# Processing of Semiconducting Materials
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## Lecture - 16
## Defeets in Crystals – II

Let us resume our discussion on the defects in semiconductor. And we have discussed about the vacancy type of defects and dislocation. There are two types of defects we have discussed, but very clearly we have not discussed, what are the actual defects that are there inside the crystal, during the growth in silicon or gallium arsenide? That was the general type of discussion that, those are the defects that occur in semiconductor.

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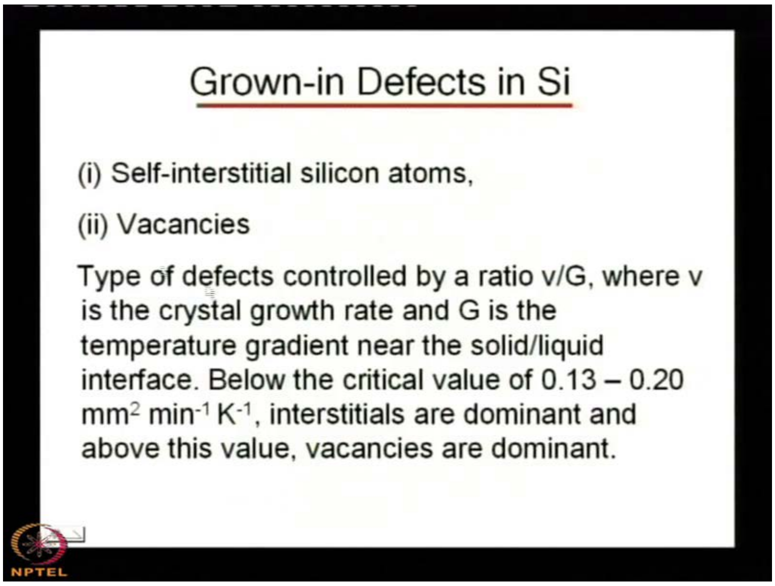

Grown-in Defects in Si

(i) Self-interstitial silicon atoms,

(ii) Vacancies

Type of defects controlled by a ratio v/G, where v is the crystal growth rate and G is the temperature gradient near the solid/liquid interface. Below the critical value of 0.13 – 0.20 $mm^2 min^{-1} K^{-1}$, interstitials are dominant and above this value, vacancies are dominant.

Now if you see this presentation, you find that there are some grown-in defects in silicon. Those grown-in defects in silicon are mostly of two types. One is self interstitial silicon atoms and another is vacancies. Now, when we talk about self interstitial silicon atoms means, in a silicon crystal the host matrix is silicon. And there are interstitial sites as well. So on those interstitial sites, if the silicon occupy those sites, then it is known as the self interstitial silicon atoms. And there will be vacancies as well which we have discussed. Now, when there will be interstitial silicon atoms or vacancies, it will be governed by a ratio which is given by v by G, where v is the crystal growth rate and G is the temperature gradient near the solid liquid interface. So that means, you have to take care of this ratio. One is the crystal growth, which is in the numerator and in the denominator you find that the temperature gradient, near the solid liquid interface.

So, if this v by G ratio lies between 0.13 to 0.2, then, the interstitials defects will be formed; that means, it will depend on v by G ratio and if you if v by G is from 0.13 to 0.2, then you will find that, the grown-in defects in silicon will be dominated by the self interstitial silicon atoms. But if it is above 0.13 to 0.2, then you will find that the vacancies will be created. So it is basically the ratio between the crystal growth rate and the temperature gradient. So that is why, you have to very carefully choose the growth rate and the temperature gradient, because if the growth rate is very, very less, then what will happen, economically it is not viable. For a silicon crystal to grow, you have to wait for several days. So that means economically it is not viable. But if the growth rate is vey faster, then we’ll find that the vacancies will be dominant.

And if there are more vacancies in the crystal, then that crystal cannot be used for the fabrication of microelectronic integrated circuit, because we are concerned about those thing, the primary application of silicon waferin electronic industry. And the temperature gradient can be very usefully controlled by a computer. That is that you can make, but the crystal growth rate is the very, very important thing to this ultimately v by G ratio determines, whether it will be interstitial or whether it will be vacancy.

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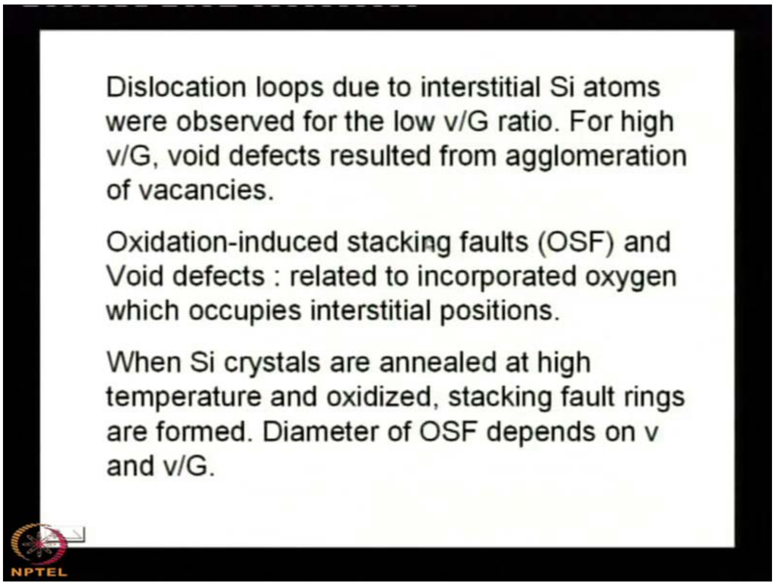

Dislocation loops due to interstitial Si atoms were observed for the low v/G ratio. For high v/G, void defects resulted from agglomeration of vacancies.

Oxidation-induced stacking faults (OSF) and Void defects : related to incorporated oxygen which occupies interstitial positions.

When Si crystals are annealed at high temperature and oxidized, stacking fault rings are formed. Diameter of OSF depends on v and v/G.

Then another thing is that, the dislocation loops due to interstitial silicon atoms, were observed for the low v by G ratio. So that means, if this v by G ratio is low, then dislocation loops will formed because of the interstitial silicon atoms. For high v by G ratio what will happen? Because as we have seen earlier, that if v by G ratio is high you see that and above this value the vacancies are dominant so that means if v by G ratio is high, high means it is greater than say 0.2millimetre square per minute per Kelvin. Then you will find that, the defects will agglomerate to form vacancy, to form void. All the vacancies will agglomerate and a void will be created in the crystal itself.

That means, when vacancies agglomerate, then void will be created. And you know that, void what is void inside the crystal. That means it is there is that is dead space basically, inside there is nothing, no atom is there inside the crystal matrix for a particular orientation, for a particular position. So then that part will also not be useful for the growth of any device. Another thing is that...

Student: Sir, what is dislocation loop?

What is dislocation loop that we have discussed in my last lecture. In my last lecture you find that we have concentrated on our discussion on the dislocation. Basically there are two types of dislocation. One is the edge dislocation, another is the screw dislocation. And basically the dislocation lines, it is of the order of say nanometre, 100 nanometre, 50 nanometre, 80 nanometre. And that line basically acts as the precipitate centre for the impurity. Particularly the heavier impurity. So, then there will be the precipitation of the impurity in the defects sides, in the dislocation loop and that crystal will not be useful for any device application.

And then you find that another is defect is the oxidation induced stacking fault, O S F. Oxidation induced stacking fault and a it is basically related to the incorporation of oxygen, which occupies interstitial position; that means, if you take a silicon crystal and sometimes for high temperature annealing and oxidation or diffusion type of thing, you will find that, when silicon crystal are annealed at high temperature and oxidized, you find that the oxygen will be incorporated in the crystal in the interstitial position. So in the interstitial position, there will be oxygen as well. And those oxygen, will give you some stacking fault of defect, which is the void defect and what happens actually?

Now, those voids are decorated or covered by SiO2, silicon oxide. So basically there will be void inside the crystal and inside the void the void walls will be covered by SiO2 silicon dioxide.

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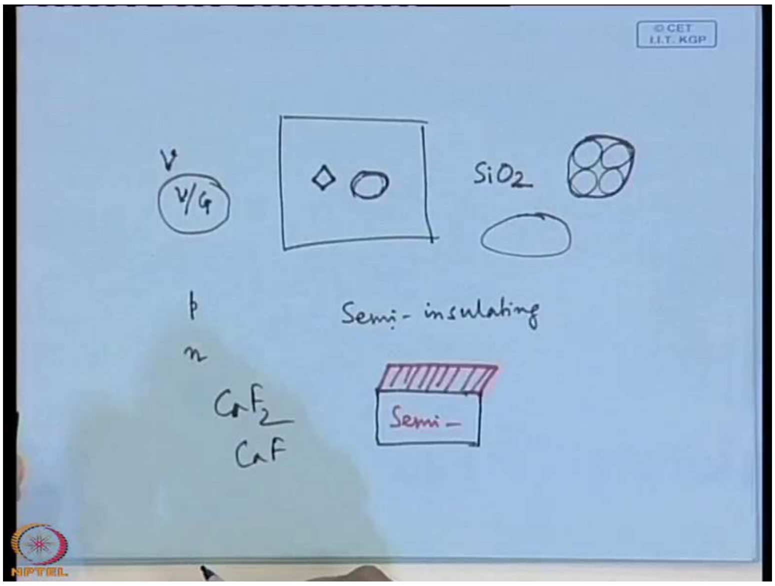

So if you find that there is a crystal matrix like this. Say this is a void inside a crystal. And the inner walls of the void, inner walls of the void will be covered by SiO2. Now from where the oxygen comes, oxygen comes from the annealing or oxidation, during annealing and oxidation or say during diffusion of the impurity atom in the crystal lattice. Now, sometimes this O S F is known as the ring O S F. Ring means it looks like a ring. It is basically circular

If you take the T m picture of this wafer, you will find that there will be some O S F ring. That means, it is oxygen induced stacking fault. And those rings are basically formed, say due to different kinds of defects. There are many defects inside and the edge of the defects form the ring, the edge of the defects form the ring, which is known as the oxidation induced stacking fault. And the diameter of O S F depends on v and v by G ratio; that means is the rate of crystal growth v and v by G ratio is the ratio between the rate of crystal growth and the temperature gradient in the liquid solid interface. So as we discus those things, we will find that, basically it is the crystal pull rate or the growth rate and the gradient in temperature, which play the critical role for the defect induced inside the crystal during growth, particularly for silicon.

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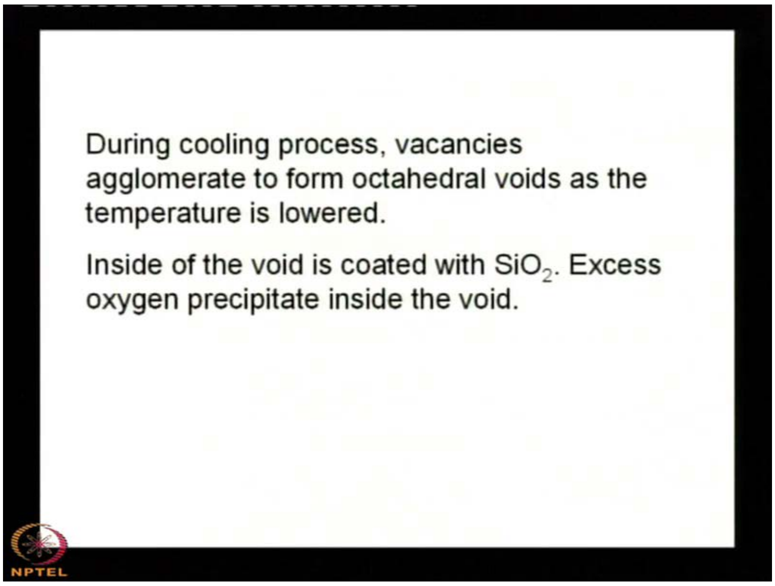

During cooling process, vacancies agglomerate to form octahedral voids as the temperature is lowered.

Inside of the void is coated with $SiO_2$. Excess oxygen precipitate inside the void.

Then another thing is that, say a silicon crystal is being oxidized or some diffusion implantation is carried out. Then as the temperature is cooled down, vacancies agglomerate to form octahedral voids, as the temperature is lowered. Now what is octahedral voids? Octahedral means which have eight faces. So basically say this these are four faces and similarly these are four faces, so eight faces will be created. And the and the voids are basically not in circular in shape, though we have shown you that circular type of, so actually it looks like this type of thing.

Here four we have shown, there are other fours on the back side. So octahedral formation of the voids take place as the temperature is lowered, and it happens during the cooling process. And as I have told you that inside the void is coated with SiO2 and excess oxygen precipitate inside the void and SiO2 is formed. So it is very critical a thing, so far as the defect inside a silicon crystal is concerned and not that only the vacancies will be formed or the dislocation will be formed. There are many types of defects which can be formed depending on the value of the crystal pool rate and the gradient in temperature.

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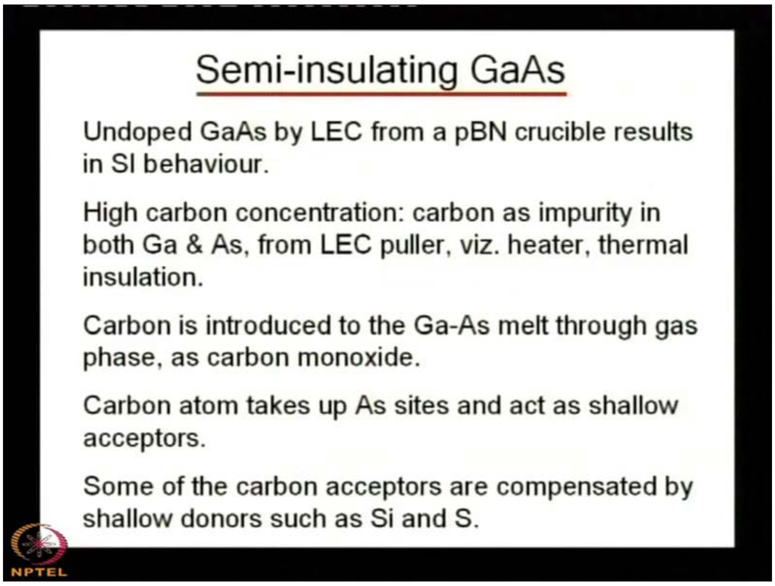

## Semi-insulating GaAs

Undoped GaAs by LEC from a pBN crucible results in SI behaviour.

High carbon concentration: carbon as impurity in both Ga & As, from LEC puller, viz. heater, thermal insulation.

Carbon is introduced to the Ga-As melt through gas phase, as carbon monoxide.

Carbon atom takes up As sites and act as shallow acceptors.

Some of the carbon acceptors are compensated by shallow donors such as Si and S.

Now, so far as the gallium arsenide is concerned, we find that apart from N-type and P-type gallium arsenide, there is another type of gallium arsenide which is known as the semi insulating gallium arsenide. We have discussed this thing little bit in my last lecture.

Student: (( ))

So it is semi insulating type of semi insulating gallium arsenide. So we have p-type, we have n-type and we have semi insulating type, which is not seen in case of silicon. So far as silicon is concerned or germanium is concerned, there is no semi insulating type of crystal. Now, what are the advantages of semi insulating type of crystal? The advantage of semi insulating type of crystal is that, as the name implies it is almost insulating in nature. If you see a an N-type semi conductor, it is highly conducting, the resistivity is very, very low.

For P-type, it is also conducting in nature, though the mobility or the resistivity, mobility will be less compared to n-type generally and the resistivity will be high compared to n-type. But insulating means, it is neither N-type nor P-type. Its resistivity is very, very high. Then why we use this? Where we use this? We use that semi insulating material for the crystal growth. Because you see that if the gallium arsenide is grown, than what is the substrate? the substrate will be gallium arsenide.

Then only the lattice matching will be possible, right. Now suppose you want to grow n-type gallium arsenide or P-type gallium arsenide, then what you will prefer? If you grow on semi insulating substrate, then the contribution of the substrate will not be there, if you measure the electrical properties of the grown N or P layer. So that is beauty of the application of semi insulating substrate in epitaxy, right. It is during epitaxy, we use semi insulating substrate. Because it will not contribute to the electrical property, because it is insulating in nature; that means, you are growing the film on the on an insulating material. So the electrons or holes will not be available for the conduction process from the substrate to the epitaxial layer.

That means this is your substrate. And you have grown say one film on it. That is epitaxial film. Now if you measure the electrical conductivity of this grown field, if you measure the conductivity of this grown field, what you will find? You expect that, the electrons or the holes will come from the layer only not from the substrate. If it comes from the substrate then, you will not be able to determine the resistivity of the grown layer. So that is why it is better that, you grow a layer on a semi insulating substrate, semi insulating substrate. Then the contribution of the substrate will not be there on the epitaxially grown film.

So that is an advantage of the semi insulating substrate. Then lattice matching will be there, because it is also gallium arsenide, it is also gallium arsenide. So lattice matching will be there, but there will be no contribution of the electrical characteristics from the substrate. So, that means it will only governed by the electrons or holes of the layers, which you are growing.

Student: Sir this is equivalent to our intrinsic semiconductor.

Yes, you can say that, the semi insulating is an intrinsic semiconductor, but at say for silicon intrinsic semiconductor or gallium arsenide intrinsic semiconductor, it is not semi insulating, though the resistivity is high, but it is almost insulator; that means very, very high resistivity is there greater than the normal intrinsic semiconductor. And another thing is that you see that this semi insulating gallium arsenide is grown by the method of liquid encapsulated czochralski technique. That we have discussed, and probably you can remember that LEC technique is nothing but the melt by B2O3 boron oxide to avoid decomposition of the group five element from the crystal surface. As the temperature is high, they say the growth temperature is almost the melting point of gallium arsenide or indium phosphate. For gallium arsenide the melting point is how much? Very, very high. It is 1240 almost. 1237, 38 degree centigrade. So, as the temperature approaches that the melting point of gallium arsenide say... arsenic.

Arsenic will start evaporating from the surface. The surface will be decomposed. To avoid the decomposition of the surface, because if arsenic evaporates then what will happen? There will be arsenic vacancy and the material will be non stoichiometric, the material will be non stoichiometric, because in single crystal we always prefer growth of stoichiometric material. So that the composition, the ratio of the atoms will be in a particular integer value, say a calcium fluoride, what is the value, what is the formula, c a F 2. So that means, one atom of calcium and two atoms of fluorine are there. So that is why it is stoichiometric. If you find that it is like this thing, then what is this, it is non-stoichiometric.

Because the normal composition of C a F 2 is, one is to two. Here it is one is to one. So that is why it is non-stoichiometry. So, as the temperature as the arsenic evaporates from the surface, obviously gallium will also evaporate; do not think that only arsenic will evaporate, but why we talking about arsenic more and more? It is because the vapour pressure of arsenic is higher than gallium. So the evaporation of arsenic will be faster than the evaporation of gallium. Gallium will also evaporate, but the depend, it will depend on the vapour pressure of the element in the material.

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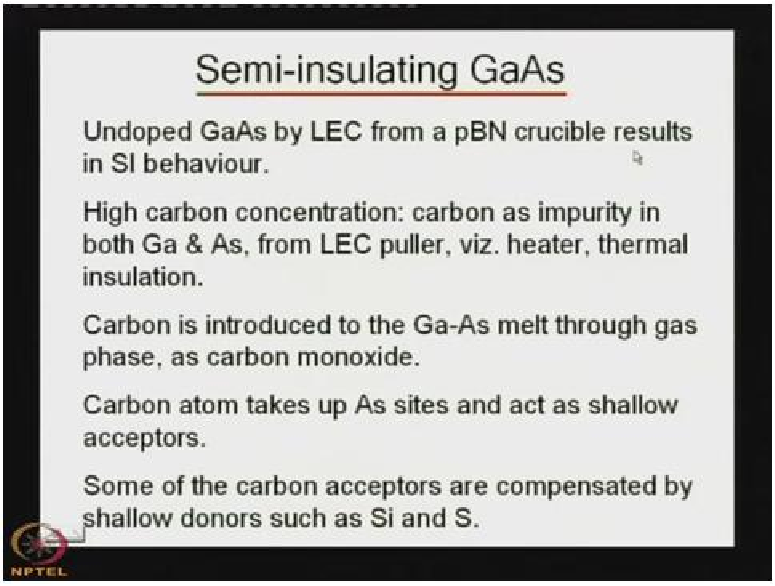

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Now, you see that for undoped gallium arsenide by LEC, and we use the paralytic boron crucible. Why we use the paralytic boron crucible? It is because, if you use the silica crucible, then what will happen? Oxygen will mix in the melt. To avoid oxygen contamination we use paralytic boron nitrite.

There is a another reason here. The reason is that, b 2 o 3, which is covering the surface of the melt, reacts with silica and graphite crucible. It is reactive. It is not reactive with gallium arsenide. But it is reactive with the crucible material the crucible material if the material is say...

Student: Silica.

Silica or graphite. That is why paralytic boron nitride is used though it is very costly material. So we find that the semi insulating material is obtained from undoped gallium arsenide grown by LEC technique, using paralytic boron nitrite crucible. But, there will be high carbon concentration. Why there will be high carbon concentration, what is the source of carbon? Because you are not using graphite crucible, then where is the source of carbon? The source of carbon is from arsenic and gallium. Because, even you purify arsenic and gallium to the level of 9 and 10 and 11 and there will be some trace amount of carbon inside the material. That is one source. Second source is the heater and thermal insulation; that means the LEC puller the crystal growth arrangements; that is known as LEC puller.

There will be heater and thermal insulation. And carbon is introduced to the gallium arsenide melt through gas phase as carbon monoxide. So that means, from the furnace, from the insulator, thermal insulators you are using many kinds of materials and you know that almost all materials contain some amount of carbon. So if you do not even if you do not use graphite crucible, carbon will be there and it will mix in the melt as carbon monoxide in the gas phase. Now this is the source of carbon. And carbon atom inside the material; that means inside gallium arsenide, takes up arsenic sites and acts as shallow acceptors. So that means what will happen, there is a gallium arsenide crystal and carbon will occupy the arsenic sites and it will act as a shallow acceptor. What is shallow acceptor?

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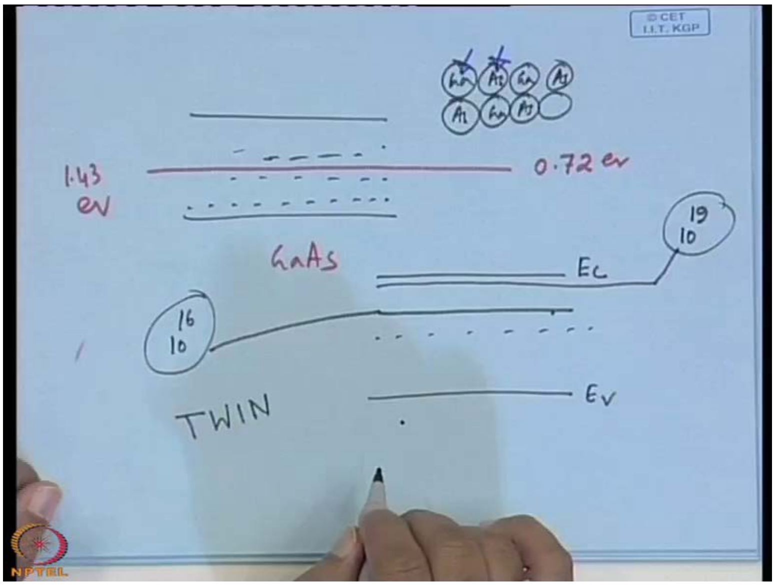

Why it is known as shallow? It is because...

Student: It is above the valence band.

Yes, it is just above the valence band. That is why it is known as shallow acceptor. Or shallow donors means, it is just below the conduction bandage. Bottom of the conduction band. If it is a deep inside the material, near the mid gap then it is known as the

Student: Deep level.

Deep level. That means say, this position is the mid gap. If it is gallium arsenide, then what is value of band gap, 1.43 electron volt. So what is the position of the mid gap, 0.71 or 72 electron volt. So that is position of mid gap when it will be near to 0.7 electron volt; that means, it is either here or it is there. If it is acceptor type, then it is below the mid gap. It if it is donor type, it is above the mid gap. But its value will be very near to the mid gap energy of which is for gallium arsenide is 0.72 electron volt. Then normally carbon atom takes up arsenic sites and act as shallow acceptors. Some of the carbon acceptors are compensated by shallow donors such as silicon and sulphur. What is compensation, what is compensation what do you mean by compensation in semiconductors?

Student: (( ))

(( )) acceptors and donors are present in a same way.

Actually what happens, suppose you have a n-type material. Say the concentration of the electron is 10 to the power 17 say. And you want to make it p-type. You are starting with an n-type material and you want to make it P-type. Then, as you go on increasing the acceptor level, if you dope it with some acceptors atom, then what will happen, say...

Student: (( ))

There was 10 to the power 17 electrons. So first you need 10 to the power 17 holes to compensate 10 to the power 17 electrons. And then even if you increase the acceptor concentration, it will be p-type. p type So that is known as the compensation. And you see that, when carbon takes up arsenic sites, it will be it will act as shallow acceptors, and those acceptors will be compensated by shallow donors such as silicon and sulphur, which are also present in the gallium arsenide crystal some of the carbon acceptors not all the carbon acceptors. Then what will happen to the other carbon acceptors? So if there is x number of carbon acceptors and y has been compensated by shallow donors like silicon and sulphur, then the remaining x minus y to be compensated by some other means.

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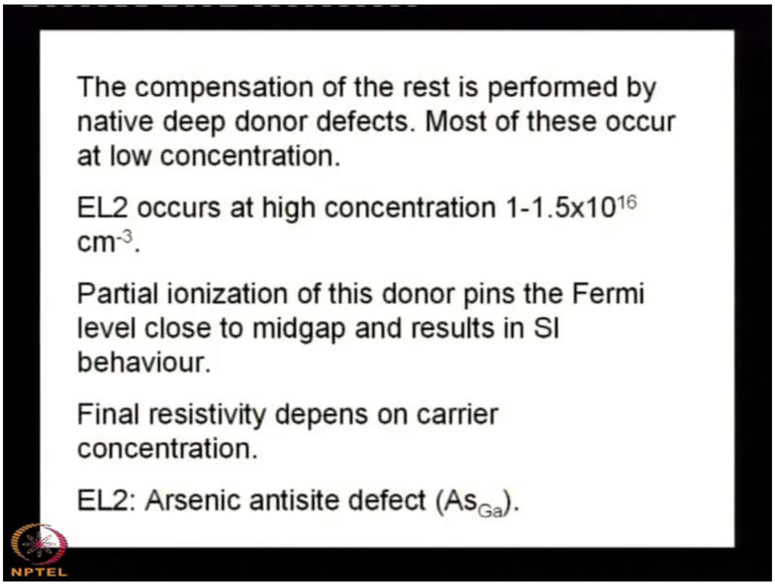

The compensation of the rest is performed by native deep donor defects. Most of these occur at low concentration.

EL2 occurs at high concentration 1-1.5x$10^{16}$ $cm^{-3}$.

Partial ionization of this donor pins the Fermi level close to midgap and results in SI behaviour.

Final resistivity depens on carrier concentration.

EL2: Arsenic antisite defect ($As_{Ga}$).

So that means is the rest is the compensation of the rest is, performed by native deep donor defects, deep donor defects Deep donor defects means, they are near to the mid gap. And most of these occur at low concentration. But there is one defect which is known as EL2 that is very important. EL2 E and L stands for electron level, E and L stands for electron level EL2 basically the electron level 2. There may be EL1, EL3, EL5, EL7, there may be electron levels. So electron levels means those are basically the donor levels. Hole levels are basically the acceptor levels. So like EL there may be AL, acceptable levels. But one EL2 is there, having concentration very high concentration. Very high means, it is 1 to 1.5 into 10 to the power 16 per centimetre cube.

So that is the concentration of EL2 inside gallium arsenide. And partial ionization of this donor, pins the fermi level close to mid gap and results in semi insulating behaviour. Pins the Fermi level means, what is meaning of pinning of Fermi level. Pinning of Fermi level means, it is fixing the Fermi level, so that the Fermi level is unable to move. What we find that if the electron concentration increases Fermi level moves more towards the conduction bandage. If there is more concentration of electrons than if there is more concentration of holes than electrons, then what will happen? The Fermi level moves closer to the valence band. So that means whether it will be P-type or n-type, it can be determined from the position of the Fermi level. Say this is your material. This is the intrinsic level and it is the conduction bandage, it is the valence bandage. If the electron concentration is 10 to the power say 19. Then say this is the position of the Fermi level. For 10 to the power 19. If it is 10 to the power 16, then where should be the position?

Student: Below.

It will be near to the...

Student: (( ))

Yes right. So; that means the position of the Fermi level changes depending on the...

Student: Concentrations.

Concentration of the electrons or holes. But if you pin the Fermi level, you know the effect of pinning in a notice board. Suppose this is a notice, and you are pinning it on the notice board; that means it is fixed, it cannot move. So that means, the pinning of the Fermi level happens means, that the electron concentration cannot be changed. So that is why the semi insulating behaviour is there. It is very near to the mid gap. And it is due to the appearance of EL2 defect in the semi in the gallium arsenide crystal. And though the final resistivity depends, it will be depend. Depends on carrier concentration of carbon, but EL2 is basically the arsenic anti site defect, there is some controversy over the atomic identification of EL2 what is EL2?

Because people have obtained one level near the mid gap energy, but what is EL2? EL2 is nothing but a arsenic anti site defect. What is arsenic anti site defect? That is arsenic occupied the gallium position. Anti site, arsenic is not in its own site. If you find that this is your gallium arsenide, gallium arsenic gallium arsenic say this is gallium, it is arsenic, it is gallium; it is arsenic, then it is arsenic, it is gallium, it is arsenic, it is gallium. So if this happens, then see this is the position of the arsenic and this is the position of gallium.

If arsenic occupies the gallium site, if arsenic occupies the gallium site, then it is known as the anti site defect, arsenic anti site defect. And EL2 is nothing but the arsenic anti site defect. So EL2 is very important because EL2 gives you the semi insulation property, in case of gallium arsenide. It is basically a deep level defect and its concentration is very high, its almost 1.5 into 10 to the power 16 per centimetre cube. And its ionization pins the Fermi level close to the mid gap. Pins the Fermi level means, Fermi level is unable to move...

Ionization is what do you mean by ionization? Ionization means when you dope a material, suppose you are doping silicon with phosphorous so from where the electron comes? The electron comes from the ionization of phosphorous atom. Then what happens, one electron it donate to the silicon crystal matrix and immobile ion of phosphorous will be there inside the crystal matrix. So here also the same thing happens. Without ionization the impurity atom or the defect has no role to play. Without ionization it cannot do anything; that means either it will donate electrons or it will be preparing for to accept the holes. And that is possible only when it is ionised. And for ionisation, you need energy. But we observe that for gold and silver deep need to be occupy the ionization energy is also high.

Student: Yes same thing happens.

Yes obviously. The same thing happens obviously. And when it happens,, say during annealing or some temperature gradient during the crystallization, it gets huge energy. And at that time it ionized, and it pins the Fermi level. So energy is there, energy can be is available, because you know that 1237 is the temperature for the gallium arsenide crystal growth. So it is very huge energy. And sometimes some of the processing is done at high temperature, thermal annealing is there. So there also the deep level can except energy and the source of energy is basically the thermal energy. It can ionize and then it will pin the Fermi level at the mid gap. So it will and the Fermi levels will be unable move, right.

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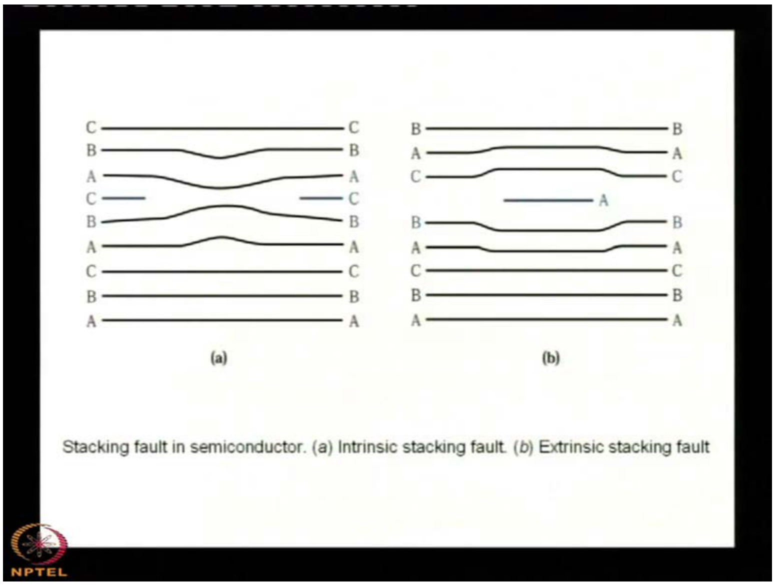

Stacking fault in semiconductor. (*a*) Intrinsic stacking fault. (*b*) Extrinsic stacking fault

And then other type of defect are there. One is the a stacking fault type of defect. Stacking fault means, you see that, in a crystal matrix the layers are organized in this manner C B A C B A C B A. And, one layer is missing. Layer C is missing. So if layer C is missing, then it is known as the stacking fault. One layer is missing. And you see that since this layer is missing, then just above and below that layer, there are some deformation in the crystal. You see this presentation that there is some deformation in the crystal. And these deformation is not condiship for device processing. Similarly there can be another type of stacking fault you see that the organization of this layer is B A C B A C B A C etcetera. And one new layer A say is inserted between this C and B.

So if an additional layer is inserted here, then also the it is known as the stacking fault. And just above and below this a level or a layer, you find that there is some distortion in the crystal. So it will give you the lattice trend. When this is the insertion, it is known as the extrinsic stacking fault. And if the there is an absence of the layer, it is known as the intrinsic stacking fault. So apart from this stacking fault, there may be twin type of defect T W I N TWIN. T W I N TWIN So that means, that crystal direction is different. Different crystal directions are there. That is why that is known as the twin. Another thing can be the one is stacking fault another is twin and third one is say precipitated type of defect, which is known as the volume defect precipitated type of defect which is known as the volume defect this is twin is an area defect. Dislocation is a line defect. Vacancy or interstitial is point defect.

Student: Point defect.

So there is another type of area defect apart from twin and stacking fault

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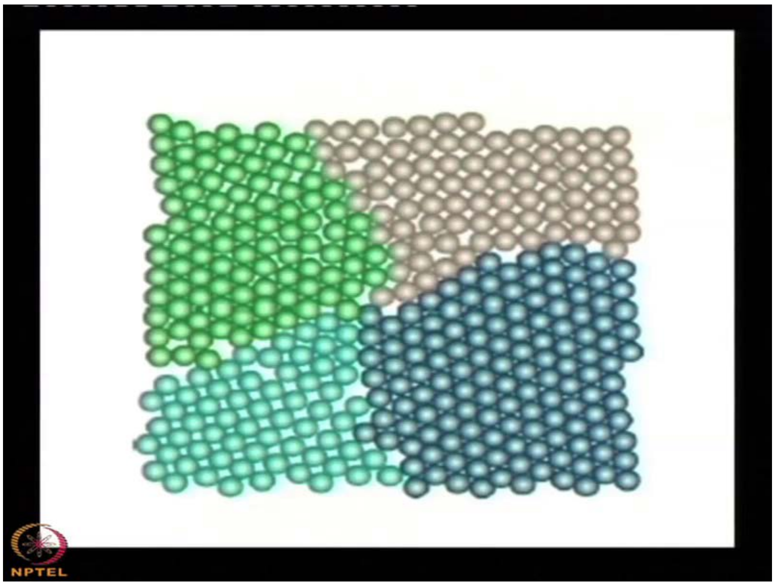

This is the grain boundary this is the grain boundary and this grain boundary will find that there are different grain size; that means this is a crystal having a particular orientation. This is another crystal having another orientation, this is the third type of crystal having another type of orientation. And you see that when electrons move from this grain to that grain; that means say from grey to green, what will happen, there is a boundary and this boundary is not perfectly oriented. Similarly you see that this boundary is not perfectly oriented.

There are many boundaries. This grain, there four grains here and you see that there are four boundaries. 1, 2, 3 and 4 and apart from those boundaries there are voids inside the boundary you see. So those act as the local distortion and when electrons will move from one grains to another grain, then electrons will be scattered at the grain boundary. So during scattering, its motion will be hampered, obstructed. And so the mobility will be decreased. So it happens during polycrystalline material. In single crystal generally, only one grain is there throughout the crystals matrix, say this grain. This grain is repeated; that means it is single crystal. That is a perfect orientation, free from any kinds of grain boundary. But in a polycrystalline material you will find that, there will be grains and electrons will move throughout the crystal.

So if this is a crystal, so the electrons will move from this end to that end. Then only you will get some mobility. But if the if inside the material there are different kinds of grains, and due to the scattering at the grain boundary, the motion of the electrons will be jeopardized and consequently the mobility will be less.

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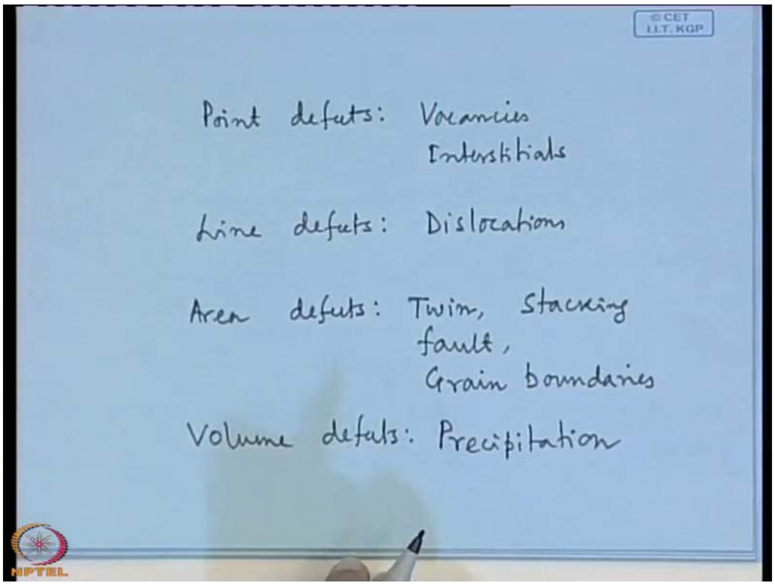

Point defects: Vacancies
Interstitials

Line defects: Dislocations

Area defects: Twin, Stacking
fault,
Grain boundaries

Volume defects: Precipitation

So we find that so far as the point defect is concerned, point defect, you have what are the defects, vacancies, interstitials defect etcetera. Then there is line defects, these line defects are basically the dislocations. It can be edge dislocation, it can be screw dislocation. Then there is area defect. It is twin, stacking fault, yes stacking fault grain boundaries. And the last one is the volume defects. Volume defect is basically the...

Student: (( ))

Precipitation. Now what is volume defect?

Student: (( )) it (( ))

Yes. But what is that? How it is created in the defect, in the material, how this defect is created in the material? Say you are doping something you are doping something you are doping silicon with boron or aluminium or phosphorous whatever be the case. It depends on the, doping depends on the solubility of the material and the solubility depends on the temperature. Solubility of phosphorous in silicon; solubility of gallium in silicon; solubility of boron in silicon, it is practically the temperature related process. If temperature increases, solubility increases. If temperature decreases, solubility decreases. Now you are growing say silicon. What is the temperature?

Student: 1400.

1400.

Student: (( ))

Degree centigrade. More than 1400 degree centigrade. So at that temperature say boron you are doping. So that means you are mixing boron with silicon and at the temperature you are growing the crystal. Then what will happen, during cooling during cooling the solubility of boron will be less. But you have mixed boron at melting point which is 1400 degree centigrade. So as the temperature is reduced or cooled down, the solubility will also be reduced.

Reduced. But where the boron will go? Boron has mixed at that temperature. It is mixed up to its saturation level. Because it is it will be governed by the solubility of boron. Then as you reduce the temperature when it solidifies; that means you reduce the temperature, then there will be precipitation of boron there will be precipitation of boron...

There is a line, it may be in the line defect or it may be in the void etcetera. So that precipitation will give rise to volume type of defects inside the material. Right. So it is because of the precipitation due to the difference in solubility at low temperature. It will be precipitated. So that means, some amount of boron or any impurity will be precipitated inside the crystal matrix. And what will happen then? What will happen It is basically a silicon crystal and some foreign impurity is precipitated inside the crystal matrix, from where the space will come. Because it is very uniformly spaced, the silicon atoms are very uniformly spaced, it has particular diameter. So there will be foreign impurity precipitation inside the crystal matrix, so there will be distortion in the local crystal lattice.

And that distortion will give you the defect property. It can be dislocation; it can be void. Different kind of things can happen. If it occupies the vacancy or the interstitial it is ok. But remember that when you have doped, when you are doping a semiconductor or a material, all the vacancy and the interstitial positions are almost full, because where foreign impurity will go? Either in the vacancy or in the interstitial. So you have used boron to its highest extent. Because the solubility was in the limiting site, higher site. Then as you cool down, all the vacancy and the impure, interstitial positions are filled. So where it will go? So, it will basically push the crystal matrix. It will push the silicon atoms. And there will be distortion.

Student: (( )) pushing or replacing.

How it will replace? Where then, the replace atom where the replaced atom will go? If there is space it is ok. We do not know, but normally there will be a pull, there will be a push basically. It will push the host matrix. So that is the precipitation or the volume kind of defect.

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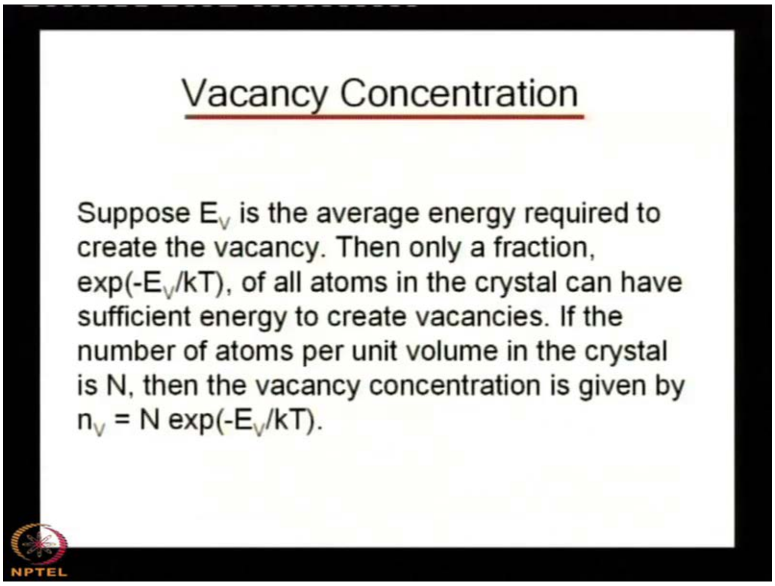

## Vacancy Concentration

Suppose $E_V$ is the average energy required to create the vacancy. Then only a fraction, $\exp(-E_V/kT)$, of all atoms in the crystal can have sufficient energy to create vacancies. If the number of atoms per unit volume in the crystal is N, then the vacancy concentration is given by $n_V = N \exp(-E_V/kT)$.

Let us move to one thing that, what is the vacancy concentration? How the vacancy concentration is measured? Is there any numerical theory using which we can measure the vacancy concentration in a material? yes Actually you see that, if E v is the average energy required to create a vacancy, then only a fraction which is given by exponential minus E v by k T of all atoms in the crystal can have sufficient energy to create vacancies. And if the number of atoms per unit volume in the crystal is capital N, then the vacancy concentration is given by capital N exponential minus E v by k T.

Now, you see that exponential minus E v by k T is the Boltzmann factor exponential minus E v by k T is the Boltzmann factor. So if E v is the average energy required to create the vacancy, then the total number of vacancy will be given by N exponential minus E v by k T, if n number of atoms per unit volume in the crystal is there. So using this expression, number of vacancy concentration equals to capital N exponential minus E v by k T. We can determine the concentration of vacancy in a crystal.

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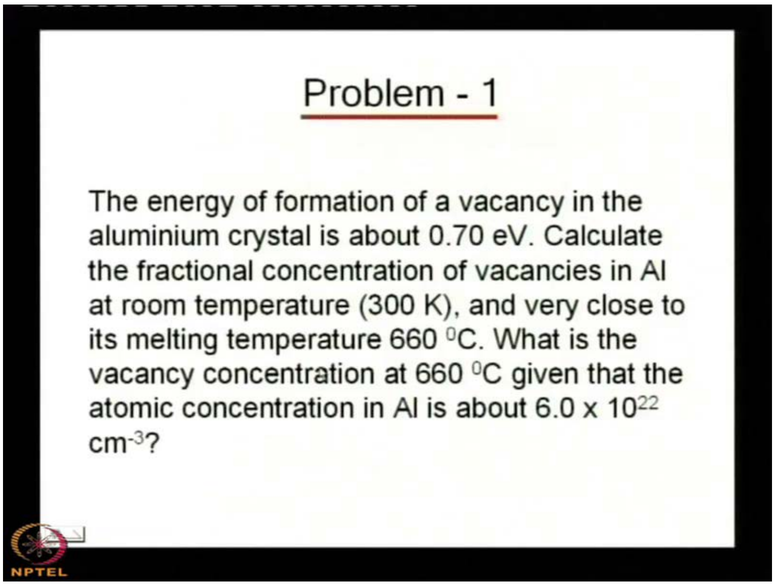

## Problem - 1

The energy of formation of a vacancy in the aluminium crystal is about 0.70 eV. Calculate the fractional concentration of vacancies in Al at room temperature (300 K), and very close to its melting temperature 660 $^0$C. What is the vacancy concentration at 660 $^0$C given that the atomic concentration in Al is about 6.0 x $10^{22}$ cm$^{-3}$?

So let us try this problem. You see that, the energy of formation of a vacancy in the aluminium crystal is about 0.7 electron volt. Calculate the fractional concentration of the vacancies in aluminium at room temperature; that means 300 K and very close to its malting temperature which is 660 degree centigrade. What is the vacancy concentration at 660 degree centigrade? Given that the atomic concentration in aluminium is about 6 into 10 to the power 12 centimetre cube inverse. So that means you have to calculate the fractional concentration of vacancies at 300 K and 660 degree centigrade. Now what is fractional concentration of vacancy?

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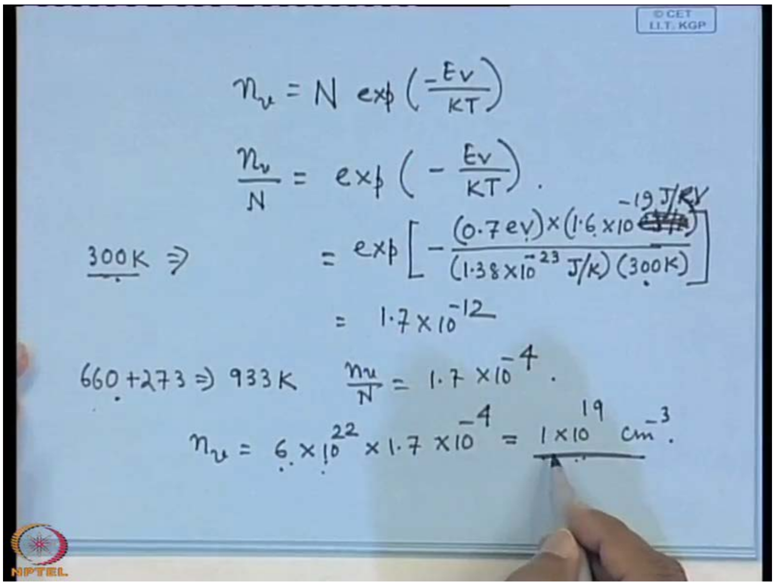

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$$n_v = N \exp\left(\frac{-E_v}{KT}\right)$$

$$\frac{n_v}{N} = \exp\left(-\frac{E_v}{KT}\right).$$

$\underline{300 K} \Rightarrow$ $$= \exp\left[-\frac{(0.7\,eV)\times(1.6\times10^{-19}\,J/eV)}{(1.38\times10^{-23}\,J/K)(300K)}\right]$$

$$= 1.7\times10^{-12}$$

$660+273 \Rightarrow 933K$ $\quad \frac{n_v}{N} = 1.7\times10^{-4}.$

$$n_v = 6\times10^{22}\times1.7\times10^{-4} = \underline{1\times10^{19}\ cm^{-3}}.$$

It is n v by N. It is n v by N. You see that n v; that means the vacancy concentration. It is given by number of atoms per c c in the crystal and exponential minus E v by K T. Fractional concentration means n v by N, that is equals to exponential minus E v by K T. That is the fractional concentration of vacancy. If E v is given, what is the value of E v?

Student: 0.7.

0.7 and you know K.

Student: K T is equal to 0.026.

It is at 300 K at 660 K it will be different. You calculate.

Student:  (( ))

You calculate the value of n v by N at two temperature, at 300 degrees Kelvin. What will be there? It will be exponential minus.

Student:  (( ))

What is E v 0.7 electron volt.

Student: 105.

What is the value?

Student: 50 (( )) n v by N equals (( )) .

0.05. n v by N is...

Student:  (( ))

1.7 1into10 to the power minus 12.

Student: 4.7 k T into (( )) k T is point (( )) (( )) Points (( ))

See exponential minus 7 E v by 1.38 into 10 to the power minus 23 joule per kelvin multiplied by 300 kelvin.

Student:  (( )) equal to (( )).

And it will be 1.6 into 10 to the power minus 19.

Student:  (( ))

Joule per Kelvin. Electron volt by Kelvin. No

Student: Sir (( ))

Joule per Kelvin.

Student: What is that (( ))?

No, no it is not joule per Kelvin, it is joule per electron volt.

Student: Sir (( )) it will be the exponential minus 30 equals 6 (( )) into (( ))

See you first see what are the values? E v is not 0.7 electron volt, but 0.7 electron volt multiplied by 1.6 into 10 to the power minus 19 joule per electron volt. Otherwise you put the value of K in terms of electron volt, not in terms of joule per Kelvin, not in terms of joule per Kelvin.

Student: Sir it will be...

If you put K equals to 1.38 into 10 to the power minus 23, then that is basically joule per Kelvin. Then also you have to use joule per electron volt in the numerator.

And directly know that we have k T in 26 (( )) Yes, you put.

Student: Sir (( )) 4 into minus 12.

Yes so that is equals to basically 1.7 into 10 to power minus 12.

Student: 2 point.

Yes it is ok. Minus 12 is...

Student: Room at room (( )).

At room at 300 K yes you see it is at 300 K. Then at 660 degree centigrade means...

Student:  (( ))

660.

Student: 9.

Plus 273.

Student: 900 and 33.

9

Student: 9 (( ))

933. So if it is 933, you see what is the value? It will be n v by N, if you put only just in this place 300 K you put 933 Kelvin and the value is here, you see it is 1.7 into 10 to the power minus 4. 10 to the power minus 4 minus.

Student: (( ))

Then what is the concentration of defect? Concentration of defect is n v equals to N, which is given by six into 10 to the power 22, multiplied by 1.7 into 10 to the power minus 4. And you will get what is the value? 1 into 10 to the power 19 centimetre cube inverse. 1 into 10 to the power 19 centimetre cube inverse. What it means, it means that 1 in 6000 site is a defect. one in 6000 site is a defect. From where I get the 6000, because the atomic concentration is 6 into 10 to the power 22 6 into 10 to the power 22 is number of atoms.

And number of vacancy is 1 into 10 to the power 19. So if you divide 6 into 10 to the power 22 by 1into 10 to the power 19, you will get 6000 that means, 1 in 6000 atomic site is a defect site in aluminium.

Student: Sir (( ))

If how many atoms are there in the aluminium crystal? It is 6 into 10 to the power 22. Now what the number of defect, 1 into 10 to the power 19.

Student: Vacancy .

Vacancy yes. So, what is the ratio, the ratio is 6000 into is to 1 the ratio is 6000 is to 1; that means per 6000 atomic site one defect is there in the aluminium at its malting point. So very high concentration of defect very high concentration of defect Because out of 6 out of 6 into 10 to the power 22 sites, if 1 into 19 sites are defect or vacancy; that means it is very high defect. And what is the origin of such high defect? It is because of the thermal expansion. yes with temperature at melting point, may be the thermal expansion is very high. And so the defect is very high. And if you, I shall compare this result with covalent crystal, say in germanium in my next class, I shall show you that this concentration is very very low in case of a covalent crystal like silicon or germanium or gallium arsenide. Is very very low compared to metal say aluminium is a metal. Its thermal expansion is very high, compared to gallium arsenide or any covalent crystal. So here the vacancies is also very high.

Student: (( ))

Problem problem is you see, that the energy of formation of a vacancy in the aluminium crystal is about 0.7 electron volt, calculate the fractional concentration of vacancies in aluminium at room temperature; that means 300 K and very close to its melting temperature 660 degree centigrade. Close to its melting temperature. Because I have we have to see that, at melting temperature what is the defect? Because when it re-crystallizes so it will with re-crystallize that defect. What is the vacancy concentration at 660 degree centigrade, given that the atomic concentration is aluminium is about 6 into 10 to the power 22 per centimetre cube, right. So this is a metal, aluminium is a metal and we see that for aluminium near its malting point 1 site per 6000 atomic site is a vacancy.