For carriers in semiconductors, the situation can be more complex. In some semiconductors, an analogous law holds for electrons in the conduction band at energies close to the minimum, $E_c$, in this band:

$$E - E_c = \frac{p^2}{2m_e^*}$$

(2.4)

A similar relationship holds for holes near the maximum energy, $E_v$, in the valence band:

$$E_v - E = \frac{p^2}{2m_h^*}$$

(2.5)

The foregoing relationships are indicated in Fig. 2.8. Such semiconductors are known as direct-band-gap semiconductors, and the most important technologically is the compound semiconductor GaAs.

In other semiconductors, the minimum of the conduction band can be at a finite value of crystal momentum, obeying a relationship:

$$E - E_c = \frac{(p - p_0)^2}{2m_e^*}$$

(2.6)

Figure 2.8. (a) Energy-crystal momentum relationships near the band edges for electrons in the conduction band and holes in the valence band of a direct-band-gap semiconductor. (b) Corresponding spatial representation of allowed energies in a semiconductor.

If $p_0 = p'_0$, the semiconductor has a direct band-gap. However, if $p_0 \neq p'_0$, the band-gap is called indirect. The most common elemental semiconductors, Ge and Si, both are indirect-band-gap materials. In each case, $p_0 = 0$ but $p_0$ is finite. Such a situation is shown in Fig. 2.9.

The valence band can exhibit a similar relationship:

$$E_v - E = \frac{(p - p'_0)^2}{2m_h^*}$$

(2.7)

Figure 2.9. Energy-crystal momentum relationships near the band edges for an indirect-band-gap semiconductor. Also shown is the energy band spatial representation.

Note that the common representation of energy relations in semiconductor devices where energy is plotted as a function of distance (as also indicated in Figs. 2.8 and 2.9) does not differentiate between direct- and indirect-band-gap semiconductors.

2.7 ENERGY DENSITY OF ALLOWED STATES

The number of allowed states per unit volume in a semiconductor is obviously zero for energies corresponding to the forbidden gap and nonzero in the allowed bands. The question arises as to just how many states for electrons are distributed within the allowed bands.

An answer can be found reasonably simply (Refs. 2.1 to 2.4), at least for energies near the edges of the allowed bands, where car-
Figure 2.10. (a) Band representation of a semiconductor. (b) Corresponding energy density of allowed states for electrons. (c) Probability of occupation of these states. (d) Resulting energy distribution of electrons and holes. Note that most are clustered near the edge of the respective band.

Riers can be treated similarly to free carriers. The number of allowed states per unit volume and energy, \( N(E) \), at an energy \( E \) near the conduction-band edge (in the absence of anisotropy) is given by

\[
N(E) = \frac{8\sqrt{2}\pi m^*}{h^3} \left( E - E_c \right)^{1/2}
\]  

(2.8)

where \( h \) is Planck’s constant. A similar expression holds for energies near the valence-band edge. These distributions of allowed states are shown in Fig. 2.10(b).

2.8 DENSITIES OF ELECTRONS AND HOLES

Knowing the density of allowed states [Eq. (2.8)] and the probability of occupation of these states [Eq. (2.1)], it is now possible to calculate the actual energy distribution of electrons and holes. The results are shown schematically in Fig. 2.10.

Owing to the nature of the Fermi-Dirac distribution function, most of the electrons in the conduction band and holes in the valence band are clustered near the band edges. The total number in either band can be found by performing an integration. The number of electrons in the conduction band per unit volume of the crystal, \( n \), is given by

\[
n = \int_{E_c}^{E_c \text{max}} f(E) N(E) dE
\]  

(2.9)

Since \( E_c \) is many \( kT \) larger than \( E_F \), \( f(E) \) for the conduction band reduces to

\[
f(E) \approx e^{-(E-E_F)/kT}
\]  

(2.10)

and the upper limit, \( E_c \text{max} \), can be replaced by infinity with little error. Therefore,

\[
n = \int_{E_c}^{\infty} \frac{8\sqrt{2}}{h^3} \frac{\pi m^*}{3/2} (E - E_c)^{1/2} e^{(E_F-E)/kT} dE
\]

(2.11)

Changing the variable of integration to \( x = (E - E_c)/kT \) gives

\[
n = \frac{8\sqrt{2}}{h^3} \frac{\pi}{3/2} (m^* kT)^{3/2} e^{(E_F-E_c)/kT} \int_{E_c}^{\infty} x^{1/2} e^{-x} dx
\]  

(2.12)

The integral in this expression is in standard form and equals \( \sqrt{\pi}/2 \). Hence,

\[
n = 2 \left( \frac{2\pi m^* kT}{h^2} \right)^{3/2} e^{(E_F-E_c)/kT}
\]  

(2.13)

\[
n = N_C e^{(E_F-E_c)/kT}
\]  

(2.14)

where \( N_C \) is a constant at fixed \( T \) known as the effective density of states in the conduction band and is defined by comparing Eqs. (2.13) and (2.14). Similarly, the total number of holes in the valence band per unit volume of the crystal is given by

\[
p = N_V e^{(E_V-E_F)/kT}
\]  

(2.15)
with \( N_V \), the effective density of states in the valence band, similarly defined.

For the idealized case of a pure and perfect semiconductor without surfaces, \( n \) equals \( p \) because each electron in the conduction band leaves a vacancy or hole in the valence band. Hence,

\[
\begin{align*}
 n &= p = n_i \\
 np &= n_i^2 = N_C N_V e^{(E_F - E_C)/kT} \\
 &= N_C N_V e^{-E_F/kT}
\end{align*}
\]

(2.16)

(2.17)

where \( n_i \) is known as the "intrinsic concentration" and \( E_F \) is the width of the forbidden gap between the conduction and valence bands. Note also from Eq. (2.16) that

\[
N_C e^{(E_F - E_C)/kT} = N_V e^{(E_V - E_F)/kT}
\]

(2.18)

which gives

\[
E_F = \frac{E_C + E_V}{2} + \frac{kT}{2} \ln \left( \frac{N_V}{N_C} \right)
\]

(2.19)

Hence, the Fermi level in a pure and perfect semiconductor lies close to midgap, being offset only by differences in the effective density of states in the conduction and valence bands.

### 2.9 BOND MODEL OF A GROUP IV SEMICONDUCTOR

Some of the more fundamental of the semiconductor properties described up to now can be looked at from a different viewpoint for a class of semiconductors represented by those belonging to group IV of the periodic table of chemical elements. Although the following "bond model" description is not universally valid for all semiconducting material, it does allow the effects of impurities upon the electronic properties of semiconductors to be introduced in a simple manner.

The characteristic lattice structure of a semiconductor from group IV of the periodic table was shown in Fig. 2.3. A schematic two-dimensional representation of the silicon lattice is shown in Fig. 2.11(a). Each silicon atom is bonded to four neighbors by covalent bonds. Each covalent bond requires two electrons. Silicon has four valence electrons, so each covalent bond shares an electron originating from the central atom and one originating from the neighboring atom.

For the case shown in Fig. 2.11(a), the semiconductor cannot conduct electricity. However, at higher temperatures, some electrons in the covalent bond can obtain enough energy to break free from the bond as shown in Fig. 2.11(b). In this case, the electrons released are free to move about throughout the crystal and can contribute to current flows. Electrons in covalent bonds in the vicinity of the broken bond can also move into the location left vacant in this bond, leaving another broken bond behind. This process also contributes to current flow.

Reverting to the terminology of previous sections, an electron released from a covalent bond can be recognized as being in the conduction band, whereas those associated with covalent bonds are in the valence band. A broken bond can be identified as a hole in the valence band. The minimum energy required to release an electron from a covalent bond is then equal to the width of the forbidden band gap in the semiconductor.

The bond model is particularly useful for discussing the effects of impurities in silicon upon its electronic properties. In the

![Figure 2.11. Schematic representation of the silicon crystal lattice.](image-url)

(a) No covalent bonds broken.
(b) One covalent bond broken, showing the motion of the released electron as well as the motion of a nearby bonded electron into the position left vacant.
next section, the effects of very specialized impurities known as dopants are described.

2.10 GROUP III AND V DOPANTS

Impurity atoms can be incorporated in a crystal structure in two ways. They can occupy positions squeezed in between the atoms of the host crystal, in which case they are known as interstitial impurities. Alternatively they can substitute for an atom of the host crystal, maintaining the regular atomic arrangement in the crystal structure, in which case they are known as substitutional impurities.

Atoms from groups III and V of the periodic table act as substitutional impurities in silicon. A portion of the lattice where a group V impurity (e.g., phosphorus) has replaced a silicon atom is shown in Fig. 2.12. Four of the valence electrons are used up in covalent bonds, but the fifth is in a different situation. It is not in a covalent bond, so it is not in the valence band. For the case shown, it is tied to the group V atom and so is not free to move through the lattice. Hence, it is not in the conduction band either.

It might be expected that only a small amount of energy is required to release this extra electron compared to that required to free electrons locked up in covalent bonds. This is in fact the case. A rough estimate of the energy required can be found by noting the similarity to an electron tied to a hydrogen atom. The expression for the ionization energy (the energy required to release the electron) in the latter case is (Refs. 2.1 to 2.4)

\[
E_i = \frac{m_0 q^4}{8\varepsilon^2 \hbar^2} = 13.6 \text{ electron volts (eV)}
\]  

(2.20)

where \(m_0\) is the electron's rest mass, \(q\) the electronic charge, and \(\varepsilon_0\) the permittivity of free space. The extra electron orbits the group V atom, which has one unneutralized positive charge. The expression for the ionization energy in this case is therefore similar. The radius of the orbit turns out to be much larger than the interatomic distance, so \(\varepsilon_0\) in Eq. (2.20) should be replaced by the permittivity of silicon (11.7\(\varepsilon_0\)). Since the orbiting electron experiences the periodic forces of the silicon lattice, the electron’s mass also should be replaced by an effective mass \((m_e*/m_0 \approx 0.2\) for silicon). Hence, the energy required to free the extra electron is given by

\[
E_i' \approx \frac{13.6(0.2)}{(11.7)^2} \approx 0.02 \text{ eV}
\]  

(2.21)

This is much less than the band-gap energy of silicon of 1.1 eV. A free electron is in the conduction band. Hence, the extra electron tied to the group V atom lies at an energy \(E_i'\) below the edge of the conduction band, as illustrated in Fig. 2.13(a). Note that this places an allowed energy level within the “forbidden” gap.

In an analogous way, a group III impurity does not have enough valence electrons to satisfy the four covalent bonds. This gives rise to a hole tied to the group III atom. The energy required to release the hole is similar to that given by Eq. (2.21). Hence, a group III atom gives rise to an allowed energy level for electrons in the forbidden gap just above the valence-band edge, as shown in Fig. 2.13(b).

![Figure 2.12. Portion of the silicon lattice where a group V atom has replaced a silicon atom.](image)

![Figure 2.13. (a) Energy of the allowed state introduced into the forbidden gap by a group V substitutional impurity. (b) Corresponding energy state for a group III impurity.](image)
2.11 CARRIER DENSITIES

Since the energy required to release the extra electron from a group V atom is small, it is not unexpected that, at room temperature, most of these electrons have acquired this energy. Hence, most have left the group V atom, with its net positive charge, behind and are free to move through the crystal. Since group V atoms donate electrons to the conduction band, they are known as donors. A more quantitative idea of the number of electrons that have obtained the small amount of energy required can be obtained by referring to Fig. 2.14. Note that the form of the Fermi-Dirac distribution function indicates that donor levels have only a small probability of being occupied.\(^1\) This means that most electrons have left the donor site and are in the conduction band.

The total number of electrons in the conduction band and holes in the valence band in this case can be found by considering the condition for charge neutrality in the semiconductor:

\[
p - n + N_D^+ = 0
\]

where \(p\) is the hole density in the valence band, \(n\) the density of conduction band electrons, and \(N_D^+\) the density of ionized donors (i.e., positive charges left behind when the electron departs). The other important equation comes from Eq. (2.17):

\[
np = n_f^2
\]

This relation is more general than for the case of pure semiconductors previously discussed. Equations (2.14), (2.15), and (2.22), in conjunction with the Fermi-Dirac distribution function, can be solved to give precise values for \(n\), \(p\), and \(N_D^+\) under general conditions. However, for most cases of interest in this book, the approximate but much simpler method of solution outlined below will give results of more than adequate accuracy.

Since the vast majority of donors will be ionized, \(N_D^+\) will be nearly equal to the total density of donors, \(N_D\). From Eq. (2.22), \(n\) will be greater than \(p\) and, in fact, very much greater when \(N_D^+\) be-

\(^1\) The statistics governing the occupation of the donor level are actually slightly different from those governing the occupation of levels within the allowed band. Once a donor level is occupied by a single electron of either "spin," the effective positive charge on the central donor atom is neutralized and there is no attraction that would allow occupation by a second electron of opposite spin. This results in an expression for the probability of occupation which differs slightly from the Fermi-Dirac function. That difference is not important in this book.

Figure 2.14. (a) Band representation of a group IV semiconductor with a group V substitutional impurity of density \(N_D\) per unit volume. (b) Corresponding energy density of allowed states. (c) Probability of occupation of these states. (d) Resulting energy distributions of electrons and holes. (The case shown would correspond to quite high temperatures. At more moderate temperatures, the probability of occupation of donor states by electrons would be even smaller than shown.)

comes large. Hence, the approximate solution is

\[
N_D^+ \approx N_D
\]

\[
n \approx N_D
\]

\[
p \approx n_f^2 \ll n
\]

An analogous situation occurs with group III impurities. These very easily give up their excess hole to the valence band or equivalently accept an electron from this band. Consequently, they are known as acceptors. An ionized acceptor has a net negative charge. Hence,

\[
p - n - N_A^- = 0
\]

where \(N_A^-\) is the density of ionized acceptors.

The approximate solution in this case is

\[
N_A^- \approx N_A
\]

\[
p \approx n_f^2 \ll n
\]
2.12 LOCATION OF FERMI LEVEL IN DOPED SEMICONDUCTORS

The equations for electron and hole densities derived in Eqs. (2.14) and (2.15) apply to more general cases than that for pure semiconductors. For the case of material doped with donors (commonly called n-type material), these become

$$n = N_D = N_C e^{(E_F - E_C)/kT}$$  \hspace{3cm} (2.27)

or, equivalently,

$$E_F - E_C = kT \ln \left( \frac{N_D}{N_C} \right)$$  \hspace{3cm} (2.28)

Similarly, for material doped with acceptors (p-type material),

$$p = N_A = N_V e^{(E_V - E_P)/kT}$$  \hspace{3cm} (2.29)

$$E_V - E_P = kT \ln \left( \frac{N_A}{N_V} \right)$$  \hspace{3cm} (2.30)

As the semiconductor material becomes more heavily doped, the Fermi level $E_F$ moves away from midgap and approaches the conduction band for n-type material or the valence band for p-type material, as shown in Fig. 2.15.

![Diagram of energy levels and Fermi level](image)

Figure 2.15. Energy of the Fermi level as a function of the concentration of donors and acceptors.

2.13 EFFECT OF OTHER TYPES OF IMPURITIES

Our theoretical understanding of the properties of impurities in silicon other than those from groups III and V is less developed, although the practical effects of such impurities are well known.

Just as group III and V impurities introduce an allowed energy level into the forbidden band gap of silicon, so do more general impurities. This is indicated in Fig. 2.16, which shows the al-

![Energy levels within the forbidden gap for a range of impurities in Si and GaAs](image)

Figure 2.16. Energy levels within the forbidden gap for a range of impurities in Si and GaAs. A indicates an acceptor level, D a donor level. [After S. M. Sze and J. L. Irwin, Solid-State Electronics 11 (1968), 599.]
lowed energy levels introduced by a range of impurities in the silicon as well as the compound semiconductor GaAs. Some impurities introduce multiple energy levels, as shown. Crystal defects act in a similar way to introduce allowed levels into the forbidden gap.

Impurities, particularly those which introduce energy levels near the middle of the band gap, generally degrade the properties of semiconductor devices. Impurity concentrations in the starting material used in the fabrication of these devices are therefore kept as low as technology will allow—generally less than 1 part per billion.

2.14 CARRIER TRANSPORT

2.14.1 Drift

Under the influence of an applied electric field, $\xi$, a randomly moving free electron would have an acceleration $a = \frac{q\xi}{m}$ in a direction opposite to the field, with its velocity in this direction increasing with time. The electron in a crystal structure is in a different situation. It moves with a different mass and will not continue accelerating for very long. It will eventually collide with a lattice atom, or an impurity atom, or a defect in the crystal structure. Such a collision will tend to randomize the electron's motion. In other words, it will tend to reduce the excess velocity that the electron picked up in the applied field. The "average" time between collisions is called the relaxation time, $t_r$. This will be determined by the random thermal velocity of electrons, which is generally much larger than field imparted velocities. The average velocity increase of electrons between collisions caused by the field is called the drift velocity and is given by

$$v_d = \frac{1}{2} q t_r \frac{\xi}{m_e^*}$$

(2.31)

for electrons in the conduction band. (The factor of 2 disappears if $t_r$ is averaged over all electron velocities.) The electron carrier mobility is defined by the ratio

$$\mu_e = \frac{v_d}{\xi} = \frac{q t_r}{m_e^*}$$

(2.32)

The corresponding current density flow due to conduction band electrons will be

$$J_e = q n v_d = q n \mu_e \xi$$

(2.33)

An analogous equation for holes in the valence band is

$$J_h = q \mu_h p \xi$$

(2.34)

The total current flow is just the sum of these two components. Hence, the conductivity, $\sigma$ of the semiconductor can be identified as

$$\sigma = \frac{1}{\rho} = \frac{J}{\xi} = q \mu_e n + q \mu_h p$$

(2.35)

where $\rho$ is the resistivity.

Although the analysis resulting in Eq. (2.32) is simplistic, it does allow an intuitive understanding of how the carrier mobilities, $\mu_e$ and $\mu_h$, change with changes in the density of dopants, temperature, and electric field strength.

For relatively pure semiconductors of good crystallographic quality, the collisions that randomize the carrier velocities will involve the atoms of the host crystal. However, ionized dopants are very effective scatterers because of their associated net charge. Consequently, as the semiconductor becomes more heavily doped, the average time between collisions and hence the mobility will decrease. For good-quality silicon, empirical expressions relating the carrier mobilities to the level of dopants $N$ (in cm$^{-3}$) are (Ref. 2.5)

$$\mu_e = 65 + \frac{1265}{1 + (N/8.5 \times 10^{16})^{0.72}} \text{ cm}^2/\text{V-s}$$

(2.36)

$$\mu_h = 47.7 + \frac{447.3}{1 + (N/6.3 \times 10^{16})^{0.72}} \text{ cm}^2/\text{V-s}$$

Less specialized impurities as well as crystal defects will decrease mobilities further, for similar reasons.

Increasing temperature will increase the vibration of the host atoms, making them larger "targets," again decreasing the average time between collisions as well as the carrier mobilities. This effect becomes less pronounced at high doping levels, where ionized dopants are effective carrier scatterers.

Increasing the strength of the electric field will eventually increase the drift velocities of carriers to values where they will become comparable to the random thermal velocities. Hence, the total velocity of electrons will ultimately increase with field strength, decreasing the time between collisions and the mobility.