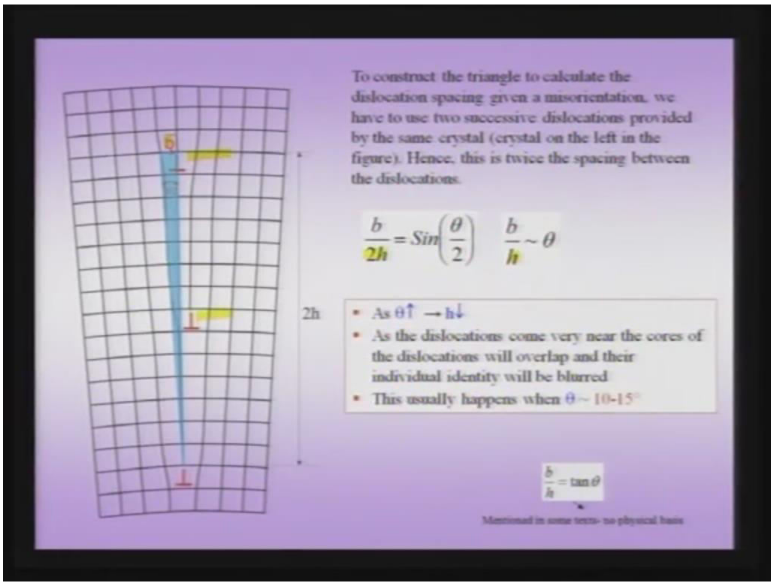

To construct the triangle to calculate the dislocation spacing given a misorientation, we have to use two successive dislocations provided by the same crystal (crystal on the left in the figure). Hence, this is twice the spacing between the dislocations.

$$\frac{b}{2h} = Sin\left(\frac{\theta}{2}\right) \qquad \frac{b}{h} \sim \theta$$

- As $\theta\uparrow \rightarrow h\downarrow$
- As the dislocations come very near the cores of the dislocations will overlap and their individual identity will be blurred
- This usually happens when $\theta \sim 10\text{-}15^\circ$

$$\frac{b}{h} = \tan\theta$$

Mentioned in some texts- no physical basis

Why in the grain boundaries can spontaneously form during the process known as polyganisation which takes place during the recovery of a cold work material. Therefore, they can have an important role in materials and as I pointed out they can spontaneously form during recovery process. So, let us summaries how this how we understand this dislocation along the grain boundary. So, we have a triangle here in which we have the burgers vector which is representative of strength of the dislocation. And depending on the burgers vector the plain the dislocation energy is returning now these dislocation noted spacing. We have noted keeps on decreasing as we increase the misorientation angle between two crystals. And at some point of time the individual independent existence of these dislocations is no longer or identification is no longer possible with increasing misorientation. And therefore, we land up with the scenario what is known as the high angle grain boundary. And depending on the when do we actually start saying high angle grain boundaries is determined as you can see from this equation.

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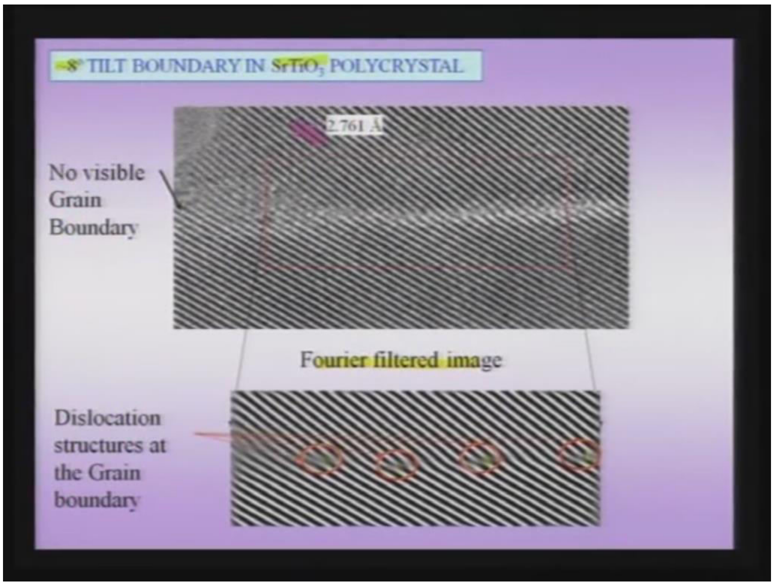

~8° TILT BOUNDARY IN SrTiO$_3$ POLYCRYSTAL

Now, this is a nice example of a low angle grain boundary though not a symmetric low angle grain boundary this material happens to be torsion tightening. And a misorientation angle between the 2 crystallites here or a 2 grains here is about 8 degrees. And the existence of this dislocations along the grain boundary you see in the image below which is nothing but a Fourier filtered image in which you can see that there are distinct dislocations which are present along the grain boundary. So, we can clearly see in high resolution lattice using an high resolution lattice range image which is been Fourier filtered that a low angle grain boundary consist of an array of dislocations.

Another important feature of this presence of these dislocations along a low angle grain boundaries and as pointed out by especially why does this arrangement of dislocations along to create low angle grain boundary take place during polygonization is that the compressive field of one dislocation. Cancel the tensile field of the other dislocation partially. And therefore, to such a boundary has no longer in stress field that is all the stress field is localized to only to grain boundary region unlike an isolated dislocation. And this is the motivation for a crystal to actually throughout such kind of low angle grain boundaries during a polygonization process.

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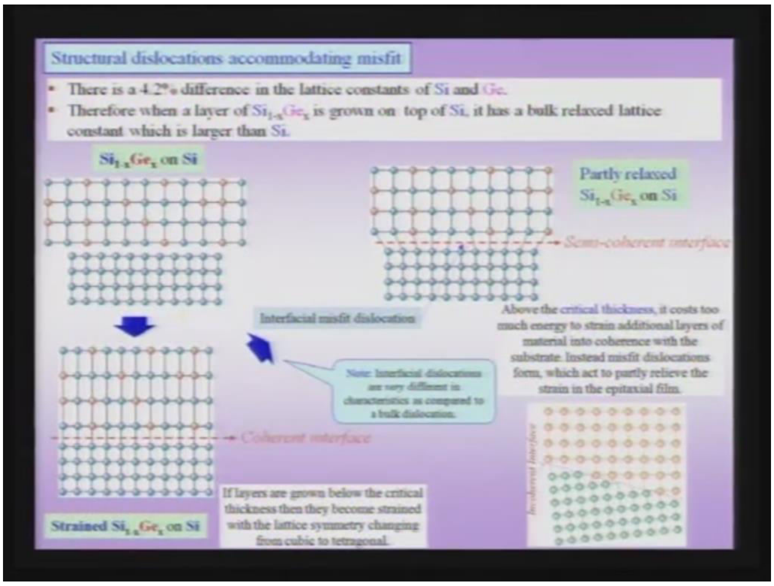

Structural dislocations accommodating misfit

- There is a 4.2% difference in the lattice constants of Si and Ge.
- Therefore when a layer of $Si_{1-x}Ge_x$ is grown on top of Si, it has a bulk relaxed lattice constant which is larger than Si.

Above the critical thickness, it costs too much energy to strain additional layers of material into coherence with the substrate. Instead misfit dislocations form, which act to partly relieve the strain in the epitaxial film.

Note: Interfacial dislocations are very different in characteristics as compared to a bulk dislocation.

If layers are grown below the critical thickness then they become strained with the lattice symmetry changing from cubic to tetragonal.

Now, let us consider how structural dislocation can accommodate linear midfield. So, let us consider a nice example for this which is the growth of silicon germanium to some composition. So, you can for example, consider silicon 50 percent germanium, 50 percent diamond cubic structure which is grown on a silicon substrate. So, this could be the silicon substrate and this could be the G s i alloy. And if you consider silicon it is got a four point two lattice parameter in midfield with germanium. And this alloy itself has a lattice parameter in midfield. Therefore, with these substrate which is silicon now when epitoxically grow such a film on the top of substrate. The film has a tetragonal distortion and is forced to grow when especially as a thin layer on top of the silicon such that the lattice plains are continuous here. So, you can see that in this schematic which is of course, an exploitative schematic that lattice plains are continuous. And such a boundary is called a coherent interface or a coherent boundary where in lattice plains are continuous. Therefore, here is the growth of gesi on the top of Silicon. And such an alloy grows epitoxically putting out a coherent interface.

But as a film grows thicker and thicker at some point of time or at some point of time or some thickness of film the energy stored at the interface or stored in the film becomes too much. And therefore, the interface breaks up into regions which are coherent or actually taking for the whole interface as a semi coherent interface. In other words a coherent interface becomes semi coherent by the presence of a midfield dislocation. And this dislocation as you can see age dislocation is accommodating linear midfield between the epitoxically film and the substrate. And again we have to note that these interfacial dislocation are very different in characteristics as compared to a bulk dislocation. As we have noted before in the case even in the normal material in the case of plasticity.

Therefore, you could have a coherent interface you could have a semi coherent interface between G s and S I where in there are interfacial midfield edge dislocation present which are partially reliving the strain between the film and the substrate. And you could also think of an interface which is totally incoherent that means there is no matching of plains between the two sides of the interface. And therefore, such an interface would be an incoherent interface. So therefore, based on the continuity or coherency we can have a coherent interface a semi coherent interface or a incoherent interface. And we can note clearly here that this dislocation here is slightly different from the grain boundary dislocation. Because the material above the dislocation and the material below the dislocation slip plain is are different.

Therefore, these are hetro hepitoxial systems that is the materials above and below the interface are different to summaries this slide. Therefore, there are structural dislocations which can accommodate linear misfate. And such this locations are like the low angle grain boundary dislocations localized the interface. And here they are performing the role of partly reliving the stresses which are caused because of the lattice mismatch between the g s i alloy and the silicon substrate. And based on coherency you can have coherent interfaces and semi coherent interfaces which have dislocations decorating the interface and in generally of course, an incoherent interface.

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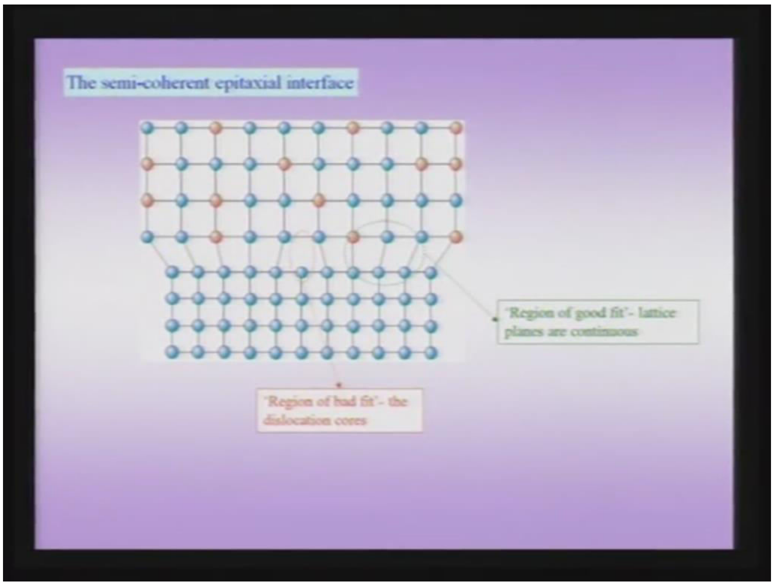

The semi-coherent epitaxial interface

'Region of good fit'- lattice planes are continuous

'Region of bad fit'- the dislocation cores

So, the semi coherent interface like in the case of a low angle grain boundary can be thought of a regions where in you have a dislocation and regions which are regions of good misfate or good fate which are separated by these dislocations. So, we can have a picture where in there are plains which are continuous from the substrate to the film like here. And there are regions where are where in there are dislocation course.

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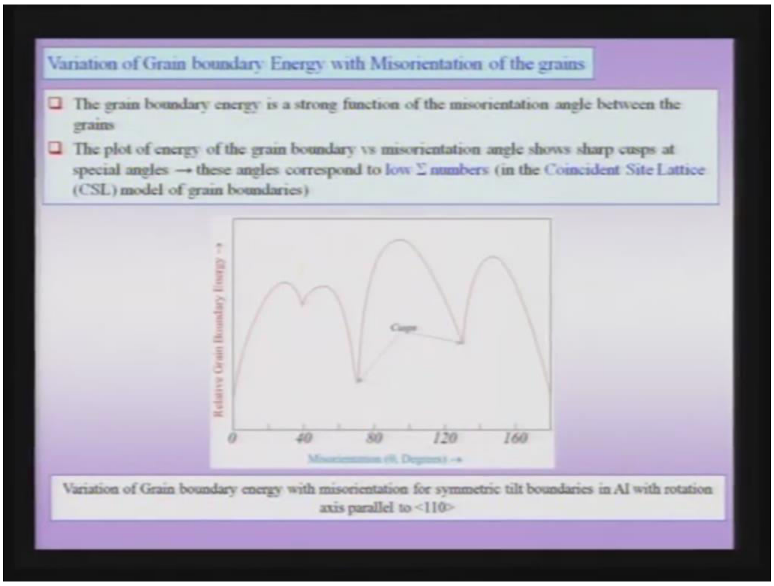

Variation of Grain boundary Energy with Misorientation of the grains

- ☐ The grain boundary energy is a strong function of the misorientation angle between the grains
- ☐ The plot of energy of the grain boundary vs misorientation angle shows sharp cusps at special angles → these angles correspond to low Σ numbers (in the Coincident Site Lattice (CSL) model of grain boundaries)

Variation of Grain boundary energy with misorientation for symmetric tilt boundaries in Al with rotation axis parallel to <110>

The grain boundary energy is a function of the misorientation between the 2 crystals. Of course, suppose you are choosing the misorientation angle axis like an tilt boundary to be a safe for an instance the 1 1 0 axis none you would if you had to plot the misorientation angle which is theta n on the x-axis with the grain boundary energy which is the y-axis. You typically you may end up getting a plot which looks like this the important feature of this plot is that for low angle boundaries the energy is small. And we had noticed that this low angle region is the region where in you can consider the grain boundary to be an array of dislocations. Then for normal angle grain boundaries you would notice that the energy is pretty high. But between this high energy mis-orientations there are cuts in the grain boundary verses the mis-orientation plot that there are some special boundaries which have a low energy. Typically such kind of boundaries or eyes when you have some a concept known as coincidence side lattice model of grain boundaries this being a elementary course.

We are not going in to the detail of what is a coincidence side lattice or how this coincidence side lattice is going to give rise to low energy. But this is important to note that the like we had noted for the case of the low angle grain boundary that the increasing mis-orientation. The energy of the boundary is going to change so, it is true for even for angle grain boundaries. But the variations is not a monotonic function in other words the variation in energy of the system as a function of the grain boundary mis-orientation. And could show a function which looks like the plot shown here which could have curves which correspond to special boundaries. So, we could in general classified 2 kinds of special boundaries those having which corresponds to this curves and those having low angle. Therefore, we can have low angle grain boundaries which as special boundaries. And those high angle grain boundaries which could also have relatively lower energy which we can which can then corresponded to something known as coincidence side lattice concept. But as we noted this grain boundary energy is a very important quantity in the behavior of the material. Because now this is going to determine how much segregation going to occur or how much of for instance grain growth or how fast the grain growth occur during an annealing or high temperature hold process?

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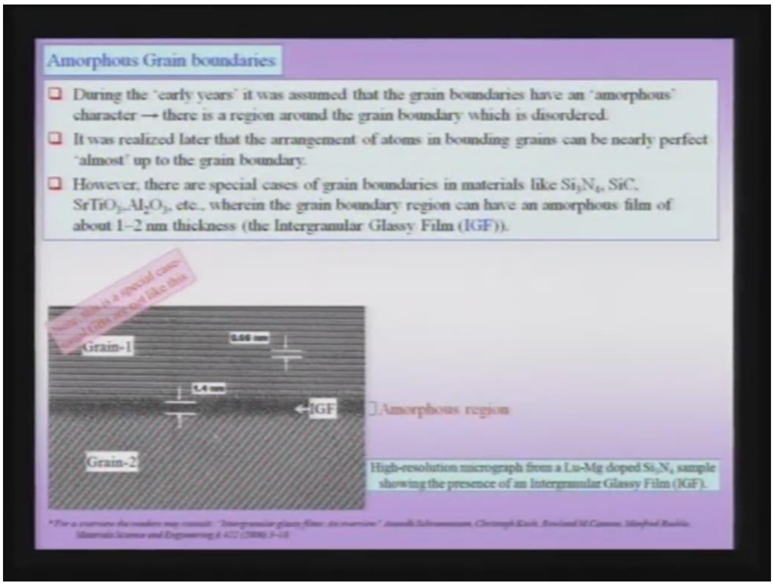

Amorphous Grain boundaries

- ☐ During the 'early years' it was assumed that the grain boundaries have an 'amorphous' character → there is a region around the grain boundary which is disordered.
- ☐ It was realized later that the arrangement of atoms in bounding grains can be nearly perfect 'almost' up to the grain boundary.
- ☐ However, there are special cases of grain boundaries in materials like Si_3N_4, SiC, $SrTiO_3$, Al_2O_3, etc., wherein the grain boundary region can have an amorphous film of about 1–2 nm thickness (the Intergranular Glassy Film (IGF)).

High-resolution micrograph from a Lu-Mg doped Si_3N_4 sample showing the presence of an Intergranular Glassy Film (IGF).

As I pointed out before, suppose you had to talk to ah material scientist in the early days that is much before some of the models of these grain boundaries worse a mental picture which is often carried by many people is that the grain boundary is a region of disorder. And we have as we have noted by looking at some other grain boundaries so far that often it is not true and often there could be an order in the grain boundary. Of course, this order could be very different from the order present in the bulk of the crystal. But there are special cases wherein you would find actually that the grain boundary region is actually totally amorphous or it is classy. And such an example is shown in the high resolution lattice image which is in the micrograph as below.

So, this micrograph below shows a grain boundary in silicon nitrate between two this grain there is a grain one of silicon nitrate above. And there is a grain two of silicon nitrate below and there are there there fringes corresponds to lattice plain in this two crystallites. But, the important thing to focus here is the grain boundary region. And you would notice that the grain boundary region is glassy or amorphous so even amorphous region at the grain boundary. But it is to be noted this it occurs in very special cases as in this case this is silicon grain boundary in silicon nitrate. Such kind of amorphous grain boundaries can also found in other special system like silicon carbide tension tightening and alumina. But if you take a general grain boundary in aluminum or copper you would not typically find these kind of amorphous grain boundary.

And to summaries this slide though most grain boundaries can have a very good order in them. There are possibilities of having grain boundaries which have an disordered and amorphous layer. And these examples can be found for instance in silicon nitrate or tension tightening where in you have a thin layer. Of course, this layer is of the order of a nano meter or 1 to 2 nano meters which is an amorphous region. And the grain boundary region itself is totally amorphous or not does not have crystalline order as in the side of the crystal.

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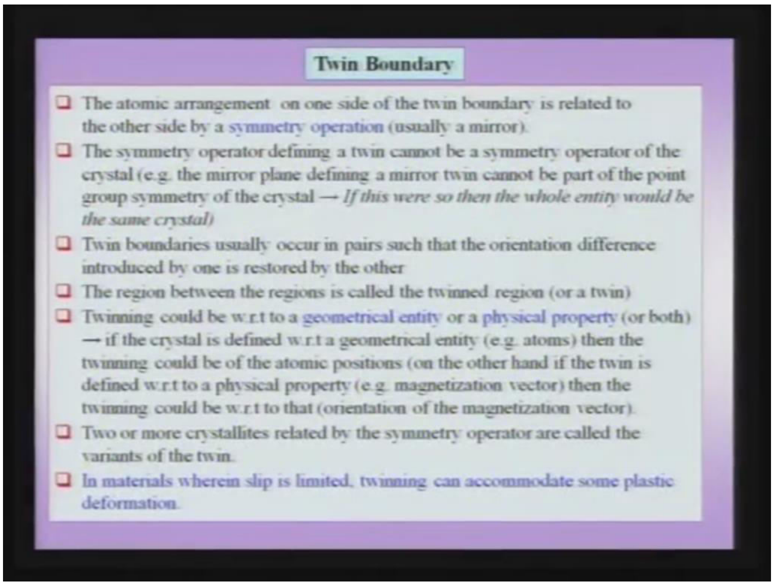

Twin Boundary

- ☐ The atomic arrangement on one side of the twin boundary is related to the other side by a symmetry operation (usually a mirror).
- ☐ The symmetry operator defining a twin cannot be a symmetry operator of the crystal (e.g. the mirror plane defining a mirror twin cannot be part of the point group symmetry of the crystal → *If this were so then the whole entity would be the same crystal)*
- ☐ Twin boundaries usually occur in pairs such that the orientation difference introduced by one is restored by the other
- ☐ The region between the regions is called the twinned region (or a twin)
- ☐ Twinning could be w.r.t to a geometrical entity or a physical property (or both) → if the crystal is defined w.r.t a geometrical entity (e.g. atoms) then the twinning could be of the atomic positions (on the other hand if the twin is defined w.r.t to a physical property (e.g. magnetization vector) then the twinning could be w.r.t to that (orientation of the magnetization vector).
- ☐ Two or more crystallites related by the symmetry operator are called the variants of the twin.
- ☐ In materials wherein slip is limited, twinning can accommodate some plastic deformation.

The next two dimensional interface, we consider is a twin boundary. The twin boundary is a very special kind of a boundary which is in wherein some sense very regular kind of a boundary as compared to any other defects in the material. Or any other two dimensional defects in a material the atomic arrangement on one side of the twin boundary is related to other side by a symmetry operation this symmetry operation is typically in mirror. And therefore, you have something known as mirror twin boundary or the mirror twin. But in addition you can also have inversion twin and rotational twins So, we will take up one example at least of a mirror twin and also of a rotational twin during the course of these lectures. It is obvious that the symmetry operator defining the twin itself cannot be a symmetry operator of the crystal. Because if it is a symmetry operator of the crystal the crystal actually will continue across a interface. And therefore, we will have no distinct boundary.

And therefore, we can have no twin that means the symmetry operator for instance some mirror cannot be a mirror plain of the crystal that means it is not one of the existing symmetry operators of the crystal. And it has to the mirror plain has to be different from the symmetry operator of the crystal it is been often noted. And we will see this using a micrograph the twin boundary typically occurs in pairs and the orientation difference created by one twin boundary is restored by the other the region between the twin boundaries is called the twin region or a twin. Therefore, you have a twin and the bounding surface of the twin are called twin boundaries. We have earlier noted when defining a crystal that a crystal can be defined with respect to a geometrical entity a physical property or a combination of both.

Therefore when we are talking about twin which is now again a concept of invokes symmetry therefore, like the crystal Therefore, you could have a twin boundary a mirror twin for example, which could be reflecting physical property or which could be reflecting atomic position. Therefore, you could have a twin boundary which is with respect to a geometrical entity or a physical property or a very special cases. We can even visualize a twin boundary which is with respect to both geometrical entity and the physical property. Now, two or more crystallites related by symmetry operator are called variants of the twin. Now, the importance of twinning becomes very very obvious especially when we are talking about plastic deformation or permanent deformation. We have noted that one of the most important vehicles of the plastic deformation is the dissolution. But there could be systems wherein a plasticity by slip or by motion dislocation is limited.

This could be for instance bcc crystal of low temperature and such materials twinning becomes an important mechanism by which plastic deformation or permanent deformation is achieved. Therefore, twinning is not only an important structural defect from the point of view of its association in symmetry. But it can play an important role in plastic deformation especially in systems wherein slip is limited or wherein the strain rates are very high. Therefore, materials wherein slip is limited twinning can accommodate some amount of plastic deformation to summaries this slid once more a twin can be with respect to a geometrical entity or a physical property. And one side of the twin boundary is related to other side of the twin boundary by a symmetry operation which is not the symmetry operation of the crystal. And this symmetry operation could be typically a mirror but, it could also be an inversion or a rotation.

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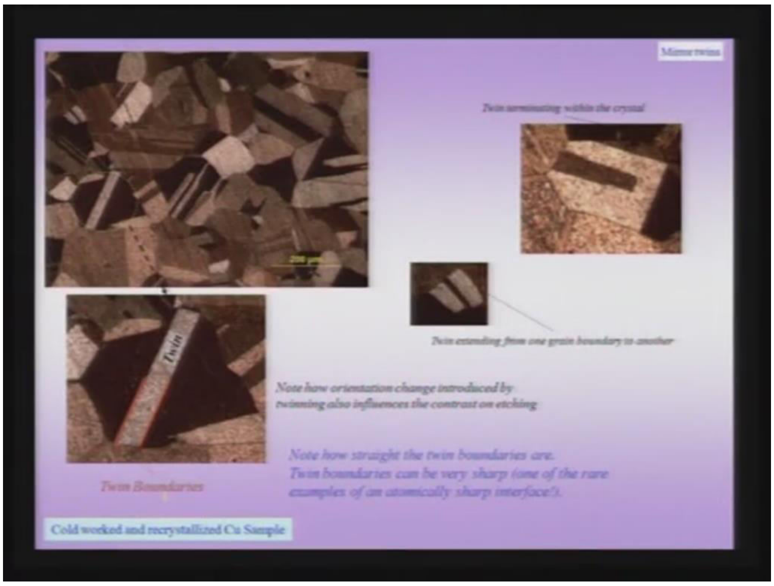

Mirror twins

Twin terminating within the crystal

Twin extending from one grain boundary to another

Note how orientation change introduced by twinning also influences the contrast on etching

Note how straight the twin boundaries are.
Twin boundaries can be very sharp (one of the rare examples of an atomically sharp interface!).

Twin Boundaries

Cold worked and recrystallized Cu Sample

So, let us first jump and see an actual micrograph wherein we have some twins. Therefore for instance this region within the crystal so this is a grain which you can see here let me so this is my grain here. And within this grain you can clearly see there are two boundaries the region between these two boundaries is a twin boundary. And since these are two dimensional interfaces this plain actually extends in to the slide. So, you tweet have two twin boundaries one introduces misorientation which is canceled by other the other. And the region between the two twin boundaries is the twin we are talking about is this is the sample which is nothing but cold work and crystallize copper wherein you can see there are lot of twins in the structure the.

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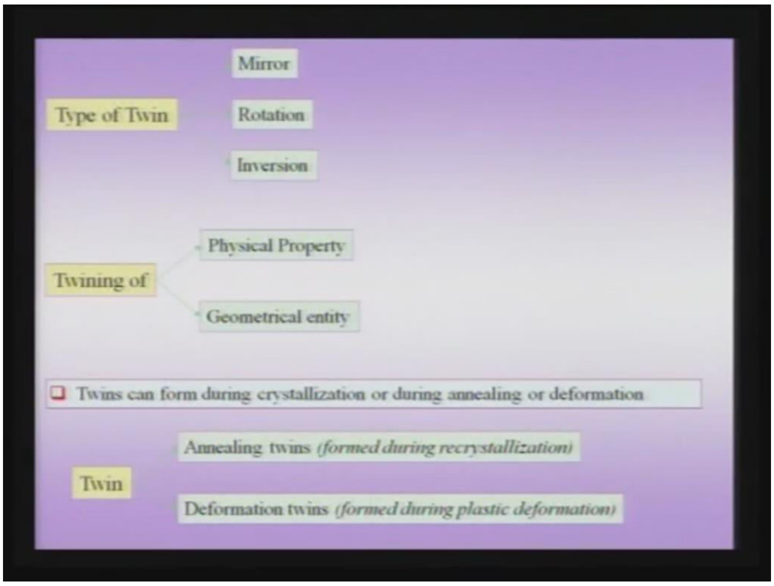

Type of Twin

- Mirror
- Rotation
- Inversion

Twining of

- Physical Property
- Geometrical entity

❑ Twins can form during crystallization or during annealing or deformation

Twin

- Annealing twins *(formed during recrystallization)*
- Deformation twins *(formed during plastic deformation)*

So, let us go back and try to understand that what kind of twins are possible. And as we have pointed out before twins can be mirror twins rotational twins or inversion twins. Twining can be with respect to physical property or a geometrical entity additionally by the process by which twins are created also twining can be classified. Twins can be created during annealing like we had seen in the case below of a cold work copper. But twins also can be created by deformation which I stole by the twins which accommodates plasticity. Therefore, you can have annealing twins which are created during re-crystallization or you can have deformation twins which are created during plastic deformation of a material.

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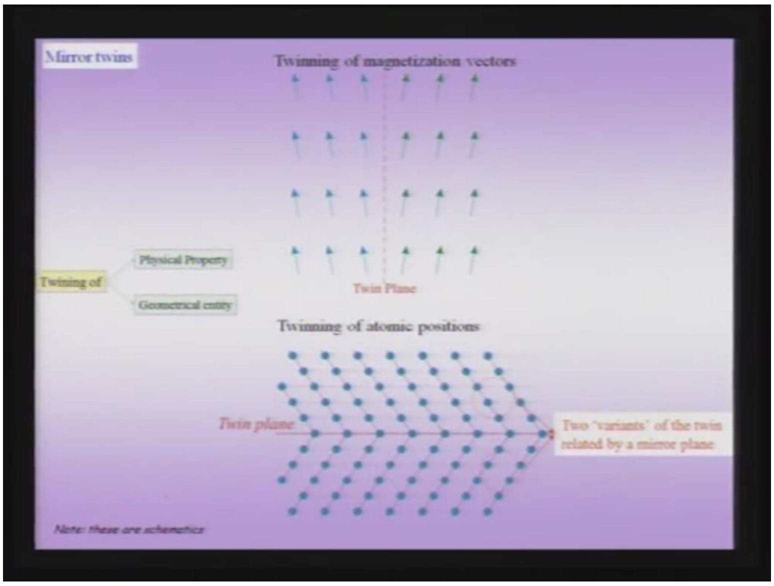

Mirror twins

Twining of

Physical Property

Geometrical entity

Twinning of magnetization vectors

Twin Plane

Twinning of atomic positions

Twin plane

Two 'variants' of the twin related by a mirror plane

Note: these are schematics

Typically twins are observed or twining is more observed in a material wherein the staking fault energy is small. And we will soon see why that criteria is important for instance I was pointing out that actually you can have a mirror twin wherein a physical property could be reflected for instance this is my twin plain or mirror plain. And this is the crud schematic showing how a physical property like a magnetization vector can be reflect across a interface. But, more commonly we are talking about twins wherein you have a geometrical entity like a atomic position which is reflected. And therefore, you can see an image below wherein you can see that these is a twin plain which passes through the middle. And the atoms across the plain are reflected by this mirror plain before if you have atom here you would have an atom corresponding to that which is reflected in the atomic plain mirror; you have an atom here and atom here.

Therefore, you can see atomic plains are also reflected by this mirror. So, this is a twin plain and these two are the two variants of twin which we have talk about one of the important things which we are stark striking when you look at a boundary like this is that unlike the grain boundary we saw is curling. And going across the material in a very random fashion the twin boundaries are very straight and sharp. In fact the straight fact can easily be seen from an optical micrograph as here but, the to notice actually that the atomically sharp you need to go an high resolution lattice range image with a atomic resolution. But you would notice that that if you took such an image that the twin boundary is atomically sharp. So, this is one of the rare examples of a boundary which is not only straight. But also atomically sharp so unlike the grain boundary which could have a certain region around it which could even as we saw in the extern example be amorphous. And typical grain boundaries are not straight the twin boundary are a very special kind of a boundary which can be atomically sharp and actually can be very very straight.

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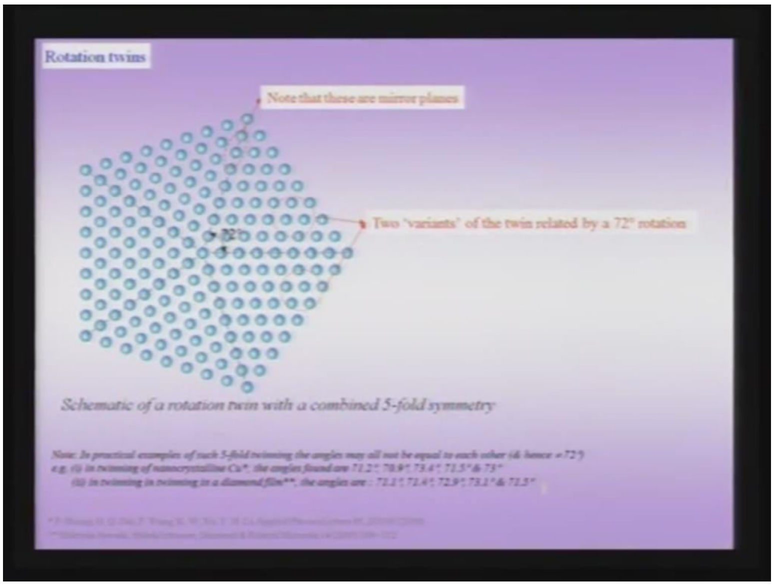

Rotation twins

Note that these are mirror planes

Two 'variants' of the twin related by a 72° rotation

Schematic of a rotation twin with a combined 5-fold symmetry

Note: In practical examples of such 5-fold twinning the angles may all not be equal to each other (& hence ≠72°)
e.g. (i) in twinning of nanocrystalline Cu*, the angles found are 71.2°, 70.9°, 73.4°, 71.5° & 73°
(ii) in twinning in twinning in a diamond film**, the angles are : 71.1°, 71.4°, 72.9°, 73.1° & 71.5°

As I told you that twins can be created by other symmetry operations like the rotation. And in this figure we see that how a rotation is created in this rotational twin we have five variants. So, we can label these 5 numbers these 5 variants as the first variant the second variant; the third variant; the fourth variant and the fifth variant. Therefore, there are 5 variants and if you think of rotation axis which passes through the center of this figure. Then you can think of one crystal rotated with respect to other crystal And the rotation is approximately 72 degrees. If you actually in real crystals you will find that the an studies have been done on nano crystalline copper or twining in diamond films the angle is close to 72 degrees. But, rarely at exactly at 72 degrees but the important thing to note that actually you can see that one crystal is rotated with respect to the other crystal.

And this rotation is carried forwarded 5 times to create the 5 variants which of the 5 variants of the crystal. And if one have to take what is known as the selected area the fraction pattern from a region around the center. You will actually observe fivefold symmetry it is as if distinct variant mimics an higher symmetry. Because the crystal itself does not have five fold symmetry. But the combination of this five variants of the twin can mimic an higher symmetry which in this case can be a fivefold symmetry. Therefore, you can have reflection twins as in the example we consider before wherein there is a mirror plain. And there is reflection of atomic position but in addition to that we can also have a rotation twin wherein one variant is rotated with respect to other by a rotation operation. And as before that rotation operation should not be inherent to the crystallite otherwise we will land up with the single crystal and not with 5 variants.

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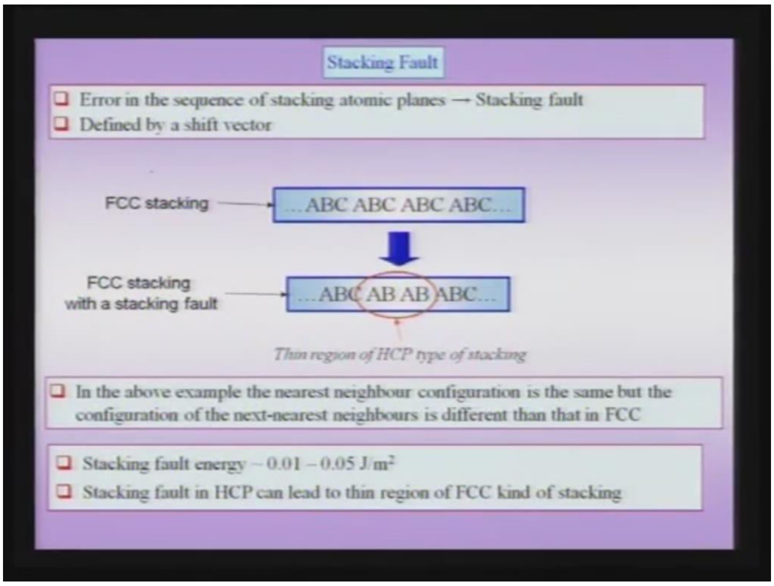

Stacking Fault

- ☐ Error in the sequence of stacking atomic planes → Stacking fault
- ☐ Defined by a shift vector

FCC stacking → ...ABC ABC ABC ABC...

FCC stacking with a stacking fault → ...ABC AB AB ABC...

Thin region of HCP type of stacking

- ☐ In the above example the nearest neighbour configuration is the same but the configuration of the next-nearest neighbours is different than that in FCC

- ☐ Stacking fault energy – 0.01 – 0.05 J/m^2
- ☐ Stacking fault in HCP can lead to thin region of FCC kind of stacking

Next, we come to another class of defects which is known as the stacking fault we had noted before that how we can understand the structure of a the cubic close pack structure. And hexagonal close pack structure as a stacking of a hexagonal plains which finally, leads to what we may call the close packing or the closest packing which is about 74 percent atomic packing fraction now it would be so that in an. And we have noted that for instance in an F C C or a cubic close pack crystal the stacking sequence is A B C A B C A B C A B C. And for an similarly, for an F C C crystal it will be A B a b A B it could so happen that during crystal grow there could be actually a defect introduced when the stacking sequence is disturbed for whatever reason. Now, for instance you have perfect crystal which is A B C A B C A B C A B C and obviously that stacking direction being the one; one direction of the cubic close pack crystal.

So, it could so happen when we are talking about a defected crystal that you have A B C A B C packing. But suddenly some region there is an A B a b packing this is created if an layer which originally had to be a C layer shifted in such a way that it now behaves like ca layer. Therefore, you have a region in the crystal or in this which looks like an H C P local therefore, the packing sequence of A B C A B C is disturbed. And there is one layer in between which originally should have been C layer, but shifted with respect to the its original expected position therefore, it sitting in a position. Therefore, can be called as a a layer therefore, locally you have a region which is A B A B packing which is like an H C p packing this fault in stacking is called as stacking fault. And is often found in materials which have low stacking fault energy like for instance in the important point to note when you are talking about stacking faults is that the region. The second nearest neighbors are not distributed it is the nearest neighbors which are distributed.

Therefore, in the materials wherein the interactions of second order are not that strong it is more observed that you will actually produce a stacking fault. This is very similar in some sense to the twining which we are considered that actually its nearest neighbors are perfectly ordered. So, these nearest neighbors these nearest neighbors are perfectly ordered. So, it is only the next nearest neighbor the one which is we are to go one further. So, if I have to label this atoms this 1 2 3 then 1 and 2 are as expected. But 1 and 3 are not as expected if 3 wherein the right position with respect to this crystal one. Then it should have actually continued and it should have been expected to be here, but it is not there. Therefore, you have a shift that means that the second nearest neighbors coordination has been affected which is very similar to the case of the stacking fault wherein again the second nearest neighbors coordinates is affected. So, materials wherein the second nearest neighbor coordination is not contributing to much to the energy. You can have a stacking fault energy and typically stacking fault energies coming the values of 0.1 to 0.5 Joules per meter square.

And if you were here talking about stacking fault in an cubic close pack crystal leading to a small region which is similar to H C P crystal. The converse is true for when you talking about stacking fault in an H C P crystal in which case the stacking fault in an H C P crystal can lead to an thin region which is having a packing you would except for a cubic close pack crystal. Now, if you are talking about a crystal, wherein you are expecting a thin region which is of H C P type, these two this regions can be thought of as bound by 2 partial dislocations in an S V crystal. And we have noted before that these are called sharply partial dislocations to summaries stacking fault is a two dimensional defect which can be thought of as a fault in the stacking sequence in a close pack crystal.

So, if you would have an A B C A B C A B C A B C sequence which would give you a perfect cubic close back crystal when you are looking along the one one direction. Now, if you had region wherein the expected C position is shifted and you have a position. Then you have region which looks like a H C P crystal. And this H C P region can be thought of as a bounded by two partial dislocations which are known as the partial dislocations. And such an material in which you have often find stacking faults are materials wherein you have low stacking fault energy which is nothing but the second order interactions being weak as compared to the first order interactions. So, a stacking fault in a cubic close pack crystal is a small region which looks like a H C P crystal and vice versa that in an H C P crystal. You can think of a stacking fault being a region wherein you have a cubic close pack of an occurrence.

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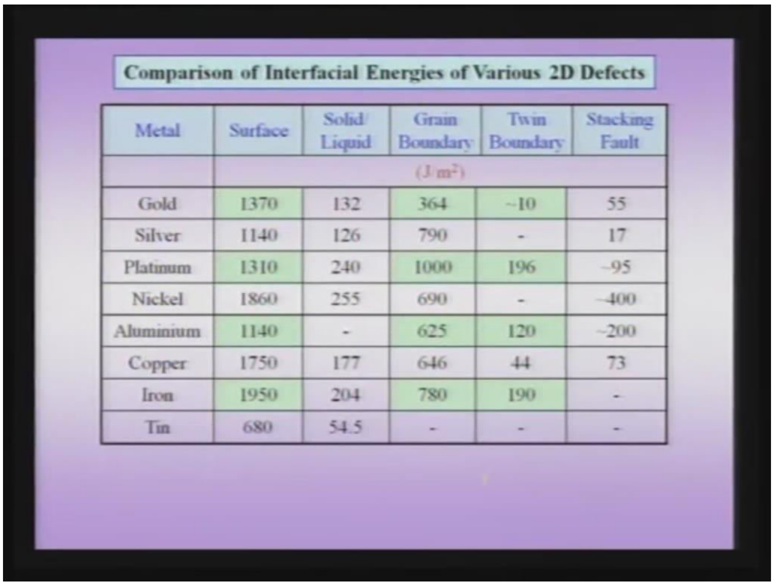

Comparison of Interfacial Energies of Various 2D Defects

Metal	Surface	Solid/ Liquid	Grain Boundary	Twin Boundary	Stacking Fault
	(J/m^2)				
Gold	1370	132	364	~10	55
Silver	1140	126	790	-	17
Platinum	1310	240	1000	196	~95
Nickel	1860	255	690	-	~400
Aluminium	1140	-	625	120	~200
Copper	1750	177	646	44	73
Iron	1950	204	780	190	-
Tin	680	54.5	-	-	-

Now, we have talked about various defects for instance we have talked about the surface we have talked about the green boundary; we have talked about the win boundary. And finally, now we talked about the stacking faults which we all considered to be two dimensional defects. And we were very clear that we were talking about two dimensional defects. We said that even though it is not ii is not geometrical two dimensional that it is not localized to just a plain but, often they disturbances. And the affect of the interface is could be a few atomic diameters especially for the grain boundary. But, in some cases it could be very atomically sharp. And the disturbances are very localized to the interfaces like in the case of the twin boundary. But an important exercise is to see the comparity or the relative energies of all these boundaries and it is clear. And the once which are highlighted for these we have list it which we have certain F C C crystals and also a B C C crystals. You know that typically the surface energy is the highest, because you are actually cutting all the bonds above the plain.

And therefore, it costing lot of energy to the surface to create the surface. And we are again to reiterate the energy we are talking about are with respect to the perfect crystal their positive energies. And not with respect to their isolated atoms that means they, they might be lower in energies as compared to isolated atoms. But the state of energy of an surface or any of the interface is higher with respect to the perfect crystal a grain boundary. On the other hand we have noted is that for instance an M F C crystal the co-ordination number around the grain boundary will not be 12, it will be smaller. And therefore, it has an higher energy but definitely a lower energy as compared to the surface energy. And you can note for that for instance it is about 1370 Joules per meter square to put a square. It is about 360 Joules per meter square to put a grain boundary and a twin boundary energy and like the stacking fault energy are smaller values compared to the grain boundary of the surface energy. And this trend can be repeatedly seen here the surface energy is high for platinum grain boundary energy is somewhere intermediate while the twin boundary is lower in energy for aluminum again the surface energy is very high.

And the grain boundary energy is somewhere intermediate while the twin boundary is small when you are looking at stacking fault energies if you compare for instance copper and an. Aluminum you will notice that aluminum has high stacking fault energy while copper has a low stacking fault energy. In other words if you want to use a different language in aluminum regular dislocations has find will find it difficult to split in to a sharkly partials Because if splits in to sharkly partials it will produces a stacking fault and it causes lot of energy to put a stacking faults. Therefore, in aluminum perfect dislocations will tend to remain perfect dislocations. And would not tend to split into sharkly partials while in a material like copper you would find that there is higher density of stacking faults and full dislocations would tend to split in to partial dislocations. Therefore, to summarize the concept of 2 d effects and to compare their energies lets go back to the starting point of these interfaces.

We talked about the most general word is an interface can connect any kind of 2 materials. It can be between gas and a solid it could be between a solid and a solid or it could be between liquid and a solid. But the most important one we are concern for now in this set of lectures in the structure materials lecture is the one between 2 solids surface is the one we are considered before is between a gas or vacuum and a solid. So the interface we are talking about here are typically between 2 solids, we are noted that we can actually classify interfaces based on many methods.

It could based on the bonding order based on the orientation of the grains or the mis-orientation between the 2 sides of the interface it could be based on chemistry. Or could be based on the kind of the phase which is present around the interface the most important of the plot is the grain boundary. And we are noted like all the other interfaces that the grain boundary is associated with the energy which is responsible for many physical phenomenon including segregation and grain growth. And we have to note that we are also noted how to create a grain boundary by macroscopic method like mis-orientation cuts. And also how work at the unit cell to actually make the grain boundary or shift one crystal with respect to the other and therefore, at the unit cell level.

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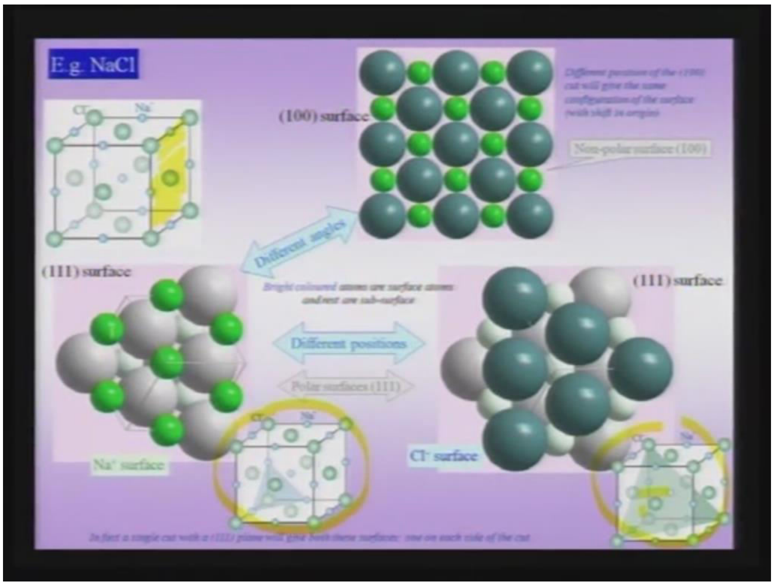

E.g. NaCl

Different position of the (100) cut will give the same configuration of the surface (with shift in origin)

Bright coloured atoms are surface atoms and rest are sub-surface

In fact a single cut with a (111) plane will give both these surfaces: one on each side of the cut

We are worried about actual atoms which are going to sit at the surface for instance in a sodium chloride. You could have a polar surface which has only for instance chlorine atoms or sodium atoms. And similarly, in an ordered structure you could have a surface which is of one kind of an atom on other kind of an atom.

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Type of boundary	Energy (J/m^2)
Grain boundary between BCC crystals	0.89
Grain boundary between FCC crystals	0.85
Interface between BCC and FCC crystals	0.63

Grain boundaries in $SrTiO_3$

So, we have noted that typically grain boundaries could be do not straight they are you know curving. But in special cases you could also have straight grain boundaries. And we noted that very special cases of grain boundaries are what are called the low angle grain boundaries which can be thought of as an array of dislocations like in the case here. And we noted that these low angle grain boundaries have no long range stress fields unlike a single dislocation. And as a mis-orientation angle increases the spacing between the dislocations tends to decrease they tend to go towards each other.

Further we had noted that these there is a other class of a interface wherein you have to invoke the concept of the structural dislocations which is the case of an hetro hepitoxial interface which becomes for instance during the hepitoxial growth. You have these semi coherent interfaces coherent interface becoming semi coherent interfaces with the formation of the misfield segment of a dislocation which is as you pointed out a very different kind of dislocation as compared to the statistically stored dislocation. And the reason that this strategy work is that the crystal is now split into regions. Which are having good field and the regions, which have bad field, which are along the porous of the dislocation? But also noted that the grain boundary energy is not a constant it depends on the mis-orientation angle and the mis-orientation verses energy when actually is not a monotonic function. And actually can have can be a very sharply varying function with curves we noted that these curves like low angle grain boundary corresponds are a special boundaries.

And they are treated separately you also noted another class of a special boundary which we call the amorphous boundary which is call only in the selected systems. So, another if I take a grain boundary in copper or take a grain boundary in some of the materials like titanium or some of the alloys or nail ordered structure. You would not find any glassy fill along the grain boundary. Because the grain boundary would be actually pretty order. But in this very special materials you can actually have an region of the grain boundary which is amorphous or glassy. We also talked about the twin boundary and the important thing we said about the twin boundary is that there are 2 variants of a twin which are connected by a symmetry operation which is not an inherent symmetry operation of either of the crystal. And we can have twins which are mirror twins rotation twins and inversion twins.

And we would also noted that twining can also play an important role in plasticity especially in materials wherein plasticity by slip is severally limited. Therefore, we can have annealing twins which are produced during re-crystallization or we can have twins, which is produced during plastic deformation. So, this was the typical example of annealing twin produced in re-crystalized copper, we could also we also saw an example of an rotation twin. And we had noted that a rotation twin can mimic an higher symmetry which is not present in the individual variant finally, we had considered stacking fault. And we noted that the stacking fault energy is typical lower than the for instance the surface energy of the grain boundary energy. And we had noted that stacking fault is a concept that we invoke for close pack crystals finally, while making comparisons. We said that the surface energy is typically higher than the grain boundary energy which is typically higher than the twin boundary or the stacking fault energy.