Case II: In this case, as shown in Fig. 14.2(b), a large band gap E_g exists ($E_g > 3$ eV). There are no electrons in the conduction band, and therefore no electrical conduction is possible. Note that the energy gap is so large that electrons cannot be excited from the valence band to the conduction band by thermal excitation. This is the case of *insulators*.

Case III: This situation is shown in Fig. 14.2(c). Here a finite but small band gap ($E_g < 3$ eV) exists. Because of the small band gap, at room temperature some electrons from valence band can acquire enough energy to cross the energy gap and enter the *conduction band*. These electrons (though small in numbers) can move in the conduction band. Hence, the resistance of *semiconductors* is not as high as that of the insulators.

In this section we have made a broad classification of metals, conductors and semiconductors. In the section which follows you will learn the conduction process in semiconductors.

14.3 Intrinsic Semiconductor

We shall take the most common case of Ge and Si whose lattice structure is shown in Fig. 14.3. These structures are called the diamond-like structures. Each atom is surrounded by four nearest neighbours. We know that Si and Ge have four valence electrons. In its crystalline structure, every Si or Ge atom tends *to share* one of its four valence electrons with each of its four nearest neighbour atoms, and also *to take share* of one electron from each such neighbour. These shared electron pairs are referred to as forming a *covalent bond* or simply a *valence bond*. The two shared electrons can be assumed to shuttle back-and-forth between the associated atoms holding them together strongly. Figure 14.4 schematically shows the 2-dimensional representation of Si or Ge structure shown in Fig. 14.3 which overemphasises the covalent bond. It shows an idealised picture in which no bonds are broken (all bonds are intact). Such a situation arises at low temperatures. As the temperature increases, more thermal energy becomes available to these electrons and some of these electrons may break–away (becoming *free* electrons contributing to conduction). The thermal energy effectively ionises only a few atoms in the crystalline lattice and creates a *vacancy* in the bond as shown in Fig. 14.5(a). The neighbourhood, from which the free electron (with charge $-q$) has come out leaves a vacancy with an effective charge ($+q$). This *vacancy* with the effective positive electronic charge is called a *hole*. The hole behaves as an *apparent free particle* with effective positive charge.

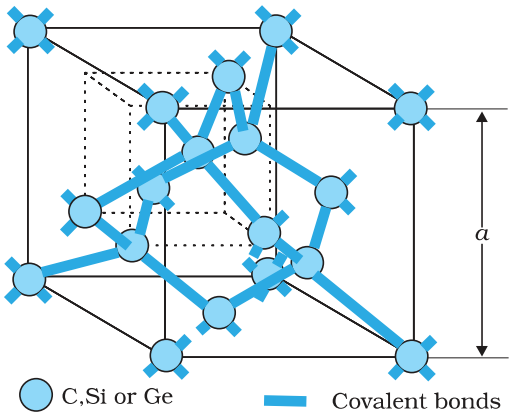


FIGURE 14.3 Three-dimensional diamond-like crystal structure for Carbon, Silicon or Germanium with respective lattice spacing a equal to 3.56, 5.43 and 5.66 Å.

In intrinsic semiconductors, the number of free electrons, n_e is equal to the number of holes, n_h. That is

$$n_e = n_h = n_i \qquad (14.1)$$

where n_i is called intrinsic carrier concentration.

Semiconductors posses the unique property in which, apart from electrons, the holes also move.

Suppose there is a hole at site 1 as shown in Fig. 14.5(a). The movement of holes can be visualised as shown in Fig. 14.5(b). An electron from the covalent bond at site 2 may jump to the vacant site 1 (hole). Thus, after such a jump, the hole is at site 2 and the site 1 has now an electron. Therefore, apparently, the hole has moved from site 1 to site 2. Note that the electron originally set free [Fig. 14.5(a)] is not involved in this process of hole motion. The free electron moves completely independently as conduction electron and gives rise to an electron current, I_e under an applied electric field. Remember that the motion of hole is only a convenient way of describing the actual motion of *bound* electrons, whenever there is an empty bond anywhere in the crystal. Under the action of an electric field, these holes move towards negative potential giving the hole current, I_h. The total current, I is thus the sum of the electron current I_e and the hole current I_h:

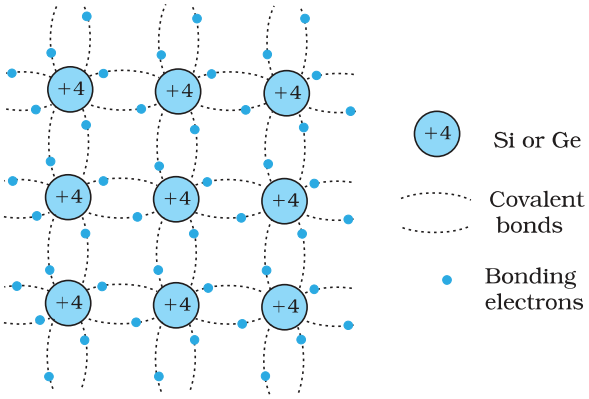


FIGURE 14.4 Schematic two-dimensional representation of Si or Ge structure showing covalent bonds at low temperature (all bonds intact). +4 symbol indicates inner cores of Si or Ge.

$$I = I_e + I_h \qquad (14.2)$$

It may be noted that apart from the *process of generation* of conduction electrons and holes, a simultaneous *process of recombination* occurs in which the electrons *recombine* with the holes. At equilibrium, the rate of generation is equal to the rate of recombination of charge carriers. The recombination occurs due to an electron colliding with a hole.

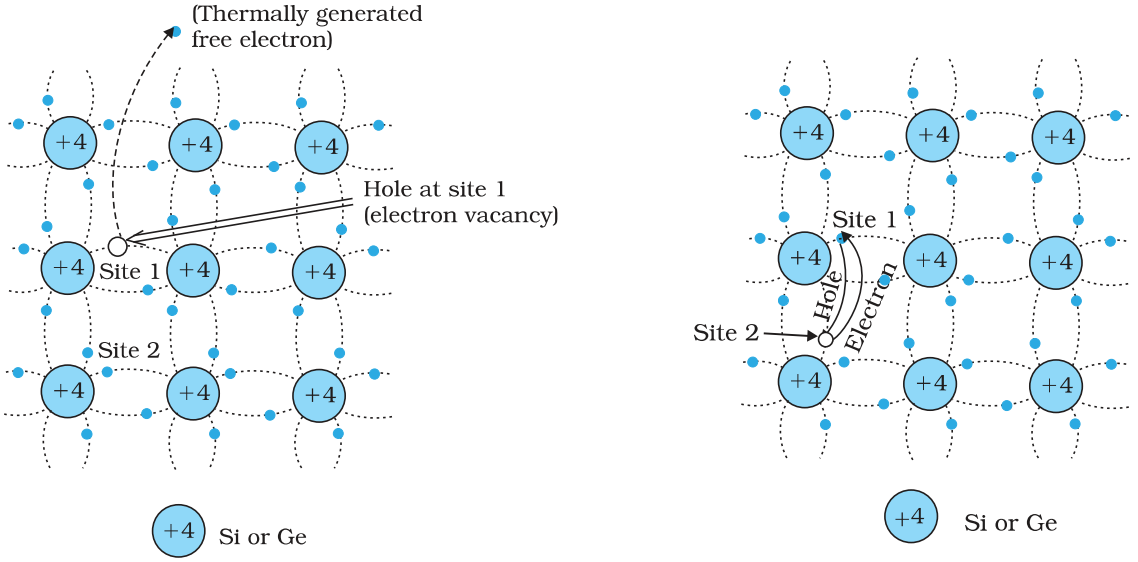


FIGURE 14.5 (a) Schematic model of generation of hole at site 1 and conduction electron due to thermal energy at moderate temperatures. (b) Simplified representation of possible thermal motion of a hole. The electron from the lower left hand covalent bond (site 2) goes to the earlier hole site1, leaving a hole at its site indicating an apparent movement of the hole from site 1 to site 2.

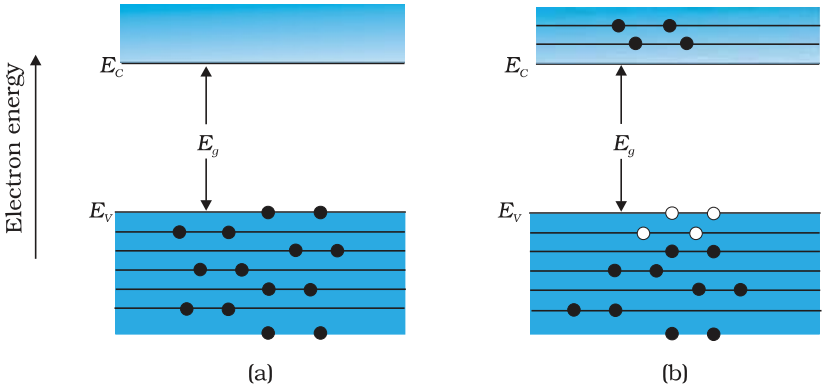


FIGURE 14.6 (a) An intrinsic semiconductor at $T = 0$ K behaves like insulator. (b) At $T > 0$ K, four thermally generated electron-hole pairs. The filled circles (•) represent electrons and empty fields (○) represent holes.

An intrinsic semiconductor will behave like an insulator at $T = 0$ K as shown in Fig. 14.6(a). It is the thermal energy at higher temperatures ($T > 0$K), which excites some electrons from the valence band to the conduction band. These thermally excited electrons at $T > 0$ K, partially occupy the conduction band. Therefore, the energy-band diagram of an intrinsic semiconductor will be as shown in Fig. 14.6(b). Here, some electrons are shown in the conduction band. These have come from the valence band leaving equal number of holes there.

EXAMPLE 14.1

Example 14.1 C, Si and Ge have same lattice structure. Why is C insulator while Si and Ge intrinsic semiconductors?

Solution The 4 bonding electrons of C, Si or Ge lie, respectively, in the second, third and fourth orbit. Hence, energy required to take out an electron from these atoms (i.e., ionisation energy E_g) will be least for Ge, followed by Si and highest for C. Hence, number of free electrons for conduction in Ge and Si are significant but negligibly small for C.

14.4 EXTRINSIC SEMICONDUCTOR

The conductivity of an intrinsic semiconductor depends on its temperature, but at room temperature its conductivity is very low. As such, no important electronic devices can be developed using these semiconductors. Hence there is a necessity of improving their conductivity. This can be done by making use of impurities.

When a small amount, say, a few parts per million (ppm), of a suitable impurity is added to the pure semiconductor, the conductivity of the semiconductor is increased manifold. Such materials are known as *extrinsic semiconductors* or *impurity semiconductors*. The deliberate addition of a desirable impurity is called *doping* and the impurity atoms are called *dopants*. Such a material is also called a *doped semiconductor*. The dopant has to be such that it does not distort the original pure semiconductor lattice. It occupies only a very few of the original semiconductor atom sites in the crystal. A necessary condition to attain this is that the sizes of the dopant and the semiconductor atoms should be nearly the same.

There are two types of dopants used in doping the tetravalent Si or Ge:

(i) Pentavalent (valency 5); like Arsenic (As), Antimony (Sb), Phosphorous (P), etc.

(ii) Trivalent (valency 3); like Indium (In), Boron (B), Aluminium (Al), etc.

We shall now discuss how the doping changes the number of charge carriers (and hence the conductivity) of semiconductors. Si or Ge belongs to the fourth group in the Periodic table and, therefore, we choose the dopant element from nearby fifth or third group, expecting and taking care that the size of the dopant atom is nearly the same as that of Si or Ge. Interestingly, the pentavalent and trivalent dopants in Si or Ge give two entirely different types of semiconductors as discussed below.

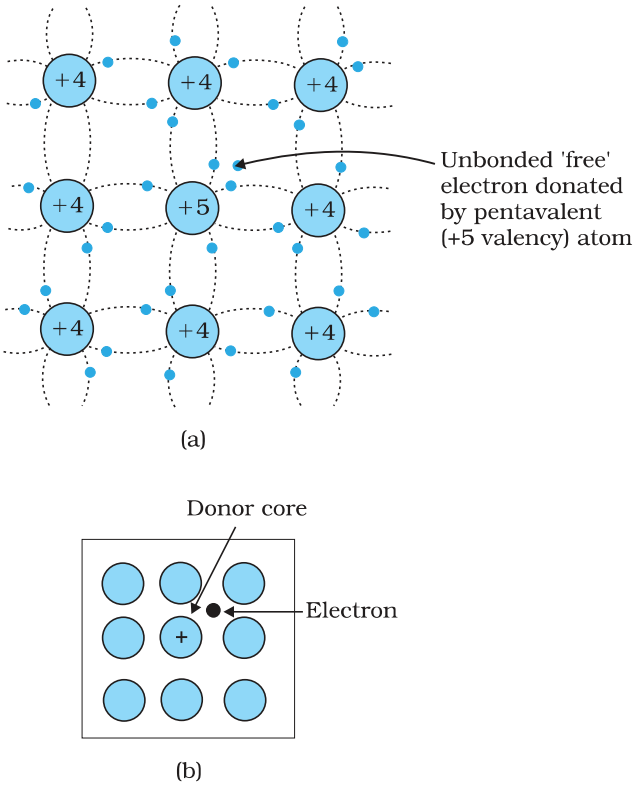


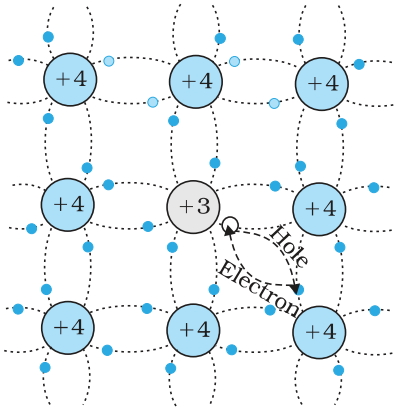
FIGURE 14.7 (a) Pentavalent donor atom (As, Sb, P, etc.) doped for tetravalent Si or Ge giving n-type semiconductor, and (b) Commonly used schematic representation of n-type material which shows only the fixed cores of the substituent donors with one additional effective positive charge and its associated extra electron.

(i) n-type semiconductor

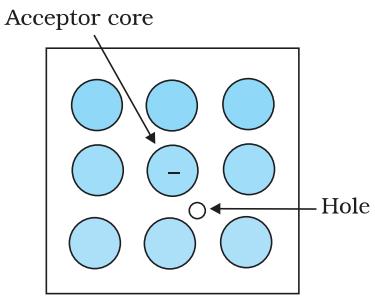
Suppose we dope Si or Ge with a pentavalent element as shown in Fig. 14.7. When an atom of +5 valency element occupies the position of an atom in the crystal lattice of Si, four of its electrons bond with the four silicon neighbours while the fifth remains very weakly bound to its parent atom. This is because the four electrons participating in bonding are seen as part of the effective core of the atom by the fifth electron. As a result the ionisation energy required to set this electron free is very small and even at room temperature it will be free to move in the lattice of the semiconductor. For example, the energy required is ~ 0.01 eV for germanium, and 0.05 eV for silicon, to separate this electron from its atom. This is in contrast to the energy required to jump the forbidden band (about 0.72 eV for germanium and about 1.1 eV for silicon) at room temperature in the intrinsic semiconductor. Thus, the pentavalent dopant is donating one extra electron for conduction and hence is known as *donor* impurity. The number of electrons made available for conduction by dopant atoms depends strongly upon the doping level and is independent of any increase in ambient temperature. On the other hand, the number of free electrons (with an equal number of holes) generated by Si atoms, increases weakly with temperature.

In a doped semiconductor the total number of conduction electrons n_e is due to the electrons contributed by donors and those generated intrinsically, while the total number of holes n_h is only due to the holes from the intrinsic source. But the rate of recombination of holes would increase due to the increase in the number of electrons. As a result, the number of holes would get reduced further.

Thus, with proper level of doping the number of conduction electrons can be made much larger than the number of holes. Hence in an extrinsic



(a)



(b)

FIGURE 14.8 (a) Trivalent acceptor atom (In, Al, B etc.) doped in tetravalent Si or Ge lattice giving p-type semiconductor. (b) Commonly used schematic representation of p-type material which shows only the fixed core of the substituent acceptor with one effective additional negative charge and its associated hole.

semiconductor doped with pentavalent impurity, electrons become the *majority carriers* and holes the *minority carriers*. These semiconductors are, therefore, known as n-*type semiconductors*. For n-type semiconductors, we have,

$$n_e >> n_h \qquad (14.3)$$

(ii) p-type semiconductor

This is obtained when Si or Ge is doped with a trivalent impurity like Al, B, In, etc. The dopant has one valence electron less than Si or Ge and, therefore, this atom can form covalent bonds with neighbouring three Si atoms but does not have any electron to offer to the fourth Si atom. So the bond between the fourth neighbour and the trivalent atom has a vacancy or hole as shown in Fig. 14.8. Since the neighbouring Si atom in the lattice wants an electron in place of a hole, an electron in the outer orbit of an atom in the neighbourhood may jump to fill this vacancy, leaving a vacancy or hole at its own site. Thus the *hole* is available for conduction. Note that the trivalent foreign atom becomes effectively negatively charged when it shares fourth electron with neighbouring Si atom. Therefore, the dopant atom of p-type material can be treated as *core of one negative charge* along with its associated hole as shown in Fig. 14.8(b). It is obvious that one *acceptor* atom gives one *hole*. These holes are in addition to the intrinsically generated holes while the source of conduction electrons is only intrinsic generation. Thus, for such a material, the holes are the majority carriers and electrons are minority carriers. Therefore, extrinsic semiconductors doped with trivalent impurity are called p-*type semiconductors*. For p-type semiconductors, the recombination process will reduce the number (n_i)of intrinsically generated electrons to n_e. We have, for p-type semiconductors

$$n_h >> n_e \qquad (14.4)$$

Note that *the crystal maintains an overall charge neutrality as the charge of additional charge carriers is just equal and opposite to that of the ionised cores in the lattice.*

In extrinsic semiconductors, because of the abundance of majority current carriers, the minority carriers produced thermally have more chance of meeting majority carriers and thus getting destroyed. Hence, the dopant, by adding a large number of current carriers of one type, which become the majority carriers, indirectly helps to reduce the intrinsic concentration of minority carriers.

The semiconductor's energy band structure is affected by doping. In the case of extrinsic semiconductors, additional energy states due to donor impurities (E_D) and acceptor impurities (E_A) also exist. In the energy band diagram of n-type Si semiconductor, the donor energy level E_D is slightly below the bottom E_C of the conduction band and electrons from this level move into the conduction band with very small supply of energy. At room temperature, most of the donor atoms get ionised but very few ($\sim 10^{-12}$) atoms of Si get ionised. So the conduction band will have most electrons coming from the donor impurities, as shown in Fig. 14.9(a). Similarly,

for p-type semiconductor, the acceptor energy level E_A is slightly above the top E_V of the valence band as shown in Fig. 14.9(b). With very small supply of energy an electron from the valence band can jump to the level E_A and ionise the acceptor negatively. (Alternately, we can also say that with very small supply of energy the hole from level E_A sinks down into the valence band. Electrons rise up and holes fall down when they gain external energy.) At room temperature, most of the acceptor atoms get ionised leaving holes in the valence band. Thus at room temperature the density of holes in the valence band is predominantly due to impurity in the extrinsic semiconductor. The electron and hole concentration in a semiconductor *in thermal equilibrium* is given by

$$n_e n_h = n_i^2 \qquad (14.5)$$

Though the above description is grossly approximate and hypothetical, it helps in understanding the difference between metals, insulators and semiconductors (extrinsic and intrinsic) in a simple manner. The difference in the resistivity of C, Si and Ge depends upon the energy gap between their conduction and valence bands. For C (diamond), Si and Ge, the energy gaps are 5.4 eV, 1.1 eV and 0.7 eV, respectively. Sn also is a group IV element but it is a metal because the energy gap in its case is 0 eV.

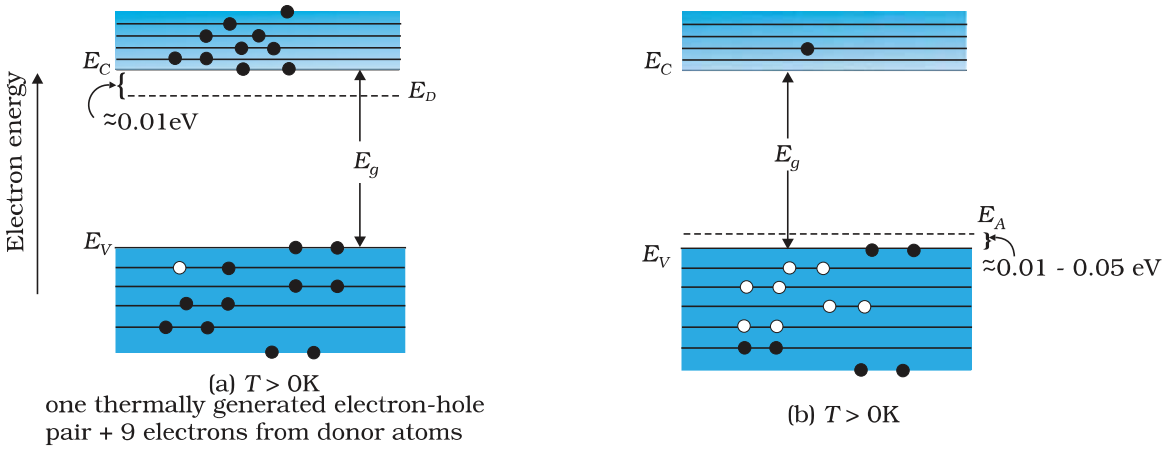


FIGURE 14.9 Energy bands of (a) n-type semiconductor at $T > 0$K, (b) p-type semiconductor at $T > 0$K.

Example 14.2 Suppose a pure Si crystal has 5×10^{28} atoms m^{-3}. It is doped by 1 ppm concentration of pentavalent As. Calculate the number of electrons and holes. Given that $n_i = 1.5 \times 10^{16}$ m^{-3}.

Solution Note that thermally generated electrons ($n_i \sim 10^{16}$ m^{-3}) are negligibly small as compared to those produced by doping.
Therefore, $n_e \approx N_D$.
Since $n_e n_h = n_i^2$, The number of holes
$n_h = (2.25 \times 10^{32})/(5 \times 10^{22})$

$\sim 4.5 \times 10^{9}$ m^{-3}

EXAMPLE 14.2