Chapter

2

REVIEW OF SEMICONDUCTOR PROPERTIES

2.1 INTRODUCTION

In Chapter 1, the properties of sunlight were reviewed. It is now appropriate to look at the properties of the other important component in photovoltaic solar energy conversion, semiconducting material.

The aim of this chapter is *not* to treat the properties of semiconductors rigorously from fundamentals. Rather, it is to highlight those properties of semiconductors that are important in the design and operation of solar cells. As such, the chapter may suffice for quick revision for readers already acquainted with these properties while containing adequate information to allow those not as well acquainted to establish a framework on which subsequent material can be supported. To strengthen this framework, readers in the latter category are referred to one of the many textbooks specifically directed at treating semiconductor properties more fundamentally (Refs. 2.1 to 2.4).

2.2 CRYSTAL STRUCTURE AND ORIENTATIONS

Most of the photovoltaic materials described in this book are *crystalline*, at least on a microscopic scale. Ideal crystalline material is characterized by an orderly, periodic arrangement of the atoms of which it is composed.

In such an orderly arrangement, it is possible to build up the entire crystal structure by repeatedly stacking a small subsection. The smallest such section with which this is possible is known as a *primitive cell.* Such primitive cells naturally contain all the information required to reconstruct the locations of atoms in the crystal but often have awkward shapes. Consequently, it can be more convenient to work with a larger *unit cell* which also contains this information but generally has a simpler shape. For example, Fig.2.1(a) shows the unit cell for an atomic arrangement known as face-centered-cubic and Fig. 2.1(b) shows the corresponding primitive cell. The directions defining the outline of the unit cell are orthogonal, whereas this is not the case for the primitive cell. The length of the edge of the unit cell is known as the *lattice constant.*

The orientation of planes within the crystal can be expressed in terms of the unit cell structure by using the system of *Miller indices.* The vectors defining the outline of the unit cell are used as the basis of a coordinate system as in Fig. 2.1(a). A plane of the orientation in question is imagined passing through the origin of the coordinate system. Then the next plane parallel to this which passes through atomic sites along each of the coordinate axis is considered. An example is shown in Fig. 2.2. The intercepts in this case along each of the axes are 1, 3, and 2 atoms from the origin. Taking inverses gives 1, $\frac{1}{3}$, and $\frac{1}{2}$. The smallest integrals with the same ratio are 6, 2, and 3. This plane is then expressed in Miller indices as the (6 2 3) plane. Negative intercepts are indicated by a bar over the top of the corresponding index (e.g., - 2 would be written as $\bar{2}$).

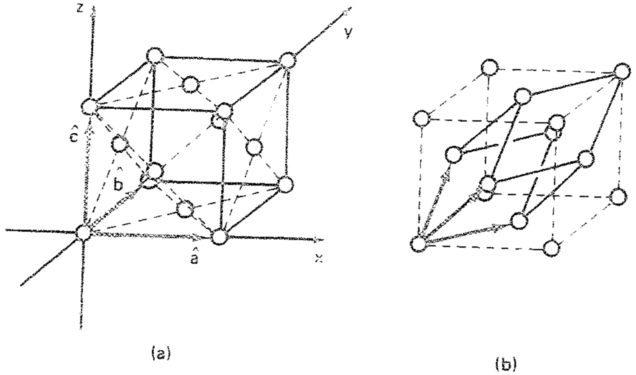

Figure 2.1. (a) Unit cell for the face-centered-cubic atomic arrangement. The unit cell is selected in this case so that the directions defining its outline are orthogonal. The vectors $\hat{a}$, $\hat{b}$, and $\hat{c}$ are unit vectors in each of these directions. (b) Primitive cell for the same atomic arrangement.

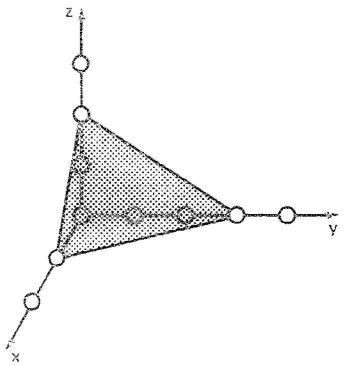

Figure 2.2. Sketch of a plane in a crystal described by the Miller indices (6 2 3).

Directions within the crystal are expressed in a condensed form of vector notation. A vector in the direction of interest is scaled so it is expressed in the form $h\hat{a} + k\hat{b} + l\hat{c}$, where $\hat{a}$, $\hat{b}$, and $\hat{c}$ are unit vectors along each of the axes of the coordinate system as in Fig. 2.1(a) and h, k, and l are integers. This direction is then described as the $[h\ k\ l]$ direction. The use of square brackets distinguishes directions from Miller indices. Note that for cubic unit cells, the $[h\ k\ l]$ direction is perpendicular to the $(h\ k\ l)$ plane.

Finally, there are planes within the crystal structure which are equivalent. For example, for the face-centered-cubic lattice of Fig. 2.1(a), differences between the (100), (010), and (001) planes depend only on the choice of origin. Collectively, the corresponding set of equivalent planes is known as the {100} set, with braces reserved for this use.

Figure 2.3(a) shows the atomic arrangement found in many of the semiconductors important in solar cell technology. This is the arrangement for silicon (Si) crystals as well as for crystals of gallium arsenide (GaAs) and cadmium sulfide (CdS). The latter are *compound* semiconductors involving more than one type of atom in the crystal structure. The arrangement shown is generally referred to as the *diamond lattice* or *zincblende lattice* (for compound semiconductors such as GaAs). The unit cell is cubic, as indicated. Figure

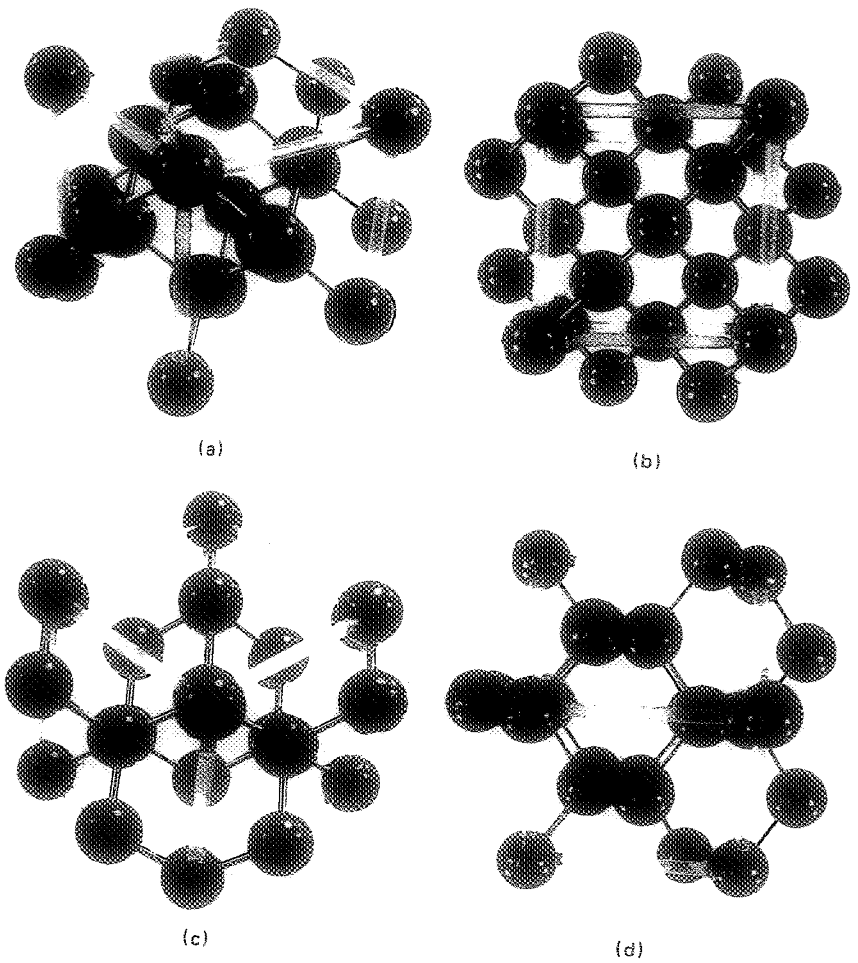

Figure 2.3. (a) Model of the diamond lattice which indicates the atomic structure of many of the semiconductors of importance in solar cells. Also shown is the outline of the unit cell. (b) View of the same structure looking in the [100] direction. (c), (d) Views in the [111] and [110] directions, respectively.

2.3(b)-(d) show atomic arrangements looking at the lattice from selected directions. These highlight the substantial differences in the physical arrangement of atoms in different directions which give rise to directional variations of importance in solar cell work (e.g., see Exercise 2.2).

2.3 FORBIDDEN ENERGY GAPS

An electron in free space has an essentially continuous range of energy values that it can attain. The situation in a crystal can be quite different.

Electrons associated with isolated atoms have a well-defined set of discrete energy levels available to them. As several atoms are brought closer together, the original levels spread out into bands of allowed energy as indicated in Fig. 2.4. When the atoms are in ordered arrangements as in crystals, there will be characteristic distances between them. Figure 2.4(a) shows the case of a crystal where the characteristic separation between atoms, d, is such that the crystal has bands of energies allowed to electrons (corresponding to the atomic energy levels) separated by bands of forbidden energy. A different situation is shown in Fig. 2.4(b), where the bands have overlapped to give virtually a continuum of allowed energies at the value of d characteristic of a different crystalline material.

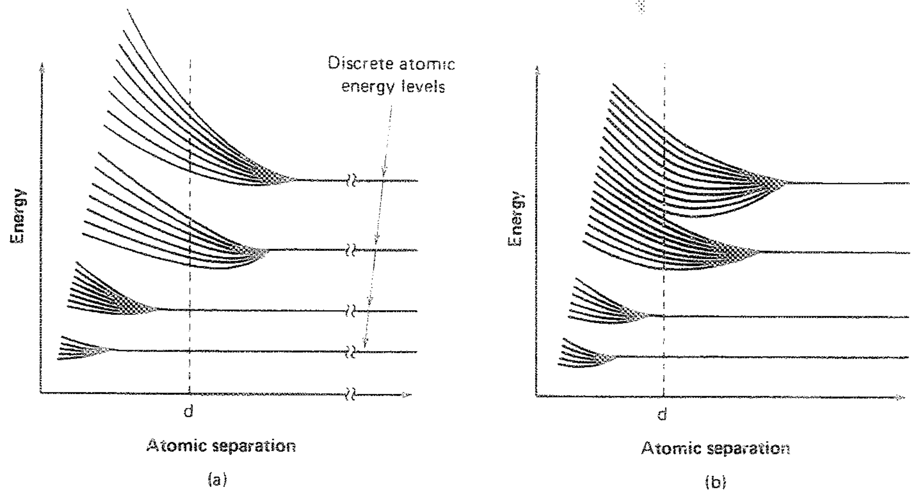

Figure 2.4. Schematic indicating how the discrete energies allowed to electrons in an isolated atom split up into bands of allowed energies when a number of similar atoms are brought together in a crystal:

(a) For this case, d, the characteristic spacing of atoms in a crystal, is such that there are bands of energies allowed to electrons separated by bands of forbidden energy.

(b) In this case, d is such that the uppermost bands have overlapped.

2.4 PROBABILITY OF OCCUPATION OF ALLOWED STATES

At low temperatures, electrons in a crystal occupy the lowest possible energy states.

At first sight, it might be expected that the equilibrium state of a crystal would be one in which the electrons are all in the lowest allowed energy level. However, this is *not* the case. A fundamental physical theorem, the *Pauli exclusion principle*, implies that each allowed energy level can be occupied by, at most, two electrons, each of opposite "spin." This means that, at low temperatures, all available states in the crystal up to a certain energy level will be occupied by two electrons. This energy level is known as the *Fermi level* (E_F).

As the temperature increases, some electrons gain energy in excess of the Fermi level. The probability of occupation of an allowed electron state of any given energy E can be calculated from statistical considerations for this more general case, taking into account the constraints imposed by the Pauli exclusion principle (Refs. 2.1 to 2.4). The result is the *Fermi-Dirac distribution function* $f(E)$, given by

$$f(E) = \frac{1}{1 + e^{(E - E_F)/kT}} \qquad (2.1)$$

where k is a constant known as *Boltzmann's constant* and T is the absolute temperature. This function is plotted in Fig. 2.5. Near absolute zero, $f(E)$ is essentially unity, as expected, up to an energy equal to E_F, and zero above E_F. As the temperature increases, there is a smearing out of the distribution, with states of energy higher than E_F having a finite probability of occupation, and states of energy below E_F having a finite probability of being empty.

It is now possible to describe the differences among metals, insulators, and semiconductors in terms of electronic band structure. Metals have an electronic structure such that E_F lies within an allowed band (Fig. 2.6). The cause of this may be that there are insufficient electrons available to fill an available band if the band structure is as shown in Fig. 2.4(a), or alternatively, that there are overlapping bands as in Fig. 2.4(b). Insulators have one band fully occupied by electrons and a large energy gap between this band and the next highest band, which is devoid of electrons at low temperatures. From the discussion in the earlier part of this section, it follows that E_F must lie within the forbidden band (Fig. 2.6).

A band in which there are no electrons obviously cannot make

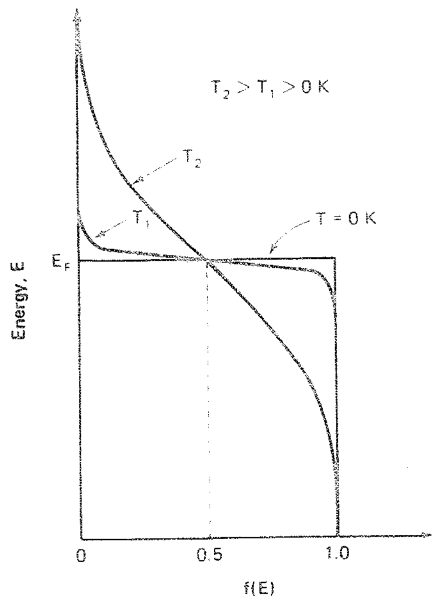

Figure 2.5. Fermi-Dirac distribution function. States above the Fermi level, E_F, have a low probability of being occupied by electrons, whereas those below are likely to be so occupied.

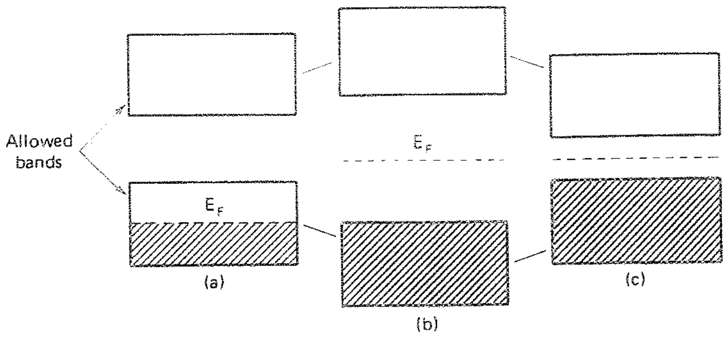

Figure 2.6. Diagrams showing the way in which allowed states are occupied by electrons in:

(a) A metal.
(b) An insulator.
(c) A semiconductor.

any contribution to current flow in the crystal. More surprisingly, *neither can a completely full band.* To contribute to such flow, an electron must extract energy from the applied field. In a completely filled band, this is not possible. There are no vacant allowed energy levels in the vicinity into which an electron can be excited. Hence, an insulator does not conduct electricity, whereas a metal, with an abundance of such levels, does.

A semiconductor is just an insulator with a narrow forbidden band gap. At low temperatures, it does not conduct. At higher temperatures, there is sufficient smearing out of the Fermi-Dirac distribution function to ensure that some levels in the originally completely filled band (*valence band*) are now vacant and some in the next-highest band (*conduction band*) are occupied. The electrons in the conduction band, with an abundance of unoccupied energy states in the vicinity, can contribute to current flows. Since there are now unoccupied levels in the valence band, an additional contribution also comes from electrons in this band.

2.5 ELECTRONS AND HOLES

A very simple but reasonably good analogy to current flow processes in a semiconductor is provided by an idealized two-level parking station (Fig. 2.7). Consider the case where the bottom level of this station is completely filled with cars and the top level completely empty, as in Fig. 2.7(a). Then there is no room for any car to move. If one car is moved from the first to the second level as in Fig. 2.7(b), the car on the second level is free to move as much as desired. This corresponds to an electron in the conduction band in a semiconductor. There will now be a vacant position on the lower level. Cars adjacent to this position can move into it, leaving a new vacant position behind. Hence, car motion is now possible on the lower level as well. This motion corresponds to the motion of electrons in the valence band. Instead of regarding the motion on the lower level as the result of the movements of a number of cars, it can be more simply described as the motion of the single vacant position. Similarly, in a crystal it is easier to think in terms of the motion of vacant states in the valence band. In many situations the correct motion of the vacancy can be predicted if it is regarded as a physical particle of positive charge commonly called a *hole*. Hence, current flow in a semiconductor can be regarded as being due to the sum of the motion of electrons in the conduction band and holes in the valence band.

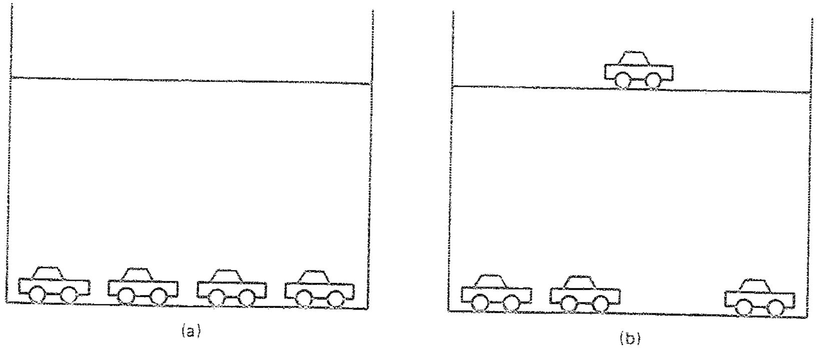

Figure 2.7. Simple "parking-station" analog of conduction processes in a semiconductor:
(a) No movement possible.
(b) Movement possible on both upper and lower levels.

2.6 DYNAMICS OF ELECTRONS AND HOLES

The motion of electrons and holes in semiconductors in response to applied forces differs from that of particles in free space. In addition to the applied force, there is always the effect of the periodic forces of the crystal atoms. However, results of quantum mechanical calculations indicate that, in most situations of interest herein, concepts developed for particles in free space can be applied to electrons and holes in semiconductors, with some modifications.

For example, in the case of electrons in a crystal lying within the conduction band, Newton's law becomes

$$F = m_e^* a = \frac{dp}{dt} \tag{2.2}$$

where F is the applied force, m_e^* an "effective mass" of the electron which incorporates the effect of the periodic force of the lattice atoms, and p is known as the crystal momentum analogous to free-space momentum.

For a free electron, energy and momentum are related by a parabolic law,

$$E = \frac{p^2}{2m} \tag{2.3}$$

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:

$$E - E_c = \frac{p^2}{2m_e^*} \tag{2.4}$$

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

$$E_v - E = \frac{p^2}{2m_h^*} \tag{2.5}$$

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:

$$E - E_c = \frac{(p - p_0)^2}{2m_e^*} \tag{2.6}$$

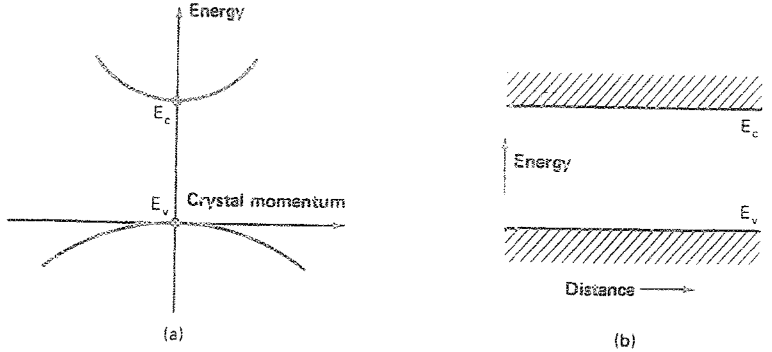

Figure 2.8. (a) Energy–crystal momentum relationships near the band edges for electrons in the conduction band and holes in the valence band of a direct-band-gap semiconductor. (b) Corresponding spatial representation of allowed energies in a semiconductor.

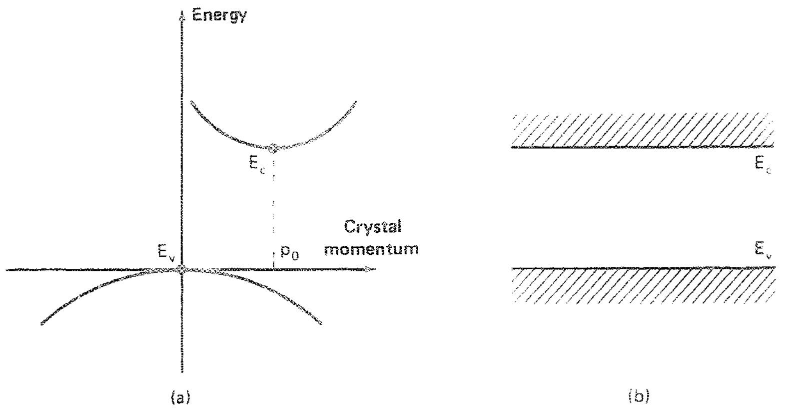

Figure 2.9. Energy–crystal momentum relationships near the band edges for an indirect-band-gap semiconductor. Also shown is the energy band spatial representation.

The valence band can exhibit a similar relationship:

$$E_v - E = \frac{(p - p_0')^2}{2m_h^*} \tag{2.7}$$

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.

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-

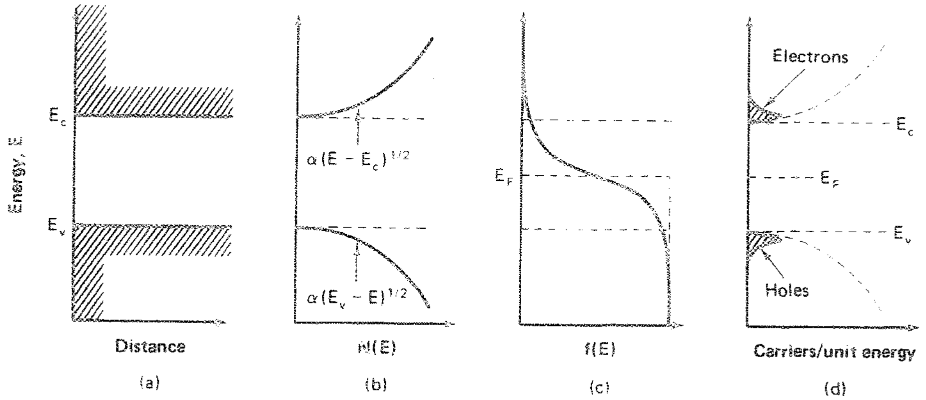

Figure 2.10. (a) Band representation of a semiconductor. (b) Corresponding energy density of allowed states for electrons. (c) Probability of occupation of these states. (d) Resulting energy distribution of electrons and holes. Note that most are clustered near the edge of the respective band.

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

$$N(E) = \frac{8\sqrt{2}\pi m_e^{*3/2}}{h^3} (E - E_c)^{1/2} \tag{2.8}$$

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

$$n = \int_{E_c}^{E_{c\,\max}} f(E)\, N(E)\, dE \tag{2.9}$$

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

$$f(E) \approx e^{-(E - E_F)/kT} \tag{2.10}$$

and the upper limit, $E_{c\,\max}$, can be replaced by infinity with little error. Therefore,

$$\begin{aligned} n &= \int_{E_c}^{\infty} \frac{8\sqrt{2}\,\pi m_e^{*3/2}}{h^3} (E - E_c)^{1/2} e^{(E_F - E)/kT}\, dE \\ &= \frac{8\sqrt{2}\,\pi}{h^3} m_e^{*3/2} e^{E_F/kT} \int_{E_c}^{\infty} (E - E_c)^{1/2} e^{-E/kT}\, dE \end{aligned} \tag{2.11}$$

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

$$n = \frac{8\sqrt{2}\,\pi}{h^3} (m_e^* kT)^{3/2} e^{(E_F - E_c)/kT} \int_0^{\infty} x^{1/2} e^{-x}\, dx \tag{2.12}$$

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

$$n = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} e^{(E_F - E_c)/kT} \tag{2.13}$$

$$\boxed{n = N_C e^{(E_F - E_c)/kT}} \tag{2.14}$$

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

$$\boxed{p = N_V e^{(E_v - E_F)/kT}} \tag{2.15}$$

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,

$$n = p = n_i \tag{2.16}$$

$$\begin{aligned} np = n_i^2 &= N_C N_V e^{(E_v - E_C)/kT} \\ &= N_C N_V e^{-E_g/kT} \end{aligned} \tag{2.17}$$

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

$$N_C e^{(E_F - E_C)/kT} = N_V e^{(E_v - E_F)/kT} \tag{2.18}$$

which gives

$$E_F = \frac{E_c + E_v}{2} + \frac{kT}{2} \ln \left(\frac{N_V}{N_C} \right) \tag{2.19}$$

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. 2.8. 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

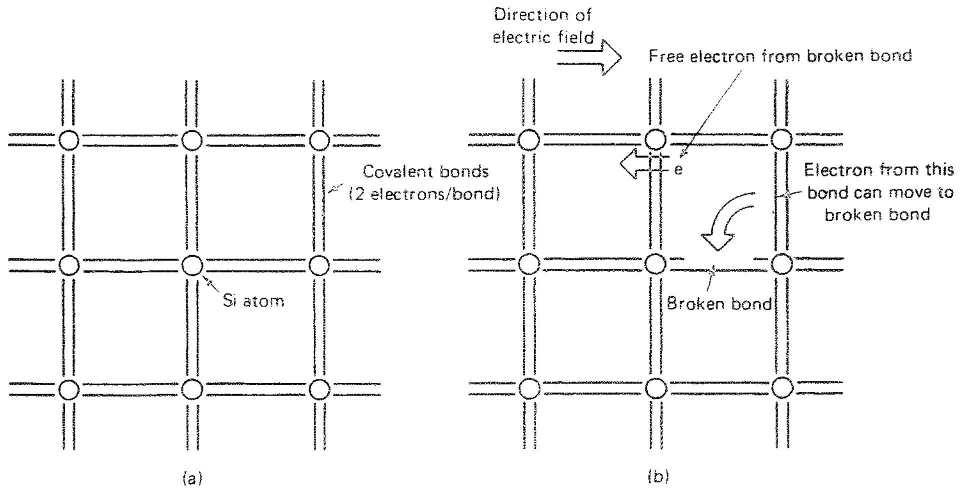

Figure 2.11. Schematic representation of the silicon crystal lattice.

(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)

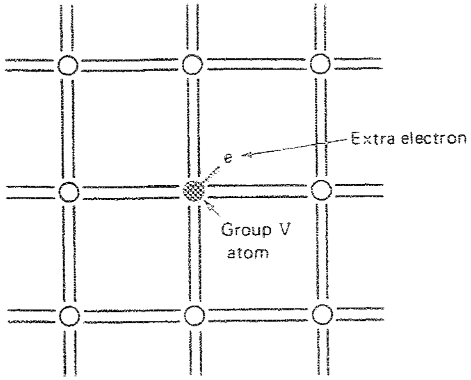

Figure 2.12. Portion of the silicon lattice where a group V atom has replaced a silicon atom.

$$E_i = \frac{m_0 q^4}{8\epsilon_0^2 h^2} = 13.6 \text{ electron volts (eV)} \qquad (2.20)$$

where m_0 is the electron's rest mass, q the electronic charge, and ϵ_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 ϵ_0 in Eq. (2.20) should be replaced by the permittivity of silicon ($11.7\epsilon_0$). Since the orbiting electron experiences the periodic forces of the silicon lattice, the electron's mass also should be replaced by an effective mass ($m_e^*/m_0 \simeq 0.2$ for silicon). Hence, the energy required to free the extra electron is given by

$$E_i' \approx \frac{13.6(0.2)}{(11.7)^2} \approx 0.02 \text{ eV} \qquad (2.21)$$

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).

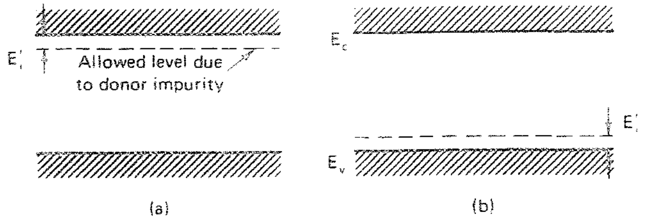

Figure 2.13. (a) Energy of the allowed state introduced into the forbidden gap by a group V substitutional impurity. (b) Corresponding energy state for a group III impurity.

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:

$$p - n + N_D^+ = 0 \tag{2.22}$$

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):

$$np = n_i^2 \tag{2.23}$$

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.

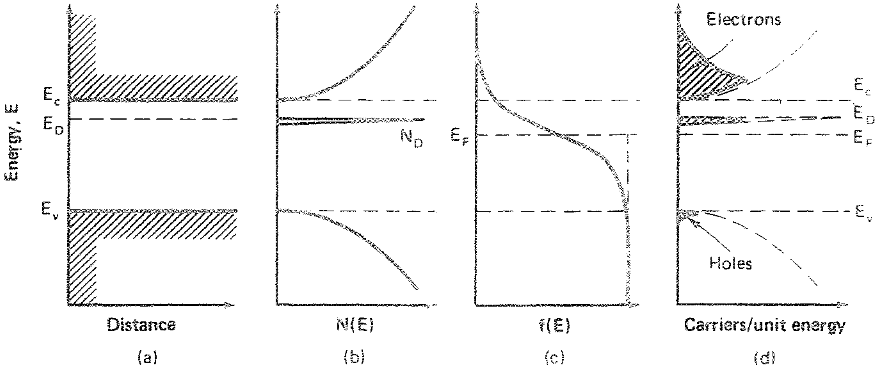

Figure 2.14. (a) Band representation of a group IV semiconductor with a group V substitutional impurity of density N_D per unit volume. (b) Corresponding energy density of allowed states. (c) Probability of occupation of these states. (d) Resulting energy distributions of electrons and holes. (The case 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.)

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 becomes large. Hence, the approximate solution is

$$\begin{aligned} N_D^+ &\approx N_D \\ n &\approx N_D \\ p &\approx \frac{n_i^2}{N_D} << n \end{aligned} \tag{2.24}$$

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,

$$p - n - N_A^- = 0 \tag{2.25}$$

where N_A^- is the density of ionized acceptors.

The approximate solution in this case is

$$\begin{aligned} N_A^- &\approx N_A \\ p &\approx N_A \\ n &\approx \frac{n_i^2}{N_A} << p \end{aligned} \tag{2.26}$$

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[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.

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

$$n = N_D = N_C e^{(E_F - E_c)/kT} \tag{2.27}$$

or, equivalently,

$$E_F - E_c = kT \ln \left(\frac{N_D}{N_C}\right) \tag{2.28}$$

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

$$p = N_A = N_V e^{(E_v - E_F)/kT} \tag{2.29}$$

$$E_v - E_F = kT \ln \left(\frac{N_A}{N_V}\right) \tag{2.30}$$

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.

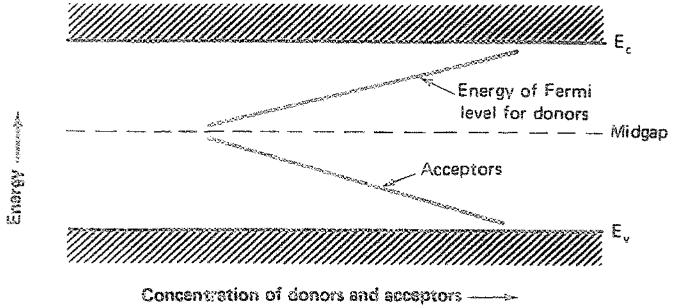

Figure 2.15. Energy of the Fermi level as a function of the concentration of donors and acceptors.

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-

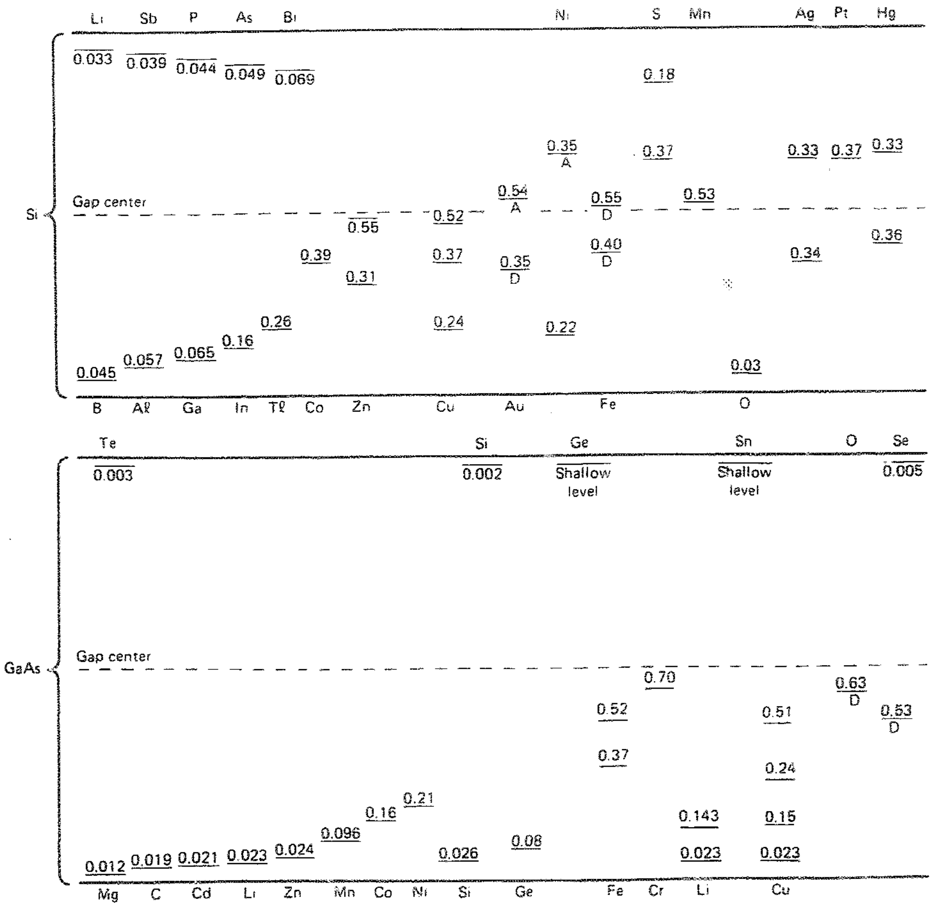

Figure 2.16. Energy levels within the forbidden gap for a range of impurities in Si and GaAs. A indicates an acceptor level, D a donor level. [After S. M. Sze and J. Irwin, *Solid-State Electronics 11* (1968), 599.]

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, ξ, a randomly moving free electron would have an acceleration $a = \xi/m$ 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

$$v_d = \frac{1}{2}at = \frac{1}{2}\frac{qt_r}{m_e^*}\xi \tag{2.31}$$

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

$$\mu_e = \frac{v_d}{\xi} = \frac{qt_r}{m_e^*} \tag{2.32}$$

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

$$J_e = qnv_d = q\mu_e n\xi \tag{2.33}$$

An analogous equation for holes in the valence band is

$$J_h = q\mu_h p\xi \tag{2.34}$$

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

$$\sigma = \frac{1}{\rho} = \frac{J}{\xi} = q\mu_e n + q\mu_h p \tag{2.35}$$

where ρ is the resistivity.

Although the analysis resulting in Eq. (2.32) is simplistic, it does allow an intuitive understanding of how the carrier mobilities, μ_n and μ_p, 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)

$$\begin{aligned} \mu_e &= 65 + \frac{1265}{1 + (N/8.5 \times 10^{16})^{0.72}} \text{ cm}^2/\text{V-s} \\ \mu_h &= 47.7 + \frac{447.3}{1 + (N/6.3 \times 10^{16})^{0.76}} \text{ cm}^2/\text{V-s} \end{aligned} \tag{2.36}$$

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.

2.14.2 Diffusion

Apart from motion by drift, carriers in semiconductors can also flow by diffusion. It is a well-known physical effect that any excess concentration of particles such as gas molecules will tend to dissipate itself unless constrained. The basic cause of this effect is the random thermal velocity of the particles involved.

The flux of particles is proportional to the negative of the concentration gradient (Fig. 2.17). Since current is proportional to the flux of charged particles, the current density corresponding to a one-dimensional concentration gradient of electrons is

$$J_e = qD_e \frac{dn}{dx} \tag{2.37}$$

where D_e is a constant known as the diffusion constant. Similarly, for holes

$$J_h = -qD_h \frac{dp}{dx} \tag{2.38}$$

Note the sign difference between Eqs. (2.37) and (2.38), which is due to the opposite types of charges involved. Drift and diffusion processes are fundamentally related and the mobilities and diffusion constants are not independent. They are interconnected by the *Einstein relations*

$$D_e = \frac{kT}{q}\mu_e \qquad \text{and} \qquad D_h = \frac{kT}{q}\mu_h \tag{2.39}$$

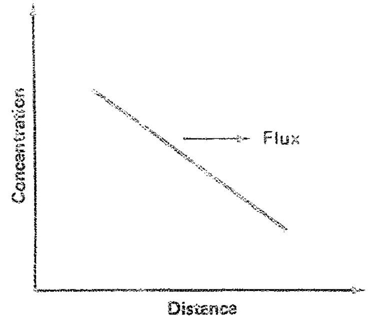

Figure 2.17. Diffusive flux of carriers in the presence of a concentrator gradient.

kT/q is a parameter that will appear often in relation to solar cells. It has the dimensions of voltage and the value of 26 mV at room temperature, a value worth committing to memory!

2.15 SUMMARY

The major points arising from this chapter are the following. Semiconductors have an electronic structure such that one band of allowed states virtually completely occupied by electrons (the valence band) is separated by a forbidden energy gap from the next band of allowed states, which is virtually devoid of electrons (the conduction band). Current flow in semiconductors is due to both motion of electrons in the conduction band and the effective motion of vacancies or holes in the valence band. In many situations, electrons in the conduction band and holes in the valence band can be regarded as free particles, provided that an "effective" mass is used to include the effect of periodic forces of the host atoms in the crystal. Most conduction-band electrons have energies close to that of the conduction-band edge, whereas most holes have energies close to that of the valence-band edge.

Semiconductors can be divided into "direct"- and "indirect"-band-gap types, depending on the form of the relationship between the energy of electrons in the conduction band and their crystal momentum.

Specialized impurities known as dopants, when introduced into semiconductors, can control the relative concentrations of electrons in the conduction band of a semiconductor and holes in the valence band. Carriers in these bands can flow by drift and diffusion when the appropriate perturbations are present.

In Chapter 3, additional electronic processes occurring within semiconductors when disturbed by light are described. From the fundamental mechanisms discussed in this and the next chapter, a single system of self-consistent equations will be synthesized. This system will be used in later chapters to establish the principles of solar cell design.

EXERCISES

2.1. For a crystal with a cubic unit cell, indicate on a sketch of the cell the following crystal planes: (a) (100); (b) (010); (c) (110); (d) (111).

2.2. (a) Silicon solar cell performance can be improved by selectively etching the cell surface to reduce reflection losses. Figure 7.6 shows a silicon crystal surface originally orientated parallel to the (100) plane which has been attacked by a chemical etch that etches at different rates in different directions through the crystal. This exposes the square-based pyramids shown. Given that the sides of the pyramids are all members of the {111} equivalent set of planes, find the angle between opposite faces of the pyramids.

(b) A fraction R of light incident normally on the original silicon surface was reflected. Neglecting dependencies upon angle of incidence and wavelength, show that fraction reflected after the selective etch is reduced to *slightly less* than R^2.

2.3. One method of introducing impurities into silicon in controlled quantities is a technique known as *ion implantation*. Ions of the desired impurity are accelerated to high velocity and directed at the silicon surface. If the ions impinged parallel to each of the crystal directions shown in Fig. 2.3(b)-(d), in which case would you expect the ions to penetrate the greatest distance into the silicon?

2.4. An allowed state for an electron in a semiconductor lies at an energy equal to 0.4 eV above the Fermi level. What probability has this state of being occupied by an electron under thermal equilibrium conditions at 300 K?

2.5. Assuming that the effective masses of electrons and holes are equal to the free electron mass, calculate the effective density of states in the conduction and valence bands for silicon at 300 K. Assuming a band gap of 1.1 eV, find the intrinsic concentration in silicon at this temperature.

2.6. (a) Silicon is uniformly doped with 10^{22} phosphorus atoms/m^3. Assuming that all these donor impurities are ionized, estimate the concentration of electrons and holes in this material under thermal equilibrium at 300 K. Hence, calculate the energy of the Fermi level in this material below the conduction-band edge.

(b) Given that the donor level for phosphorus lies 0.045 eV below the conduction-band edge, calculate the probability that this level is occupied by an electron and hence check on the assumption that all donors are ionized. (Use $N_C = 3 \times 10^{25}$ m^{-3}, $N_V = 10^{25}$ m^{-3}, and $n_i = 1.5 \times 10^{16}$ m^{-3}.)

2.7. Using Eq. (2.36) for the electron and hole mobilities in silicon, estimate the resistivity of the silicon specimen of Exercise 2.6.

2.8. Estimate the average time between collisions with the host atoms for electrons in the conduction band of lightly doped silicon.

2.9. An electric field of 10^4 V/m is applied to a specimen of silicon at 300 K doped with 10^{22} donors/m^3. Given that the thermal velocity is 10^5 m/s, compare the drift and thermal velocities for conduction-band electrons. At what value of the field strength will these be comparable?

2.10. In a section of silicon at 300 K, the field strength is zero and conduction band electrons have a concentration that varies from 10^{22} per m^2 to 10^{21} per m^2 over a distance of 1 μm. Assuming a linear variation of electrons, calculate the corresponding current density.

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