Condensed Matter Physics

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Lecture - 36
Semiconductors

We will start a discussion of semiconductors one of the most important class of materials in solids which have a wide range of technological application. In fact progress in semiconductor technology has revolutionized the area of modern electronics. Semiconductors are materials, which have electrical conductivities, as it is obvious from the name lying between the electrical conductivity of a good conductor like a metal and a perfect insulator.

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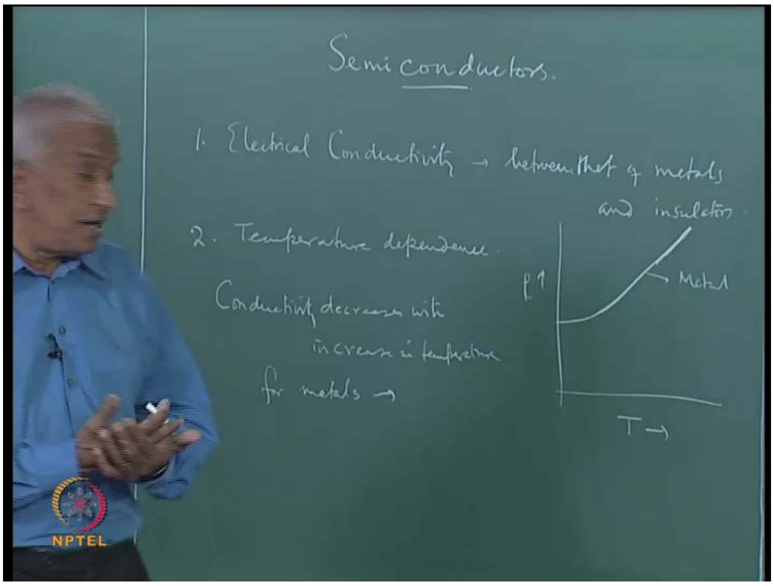

Semiconductors.

1. Electrical Conductivity → between that of metals and insulators

2. Temperature dependence.

Conductivity decreases with increase in temperature

for metals →

So, conductivities - electrical conductivity between that of metal and insulators.

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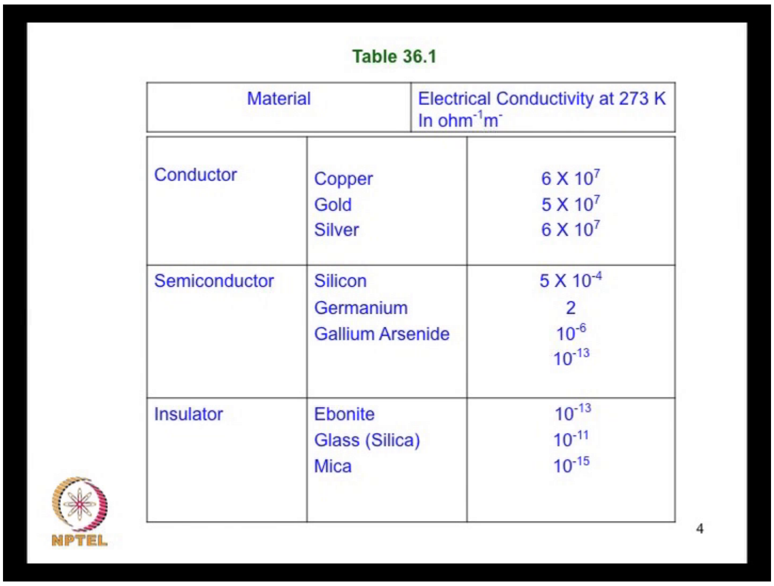

Table 36.1

Material		Electrical Conductivity at 273 K In ohm^{-1}m^{-}
Conductor	Copper Gold Silver	6 X 10^7 5 X 10^7 6 X 10^7
Semiconductor	Silicon Germanium Gallium Arsenide	5 X 10^{-4} 2 10^{-6} 10^{-13}
Insulator	Ebonite Glass (Silica) Mica	10^{-13} 10^{-11} 10^{-15}

For example, we have given in table form. The conductivities of good conductors such as copper, gold and silver; insulators like ebonite, glass and mica; and semiconductors - the standard semiconductors are silicon, germanium and gallium arsenide. The electrical conductivity values at 0 degree Celsius or 273 Kelvin is given in the last column, and it is clear that the conductors have conductivity values of which are very high compared to those a semiconductor which in turn are very high compared to those are insulators. So, the electrical conductivities spans something like from the 18, 19 orders of magnitude among common materials. So, this is a very remarkable variation that is the first feature.

The second feature is that you have a temperature dependence of the electrical conductivity or resistors. We all know that indicates of a metal, electrical resistance versus temperature is linear and then becomes non-linear and become this is for a metal. So, it has a linear variation and then the resistivity decreases with temperature; as the temperature is decrease, the resistivity decreases. So, you see that the resistivity increases, therefore the conductivity decreases electrical conductivity decreases decreases with increasing temperature for a metal, so there are said to have the resistivity increases. Whereas in the case of a semiconductor conductivity increases with increasing temperature.

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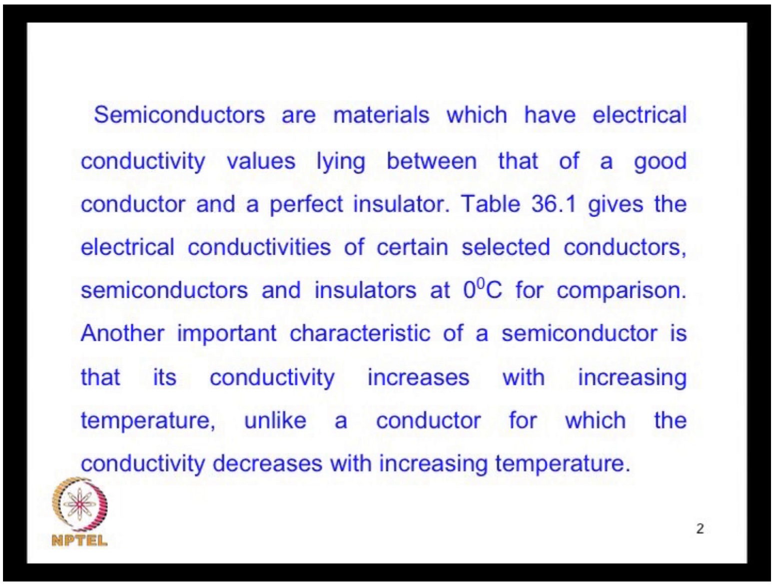

Semiconductors are materials which have electrical conductivity values lying between that of a good conductor and a perfect insulator. Table 36.1 gives the electrical conductivities of certain selected conductors, semiconductors and insulators at 0^0C for comparison. Another important characteristic of a semiconductor is that its conductivity increases with increasing temperature, unlike a conductor for which the conductivity decreases with increasing temperature.

Unlike whereas, semiconductor conductivity increases, so this is called a positive temperature coefficient. So, this has a positive temperature coefficient of resistance. So, this is known as ptc. Whereas, the metals is known as ntc, it has a negative temperature coefficient. So, this is another important difference between the behavior way temperature variation of the conductivity of a semiconductor versus that of a metal.

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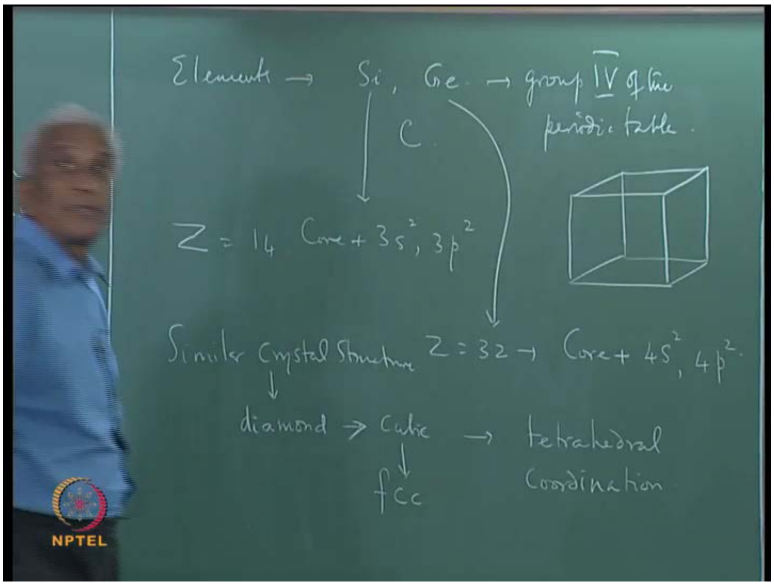

Now, what are semiconductors? The typical semiconductor elements are as I already mentioned silicon and germanium. Both these elements belongs to the group four of the periodic table. Another important element, which form is in the group four is carbon. So, carbon, silicon, germanium have identical electronic configuration. And this is the reason why all of them behave like semiconductors. For example, silicon has an atomic number fourteen, therefore, it has an electronic configuration in which there are four electron with outermost 3S 2 core plus 3S 2 and 3P 2 electrons.

Germanium has an atomic number of 32, germanium has an atomic number of 32 and that as an electron configuration which is 4 s 2 and 4 p 2. Essential thing is this is the 3 s and 3 p shell this is 4 s and 4 p shell, but in both cases the s and p outermost s and p shall are occupied by 2 electrons each. So, that is why the electron configurations are similar. So, that is why there has similar physical and chemical properties, they have indeed similar crystal structure. In fact, it is also similar to that of carbon, but in its form as diamond. So, this crystal structure is that of diamond which is nothing but carbon, so the diamond has a cubic crystal structure. So, this diamond structure is shown in a picture.

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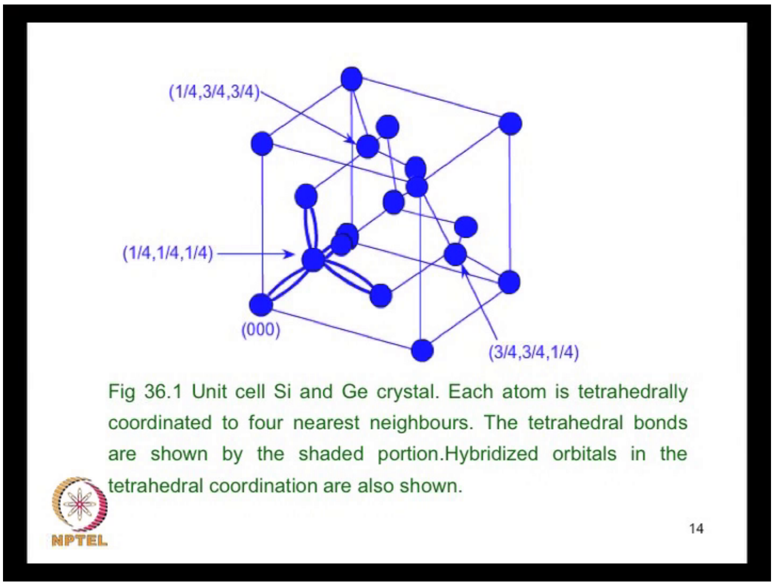

Fig 36.1 Unit cell Si and Ge crystal. Each atom is tetrahedrally coordinated to four nearest neighbours. The tetrahedral bonds are shown by the shaded portion.Hybridized orbitals in the tetrahedral coordination are also shown.

So, figure shows the unit cell of silicon and germanium crystal. In this, we will discuss this in great detail, but this is the main feature. Each atom of silicon is tetrahedrally coordinate, have a cube and each atom of silicon is tetrahedrally coordinated, auto four near neighbor - tetrahedrally coordinates. Tetrahedron means the near neighbor is 4. So, each silicon is coordinated to 4 near neighbor silicon. So, there are tetrahedral bonds which are shown by shaded portions.

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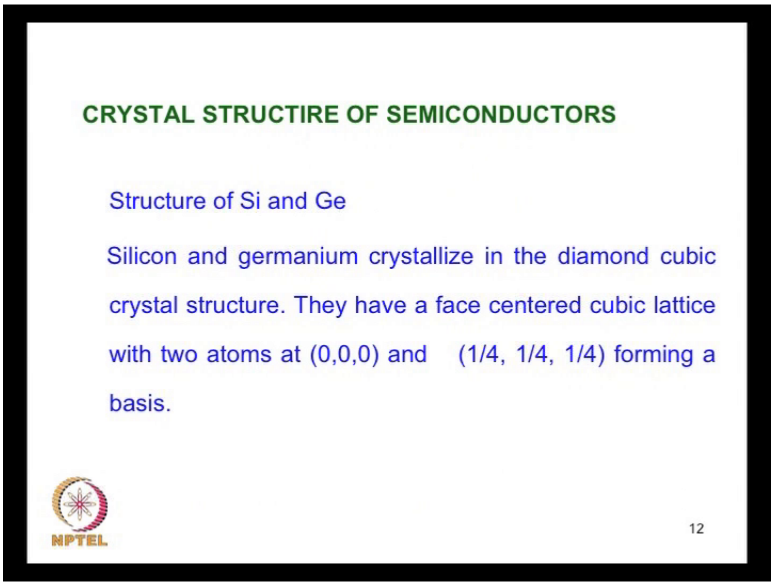

CRYSTAL STRUCTIRE OF SEMICONDUCTORS

Structure of Si and Ge

Silicon and germanium crystallize in the diamond cubic crystal structure. They have a face centered cubic lattice with two atoms at (0,0,0) and (1/4, 1/4, 1/4) forming a basis.

So, this structure is basically a face centered cubic – FCC. What does it mean that; that means, that there are times not only here, but all so at the face centred, and it is these are atoms which are tetrahedrally coordinate. So, the basis is a simple cubic lattice with two molecules in the unit cell one here and another at one-forth, one-fourth, one-forth. These are the two atoms, which form the basis, so this is what gives you the tetrahedral coordination. So, the tetrahedral mean the angle is 109 degrees 46 minutes.

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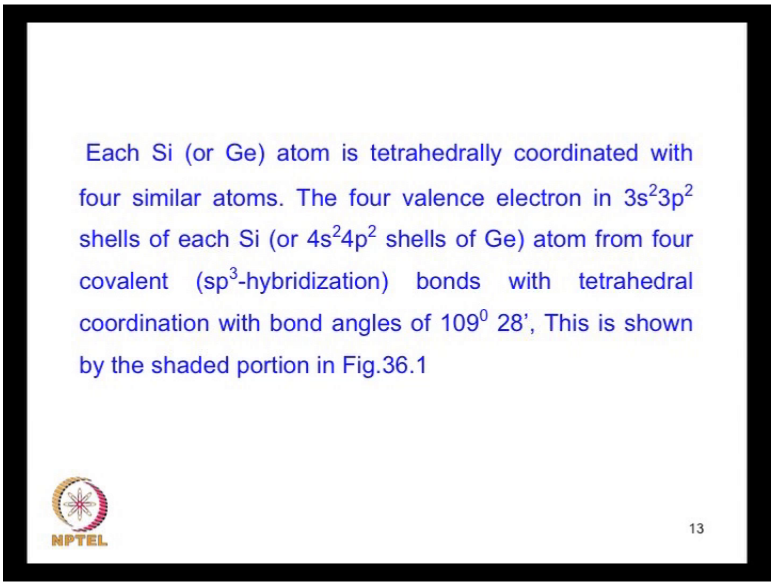

Each Si (or Ge) atom is tetrahedrally coordinated with four similar atoms. The four valence electron in $3s^2 3p^2$ shells of each Si (or $4s^2 4p^2$ shells of Ge) atom from four covalent (sp^3-hybridization) bonds with tetrahedral coordination with bond angles of 109^0 28’, This is shown by the shaded portion in Fig.36.1

So, these bonds are shown, basically what is happening is that you have two electrons here, one of these get electrons get promoted.

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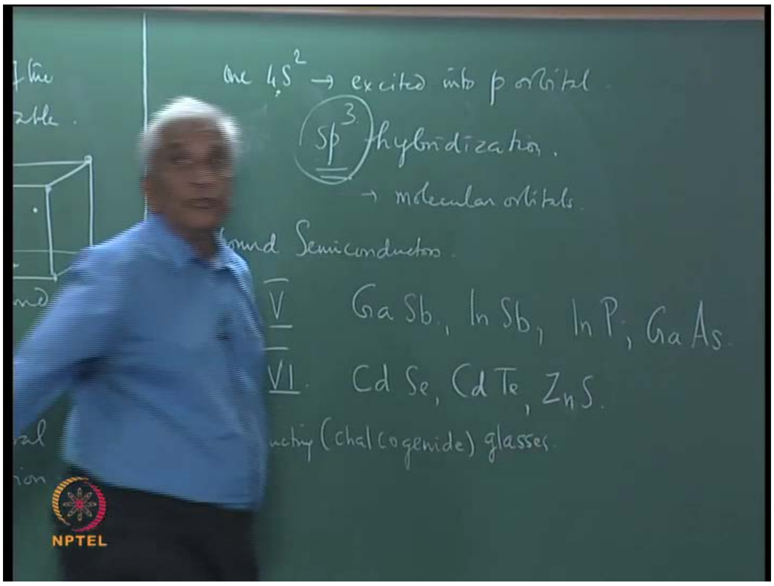

In the molecular orbital picture of the bond formation, you have one 4 S 2 electron excited into P orbital, and then you have one electron here 4 s 1. And then you have three electron and forming on S p 3 hybridization that is this electron which is excited joints with these and you have this electron with three electrons in the p shell including the one electron which is excited into the p shell. And you have the remaining electron and 3 p electrons combine together to form S P 3 hybridized molecular orbital. These are the ones; we form covalent bonds, which are shown by the shaded region in the figure.

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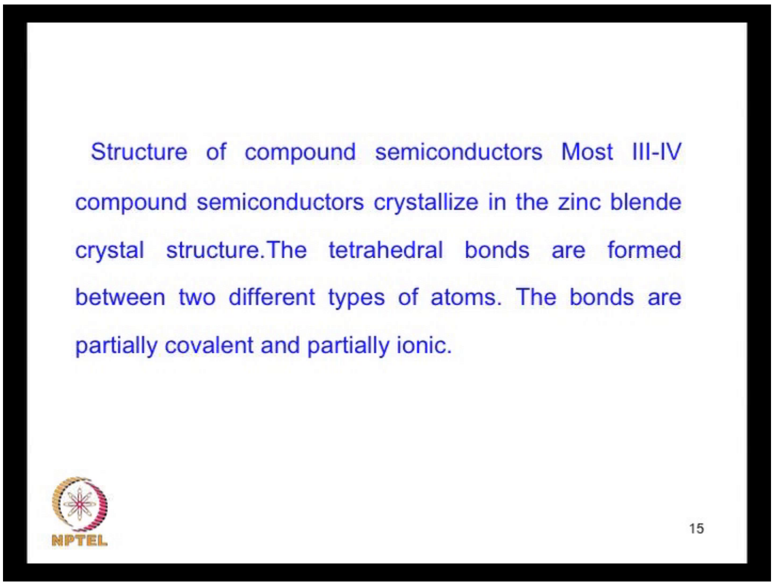

Structure of compound semiconductors Most III-IV compound semiconductors crystallize in the zinc blende crystal structure.The tetrahedral bonds are formed between two different types of atoms. The bonds are partially covalent and partially ionic.

This is also the case with most compounds semiconductors, the compound semiconductors are formed by combining a group three element with a group five element or a group two element with a group six element.

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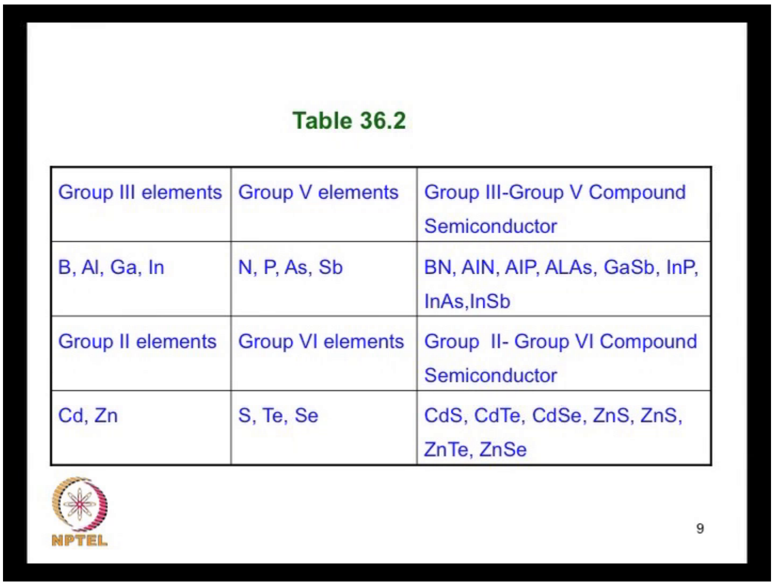

Table 36.2

Group III elements	Group V elements	Group III-Group V Compound Semiconductor
B, Al, Ga, In	N, P, As, Sb	BN, AIN, AIP, ALAs, GaSb, InP, InAs,InSb
Group II elements	Group VI elements	Group II- Group VI Compound Semiconductor
Cd, Zn	S, Te, Se	CdS, CdTe, CdSe, ZnS, ZnS, ZnTe, ZnSe

So, both are compound semiconductors. The table shows these. So, you have group two elements and group three elements and group five elements giving you things like gallium, antimonite, indium, antimonite and so on. Indium phosphate, gallium arsenide things like that, so these are all three-five compounds. In the other case two six compounds it is materials like cadmium selenite, cadmium telluride and so on, zinc sulphide, usually sulphur selenium, tellurium form the sixth group, so cadmium, zinc etcetera are in the second group. So, forming compounds of this kind, so these are the two-six compound semiconductors. These also have similar crystal structure.

You also have classes the compound semiconductors prepared in glass c form chalcogens, the sulphur selenium solarium are known as chalcogens and therefore, these are known also has chalcogenide glasses. So, preparing glassy form they are the class called the semiconducting glasses they have also acquired a lot of technological importance. So, that is regarding the basic structure and basic chemistry chemical and nature of these various kinds of semiconductor now we also have two important classes of semiconductors.

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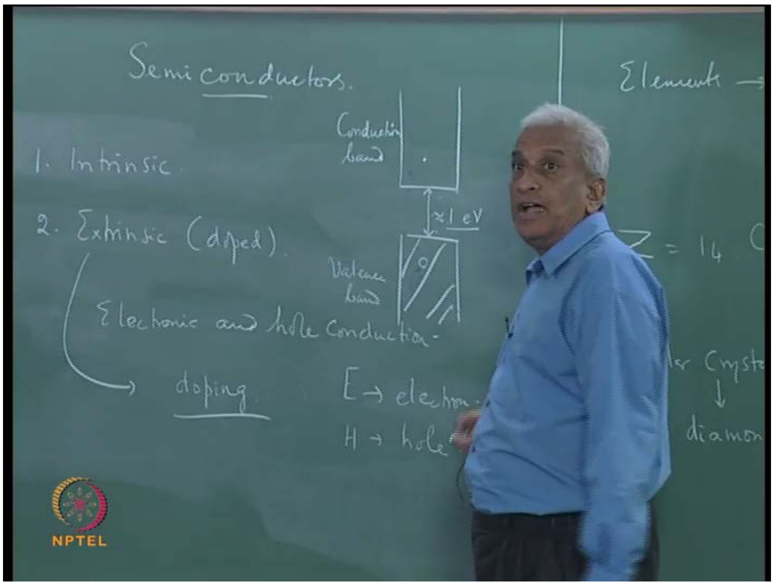

There are one is known as intrinsic semiconductor, second-class is extrinsic or doped semiconductor, because we have seen from our discussion of the energy band structure that the band structure electronic structure consist of an occupied valence band and an unoccupied conduction band, and the energy gap is rather low it is of the order of one electron volt say. So, the energy gap is such that it is sufficiently small for carriers to be a as already discuss, carriers can be excited across this the energy gap even thermally by at sufficiently high temperatures.

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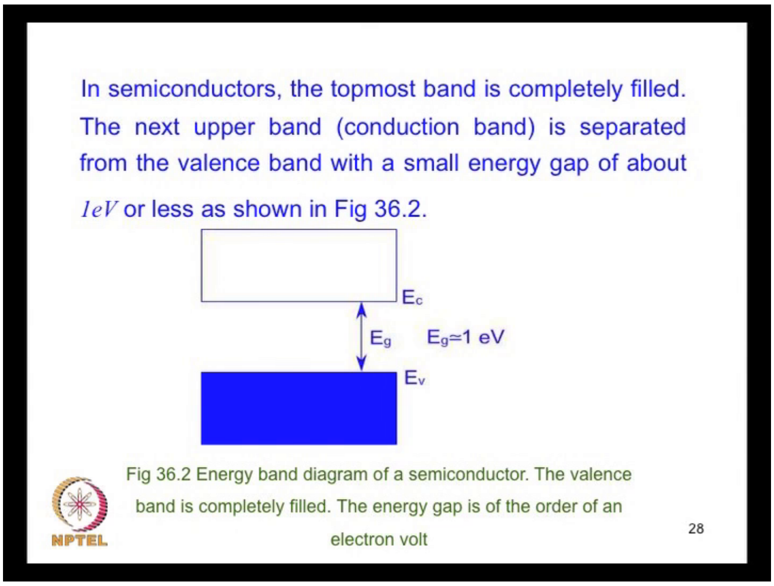

In semiconductors, the topmost band is completely filled. The next upper band (conduction band) is separated from the valence band with a small energy gap of about $1eV$ or less as shown in Fig 36.2.

Fig 36.2 Energy band diagram of a semiconductor. The valence band is completely filled. The energy gap is of the order of an electron volt

For example, room temperature and above, the carriers can be excited thermally some of the carriers. So, the intrinsic conductivity depends on the thermal activation of these carriers across the energy gap. So, then there are is an electron excited into the empty conduction band and a hole left behind in the valence band. Both the electron and hole move in opposite direction producing conduction. So, you have an electronic conduction and if hole conduction in a semiconductor, this is another major difference.

So, you have electronic and hole conduction; how do we know this we know these by performing hall effect measurements. This is why in an intrinsic semiconductor, the conduction is produced thermally or by natural means automatically without doing anything by just thermal activation. Whereas, in the case of an extrinsic semiconductor, the electrical properties are controlled by adding impurities in extremely small concentration, so you call that doping, controlled impurities in an extremely pure material. Specific impurities are added we will discuss this later in detail.

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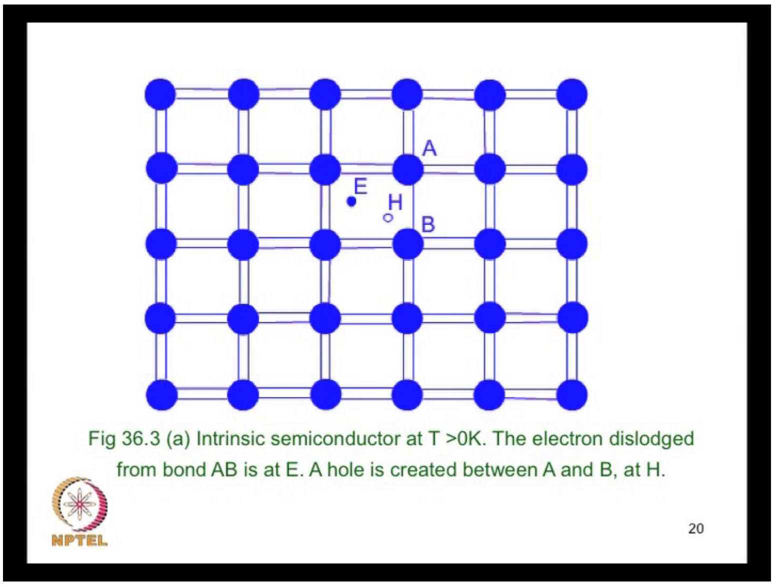

Fig 36.3 (a) Intrinsic semiconductor at T >0K. The electron dislodged from bond AB is at E. A hole is created between A and B, at H.

In order to understand what happened let us look at the intrinsic semiconductor at a finite temperature which is above 0 Kelvin. Let us look at a particular site where there are see all the bonds here are shown by two dashes two lines. And this means the number of bonds, the number of lines is equal to the number of bonds. Now suppose we consider an electron, yes that is marked E, now because this electron has been lost by the atom A and therefore, you have only one line. So, you have what is shown here is just the tetrahedral arrangement in three dimensions is projected onto two-dimensions. So, the four tetrahedral bonds are shown schematically in this manner.

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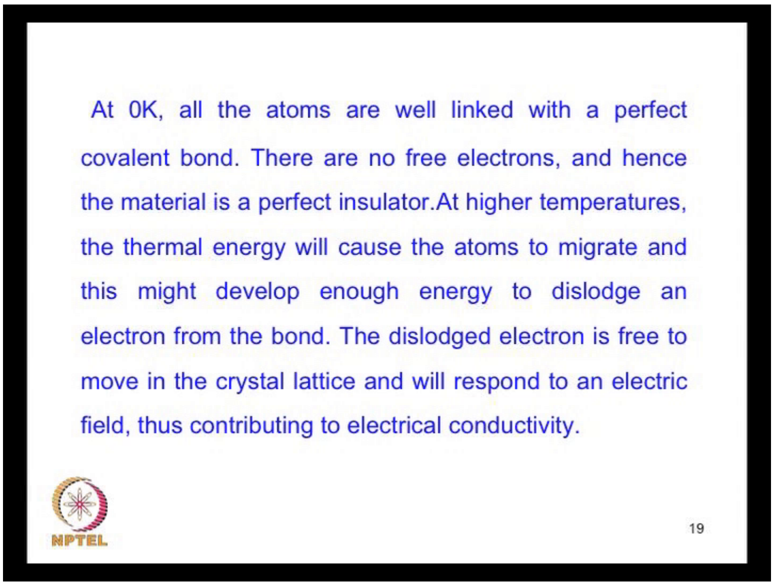

At 0K, all the atoms are well linked with a perfect covalent bond. There are no free electrons, and hence the material is a perfect insulator.At higher temperatures, the thermal energy will cause the atoms to migrate and this might develop enough energy to dislodge an electron from the bond. The dislodged electron is free to move in the crystal lattice and will respond to an electric field, thus contributing to electrical conductivity.

At 0 Kelvin all the atoms are well linked with a perfect covalent bond. And there are no free electron, there is no conduction, the semiconductor is a perfect insulator. But as the temperature is increased the thermal energy will cause the atoms to migrate. Once the electron gains enough thermal energy, it gets dislodged from this bond. So, the dislodged electron is now free to move in the crystal lattice, and this electron will now respond to an electric field, thus contributing to electrical conductivity.

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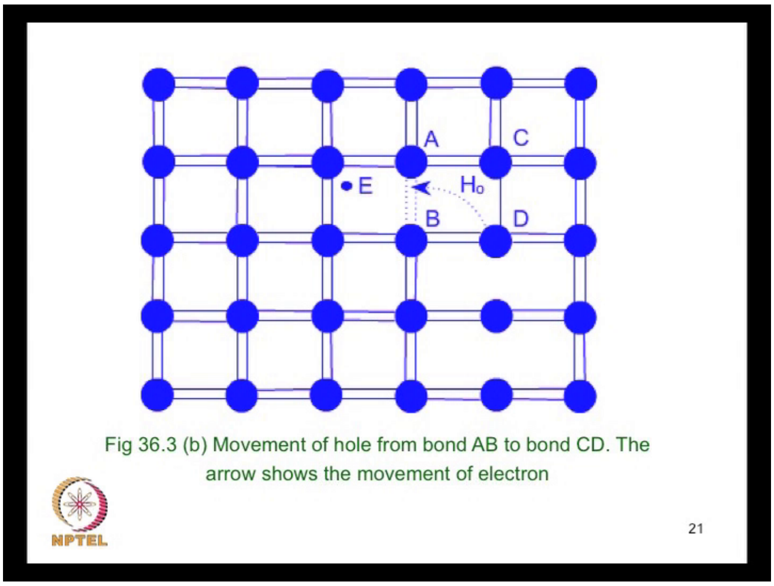

Fig 36.3 (b) Movement of hole from bond AB to bond CD. The arrow shows the movement of electron

Now in this figure the dislodged electron where shown by the letter E. So, the bond A B as last one electron. So, it has only a single link. So, between A and B, there is a missing link or a missing electron. A missing electron is shown as a hole H by the letter H. The electron these by the letter E in the figure, while H is for hole. So, when the electric field is applied, the electron moves in the direction opposite to that of the applied field, while the hole moves in the opposite direction. Now the missing link in the bond A B may be restored, if it captures another electron from a neighboring bond and then the hole moves on to that new side.

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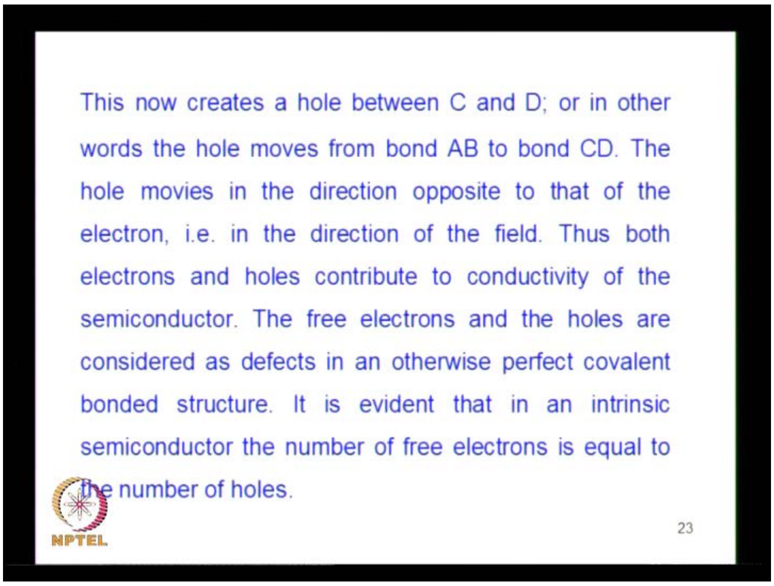

This now creates a hole between C and D; or in other words the hole moves from bond AB to bond CD. The hole movies in the direction opposite to that of the electron, i.e. in the direction of the field. Thus both electrons and holes contribute to conductivity of the semiconductor. The free electrons and the holes are considered as defects in an otherwise perfect covalent bonded structure. It is evident that in an intrinsic semiconductor the number of free electrons is equal to the number of holes.

So, this creates a hole now if it moves between c and d rather than from A and B because A B as captured an electron. So, the hole moves in the direction opposite to that of the electron it is along the direction of the field both the electrons and holes contribute to the conductivity the free electron and the holes are considered as defects in an otherwise perfect covalent bonded structure. So, in an intrinsic semiconductor the number of holes and the number of electrons are equal this is an important concept. Whereas, in the case of an extrinsic semiconductor as we already saw we have to add impurities or doped with impurities.

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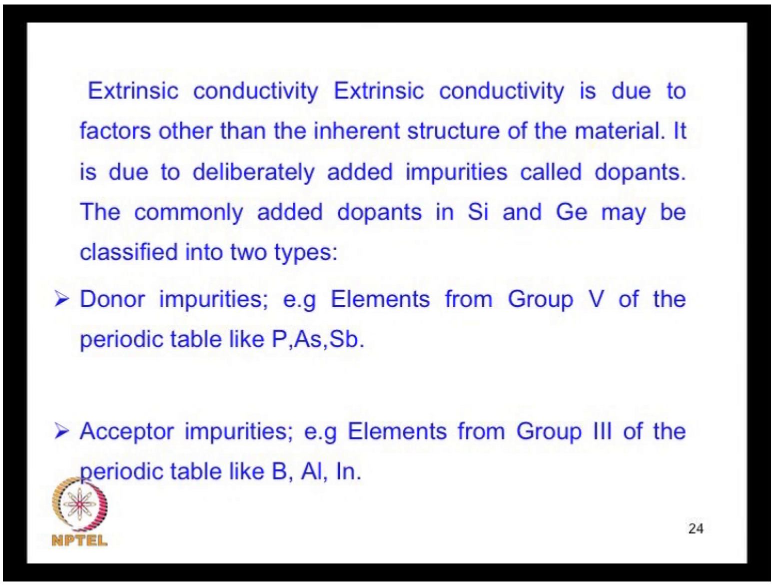

Extrinsic conductivity Extrinsic conductivity is due to factors other than the inherent structure of the material. It is due to deliberately added impurities called dopants. The commonly added dopants in Si and Ge may be classified into two types:

- Donor impurities; e.g Elements from Group V of the periodic table like P,As,Sb.

- Acceptor impurities; e.g Elements from Group III of the periodic table like B, Al, In.

Now, the impurities can be of two types. The impurities which are added can be either donor impurities or acceptor impurities. A donor impurity is one which donates an electron for example, an element from group 5 in the periodic table, we already saw these elements like phosphorus, arsenic and tumanic; whereas, acceptor impurities are one which are from an element from group 3 such as bismuth, aluminum, indium. So, these are added in extremely small quantities in at the part per million.

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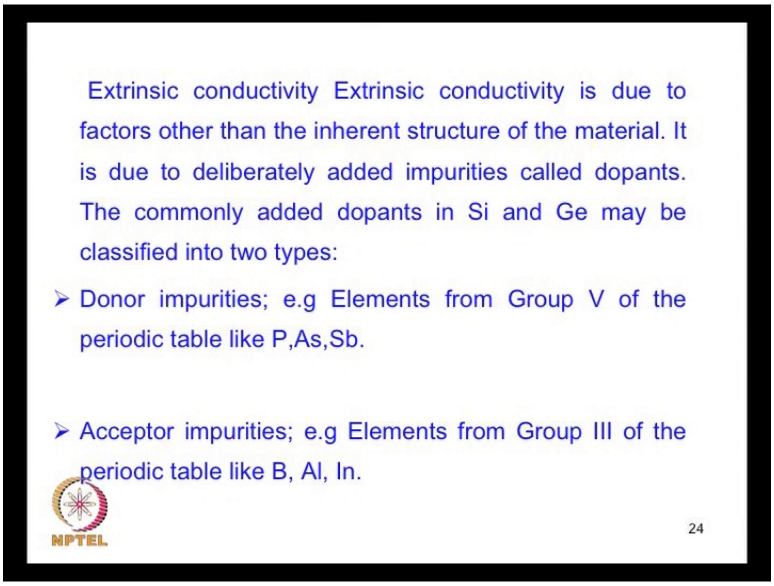

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- Donor impurities; e.g Elements from Group V of the periodic table like P,As,Sb.
- Acceptor impurities; e.g Elements from Group III of the periodic table like B, Al, In.

If it is a donor impurity, you added an electron, so it is said to give n type conductivity because it is electronic conduction since in charge on the electron is negative it is called n type semiconductors. When you doped a pure material semiconductor silicon or germanium with a controlled amount of donor impurities from group 5 of the periodic table, for example, give result in an n-type semiconductor. Whereas, if you have and acceptor, this will give me p-type semiconductor, because it accepts an electron and thus creates a hole. So, the conduction is by an excess of holes and the hole has a positive charge, it moves in the direction opposite to that of the electron in a electric field. So, this is usually from these. So, therefore, you have n-type semiconductors and p-type semiconductors.

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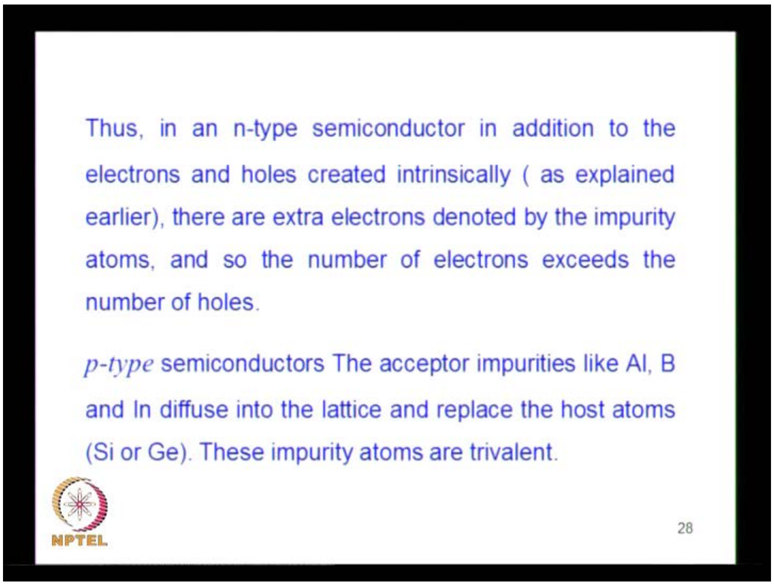

Thus, in an n-type semiconductor in addition to the electrons and holes created intrinsically (as explained earlier), there are extra electrons denoted by the impurity atoms, and so the number of electrons exceeds the number of holes.

p-type semiconductors The acceptor impurities like Al, B and In diffuse into the lattice and replace the host atoms (Si or Ge). These impurity atoms are trivalent.

So, in an n-type semiconductor, in addition to the electrons and holes which are created intrinsically by say thermal activation, there are additional electrons which are donated by the impurity atoms. And so, the number of electrons exceeds the number of holes, here n e - the electron concentration is greater than n h - the hole concentration. So, electrons are known as the majority carriers. Whereas, in a p-type semiconductor, the number of holes exceeds the number of electron, and therefore, holes are the majority carriers. Therefore, holes in an n-type material are also known as minority carriers; similarly, here the electrons are minority carriers. Each impurity atom creates a hole in the case of a p-type semiconductor, and the holes move in the direction of an applied field contributing to a hole conduction, so the number of holes exceeds that of electron. The amount of donor or acceptor impurities usually added is extremely small 10 to 100 phosphor ppm - parts per million, so that is the usual concentration. In order to do this, it is very important that we have an extremely pure basic most crystal material, silicon or germanium to which a controlled amount is added.

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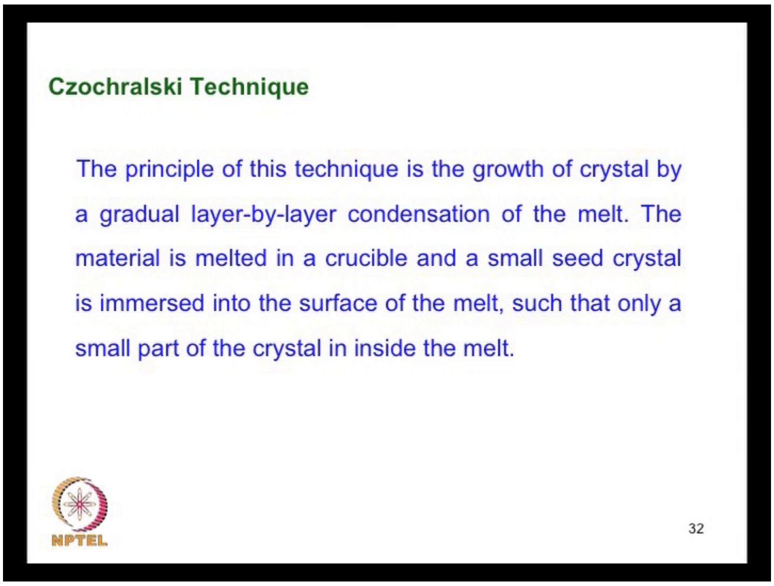

Czochralski Technique

The principle of this technique is the growth of crystal by a gradual layer-by-layer condensation of the melt. The material is melted in a crucible and a small seed crystal is immersed into the surface of the melt, such that only a small part of the crystal in inside the melt.

So, this is very important and that is why the production of semiconductors is an extremely difficult operation involving very importance techniques of crystal growth such as these Czochralski technique, zone refining and so on. We will not going to these technical aspects. So, the crystal growth crystallization of this pure semiconductor is a technology by itself.

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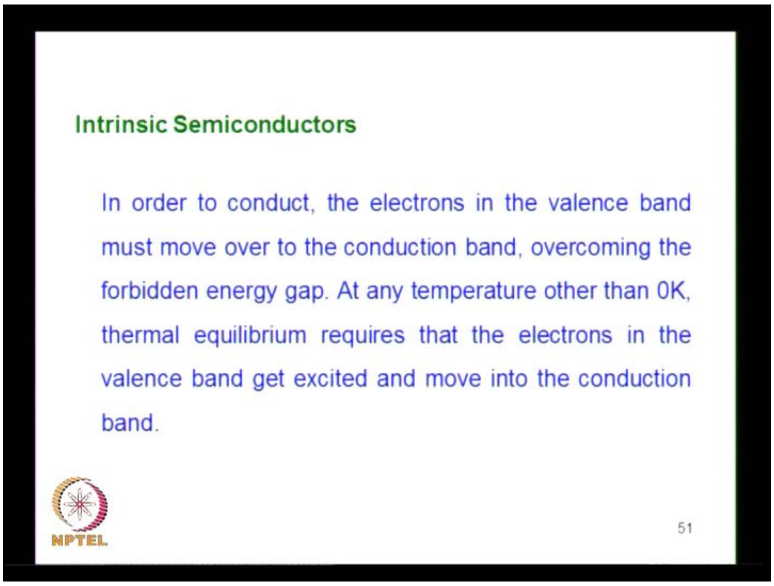

Intrinsic Semiconductors

In order to conduct, the electrons in the valence band must move over to the conduction band, overcoming the forbidden energy gap. At any temperature other than 0K, thermal equilibrium requires that the electrons in the valence band get excited and move into the conduction band.

Now if you want to understand the nature of conduction in a quantitative manner, we have two discuss a in terms of for an intrinsic semiconductor will go by carrier concentration, how to determine the carrier concentration in an intrinsic semiconductor.

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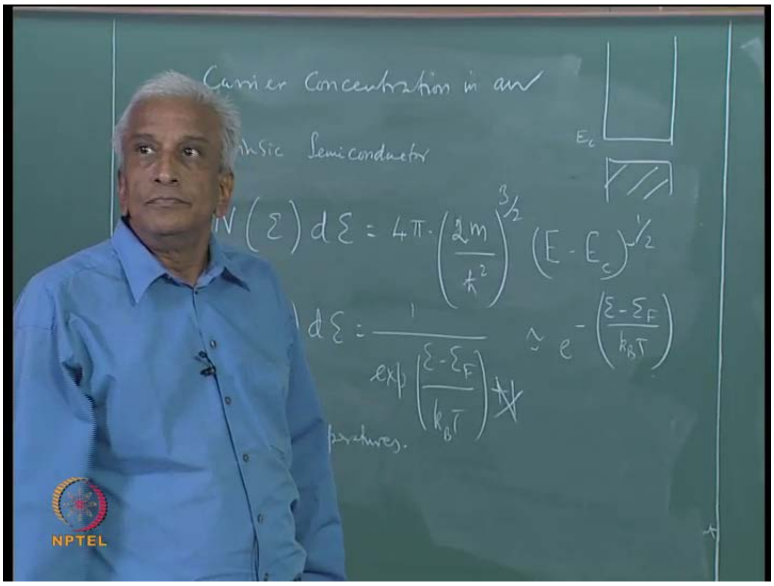

In order to know this, we have to know the number of electrons and holes. So, for this we have to go back to is so-called electron density a states.

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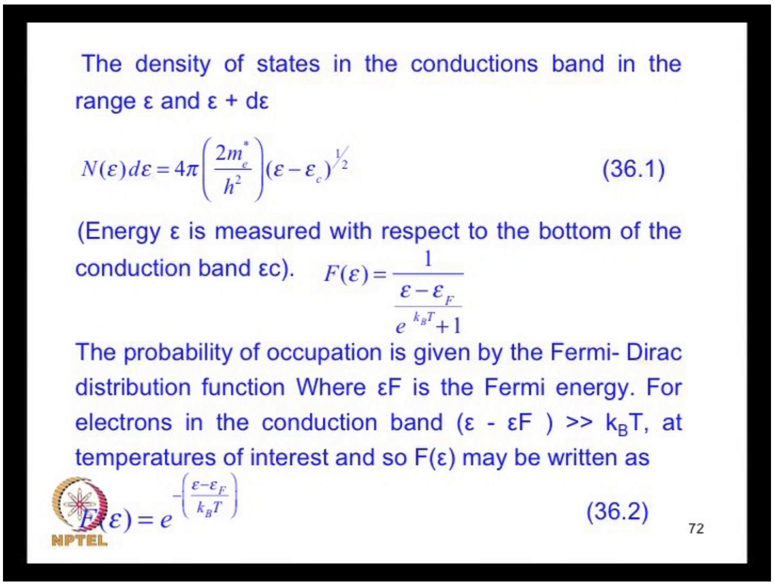

The density of states in the conductions band in the range ε and ε + dε

$$N(\varepsilon)d\varepsilon = 4\pi\left(\frac{2m_e^*}{h^2}\right)(\varepsilon-\varepsilon_c)^{1/2} \qquad (36.1)$$

(Energy ε is measured with respect to the bottom of the conduction band εc). $F(\varepsilon)=\frac{1}{e^{\frac{\varepsilon-\varepsilon_F}{k_BT}}+1}$

The probability of occupation is given by the Fermi- Dirac distribution function Where εF is the Fermi energy. For electrons in the conduction band (ε - εF) >> k_BT, at temperatures of interest and so F(ε) may be written as

$$F(\varepsilon)=e^{-\left(\frac{\varepsilon-\varepsilon_F}{k_BT}\right)} \qquad (36.2)$$

So, in order to find the concentration of carriers, we have to go to the number density of states N of e de which is 4 phi times 2 m by h cross squire to the power 3 by 2 times e minus e c to the power half this is because in the band structure of a semiconductor. This is taken off the bottom of the conduction band is taken as e and the energy is major from this, so that is why the energy term becomes e minus. In addition, we have the Fermi Dirac distribution function, which is 1 by exponential e minus e F by k B T plus 1. But at high temperatures, when the temperature is sufficiently high that e minus e F by k B T, the exponential is large compared to this. We can forget about this and this can be written as e to the power minus e minus e F by k B T combining these two expressions.

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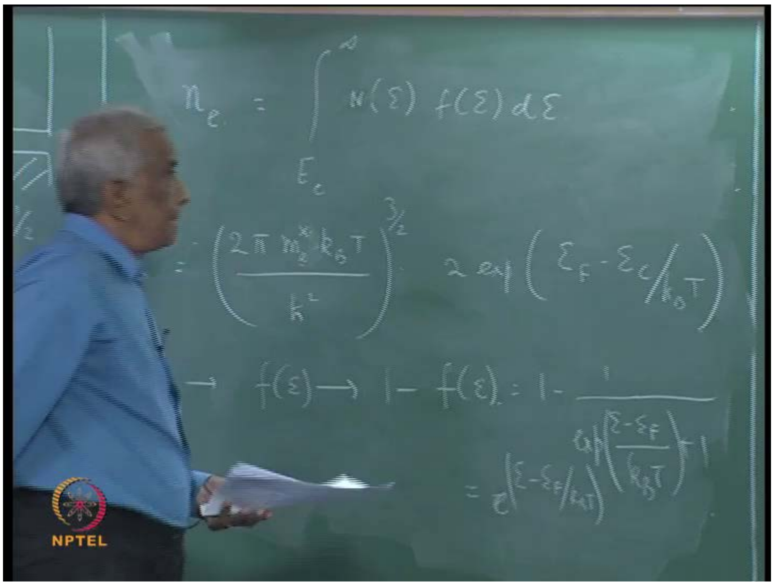

We get the expressions for the number of electrons in an energy interval e t by de and if I integrate it from E C to infinity that will give the number of electrons. So, if we carry out the integration, we arrive at the result 2 phi m k B T by h cross squire 3 power 3 by 2 into 2 exponential E F minus E C by k B T that will be the carrier concentration. Here of course, we do not write m as the mass of the free electrons since this electron e is in the periodic potential, we replace it by the m star, the effective mass. And we denote this as the effective mass of the electron by writing me star. Similarly we can calculate the hole concentration where we have to write instead of f of e should be replaced by 1 minus f of e, because this dependence on the probability of a state e not occupied or unoccupied when it is empty then the electron get in to it. And therefore, this depends on the number of vacancies, so it will be one minus f of e and that again gives you 1 minus 1 by and that will give you e to the power e minus e F by… So, they should be use in order to find the hole concentration, and we be integrate from the minus infinity to their top of the valence band, because that is where the holes exists. So, this is from minus infinity to the top of the valence band e V.

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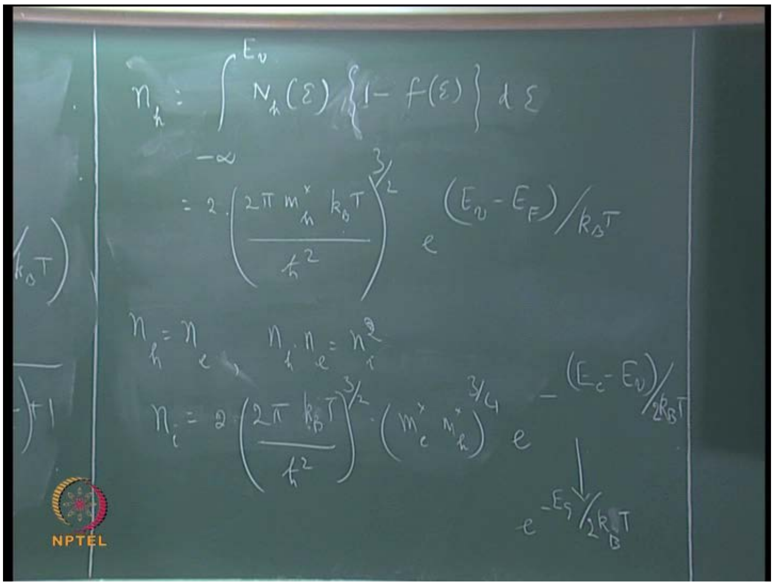

$$n_h = \int_{-\infty}^{E_v} N_h(\varepsilon)\left\{1 - f(\varepsilon)\right\} d\varepsilon$$

$$= 2\left(\frac{2\pi m_h^* k_B T}{\hbar^2}\right)^{3/2} e^{(E_v - E_F)/k_B T}$$

$$n_h = n_e, \quad n_h \cdot n_e = n_i^2$$

$$n_i = 2\left(\frac{2\pi k_B T}{\hbar^2}\right)^{3/2} \cdot \left(m_e^* m_h^*\right)^{3/4} e^{-(E_c - E_v)/2k_B T}$$

$$\downarrow$$

$$e^{-E_g/2k_B T}$$

So, n h is integral and that use the result m h star k B T y h cross square 3 by 2 into e to the power and E v minus E F by k B T. So, the number of holes and the number of electrons whenever the hole is created here then electrons gets exacted automatically. So, that number of holes at the number of electrons are equal in an intrinsic semiconductor. Therefore, n h times n e is what I call an i square in intrinsic carriers concentration, so that from these relation can find the intrinsic carriers concentration has with a bit of algebra this can be shown to be and what is C minus e v that is nothing but a energy gap. So, this becomes just exponential minus E g by 2 k B T.

Now we are taking the square root. So, we can see that the conductivity which we proportional to the carrier concentration in intrinsic carrier concentration will depend exponentially on the argument E g by 2 k B T. So, if the energy gap, which is usually as the order of one electron volt that is the energy gap. So, and the temperature 300 k, this will be the sort of this leads to the known exponential dependence as well as the known positive temperature coefficient of a semiconductor.

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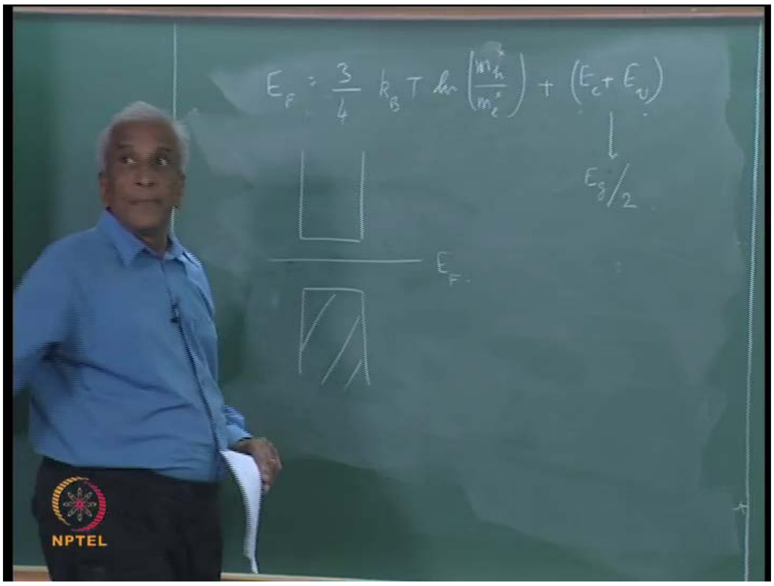

Inverting this, we can also find the Fermi energy, it turns out that the Fermi energy is three-fourth k B T m h star by m e star plus E c plus E v. If the hole and electron as the same effect you mass than this term will become 0 leaving all this and this will be E g by 2, the average of E c and E v. So, the Fermi energy lies midway between the conduction band and the valance band in a semiconductor.

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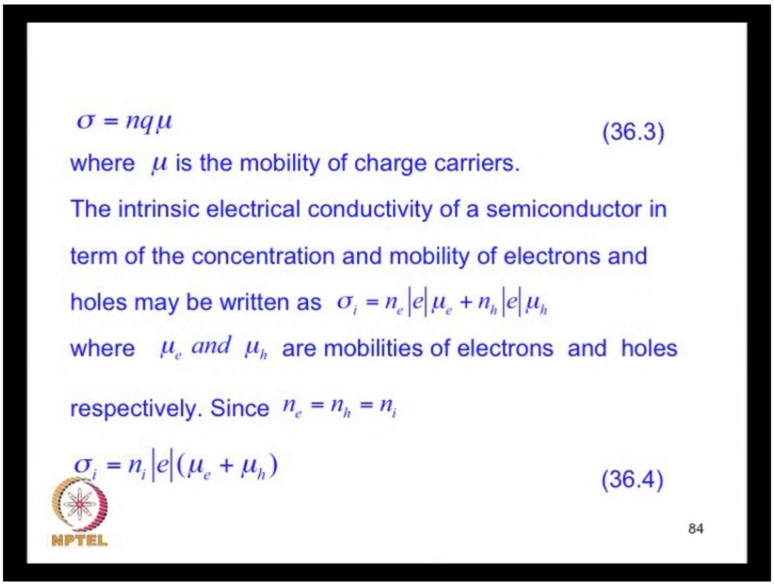

$\sigma = nq\mu$ (36.3)

where μ is the mobility of charge carriers.

The intrinsic electrical conductivity of a semiconductor in term of the concentration and mobility of electrons and holes may be written as $\sigma_i = n_e|e|\mu_e + n_h|e|\mu_h$

where μ_e *and* μ_h are mobilities of electrons and holes respectively. Since $n_e = n_h = n_i$

$\sigma_i = n_i|e|(\mu_e + \mu_h)$ (36.4)

So, the intrinsic carrier concentration goes the exponential minus E g by 2 k B T.

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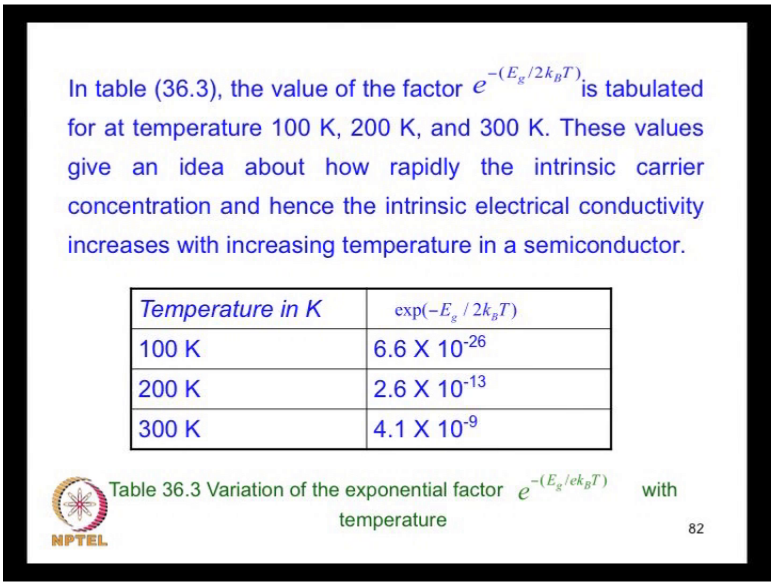

In table (36.3), the value of the factor $e^{-(E_g/2k_BT)}$ is tabulated for at temperature 100 K, 200 K, and 300 K. These values give an idea about how rapidly the intrinsic carrier concentration and hence the intrinsic electrical conductivity increases with increasing temperature in a semiconductor.

Temperature in K	$\exp(-E_g/2k_BT)$
100 K	6.6 X 10^{-26}
200 K	2.6 X 10^{-13}
300 K	4.1 X 10^{-9}

Table 36.3 Variation of the exponential factor $e^{-(E_g/ek_BT)}$ with temperature

This temperature dependent exponential term table shows the variation temperature dependence on the factor. So, the intrinsic electrical and conductivity will consist of two terms one involving the electron and another involving the hole. Well we can similarly in discuss the concentration of majority carriers in an extrinsic semiconductor, we will do that next time.

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Reference

Semiconductors
R. A. Smith
2nd edition
Cambridge University Press
1978