

# 4

## Basic Properties of Semiconductors

### 4.1. INTRODUCTION

In general, the main factors that determine basic properties (e.g., optical and electrical properties) of semiconductors are related to the chemical composition and the (crystallographic) structure, the presence of various defects and impurities (both intentional and unintentional), and the dimensions of the semiconductor or semiconductor structure (i.e., related to the quantum confinement regime). The chemical composition and the (crystallographic) structure determine the electronic band structure (e.g., the magnitude and the type of energy gap, and the carrier effective mass), which has the major influence on the semiconductor properties. The presence of various defects and impurities results in the introduction (in the energy gap of the semiconductor) of various electronic states (both shallow and deep) that affect strongly the optical and electrical properties. Finally, as will be discussed in the subsequent chapters, for the semiconductor dimensions commensurate with the de Broglie wavelength of carriers (i.e., of the order of 10 nm), quantum size effects dominate the semiconductor properties.

As mentioned in Chapter 1, the electrical conductivity of semiconductors can be varied (in both sign and magnitude) widely as a function of (i) impurity content (e.g., doping), (ii) temperature (i.e., thermal excitation), (iii) optical excitation (i.e., excitation with photons having energies greater than the energy gap  $E_g$ ), and (iv) excess charge carrier injection (e.g., in semiconductor devices). It is this capability of controlling the electrical conductivity in semiconductors that offers myriad applications of these materials in a wide variety of electronic and optoelectronic devices.

### 4.2. ELECTRONS AND HOLES IN SEMICONDUCTORS

In a semiconductor containing no impurities or defects, i.e., an *intrinsic semiconductor*, at temperatures above 0 K some thermally excited electrons are

promoted from the valence band to the conduction band. An unoccupied state in the valence band is called a *hole*, which may be regarded as a positive charge carrier that can contribute to the conduction process (see Section 3.6). Electronic transitions across the energy gap to the conduction band result in a spontaneous generation of holes in the valence band, and the generated carriers are described as *electron–hole pairs*. After a random motion through the lattice, the electron in the conduction band encounters a hole and undergoes a recombination transition. The generation of electron–hole pairs and their subsequent recombination is a continuous process, and the average time that carriers exist between generation and recombination is called the *lifetime* of the carrier. During this process of generation of electron–hole pairs, the concentration of electrons (denoted as  $n$ ) in the conduction band is equal to the concentration of holes (denoted as  $p$ ) in the valence band. This can be expressed as

$$n = p = n_i \quad (4.2.1)$$

where  $n_i$  is the intrinsic carrier concentration.

Electrons and holes in the conduction and valence bands, respectively (carrying negative and positive electronic charges, respectively), are referred to as *free charge carriers*. In the presence of an electric field  $\mathcal{E}$ , the free charge carriers attain the *drift velocity*,  $\mathbf{v}$ , and a net current density,  $\mathbf{J}$ . (Note that the electron and hole will have the drift velocities in opposite directions.) In the case of Ohm's law (i.e.,  $\mathbf{J} = \sigma \mathcal{E}$ , where  $\sigma$  is the *conductivity*), the drift velocity is proportional to the applied electric field (i.e., for electrons  $v_n = -\mu_e \mathcal{E}$ ), and the proportionality constant  $\mu_e$  is referred to as the *carrier mobility* of electrons (the mobility is a measure of the frequency of scattering events and is related to the *scattering relaxation time*  $\tau$  as  $\mu = e\tau/m^*$ ); note that in this case the direction of drift velocity is opposite to the direction of the electric field, since the charge carriers, i.e., electrons, are negatively charged. The current density for electrons and holes can be expressed as  $\mathbf{J}_n = -ne\mathbf{v}_n$  and  $\mathbf{J}_p = pe\mathbf{v}_p$ , respectively. Thus, the current densities for electrons and holes are in the same direction, since their corresponding drift velocities are in the opposite directions. The conductivity  $\sigma$  for electrons and holes can be written as  $\sigma_n = ne\mu_e$  and  $\sigma_p = pe\mu_h$  (where  $e = 1.602 \times 10^{-19}$  C is the electron charge). Since both electrons and holes contribute to the current in intrinsic semiconductors (i.e.,  $n=p$ ), the bulk conductivity  $\sigma$  must in principle be expressed as

$$\sigma = ne\mu_e + pe\mu_h \quad (4.2.2)$$

where  $\mu_e$  and  $\mu_h$  are the mobilities of electrons and holes, respectively. However, the electrons have the major contribution to the current, since typically  $\mu_e > \mu_h$  (for values of  $\mu_e$  and  $\mu_h$  see Table B1 in Appendix B); this is due to the inverse relationship between the carrier mobility and the carrier effective mass.

The carrier mobility is determined by random scattering processes, among which the main mechanisms in semiconductors include *impurity scattering* and the intrinsic *phonon (lattice) scattering*. Impurity scattering sources include both the ionized and neutral donor and acceptor atoms that are used to dope the

semiconductor to the desired conductivity level. In general, impurity scattering may also arise due to unintentionally introduced impurities and native defects and their complexes. The ionized donor and/or acceptor scattering is due to the Coulomb attraction or repulsion between the charge carriers and these ionized impurities. The scattering by neutral impurity atoms becomes considerable at sufficiently low temperatures at which a substantial number of the impurity atoms becomes neutral. The intrinsic scattering mechanisms may also include, besides phonon scattering, carrier–carrier scattering and inter-valley scattering. Typically, carrier–carrier scattering may have a significant contribution only in heavily doped semiconductors under degenerate conditions or under high-field conditions, and inter-valley scattering may occur in materials having several minima in the conduction band. The phonon (lattice) scattering mechanism usually involves two types of phonon scatterings, i.e., acoustical and optical phonon scattering mechanisms. In general, ionized impurity scattering ( $\mu_I$ ) and phonon scattering ( $\mu_{ph}$ ) are dominant electron scattering mechanisms in practical semiconductors. (In such a case, the combined mobility can be expressed as  $1/\mu = 1/\mu_I + 1/\mu_{ph}$ .) It should be noted that higher doping concentrations result in increased scattering (and lower mobilities) of the carriers by the ionized impurities.

The temperature dependence of the mobility, as described by theoretical considerations, reveals opposite temperature dependencies for the ionized impurity scattering and the phonon scattering. These are, for ionized impurity scattering,  $\mu_I \propto T^{3/2}/N_I$  (where  $N_I$  is the total impurity concentration, i.e.,  $N_d + N_a$ ), and for phonon scattering,  $\mu_{ph} \propto T^{-3/2}$ . At lower temperature regime, the carrier velocity increases with increasing temperature, resulting in the reduced time that the carriers spend in the vicinity of the scattering centers. Thus, the mobility increases with temperature. However, with further increase in temperature, the lattice vibrations become dominant, resulting in increasing probability of scattering by the lattice and in decreasing mobility. Thus, to summarize briefly, because of the opposite temperature dependences for the ionized impurity scattering and the lattice scattering, the mobility reaches a maximum at a specific temperature, which depends on the concentration of ionized impurities (i.e., with increasing impurity concentrations, the position of the maximum is shifted to increasingly higher temperatures).

#### 4.3. THE FERMI–DIRAC DISTRIBUTION FUNCTION AND THE DENSITY OF STATES

One of the most important objectives in describing a semiconductor in relation to its electrical and optical properties is to determine both the carrier concentrations and the energy distributions. These require knowledge of (i) the *probability of carrier occupancy* of a state at energy  $E$  and (ii) the density of available states, or *density of states* (DOS). The occupation statistics of energy levels by carriers is described by the *Fermi–Dirac occupation statistics*. In other words, the carrier energy distribution is described by the Fermi–Dirac statistics, and, specifically, the probability of an electron occupying a state at energy  $E$  is

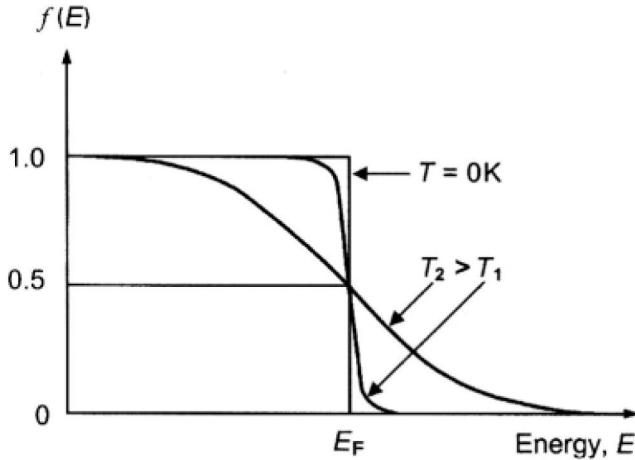


FIGURE 4.1. The Fermi-Dirac distribution function  $f(E)$  vs. energy at different temperatures.

described by the *Fermi-Dirac distribution function*  $f(E)$ , which for electrons is (see Fig. 4.1)

$$f_n(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1} \quad (4.3.1)$$

where the energy  $E_F$  is called the *Fermi energy* (also referred to as *Fermi level*), which is defined as the energy at which  $f(E) = 1/2$ , i.e., the energy for which the probability of occupation is 1/2.

Correspondingly, the hole distribution function is

$$f_p(E) = 1 - f_n(E) = \frac{1}{\exp[(E_F - E)/k_B T] + 1} \quad (4.3.2)$$

In a semiconductor, the mobile electrons are those occupying the energy state  $E$  greater than  $E_c$ . In the analysis and description of various processes in semiconductors, it is essential to calculate the electron concentration in the conduction band. In this case, the total concentration of electrons is proportional to (i) the number of states per unit volume and per unit energy [i.e., the DOS,  $g(E)$ ], over the energy interval between  $E$  and  $E + dE$  and (ii) the probability of an electron occupying a state at energy  $E$ , i.e.,  $f(E)$ . The total number of electrons in the conduction band can be determined by integrating this function over energy from the bottom energy  $E_c$  to the top energy in the conduction band. The difficulty involved in evaluating the integral in such a case is due to the fact that it would require introducing an additional parameter related to the width of the conduction band. However, since the Fermi level is much below the top of the conduction band, the upper limit for the integration can be replaced by infinity, and thus, the total number of electrons in the conduction band is

$$n = \int_{E_c}^{\infty} g_n(E) f_n(E) dE \quad (4.3.3)$$

Similarly, for holes in the valence band, the total number of holes can be expressed as

$$p = \int_{-\infty}^{E_v} g_p(E) f_p(E) dE \quad (4.3.4)$$

Thus, the evaluation of the total number of electrons and holes in their respective bands requires knowledge of the DOS  $g(E)$ . From the analysis of the case of an electron in a three-dimensional box (e.g., a cube of side  $L$ ), described in Chapter 3, the expression for its energy is

$$E_n = \frac{\hbar^2 \pi^2}{2m_e L^2} (n_x^2 + n_y^2 + n_z^2) \quad (4.3.5)$$

where the point  $(n_x, n_y, n_z)$  in the three-dimensional  $(k_x, k_y, k_z)$  space corresponds to a quantum energy state. (Note that the consideration of the electron spin actually implies two quantum states.) Thus, by counting the number of  $(n_x, n_y, n_z)$  states per unit volume over the energy range between  $E$  and  $E+dE$ , the expressions for the DOS can be determined. The volume of a unit cell in  $\mathbf{k}$ -space, occupied by one state with a specific  $k$ , is  $(2\pi/L)^3$ , or  $(2\pi)^3/V$ . In order to evaluate the number of electronic states ( $dN$ ) over the range between  $k$  and  $k + dk$ , the spherical volume between  $k$  and  $dk$ , i.e.,  $4\pi k^2 dk$ , is divided by  $(2\pi)^3/V$ . (The result should also be multiplied by a factor of two in order to account for the fact that each state with a specific value of  $k$  can be occupied by two electrons with opposite spins.) Thus, the expression for  $dN$  can be written as

$$dN = V \frac{k^2 dk}{\pi^2} \quad (4.3.6)$$

For the parabolic bands, we can write  $k = [2m_e^*(E - E_c)/\hbar^2]^{1/2}$ , and  $k dk = m_e^* dE/\hbar^2$ , and thus, the DOS can be written as

$$g_n(E) = \frac{1}{V} \frac{dN}{dE} = 4\pi (2m_e^*/\hbar^2)^{3/2} (E - E_c)^{1/2} \quad (4.3.7)$$

Thus, the expressions for the DOS for the conduction and valence bands, respectively, are

$$g_n(E) = 4\pi (2m_e^*/\hbar^2)^{3/2} (E - E_c)^{1/2} \quad (4.3.8)$$

$$g_p(E) = 4\pi (2m_h^*/\hbar^2)^{3/2} (E_v - E)^{1/2} \quad (4.3.9)$$

The Fermi–Dirac function can be expressed in a more simplified form; since  $k_B T$  at room temperature is about 0.026 eV,  $E - E_F \gg k_B T$ , and thus, for sufficiently large energies, the Fermi–Dirac function (see Eq. 4.3.1) is reduced to

the classical *Maxwell–Boltzmann function*, i.e., Eq. (4.3.1) can be approximated by

$$f_n(E) = \frac{1}{\exp[(E - E_F)/k_B T] + 1} \cong \exp[-(E - E_F)/k_B T] \quad (4.3.10)$$

By substituting Eq. (4.3.8) into Eq. (4.3.3), the electron concentration in the conduction band can be expressed as

$$n = \int_{E_c}^{\infty} g_n(E) f_n(E) dE = 2 \left( \frac{m_e^* k_B T}{2\pi\hbar^2} \right)^{3/2} F_{1/2}(\eta_n) \quad (4.3.11)$$

where  $F_{1/2}(\eta_n)$  is the Fermi integral:

$$F_{1/2}(\eta_n) = \frac{2}{\pi^{1/2}} \int_0^{\infty} \frac{x^{1/2} dx}{1 + \exp(x - \eta_n)} \quad (4.3.12)$$

and

$$\eta_n = (E_F - E_c)/k_B T \quad (4.3.13)$$

The term

$$N_c = 2 \left( \frac{m_e^* k_B T}{2\pi\hbar^2} \right)^{3/2} \quad (4.3.14)$$

is referred to as the *effective DOS* for the conduction band. Note that in this expression, for materials such as Si (with several equivalent minima with anisotropic effective masses), the effective mass for DOS calculations (i.e.,  $m_{ed}^*$ ) should be used (see Eq. 3.6.9, Chapter 3).

Analogously, by substituting Eq. (4.3.9) into Eq. (4.3.4), the hole concentration in the valence band can be expressed as

$$p = \int_{-\infty}^{E_v} g_p(E) f_p(E) dE = 2 \left( \frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2} F_{1/2}(\eta_p) \quad (4.3.15)$$

where

$$\eta_p = (E_v - E_F)/k_B T \quad (4.3.16)$$

and

$$N_v = 2 \left( \frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2} \quad (4.3.17)$$

TABLE 4.1. Effective DOS in the conduction band ( $N_c$ ) and valence band ( $N_v$ ) for selected semiconductors (at 300 K)

	Ge	Si	GaAs
$N_c (\text{cm}^{-3})$	$1.0 \times 10^{19}$	$2.8 \times 10^{19}$	$4.7 \times 10^{17}$
$N_v (\text{cm}^{-3})$	$6.0 \times 10^{18}$	$1.0 \times 10^{19}$	$7.0 \times 10^{18}$

is the effective DOS for the valence band. Note again that in this expression, the effective mass for DOS calculations should be used (see Eq. 3.6.7, Chapter 3). Effective DOS in the conduction band ( $N_c$ ) and valence band ( $N_v$ ) for selected semiconductors at 300 K are listed in Table 4.1.

For  $\eta \leq -3$ ,  $F_{1/2}(\eta)$  is approximated by  $\exp(\eta)$ , and thus, in this case, the concentration of electrons in the conduction band can be expressed as [for  $E_c - E_F \geq 3k_B T$  ( $\eta_n \leq -3$ )]

$$n = N_c \exp[(E_F - E_c)/k_B T] \quad (4.3.18)$$

and the concentration of holes in the valence band can be expressed as [for  $E_F - E_v \geq 3k_B T$  ( $\eta_p \leq -3$ )]

$$p = N_v \exp[(E_v - E_F)/k_B T] \quad (4.3.19)$$

or by substituting for  $N_c$  and  $N_v$ , using Eqs. (4.3.14) and (4.3.17)

$$n = 2 \left( \frac{m_e^* k_B T}{2\pi\hbar^2} \right)^{3/2} \exp[(E_F - E_c)/k_B T] \quad (4.3.20)$$

$$p = 2 \left( \frac{m_h^* k_B T}{2\pi\hbar^2} \right)^{3/2} \exp[(E_v - E_F)/k_B T] \quad (4.3.21)$$

To summarize briefly, from the known density of available states and the probability of occupation of these states (i.e., the Fermi-Dirac distribution function), the resulting distribution of carriers as a function of energy for an intrinsic semiconductor can be calculated. These results are shown in Fig. 4.2. In the case of the conduction band, it can be inferred from this figure that although the DOS increases with energy, the Fermi-Dirac distribution function becomes very small for higher energies; thus, the resulting distribution of carriers as a function of energy, i.e., the product  $g_n(E)f(E)$ , decreases rapidly above the conduction band edge. Similar considerations apply to the valence band case. (Note that in this case increasing energy is in opposite direction to that of electron energy.)

It is important at this juncture to distinguish between the *degenerate* and *nondegenerate* semiconductors. The conditions of  $E_c - E_F \geq 3k_B T$  and

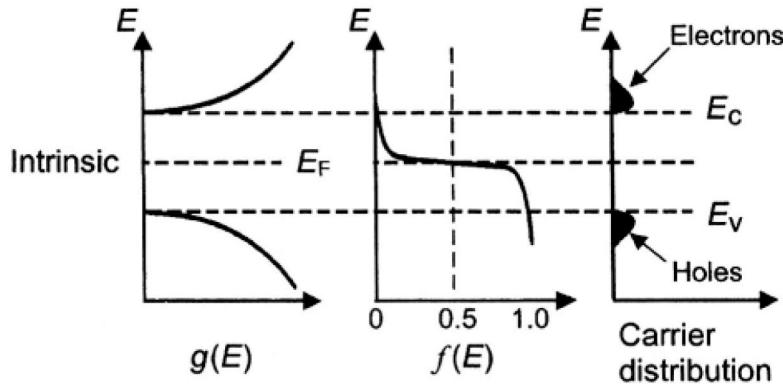


FIGURE 4.2. Schematic diagram of the density of available states, the Fermi-Dirac distribution function (i.e., probability of occupation of states), and the resulting distribution of carriers as a function of energy for an intrinsic semiconductor. The carrier concentration for electrons is a product of  $g_n(E)f(E)$ , and for holes it is  $g_p(E)[1-f(E)]$ .

$E_F - E_v \geq 3k_B T$  used earlier imply that the Fermi level position in the energy gap must be greater than  $3k_B T$  from the band edges (either conduction or valence); for such a case, the semiconductor is referred to as nondegenerate. For the case of the Fermi level being positioned within  $3k_B T$  of the band edges, or positioned inside either band, the semiconductor is referred to as degenerate.

## 4.4. INTRINSIC AND EXTRINSIC SEMICONDUCTORS

### 4.4.1. Intrinsic Semiconductors

As mentioned earlier, intrinsic semiconductors are those that do not contain impurities or defects. In such a case, the thermal activation of an electron from the valence band to the conduction band produces (i) a free electron in the conduction band and (ii) a free hole in the valence band, and the densities of electrons and holes are equal.

Typically, intrinsic semiconductors are nondegenerate, thus the equations for carrier concentrations, derived in the previous section, can be employed in this case. Thus, we can write

$$n_i = N_c \exp[(E_i - E_c)/k_B T] \quad (4.4.1)$$

$$n_i = N_v \exp[(E_v - E_i)/k_B T] \quad (4.4.2)$$

where, in this case,  $E_F = E_i$ . Using these equations, the effective densities for the conduction and valence bands, respectively, can be written as

$$N_c = n_i \exp[(E_c - E_i)/k_B T] \quad (4.4.3)$$

$$N_v = n_i \exp[(E_v - E_i)/k_B T] \quad (4.4.4)$$

Substituting these expressions for  $N_c$  and  $N_v$  in Eqs. (4.3.18) and (4.3.19) yields

$$n = n_i \exp[(E_F - E_i)/k_B T] \quad (4.4.5)$$

$$p = n_i \exp[(E_i - E_F)/k_B T] \quad (4.4.6)$$

The intrinsic Fermi energy can be derived from Eqs. (4.4.1) and (4.4.2) as

$$E_i = \frac{E_c + E_v}{2} + \frac{k_B T}{2} \ln\left(\frac{N_v}{N_c}\right) \quad (4.4.7)$$

and since  $(N_v/N_c) = (m_h^*/m_e^*)^{3/2}$ , we can also write

$$E_i = \frac{E_c + E_v}{2} + \frac{3k_B T}{4} \ln\left(\frac{m_h^*}{m_e^*}\right) \quad (4.4.8)$$

which indicates that, if  $m_h^* = m_e^*$  or  $T=0$  K, the Fermi level in an intrinsic semiconductor is positioned at mid-gap. In real cases,  $m_h^* \neq m_e^*$ , resulting in a small deviation of the Fermi level from mid-gap.

The equilibrium density of electrons and holes in a nondegenerate semiconductor is constant at a given temperature. The product of the electron and hole density, in a nondegenerate semiconductor at equilibrium, is always equal to the square of the intrinsic carrier density, i.e.,

$$np = n_i^2 \quad (4.4.9)$$

The intrinsic carrier density (which is specific to a given semiconductor) is related to the effective conduction band (denoted as  $N_c$ ) and valence band (denoted as  $N_v$ ) densities of states, i.e.,

$$np = n_i^2 = N_c N_v \exp[(E_v - E_c)/k_B T] = N_c N_v \exp(-E_g/k_B T) \quad (4.4.10)$$

This relationship, referred to as the *mass action law*, allows (at thermal equilibrium) to determine the electron density if the hole density is known or vice versa. It should be noted that this equation signifies that, although the electron–hole pairs may be continuously generated and recombined, the product of the concentration (averaged in time) stays constant. This equation also indicates that, for a nondegenerate material in equilibrium, the  $np$  product depends on the effective conduction band and valence band densities of states, the energy gap of a semiconductor, and the temperature, and it is independent of the Fermi level position and of the individual electron and hole densities. In other words, regardless of doping, the  $np$  product is a constant at a given temperature. From this equation, the intrinsic carrier density can be written as

TABLE 4.2. The energy gap and intrinsic carrier concentration ( $n_i$ ) for selected semiconductors (at 300 K)

	Ge	Si	GaAs
$E_g$ (eV)	0.67	1.12	1.42
$n_i$ ( $\text{cm}^{-3}$ )	$2.5 \times 10^{13}$	$1.0 \times 10^{10}$	$2.0 \times 10^6$

$$n_i = (N_c N_v)^{1/2} \exp(-E_g/2k_B T) \quad (4.4.11)$$

The intrinsic carrier concentration ( $n_i$ ) for selected semiconductors (at 300 K) is listed in Table 4.2.

As can be seen from Eq. (4.4.11), the temperature dependence of the intrinsic carrier concentration is dominated by the exponential factor containing the energy gap, which itself depends on the temperature (see Section 4.10). The temperature dependence of the effective densities of states are according to Eqs. (4.3.14) and (4.3.17) that also contain the effective masses in which temperature dependences can be excluded, as these are small in comparison. The dependence of the intrinsic carrier concentration in Si and GaAs on temperature is shown in Fig. 4.3.

As can be seen from Eq. (4.4.11) and Table 4.2 (showing the exponential dependence of the carrier concentration on the energy gap), at room temperature, for the change in energy gap from 0.67 (for Ge) to 1.42 eV (for GaAs), the intrinsic carrier concentration varies by seven orders of magnitude; so does the number of carriers (both electrons and holes) available for charge transport.

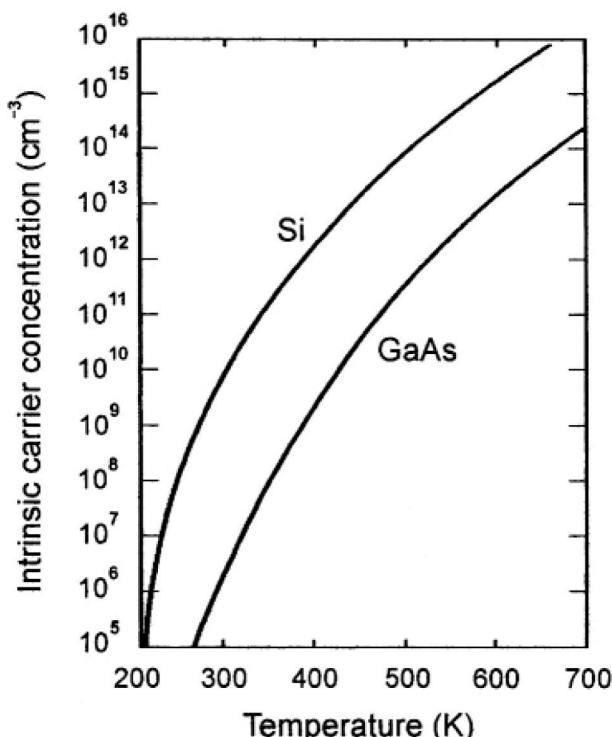


FIGURE 4.3. Dependence of the intrinsic carrier concentration on temperature in Si and GaAs.

As mentioned earlier (see Section 4.2), in semiconductors, both electrons and holes contribute to the current; thus in general, the bulk conductivity  $\sigma$  of an intrinsic semiconductor is expressed as

$$\sigma = ne\mu_e + pe\mu_h \quad (4.4.12)$$

where  $n$  and  $\mu_e$  are the concentration and mobility of electrons, respectively, and  $p$  and  $\mu_h$  are the concentration and mobility of holes, respectively, and  $e$  is the carrier charge. Thus, in the case of an intrinsic semiconductor (i.e.,  $n = p = n_i$ ), from Eq. (4.4.11) and equations for the effective densities of states for the conduction and valence bands (see Eqs. 4.3.14 and 4.3.17), we can write

$$n = p = \text{constant} \times T^{3/2} \exp(-E_g/2k_B T) \quad (4.4.13)$$

and

$$\sigma = \text{constant} \times e(\mu_e + \mu_h)T^{3/2} \exp(-E_g/2k_B T) = \sigma_0 \exp(-E_g/2k_B T) \quad (4.4.14)$$

Thus, by plotting  $\ln \sigma$  as a function of  $1/T$  (which yields a straight line), the energy gap  $E_g$  can be derived from the slope  $(-E_g/2k_B)$ . (In this case the  $T^{3/2}$  variation and the temperature variation of  $E_g$  are disregarded as negligible in comparison with the exponential temperature variation term.) Note that the electron and hole mobilities are also dependent on temperature; however, these dependences, which are in theory dependent on  $T$  as  $\mu \propto T^{-3/2}$ , would largely cancel out the  $T^{3/2}$  dependence.

#### 4.4.2. Extrinsic Semiconductors

The availability of charge carriers in the valence and conduction bands is greatly affected by the presence of intentionally (or unintentionally) introduced impurities (i.e., foreign atoms incorporated into the crystal structure of a semiconductor). In semiconductors, some impurities are deliberately introduced to produce materials and devices with desired properties. In this case, the material is referred to as *extrinsic*, and the process of putting impurities into the lattice is called *doping*. The contribution of free carriers by dopants requires them being *ionized* (i.e., the dopants have donated or accepted an electron). The ionization of the dopants depends on the thermal energy and the position of the impurity level in the energy gap of a semiconductor.

Impurities that contribute electrons to the conduction band are called *donors*, and those that supply holes to the valence band are *acceptors*. (In this context, it should be reiterated again that impurity atoms in crystals are considered as point defects if they are detrimental in the utilization of the material or device, but if they are deliberately incorporated in the material in order to control conductivity, they are referred to as donors or acceptors.) These properties of semiconductors are discussed in the following section.

#### 4.5. DONORS AND ACCEPTORS IN SEMICONDUCTORS

As mentioned earlier, in extrinsic semiconductors, some impurities are deliberately introduced to produce materials and devices with desired properties. Such a process of putting impurities into the lattice is called doping, and those impurities that contribute (“donate”) electrons to the conduction band are called donors, and those that supply holes to the valence band (i.e., “accept” electrons) are acceptors.

Donors are substitutional impurities that have a higher valence than the atoms of the host material; when a donor impurity is ionized, an electron is donated to the conduction band, which leads to an excess of mobile electrons, and the material is referred to as *n*-type. The electrons donated to the conduction band can participate in the conduction process, whereas the donor centers become positively charged. At sufficiently low temperatures, electrons can be captured by these positively charged donor centers, which become neutral.

Acceptor impurities have a lower valence than the host, which leads to incomplete atomic bonding in the lattice; thus they capture electrons, i.e., supply holes to the valence band (the acceptor centers become negatively charged), and the semiconductor is referred to as *p*-type. At sufficiently low temperatures, holes become localized at acceptor centers, which become neutral.

Both the donor and acceptor levels are located in the forbidden energy gap (see the energy band diagram of a semiconductor in Fig. 4.4). In general, the energy levels in the gap of a semiconductor can be categorized as *shallow* and *deep levels* according to their depth from the nearest band edges. The donors and acceptors are called shallow when their levels are close to the bottom of the conduction band and the top of the valence band, respectively. *Shallow impurities* are those that require typically energies corresponding to about the thermal energy to be ionized. On the other hand, *deep impurities* require higher energies in order to be ionized,

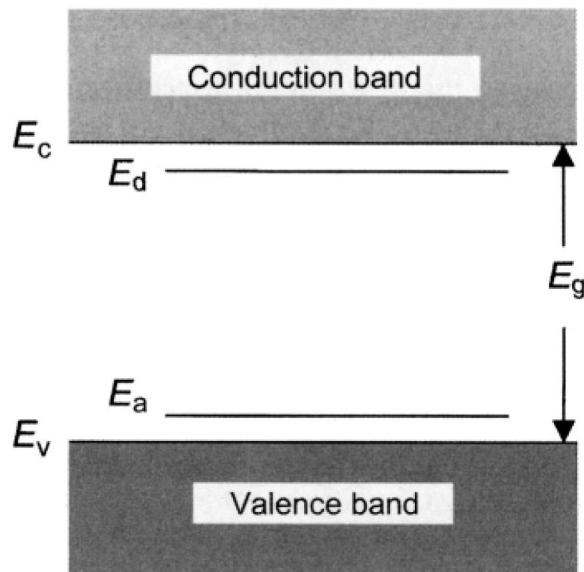


FIGURE 4.4. Schematic diagram of donor and acceptor levels located in the forbidden energy gap.

thus they are typically not expected to contribute free carriers. Such deep impurities can be effective recombination centers, i.e., centers in which electrons and holes drop and annihilate each other.

Typically, for shallow impurities, at room temperature almost the entire donor or acceptor sites are ionized, and the free carrier density corresponds to the impurity concentration. In other words, in the case of donors, the electron density  $n$  equals the concentration of donors (note that in this case  $N_d^+ \cong N_d$ ), i.e.,  $n \cong N_d$ ; and in the case of acceptors, the density of holes  $p$  equals the concentration of acceptors ( $N_a \cong N_a^-$ ), i.e.,  $p \cong N_a$ . In these cases,  $N_d$  and  $N_d^+$  are total concentration of donors and total concentration of ionized donors (positively charged), respectively; and  $N_a$  and  $N_a^-$  are total concentration of acceptors and total concentration of ionized acceptors (negatively charged), respectively.

In an extrinsic semiconductor, electrons are *majority carriers* and holes are *minority carriers* in  $n$ -type semiconductor. In  $p$ -type material, electrons are minority carriers and holes are majority carriers.

When similar concentrations of shallow donors and acceptors are present in the semiconductor, one type of impurity will cancel out the effect of the other, and the semiconductor is referred to as *compensated*. In such a case, if the donor concentration is larger and if  $N_d^+ - N_a^- \gg n_i$ , the carrier concentration is about equal to the difference between the donor and acceptor concentration, giving  $n$ -type material, i.e.,  $n \cong N_d^+ - N_a^-$ . Similar considerations can be applied if the acceptor concentration is larger than the donor concentration.

In compound semiconductors, such as the III–V binary compound GaAs, an excess of one of the components may also generate donor or acceptor states. In this case, an excess of Ga atoms would lead to a  $p$ -type material, whereas an excess of As atoms would lead to an  $n$ -type material. Also, in compound semiconductors such as GaAs, e.g., group IV element Si may occupy lattice sites either in the (group III) Ga sublattice or in the (group V) As sublattice; thus, the former case (i.e.,  $\text{Si}_{\text{Ga}}$ ) results in an  $n$ -type doping, whereas the  $\text{Si}_{\text{As}}$  case results in  $p$ -type doping. Because of the preferential occupation by the Si atoms of the Ga sublattice sites, Si is an  $n$ -type dopant in GaAs; when the concentrations of  $\text{Si}_{\text{Ga}}$  and  $\text{Si}_{\text{As}}$  are comparable, the conductivity of GaAs decreases and the material is referred to as compensated.

In the case of shallow donors, the weakly-bound excess electron is, on the average, located sufficiently far from the donor center, indicating that the specific atomic structure of the impurity can be considered as a positive point charge. Thus, the *binding energy*,  $E_D$ , of the electron to the donor impurity, or the *impurity ionization energy* (i.e., the energy required to transfer an electron from the donor level to the bottom of the conduction band), can be determined by considering an extra electron in the donor atom as a particle with an effective mass  $m^*$  moving in the presence of a positive net charge. This is analogous to a hydrogen atom embedded in the dielectric medium of the crystal. Thus, the ground-state binding energy of the extra electron becomes

$$E_D = \frac{13.6 m_e^*}{m_0 \epsilon^2} (\text{eV}) \quad (4.5.1)$$

where 13.6 eV is the ionization energy of the hydrogen atom and  $\epsilon$  is the dielectric constant of the solid, and  $m_0$  is the free electron mass. (Note that in this case, a static dielectric constant,  $\epsilon_{st}$ , should be used, see Table B1 in Appendix B.) The binding energy is measured relative to the conduction band level. In terms of the energy-band diagram, donor impurities introduce levels at energies  $E_d$  below the bottom of the conduction band  $E_c$ , thus  $E_D = E_c - E_d$  (see Fig. 4.4).

The electron orbit around the impurity atom, i.e., the spatial extent of the wave function, can also be estimated. In this case, the radius of the first Bohr orbit becomes  $r = (\epsilon m_0/m^*)a_0$ , where  $a_0$  is the radius of the first Bohr orbit in the hydrogen atom. These results indicate that for typical cases, the ionization energies are less than the room temperature energy  $k_B T$  of about 0.026 eV, and values of  $r$  are much larger than the atomic diameter. Thus, most shallow donors are expected to be ionized at room temperature, and the wave functions are expected to extend over many atomic diameters; in other words, the electron is not localized at the impurity.

Similar analysis can be considered in the case of acceptor impurities. In this case it is convenient to describe a positive hole orbiting a negatively ionized impurity atom. The donor and acceptor binding energies are expected to be somewhat different because of the difference in the effective masses of the electrons and holes (see Section 3.6). In terms of the energy-band diagram, acceptor impurities introduce levels at energies  $E_a$  above the top of the valence band  $E_v$ , thus the acceptor binding energy (i.e., the energy required to excite an electron from the valence band to the acceptor energy levels)  $E_A = E_a - E_v$  (see Fig. 4.4).

Following the arguments presented earlier for shallow impurities, in elemental group IV semiconductors, such as Si or Ge, group V elements (e.g., P, As) placed in the tetrahedral host structure can easily donate an extra electron and become donors, whereas group III elements (e.g., B, Al) can easily capture an electron from the host structure and become acceptors. As mentioned earlier, in compound semiconductors, such as GaAs, however, the same element (e.g., Si, Ge) can become a donor or an acceptor depending on whether it substitutes for Ga or As. Ionization energies of common donors and acceptors in Si and GaAs are given in Tables 4.3 and 4.4.

In the analysis of extrinsic semiconductors, it is of great importance to determine the carrier concentrations in terms of the Fermi level and other semiconductor parameters. This will allow to determine the dependence of the Fermi level on the carrier concentration in an extrinsic semiconductor.

TABLE 4.3. Ionization energies of common shallow donors and acceptors in Si

Donors	Ionization energy, $E_D$ (eV)	Acceptors	Ionization energy, $E_A$ (eV)
P	0.045	B	0.045
As	0.049	Al	0.057
Sb	0.039	Ga	0.065
Bi	0.069	In	0.16

TABLE 4.4. Ionization energies of common donors and acceptors in GaAs

Donors	Ionization energy, $E_D$ (eV)	Acceptors	Ionization energy $E_A$ (eV)
C	0.006	C	0.026
Si	0.006	Si	0.035
S	0.006	Be	0.028
Se	0.006	Zn	0.031

The distribution of electrons and holes in their corresponding bands as a function of energy for both donor-doped and acceptor-doped semiconductor can be derived from the known density of available states and the probability of occupation of these states (i.e., the Fermi–Dirac distribution function). These results are shown in Fig. 4.5. Similar to the case of an intrinsic semiconductor (see Fig. 4.2), most of the carriers in both the conduction and valence bands are distributed (as a function of energy) near the corresponding band edges. The difference in the carrier distribution in the valence and conduction bands (in both *n*- and *p*-type cases) is due to the positioning of the Fermi level. In other words, for the Fermi level located in the upper half of the energy gap, the electron population

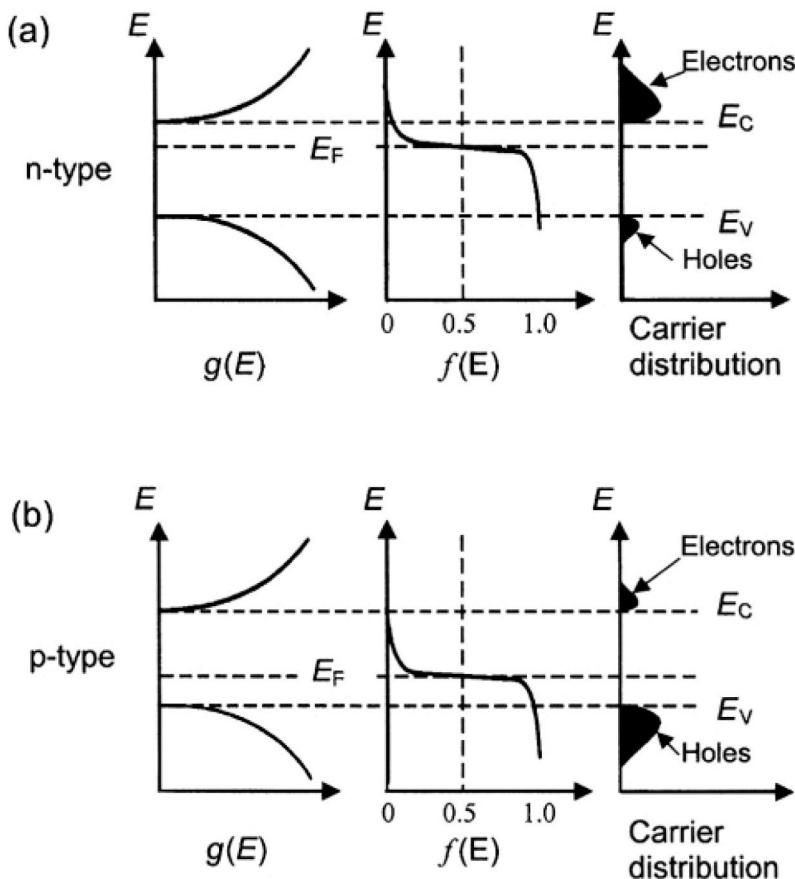


FIGURE 4.5. Schematic diagram of the DOS, the Fermi–Dirac function, and the resulting distribution of carriers as a function of energy for (a) an *n*-type semiconductor and (b) for a *p*-type semiconductor. The carrier concentration for electrons is a product of  $g_n(E)f(E)$ , and for holes it is  $g_p(E)[1 - f(E)]$ .

is higher than the hole population; whereas, for the Fermi level located in the lower half of the energy gap, the hole population is higher than the electron population.

As described earlier (see Eq. 4.4.9), for a given nondegenerate semiconductor in a thermal equilibrium, the product of the electron and hole density always equals the square of the intrinsic carrier density, i.e.,  $np = n_i^2$ . In general, a semiconductor can be considered as a reservoir of electrical charge, which includes both fixed charge (due to ionized dopant atoms that are immobile) and mobile charge (due to electrons and holes). In equilibrium, the semiconductor is neutral, and thus the condition of charge balance (or charge neutrality) between the negative and positive charges can be expressed as

$$n + N_a^- = p + N_d^+ \quad (4.5.2)$$

where  $n$  and  $p$  are the densities of mobile conduction band electrons (−) and mobile valence band holes (+), respectively; and  $N_a^-$  and  $N_d^+$  are the densities of fixed ionized acceptor atoms (−) and fixed ionized donor atoms (+), respectively. As mentioned earlier, for shallow impurities, at room temperature almost the entire donor or acceptor sites are ionized, and in this case  $N_d^+ \approx N_d$ , and  $N_a^- \approx N_a$ , and thus the charge neutrality relationship is often written as

$$n + N_a = p + N_d \quad (4.5.3)$$

Equations (4.4.9) (i.e.,  $np = n_i^2$ ) and (4.5.3) can be used to derive  $n$  and  $p$  if  $N_a$  and  $N_d$  are known (assuming total ionization and nondegenerate semiconductors). For the case of a semiconductor with  $|N_a - N_d| \gg n_i$  and  $N_a > N_d$ , the material is *p*-type, and in this case

$$p = N_a - N_d \quad (4.5.4)$$

$$n = \frac{n_i^2}{N_a - N_d} \quad (4.5.5)$$

and if  $N_d > N_a$ , the material is *n*-type, and in this case

$$n = N_d - N_a \quad (4.5.6)$$

$$p = \frac{n_i^2}{N_d - N_a} \quad (4.5.7)$$

The general expressions for carrier concentrations can be derived by eliminating  $n$  or  $p$  in Eq. (4.5.3) and using Eq. (4.4.9); thus, quadratic equations for  $n$  or for  $p$  can be written as

$$n^2 - n(N_d - N_a) - n_i^2 = 0 \quad (4.5.8)$$

$$p^2 - p(N_a - N_d) - n_i^2 = 0 \quad (4.5.9)$$

The solutions for  $n$  and  $p$  are

$$n = \frac{N_d - N_a}{2} + \left[ \left( \frac{N_d - N_a}{2} \right)^2 + n_i^2 \right]^{1/2} \quad (4.5.10)$$

$$p = \frac{N_a - N_d}{2} + \left[ \left( \frac{N_a - N_d}{2} \right)^2 + n_i^2 \right]^{1/2} \quad (4.5.11)$$

Note that since  $n$ , or  $p$ , must be  $\geq 0$ , only the positive roots are considered.

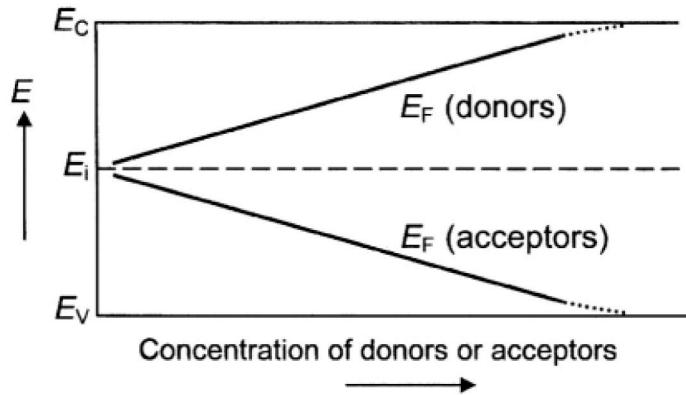
These equations, which assume total ionization of dopant sites, provide general expressions for deriving carrier concentrations in compensated semiconductors. For specific cases, these equations can be simplified. For example, considering the cases described above (see Eqs. 4.5.4 – 4.5.7), for specific cases of either  $N_a \gg N_d$  (i.e.,  $p$ -type semiconductor), or  $N_d \gg N_a$  (i.e.,  $n$ -type material), which are of practical importance in device applications, we obtain  $p \approx N_a$  and  $n \approx n_i^2/N_a$  and  $n \approx N_d$  and  $p \approx n_i^2/N_d$ , respectively.

For donor-doped (i.e.,  $n$ -type) and acceptor-doped (i.e.,  $p$ -type) nondegenerate semiconductors at equilibrium, the Fermi level can be related to the carrier concentration by using Eqs. (4.4.5) and (4.4.6), which give (assuming that all the dopants are fully ionized and  $n \approx N_d$  and  $p \approx N_a$ , for  $n$ - and  $p$ -type materials, respectively)

$$E_F = E_i + k_B T \ln (N_d/n_i) \quad (4.5.12)$$

$$E_F = E_i - k_B T \ln (N_a/n_i) \quad (4.5.13)$$

From these equations it follows that with increasing doping the Fermi level approaches the conduction band in the case of donor-doped semiconductors, and it approaches the valence band in the case of acceptor-doped materials (see Fig. 4.6). This figure, which represents the variation of the Fermi energies with dopant concentration, shows the dependence of the Fermi energy (at room temperature) of  $n$ - and  $p$ -type semiconductors as a function of dopant concentration (in log scale). The dotted segments indicate the zones corresponding to degeneracy, i.e., the energy difference between the band edge and the onset of dotted curve corresponds to  $3k_B T$ . For example, in Si such an onset of degeneracy corresponds to a donor concentration of about  $1.5 \times 10^{18} \text{ cm}^{-3}$ , and acceptor concentration of about  $0.9 \times 10^{18} \text{ cm}^{-3}$ . (Note that such semiconductors are also referred to as *highly doped* and denoted as  $n^+$ , or  $p^+$ -semiconductors.) Thus, to summarize briefly, for the case of the Fermi level being positioned within  $3k_B T$  of the band edges, or positioned inside either (conduction or valence) band, the semiconductor is referred to as degenerate, and according to the previous discussion (see Section 4.2), the exponential relationships for the carrier concentrations, i.e., Eqs. (4.3.18), (4.3.19), (4.4.5) and (4.4.6) are no longer valid.



**FIGURE 4.6.** Dependence of Fermi energy (at room temperature) of *n*- and *p*-type semiconductors as a function of dopant concentration (in log scale). The dotted segments indicate the zones corresponding to degeneracy (i.e., the energy difference between the band edge and the onset of dotted curve corresponds to  $3k_B T$ ).

It should be noted that, for increasingly high doping concentrations, the wave functions of the electrons bound to the dopant atoms begin to overlap as the average distance between the nearest dopant atoms is reduced; thus, discrete dopant (donor or acceptor) levels broaden out forming an energy band, which eventually merges with the conduction or valence band (depending on the type of doping); this is also accompanied by the narrowing of the energy gap (not shown in Fig. 4.6), which can be usually disregarded for doping concentrations below about  $10^{18} \text{ cm}^{-3}$ . It should be noted that in heavily doped semiconductors, the filling of the states near the band edges may result in the *Burstein–Moss shift* of the absorption edge (see Section 4.7). This occurs due to the fact that with an increasing doping concentration in, e.g., an *n*-type semiconductor, the Fermi level also gradually increases, and in the degenerated case, it moves above the conduction band edge. In such a case, the states for electron transitions near the conduction band edge are now occupied, resulting in the electron transitions to higher energy states, and consequently the onset of optical absorption is shifted to higher energies with increasing doping.

From Eqs. (4.5.12) and (4.5.13), it is also possible to determine the dependence of the Fermi energy on temperature for a given doping concentration. In the previous discussions, the total ionization of the dopant sites was assumed at room temperature. However, in the lower temperature cases, it is essential to consider the degree of ionization of dopant sites. The concentration of ionized donors  $N_d^+$  in relation to the total concentration of donor atoms  $N_d$  can be expressed as

$$\frac{N_d^+}{N_d} = \frac{1}{1 + g_d \exp[(E_F - E_d)/k_B T]} \quad (4.5.14)$$

where  $g_d = 2$  is the donor degeneracy factor, representing the fact that the donor state can have an electron with the spin up or down.

The concentration of ionized acceptors  $N_a^-$  in relation to the total concentration of acceptor atoms  $N_a$  can be expressed as

$$\frac{N_a^-}{N_a} = \frac{1}{1 + g_a \exp[(E_a - E_F)/k_B T]} \quad (4.5.15)$$

where  $g_a = 4$  is the acceptor degeneracy factor. In this case, in addition to spin up or down, light and heavy holes must be accounted for.

The dependence of the Fermi energy on temperature for *n*- and *p*-type semiconductors with various doping concentrations is given in Fig. 4.7. As shown in this figure, the Fermi energy approaches at higher temperatures the Fermi energy corresponding to the intrinsic material; whereas at lower temperatures, the Fermi energy in *n*- and *p*-type materials is closer to the bottom of the conduction band and the top of the valence band, respectively. The curves corresponding to  $E_c$  and  $E_v$  also show the dependence of the energy gap on temperature (see Section 4.10). Note that the intrinsic Fermi level  $E_i$ , given in Fig. 4.7, is plotted according to Eq. (4.4.8), which indicates that, for  $m_h^* = m_e^*$  (or for  $T=0$  K),  $E_i$  is positioned at mid-gap. In real cases, however, typically  $m_h^* > m_e^*$ , resulting in a small deviation of the Fermi level from mid-gap, which would result (especially at higher temperatures) to upward bending of  $E_i$  (not shown in Fig. 4.7).

As mentioned earlier, one of the most important objectives in describing a semiconductor in relation to its properties is the determination of the carrier concentrations in the material. For understanding the semiconductor device operation at different temperatures, the dependence of the carrier concentration on temperature is required. Such dependence is presented in Fig. 4.8, which shows a plot of  $\ln n$  as a function of  $1/T$  for a donor-doped semiconductor. Recalling some of the observations related to the Fermi level, (i) in an intrinsic semiconductor, the Fermi level is positioned at mid-gap and (ii) in a doped semiconductor, the Fermi energy approaches at higher temperatures the Fermi energy corresponding to

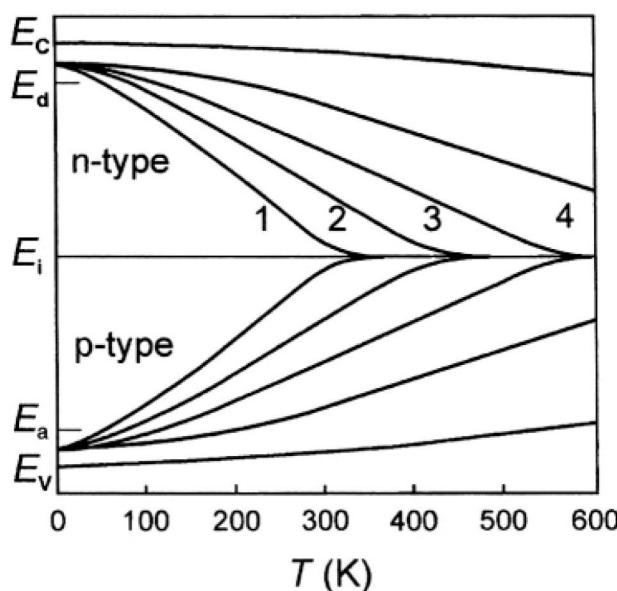


FIGURE 4.7. The dependence of the Fermi energy on temperature for *n*- and *p*-type semiconductors; the curves 1, 2, 3, and 4 correspond to increasing doping concentrations. The curves corresponding to  $E_c$  and  $E_v$  also show the dependence of the energy gap on temperature.

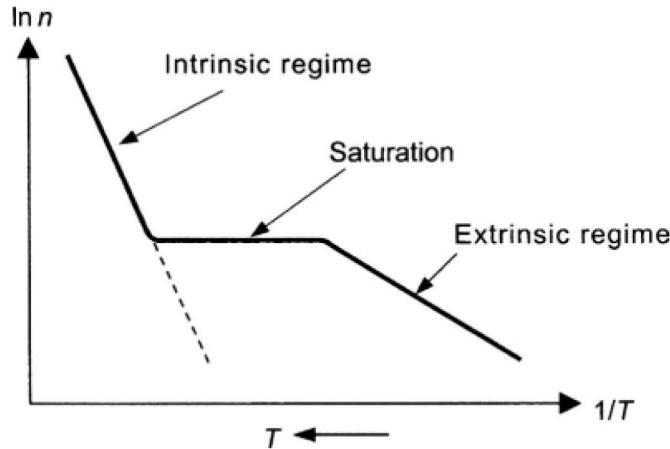


FIGURE 4.8. Dependence of the carrier concentration of a donor-doped semiconductor on temperature.

the intrinsic material; whereas at lower temperatures, the Fermi energy in *n*- and *p*-type materials is closer to the bottom of the conduction band and the top of the valence band, respectively. Three distinct regions can be distinguished in Fig. 4.8. At lower temperatures (e.g., below about 100 K for Si), carriers are excited from the dopant levels, and the carrier concentration is determined by the degree of ionization of dopant sites (see Eq. 4.5.14). This region is referred to as an *extrinsic region*. In the intermediate range (e.g., between about 100 and 400 K in Si), between the low and high temperature regimes, since all the donors are ionized, no further contribution to the carrier concentration in the conduction band with temperature is expected, but these temperatures are insufficient for the noticeable carrier excitations from the valence band to the conduction band. Thus, the carrier concentration does not change much with temperature, and the *saturation range* (or as often referred to as *exhaustion range*) is established. At higher temperatures, since all the donors are ionized and the carrier concentration in the conduction band is dominated by the thermal excitations from the valence band, the material exhibits the behavior of an intrinsic semiconductor. It should be noted that, in general, semiconductor devices operate in the saturation range, where the carrier concentrations are constant, and any changes in conductivity are predominantly due to temperature variations in mobility.

As discussed earlier, in the case of an intrinsic semiconductor, the conductivity can be expressed by Eq. (4.4.14) as

$$\begin{aligned}\sigma &= \text{constant} \times e(\mu_e + \mu_h)T^{3/2} \exp(-E_g/2k_B T) \\ &= \sigma_0 \exp(-E_g/2k_B T)\end{aligned}\quad (4.5.16)$$

In the case of an extrinsic (or doped) material, for  $n \gg p$ , the material is a *n*-type semiconductor, and for  $p \gg n$ , the material is a *p*-type semiconductor. From the temperature dependence of the conductivity it is possible to determine the dopant (or impurity) levels in semiconductors. This is because (i) of the dominant effect

of the carrier density (i.e.,  $n$  or  $p$ ) on the  $\sigma$  ( $T$ ), and (ii) of the fact that the carrier concentration, determined by a balance between the thermal generation of carriers from existing levels and recombination processes, is related to the corresponding dopant energy level in the energy gap of a semiconductor. As mentioned earlier, for the extrinsic semiconductor (e.g.,  $n$ -type material), three possible temperature regimes have to be considered. At high temperatures, since all the donors are ionized and the carrier concentration in the conduction band is dominated by the excitations from the valence band, the material exhibits the behavior of an intrinsic semiconductor; thus, the plot of  $\ln \sigma$  as a function of  $1/T$  will yield a straight line with the slope  $s = -E_g/2k_B$ . At low temperatures, on the other hand, the concentration of electrons (in the conduction band) originating from the donor levels dominates, and one can disregard the contribution of the holes to the conductivity process. In such a case, the conductivity can be expressed as

$$\sigma = \sigma_0 \exp[-(E_c - E_d)/2k_B T] \quad (4.5.17)$$

Thus, the plot of  $\ln \sigma$  as a function of  $1/T$  will yield a straight line with the slope  $s = -(E_c - E_d)/2k_B$  (see Fig. 4.9). In the intermediate range, between the low and high temperature regimes, as mentioned earlier, the saturation range is established, where the  $T^{3/2}$  term and temperature variations in mobility determine the specific shape of the curve. Similar reasoning applies to  $p$ -type semiconductors.

Thus, to summarize briefly, the shallow donor and acceptor impurities produce in the crystal relatively small perturbations that result in the formation, in the energy gap, of bound states in very close proximity to the boundaries of the valence and conduction bands. These states can contribute carriers to the respective bands, and thus control the electrical properties of a semiconductor. However, the simple hydrogenic model for impurity levels is not always applicable. In some cases impurities introduce deep levels in the fundamental energy gap of a semiconductor. In addition to the impurity-induced deep levels, a variety of defects may also give rise to bound states in the energy gap of the

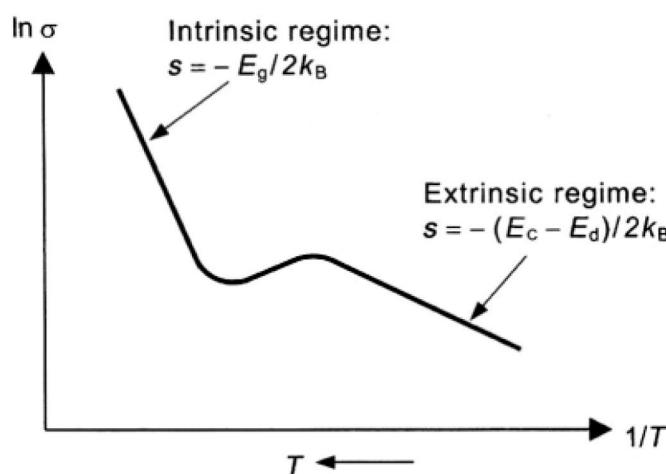


FIGURE 4.9. Variation of electrical conductivity of donor-doped semiconductor on temperature.

material. These defects can be vacancies, interstitials, antisite defects and their complexes, dislocations, stacking faults, grain boundaries, or precipitates. These states are usually located deeper in the energy gap and are more localized. The information about these deep centers is important in both the understanding and applications of semiconductors, since deep centers typically act as efficient traps and control the carrier lifetime. However, no universal theory is available to account for all these centers.

#### 4.6. NONEQUILIBRIUM PROPERTIES OF CARRIERS

Important processes related to excess minority carriers in a semiconductor include (i) *generation* of excess carriers, (ii) *diffusion* (due to the concentration gradient), (iii) *drift* (due to the applied electric field), and (iv) *recombination*. A semiconductor is considered to be in a nonequilibrium state if the equation  $np = n_i^2$  is no longer satisfied. The condition  $np > n_i^2$  implies the injection of an additional charge into a semiconductor (i.e., *carrier injection*), and it can be caused by optical excitation with photon energy greater than the energy gap, or by forward bias of a semiconductor junction device. For the case of carrier injection, two regimes are considered: *low-level injection* (the increase in carrier concentration is much smaller than the doping concentration) and the *high-level injection* (the increase in carrier concentration is commensurate to the doping concentration). The case of  $np < n_i^2$  corresponds to *carrier extraction*.

In the case of carrier injection into a semiconductor, the carrier distribution described by the Fermi–Dirac function (see Section 4.3) is no longer valid. In such a nonequilibrium case, under certain assumptions, the carrier occupation can be described by introducing the *quasi-Fermi energies*  $E_{Fn}$  and  $E_{Fp}$  for electrons and holes, respectively (these are also referred to as *quasi-Fermi levels*). This description indicates that although the electrons and holes are no longer in thermal equilibrium, they can be described by introducing different Fermi energies for electrons and holes. (This is valid under an assumption that the electrons are in thermal equilibrium in the conduction band and holes are in thermal equilibrium in the valence band.) Thus, by introducing distinct Fermi energies for electrons and holes (i.e., quasi-Fermi energies  $E_{Fn}$  and  $E_{Fp}$ ), the excess carrier densities (for a nondegenerate case) can be described by the following equations (see Eqs. 4.3.18 and 4.3.19)

$$n = N_c \exp[(E_{Fn} - E_c)/k_B T] \quad (4.6.1)$$

$$p = N_v \exp[(E_v - E_{Fp})/k_B T] \quad (4.6.2)$$

At equilibrium,  $E_{Fn} = E_{Fp} = E_F$ . (Note that with excess electron and hole injection into a semiconductor,  $E_{Fn}$  and  $E_{Fp}$  move towards the conduction and valence bands, respectively.) In a nonequilibrium case,  $E_{Fn} \neq E_{Fp}$  and these may depend