# 11 Electrical Properties of Materials

One of the principal characteristics of materials is their ability (or lack of ability) to conduct electrical current. Indeed, materials are classified by this property, that is, they are divided into conductors, semiconductors, and nonconductors. (The latter are often called insulators or dielectrics.) The **conductivity**,  $\sigma$ , of different materials at room temperature spans more than 25 orders of magnitude, as depicted in Figure 11.1. Moreover, if one takes the conductivity of superconductors, measured at low temperatures, into consideration, this span extends to 40 orders of magnitude (using an estimated conductivity for superconductors of about  $10^{20}$  1/ $\Omega$  cm). This is the largest known variation in a physical property and is only comparable to the ratio between the diameter of the universe (about  $10^{26}$  m) and the radius of an electron ( $10^{-14}$  m).

The inverse of the conductivity is called **resistivity**,  $\rho$ , that is:

$$\rho = \frac{1}{\sigma}.\tag{11.1}$$

The **resistance**, *R* of a piece of conducting material is proportional to its resistivity and to its *length*, *L*, and is inversely proportional to its cross-sectional area, *A*:

$$R = \frac{L \cdot \rho}{A}.$$
 (11.2)

The resistance can be easily measured. For this, a direct current is applied to a slab of the material. The current, *I*, through the sample (in ampères), as well as the voltage drop, *V*, on two potential probes (in volts) is recorded as depicted in Figure 11.2.



FIGURE 11.1. Room-temperature conductivity of various materials. (Superconductors, having conductivities of many orders of magnitude larger than copper, near 0 K, are not shown. The conductivity of semiconductors varies substantially with temperature and purity.) It is customary in engineering to use the centimeter as the unit of length rather than the meter. We follow this practice. The reciprocal of the ohm ( $\Omega$ ) is defined to be 1 siemens (S); see Appendix II. For conducting polymers, refer to Figure 11.20.

Ohm's Law The resistance (in ohms) can then be calculated by making use of *Ohm's law*:

$$V = R \cdot I, \tag{11.3}$$

which was empirically found by Georg Simon Ohm (a German physicist) in 1826 relating a large number of experimental observations. Another form of Ohm's law:

$$j = \sigma \cdot \mathscr{E}, \tag{11.4}$$

links current density:

$$j = \frac{I}{A},\tag{11.5}$$



FIGURE 11.2. Schematic representation of an electric circuit to measure the resistance of a conductor.

that is, the current per unit area (A/cm<sup>2</sup>), with the conductivity  $\sigma$  (1/ $\Omega$  cm or siemens per cm) and the electric field strength:

$$\mathscr{E} = \frac{V}{L} \tag{11.6}$$

(V/cm). (We use a script % for the electric field strength to distinguish it from the energy.)

#### 11.1 • Conductivity and Resistivity of Metals

The resistivity of metals essentially increases linearly with increasing temperature (Figure 11.3) according to the empirical equation:

$$\rho_2 = \rho_1 [1 + \alpha (T_2 - T_1)], \qquad (11.7)$$

where  $\alpha$  is the linear *temperature coefficient of resistivity*, and  $T_1$  and  $T_2$  are two different temperatures. We attempt to explain this behavior. We postulate that the free electrons (see Chapter 10) are accelerated in a metal under the influence of an electric field maintained, for example, by a battery. The drifting electrons can be considered, in a preliminary, classical description, to occasionally collide (that is, electrostatically interact) with certain lattice atoms, thus losing some of their energy. This constitutes the just-discussed resistance. In essence, the drifting electrons are then said to migrate in a zig-zag path through the conductor from the cathode to the anode, as sketched in Figure 11.4. Now, at higher temperatures, the lattice atoms increasingly oscillate about their equilibrium positions due to the supply of thermal energy, thus enhancing the probability for collisions by the drifting electrons. As a consequence, the resistance rises with higher



FIGURE 11.3. Schematic representation of the temperature dependence of the resistivity of copper and various copper-nickel alloys.  $\rho_{res}$  is the residual resistivity.

FIGURE 11.4. Schematic representation of an electron path through a conductor (containing vacancies, impurity atoms, and a grain boundary) under the influence of an electric field. This classical description does not completely describe the resistance in materials.



temperatures. At near-zero temperatures, the electrical resistance does not completely vanish, however (except in superconductors). There always remains a *residual resistivity*,  $\rho_{res}$  (Figure 11.3), which is thought to be caused by "collisions" of electrons (i.e., by electrostatic interactions) with imperfections in the crystal (such as impurities, vacancies, grain boundaries, or dislocations), as explained in Chapters 3 and 6. The residual resistivity is essentially temperature-independent.

On the other hand, one may describe the electrons to have a wave nature. The matter waves may be thought to be scattered by lattice atoms. Scattering is the dissipation of radiation on small particles in all directions. The atoms absorb the energy of an incoming wave and thus become oscillators. These oscillators in turn re-emit the energy in the form of spherical waves. If two or more atoms are involved, the phase relationship between the individual re-emitted waves has to be taken into consideration. A calculation<sup>1</sup> shows that for a *periodic crystal structure* the individual waves in the forward direction are *in-phase*, and thus interfere constructively. As a result, a wave which propagates through an ideal crystal (having periodically arranged atoms) does not suffer any change in intensity or direction (only its velocity is modified). This mechanism is called *coherent scattering*.

If, however, the scattering centers are not periodically arranged (impurity atoms, vacancies, grain boundaries, thermal vibration of atoms, etc.), the scattered waves have no set phase relationship and the wave is said to be *incoherently scattered*. The energy of incoherently scattered waves is smaller in the forward direction. This energy loss qualitatively explains the resistance. In

<sup>&</sup>lt;sup>1</sup>L. Brillouin, *Wave Propagation in Periodic Structures*, Dover, New York (1953).

short, the wave picture provides a deeper understanding of the electrical resistance in metals and alloys.

According to a rule proposed by **Matthiessen**, the total resistivity arises from independent mechanisms, as just described, which are additive, i.e.:

$$\rho = \rho_{\rm th} + \rho_{\rm imp} + \rho_{\rm def} = \rho_{\rm th} + \rho_{\rm res}. \tag{11.8}$$

The thermally induced part of the resistivity  $\rho_{th}$  is called the *ideal* resistivity, whereas the resistivity that has its origin in impurities  $(\rho_{imp})$  and defects  $(\rho_{def})$  is summed up in the residual resistivity ( $\rho_{res}$ ). The number of impurity atoms is generally constant in a given metal or alloy. The number of vacancies, or grain boundaries, however, can be changed by various heat treatments. For example, if a metal is annealed at temperatures close to its melting point and then rapidly quenched into water of room temperature, its room temperature resistivity increases noticeably due to quenched-in vacancies, as already explained in Chapter 6. Frequently, this resistance increase diminishes during room temperature aging or annealing at slightly elevated temperatures due to the annihilation of these vacancies. Likewise, work hardening, recrystallization, grain growth, and many other metallurgical processes change the resistivity of metals. As a consequence of this, and due to its simple measurement, the resistivity has been one of the most widely studied properties in materials research.

**Free Electrons** The conductivity of metals can be calculated (as P. Drude did at the turn to the 20th century) by simply postulating that the electric force,  $e \cdot \mathcal{E}$ , provided by an electric field (Figure 11.2), accelerates the electrons (having a charge -e) from the cathode to the anode. The drift of the electrons was thought by Drude to be counteracted by collisions with certain atoms as described above. The Newtonian-type equation (force equals mass times acceleration) of this **free electron model** 

$$m \, \frac{d\mathbf{v}}{dt} + \gamma \mathbf{v} = e \cdot \mathscr{C} \tag{11.9}$$

leads, after a string of mathematical manipulations, to the conductivity:

$$\sigma = \frac{N_f \cdot e^2 \cdot \tau}{m},\tag{11.10}$$

where v is the drift velocity of the electrons, *m* is the electron mass,  $\gamma$  is a constant which takes the electron/atom collisions into consideration (called damping strength),  $\tau = m/\gamma$  is the average time between two consecutive collisions (called the relaxation time), and  $N_f$  is the number of free electrons per cubic meter in

the material. We can learn from this equation that semiconductors or insulators which have only a small number of free electrons (or often none at all) display only very small conductivities. (The small number of electrons results from the strong binding forces between electrons and atoms that are common for insulators and semiconductors.) Conversely, metals which contain a large number of free electrons have a large conductivity. Further, the conductivity is large when the average time between two collisions,  $\tau$ , is large. Obviously, the number of collisions decreases (i.e.,  $\tau$  increases) with decreasing temperature and decreasing number of imperfections.

The above-outlined free electron model, which is relatively simple in its assumptions, describes the electrical behavior of many materials reasonably well. Nevertheless, quantum mechanics provides some important and necessary refinements. One of the refinements teaches us how many of the valence electrons can be considered to be free, that is, how many of them contribute to the conduction process. Equation (11.10) does not provide this distinction. Quantum mechanics of materials is quite involved and requires the solution of the Schrödinger equation, the treatment of which must be left to specialized texts.<sup>2</sup> Its essential results can be summarized, however, in a few words.

We know from Section 3.1 that the electrons of isolated atoms **Electron Band** (for example in a gas) can be considered to orbit at various dis-Model tances about their nuclei. These orbits constitute different energies. Specifically, the larger the radius of an orbit, the larger the excitation energy of the electron. This fact is often represented in a somewhat different fashion by stating that the electrons are distributed on different *energy levels*, as schematically shown on the right side of Figure 11.5. Now, these distinct energy levels, which are characteristic for isolated atoms, widen into **energy bands** when atoms approach each other and eventually form a solid as depicted on the left side of Figure 11.5. Quantum mechanics postulates that the electrons can only reside within these bands, but not in the areas outside of them. The allowed energy bands may be noticeably separated from each other. In other cases, depending on the material and the energy, they may partially or completely overlap. In short, each material has its distinct electron energy band structure. Characteristic band structures for the main classes of materials are schematically depicted in Figure 11.6.

<sup>&</sup>lt;sup>2</sup>See, for example, R.E. Hummel, *Electronic Properties of Materials*, 3rd Edition, Springer-Verlag, New York (2001).



FIGURE 11.5. Schematic representation of energy levels (as for isolated atoms) and widening of these levels into energy bands with decreasing distance between atoms. Energy bands for a specific case are shown at the left of the diagram.

Now, the band structures shown in Figure 11.6 are somewhat simplified. Specifically, band schemes actually possess a fine structure, that is, the individual energy states (i.e., the possibilities for electron occupation) are often denser in the center of a band (Figure 11.7). To account for this, one defines a density of energy states, shortly called the **density of states**, Z(E).

Some of the just-mentioned bands are occupied by electrons while others remain partially or completely empty, similar to a cup that may be only partially filled with water. The degree to which an electron band is filled by electrons is indicated in Figure 11.6 by shading. The highest level of electron filling within a band is called the **Fermi energy**,  $E_F$ , which may be compared with the water surface in a cup. (For values of  $E_F$ , see Appendix II). We notice in Figure 11.6 that some materials, such as insulators and semiconductors, have completely filled electron bands. (They differ, however, in their distance to the next higher band.)



FIGURE 11.6. Simplified representation for energy bands for (a) monovalent metals, (b) bivalent metals, (c) semiconductors, and (d) insulators. For a description of the nomenclature, see Appendix I. FIGURE 11.7. Schematic representation of the density of electron states Z(E) within an electron energy band. The density of states is essentially identical to the population density N(E) for energies below the Fermi energy,  $E_F$  (i.e., for that energy level up to which a band is filled with electrons). Examples of highest electron energies for a monovalent metal  $(E_M)$ , for a bivalent metal  $(E_B)$ , and for an insulator  $(E_I)$  are indicated.



Metals, on the other hand, are characterized by *partially* filled electron bands. The amount of filling depends on the material, that is, on the electron concentration and the amount of band overlapping.

We may now return to the conductivity. In short, according to quantum theory, only those materials that possess partially filled electron bands are capable of conducting an electric current. Electrons can then be lifted slightly above the Fermi energy into an allowed and unfilled energy state. This permits them to be accelerated by an electric field, thus producing a current. Second, only those electrons that are close to the Fermi energy participate in the electric conduction. (The classical electron theory taught us instead that *all* free electrons would contribute to the current.) Third, the number of electrons near the Fermi energy depends on the density of available electron states (Figure 11.7). The conductivity in quantum mechanical terms yields the following equation:

$$\sigma = \frac{1}{3} e^2 v_F^2 \tau N(E_F)$$
(11.11)

where  $v_F$  is the velocity of the electrons at the Fermi energy (called the Fermi velocity) and  $N(E_F)$  is the density of filled electron states (called the population density) at the Fermi energy. The population density is proportional to Z(E); both have the unit  $J^{-1}m^{-3}$  or  $eV^{-1}m^{-3}$ . Equation (11.11), in conjunction with Figure 11.7, now provides a more comprehensive picture of electron conduction. Monovalent metals (such as copper, silver, and gold) have partially filled bands, as shown in Figure 11.6(a). Their electron population density near the Fermi energy is high (Figure 11.7), which, according to Eq. (11.11), results in a large conductivity. Bivalent metals, on the other hand, are distinguished by an overlapping of the upper bands and by a small electron concentration near the bottom of the valence band, as shown in Figure 11.6(b). As a consequence, the electron population near the Fermi energy is small (Figure 11.7), which leads to a comparatively low conductivity. Finally, insulators have completely filled (and completely empty) electron bands, which results in a virtually zero population density, as shown in Figure 11.7. Thus, the conductivity in insulators is virtually zero (if one disregards, for example, ionic conduction; see Section 11.6). These explanations are admittedly quite sketchy. The interested reader is referred to the specialized books listed at the end of this chapter.

#### 11.2 • Conduction in Alloys

The residual resistivity of alloys increases with increasing amount of solute content as seen in Figures 11.3 and 11.8. The slopes of the individual  $\rho$  versus *T* lines remain, however, essentially constant (Figure 11.3). Small additions of solute cause a linear shift of the  $\rho$  versus *T* curves to higher resistivity values in accordance with the Matthiessen rule; see Eq. (11.8) and Figure 11.8. Various solute elements might alter the resistivity of the host material to different degrees. This is depicted in Figure 11.8 for silver, which demonstrates that the residual resistivity increases with increasing atomic number of the solute. For its interpretation, one may reasonably assume that the likelihood for interactions between electrons and impurity atoms increases when the solute has a larger atomic size, as is encountered by proceeding from cadmium to antimony.

The resistivity of *two-phase alloys* is, in many instances, the sum of the resistivity of each of the components, taking the volume fractions of each phase into consideration. However, additional factors, such as the crystal structure and the kind of distribution of the phases in each other, also have to be considered.





Some alloys, when in the ordered state, that is, when the solute atoms are periodically arranged in the matrix, have a distinctly smaller resistivity compared to the case when the atoms are randomly distributed. Slowly cooled  $Cu_3Au$  or CuAu are common examples of ordered structures.

Copper is frequently used for electrical wires because of its high conductivity (Figure 11.1). However, pure or annealed copper has a low strength (Chapter 3). Thus, work hardening (during wire drawing), or dispersion strengthening (by adding less than 1% Al<sub>2</sub>O<sub>3</sub>), or age hardening (Cu-Be), or solid solution strengthening (by adding small amounts of second constituents such as Zn) may be used for strengthening. The increase in strength occurs, however, at the expense of a reduced conductivity. (The above mechanisms are arranged in decreasing order of conductivity of the copper-containing wire.) The resistance increase in copper inflicted by cold working can be restored to almost its initial value by annealing copper at moderate temperatures (about 300°C). This process, which was introduced in Chapter 6 by the terms stress relief anneal or recovery, causes the dislocations to rearrange to form a polygonized structure without substantially reducing their number. Thus, the strength of stress-relieved copper essentially is maintained while the conductivity is almost restored to its pre-work hardened state (about 98%).

For other applications, a *high* resistivity is desired, such as for heating elements in furnaces which are made, for example, of nickel–chromium alloys. These alloys need to have a high melting temperature and also a good resistance to oxidation, particularly at high temperatures.

## 11.3 • Superconductivity

The resistivity in superconductors becomes immeasurably small or virtually zero below a critical temperature,  $T_c$ , as shown in Figure 11.9. About 27 elements, numerous alloys, ceramic materials (containing copper oxide), and organic compounds (based, for example, on selenium or sulfur) have been found to possess this property (see Table 11.1). It is estimated that the conductivity of superconductors below  $T_c$  is about  $10^{20}$  1/ $\Omega$  cm (see Figure 11.1). The transition temperatures where superconductivity starts range from 0.01 K (for tungsten) up to about 125 K (for ceramic superconductors). Of particular interest are materials whose  $T_c$  is above 77 K, that is, the boiling point of liquid nitrogen, which is more readily available than other coolants. Among the so-called

Materials	<i>T</i> <sub>c</sub> [K]	Remarks	
Tungsten	0.01		
Mercury	4.15	H.K. Onnes (1911)	
Sulfur-based organic superconductor	8	S.S.P. Parkin et al. (1983)	
Nb <sub>3</sub> Sn and Nb–Ti	9	Bell Labs (1961), Type II	
V <sub>3</sub> Si	17.1	J.K. Hulm (1953)	
Nb <sub>3</sub> Ge	23.2	(1973)	
La–Ba–Cu–O	40	Bednorz and Müller (1986)	
$YBa_2Cu_3O_{7-x}$	92	Wu, Chu, and others (1987)	
$RBa_2Cu_3O_{7-x}$	~92	R = Gd, Dy, Ho, Er, Tm, Yb, Lu	
$Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$	113	Maeda et al. (1988)	
$Tl_2CaBa_2Cu_2O_{10+\delta}$	125	Hermann et al. (1988)	
$HgBa_2Ca_2Cu_3O_{8+\delta}$	134	R. Ott et al. (1995)	

TABLE 11.1 Critical temperatures of some superconducting materials

*high-T<sub>c</sub>* superconductors are the 1-2-3 compounds such as  $YBa_2Cu_3O_{7-x}$  whose molar ratios of rare earth to alkaline earth to copper relate as 1:2:3. Their transition temperatures range from 40 to 134 K. Ceramic superconductors have an orthorhombic, layered, perovskite crystal structure (similar to BaTiO<sub>3</sub>; see Figure 11.30) which contains two-dimensional sheets and periodic oxygen vacancies. (The superconductivity exists only parallel to these layers, that is, it is anisotropic.) The first superconducting material was found by H.K. Onnes in 1911 in mercury which has a  $T_c$  of 4.15 K.

A high magnetic field or a high current density may eliminate superconductivity. In *Type I superconductors*, the annihilation of the superconducting state by a magnetic field, that is, the transi-



FIGURE 11.9. Schematic representation of the resistivity of pure and compound superconducting materials.  $T_c$  is the critical or transition temperature, below which superconductivity commences.

FIGURE 11.10. Schematic representation of the resistivity of (a) Type I (or soft) and (b) Type II (or hard) superconductors in an external magnetic field. The solids behave like normal conductors above  $H_c$  and  $H_{c2}$  respectively.



tion between superconducting and normal states, occurs sharply; Figure 11.10(a). The critical field strength  $H_c$ , above which superconductivity ceases, is relatively low. The destruction of the superconducting state in *Type II superconductors* occurs instead, more gradually, i.e., in a range between  $H_{c1}$  and  $H_{c2}$ , where  $H_{c2}$  is often 100 times larger than  $Hc_1$  [Figure 11.10(b)]. In the interval between  $H_{c1}$  and  $H_{c2}$ , normal conducting areas, called *vortices*, and superconducting regions are interspersed. The terms "Type I" and "Type II" superconductors are occasionally also used when a distinction between abrupt and gradual transition with respect to temperature is described; see Figure 11.9. In alloys and ceramic superconductors, a temperature spread of about 0.1 K has been found whereas pure gallium drops its resistance within  $10^{-5}$  K.

Type II superconductors are utilized for strong electromagnets employed, for example, in magnetic resonance imaging devices (used in medicine), high-energy particle accelerators, and electric power storage devices. (An electric current induced into a loop consisting of a superconducting wire continues to flow for an extended period of time without significant decay.) Further potential applications are lossless power transmission lines; highspeed levitation trains; faster, more compact computers; and switching devices, called *cryotrons*, which are based on the destruction of the superconducting state in a strong magnetic field. Despite their considerably higher transition temperatures, ceramic superconductors have not vet revolutionized current technologies, mainly because of their still relatively low  $T_c$ , their brittleness, their relatively small capability to carry high current densities, and their environmental instability. These obstacles may be overcome eventually, however, by using other materials, for example, compounds based on bismuth, etc., or by producing thin-film superconductors. At present, most superconducting electromagnets are manufactured by using niobium-titanium allovs which are ductile and thus can be drawn into wires.

The quantum-mechanical theory, which explains superconductivity and which was developed in 1957 by Bardeen, Cooper, and Schrieffer, is quite involved and is therefore beyond the scope of this book.

## 11.4 • Semiconductors

Semiconductors such as silicon or germanium are neither good conductors nor good insulators as seen in Figure 11.1. This may seem to make semiconductors to be of little interest. Their use-fulness results, however, from a completely different property, namely, that extremely small amounts of certain impurity elements, which are called *dopants*, remarkably change the electrical behavior of semiconductors. Indeed, semiconductors have been proven in recent years to be the lifeblood of a multibillion dollar industry which prospers essentially from this very feature. Silicon, the major species of semiconducting materials, is today the single most researched element. Silicon is abundant (28% of the earth's crust consists of it); the raw material (SiO<sub>2</sub> or sand) is inexpensive; Si forms a natural, insulating oxide; its heat conduction is reasonable; it is nontoxic; and it is stable against environmental influences.

#### Intrinsic Semiconductors

The properties of semiconductors are commonly explained by making use of the already introduced electron band structure which is the result of quantum-mechanical considerations. In simple terms, the electrons are depicted to reside in certain allowed energy regions as explained in Section 11.1. Specifically, Figures 11.6(c) and 11.11 depict two electron bands, the lower of which, at 0 K, is completely filled with valence electrons. This band is appropriately called the **valence band**. It is separated by a small gap (about 1.1 eV for Si) from the conduction band, which, at 0 K, contains no electrons. Further, quantum mechanics stipulates that electrons essentially are not allowed to reside in the gap between these bands (called the forbidden band). Since the filled valence band possesses no allowed empty energy states in which the electrons can be thermally excited (and then accelerated in an electric field), and since the conduction band contains no electrons at all, silicon, at 0 K, is an insulator.

The situation changes decisively once the temperature is raised. In this case, *some* electrons may be thermally excited across the band gap and thus populate the conduction band (Figure 11.11). The number of these electrons is extremely small for statistical reasons. Specifically, about one out of every 10<sup>13</sup> atoms contributes an electron at room temperature. Nevertheless, this num-



ber is large enough to cause some conduction, as shown in Figure 11.1. Actually, the number of electrons in the conduction band,  $N_e$ , increases exponentially with temperature, T, but also depends, of course, on the size of the gap energy,  $E_g$ , according to:

$$N_e = 4.84 \times 10^{15} \ T^{3/2} \ \exp\left[-\left(\frac{E_g}{2k_B T}\right)\right], \tag{11.12}$$

where  $k_B$  is the Boltzmann constant (see Appendix II), and the constant factor in front of  $T^{3/2}$  has the unit of cm<sup>-3</sup> · K<sup>-3/2</sup>. The conductivity depends naturally on the number of these electrons but also on their mobility. The latter is defined to be the velocity, v, per unit electric field,  $\mathcal{E}$ , that is:

$$\mu = \frac{\mathrm{v}}{\mathrm{\mathscr{C}}}.$$
 (11.13)

All taken, the conductivity is

$$\sigma = N_e \cdot \mu \cdot e, \tag{11.14}$$

where *e* is the charge of an electron (see Appendix II). The mobility of electrons is substantially impaired by interactions with impurity atoms and other lattice imperfections (as well as with vibrating lattice atoms), as explained in Section 11.1. It is for this reason that silicon has to be extremely pure and free of grain boundaries, which requires sophisticated and expensive manufacturing processes called *zone refining* or *Czochralski crucible pulling*.

From the above discussion, particularly from Eq. (11.12), it becomes evident that the conductivity for semiconductors increases with rising temperatures. This is in marked contrast to metals and alloys, for which the conductivity decreases with temperature (see Figure 11.3).



Now, the thermal excitation of some electrons across the band gap has another important consequence. The electrons that have left the valence band leave behind some empty spaces which allow additional conduction to take place in the valence band. Actually, the empty spaces are called *defect electrons* or *electron holes*. These holes may be considered to be positively charged carriers similarly as electrons are defined to be negatively charged carriers. In essence, at elevated temperatures, the thermal energy causes some electrons to be excited from the valence band into the conduction band. They provide there some conduction. Concomitantly, the electron holes which have been left behind in the valence band cause a hole current which is directed in the opposite direction compared to the electron current. The total conductivity, therefore, is a sum of both contributions:

$$\sigma = N_e \mu_e e + N_h \mu_h e, \qquad (11.15)$$

where the subscripts e and h refer to electrons and holes, respectively. The process just described is called *intrinsic conduction*, and the material involved is termed an *intrinsic semiconductor* since no foreign elements have been involved.

The Fermi energy of intrinsic semiconductors can be considered to be the average of the electron and the hole Fermi energies and is therefore situated near the center of the gap, as depicted in Figure 11.11.

The number of electrons in the conduction band can be considerably increased by adding, for example, to silicon small amounts of elements from Group V of the Periodic Table called *donor atoms*. Dopants such as phosphorous or arsenic are commonly utilized, which are added in amounts of, for example, 0.0001%. These dopants replace some regular lattice atoms in a substitutional manner; Figure 11.12. Since phosphorous has five valence



FIGURE 11.12. Two-dimensional representation of a silicon lattice in which a phosphorous atom substitutes a regular lattice atom, and thus introduces a negative charge cloud about the phosphorous atom. Each electron pair between two silicon atoms constitutes a covalent bond [see Chapter 3, particularly Figure 3.4(a)].

Extrinsic Semiconductors



FIGURE 11.13. Schematic representation of the number of electrons per cubic centimeter in the conduction band as a function of temperature for extrinsic semiconductors, assuming low doping.

> electrons, that is, one more than silicon, the extra electron, called the *donor electron*, is only loosely bound. The binding energy of phosphorous donor electrons in a silicon matrix, for example, is about 0.045 eV. Thus, the donor electrons can be disassociated from their nuclei by only a slight increase in thermal energy; see Figure 11.13. Indeed, at room temperature all donor electrons have already been excited into the conduction band.

> It is common to describe this situation by introducing into the forbidden band so-called *donor levels*, which accommodate the donor electrons at 0 K; see Figure 11.14(a). The distance between the donor level and the conduction band represents the energy that is needed to transfer the extra electrons into the conduction band (e.g., 0.045 eV for P in Si). The electrons that have been excited from the donor levels into the conduction band are free and can be accelerated in an electric field as shown in Figures 11.2 and 11.4. Since the conduction mechanism in semiconductors with donor impurities is predominated by *negative* charge carriers, one calls these materials *n-type semiconductors*.

Similar considerations may be carried out with respect to im-



FIGURE 11.14. (a) Donor and (b) acceptor levels in extrinsic semiconductors.

purities from the third group of the Periodic Table (B, Al, Ga, In). They are deficient in one electron compared to silicon and therefore tend to accept an electron. The conduction mechanism in these semiconductors with *acceptor impurities* is thus predominated by *positive* charge carriers (holes) which are introduced from the *acceptor levels* [Figure 11.14(b)] into the valence band. They are therefore called *p-type* semiconductors. In other words, the conduction in p-type semiconductors under the influence of an external electric field occurs in the valence band and is predominated by holes.

The conductivity for n-type semiconductors is

$$\sigma = N_{de} \ e \ \mu_e, \tag{11.16}$$

where  $N_{de}$  is the number of donor electrons and  $\mu_e$  is the mobility of the (donor) electrons. A similar equation holds for hole conduction.

Near room temperature, only the majority carriers need to be considered. For example, at room temperature, all donor electrons in an n-type semiconductor have been excited from the donor levels into the conduction band. At higher temperatures, however, intrinsic effects may considerably contribute to the conduction, as seen in Figure 11.13. For certain applications (high temperatures, space, military) this needs to be prevented, and semiconductor materials with wider band gaps, such as compound semiconductors (see below) are utilized.

## Compound Semiconductors

Compounds made of Group III and Group V elements, such as gallium arsenide, have similar semiconducting properties as the Group IV materials silicon or germanium. GaAs is of some technical interest because of its above-mentioned wider band gap, and because of its larger electron mobility, which aids in highspeed applications; see Appendix II. Further, the ionization energies of donor and acceptor impurities in GaAs are one order of magnitude smaller than in silicon, which ensures complete electron (and hole) transfer from the donor (acceptor) levels into the conduction (valence) bands, even at relatively low temperatures. However, GaAs is about ten times more expensive than Si and its heat conduction is smaller. Other compound semiconductors include II-VI combinations such as ZnO, ZnS, ZnSe, or CdTe, and IV-VI materials such as PbS, PbSe, or PbTe. Silicon carbide, a IV-IV compound, has a band gap of 3 eV and can thus be used up to 700°C before intrinsic effects set in. The most important application of compound semiconductors is, however, for opto-electronic purposes (e.g. for light-emitting diodes, and lasers). We shall return to this in Chapter 13.

#### Semiconductor Devices

The evolution of solid-state microelectronic technology started in 1947 with the invention of the point contact transistor by Bardeen, Brattain, and Shockley at Bell Laboratories. (Until then, vacuum tubes were used, the principle of which was invented in 1906 by Lee deForest. Likewise, silicon rectifiers have been in use since the beginning of the 20<sup>th</sup> century.) The development went via the germanium junction transistor (Shockley, 1950), the silicon transistor (Shockley, 1954), the first integrated circuit (Kilby, Texas Instruments, 1959), the planar transistor (Noyce and Fairchild, 1962), to the ultra-large–scale integration (ULSI) of today with several million transistors on one chip.

A rectifier or diode is used to "convert" an alternating current (as used in household circuits) into a direct current, which is needed for many electronic devices and for automobile batteries. A rectifier consists of a junction of p- and n-type semiconductors [manufactured by ion implanting P and B dopants into different parts of a silicon substrate; Figure 11.15(a)]. As explained above, electrons are the predominant charge carriers in n-type semiconductors, whereas holes are the majority carriers in p-type semiconductors. If a negative voltage is applied to the p-side (and consequently a positive charge to the n-side), then the resulting electrostatic attraction forces cause the charge carriers to separate, that is, they migrate to their respective ends of the device. This causes an area which is free of carriers near the junction between n and p. It is called the *barrier region* or the space charge region [Figure 11.15(a-c)]. Once a barrier region of appropriate width has been formed, no current flows in the circuit, as depicted in Figures 11.15(b), (d), and (e). This operational mode is called *reverse bias*. On the other hand, a positive charge to the p- and a negative charge to the n-side forces electrons and holes to drift towards the center, where they mutually recombine. This constitutes a current, I, in the circuit which increases (exponentially) with rising applied voltage, as depicted in Figures 11.15 (c), (d), and (e) (forward bias). This current is

$$I = I_s \left[ \exp\left(\frac{eV}{k_B T}\right) - 1 \right], \tag{11.17}$$

where *V* is the applied voltage on the device and  $I_s$  is a very small current (microamps!) which still flows during reverse bias. It is called the *saturation current* [see Figure 11.15(d)].

A solar cell (or photovoltaic device) consists of a p–n junction. If light of sufficiently large energy ( $E = \nu \cdot h$ ) falls on this device, electrons are lifted from the valence band into the conduction band. The electrons in the barrier region drift quickly to the n-side, whereas the concomitantly created holes in the va-



FIGURE 11.15. Schematic representation of (a) an unbiased p-n junction, (b) a p-n junction in reverse bias, (c) a p-n junction in forward bias, (d) current voltage characteristics of a p-n rectifier, and (e) voltage versus time curves.

lence band migrate into the p-region. This provides a potential difference (voltage) between the n and p terminals. (A more complete description makes use of the appropriate electron band diagram.)

The **bipolar junction transistor** may be considered to be an n-p diode back-to-back with a p-n diode, as depicted in Figure 11.16. The three terminals are called *emitter* (E), *base* (B), and *collector* (C). The transistor is used for amplification of a signal (music, voice) and as an effective switching device for computers. The "diode", consisting of emitter and base, is forward-biased, thus allowing an injection of electrons from the emitter into the base. In order to effectively reduce a possible electron-hole recombination in the base area, this region needs to



FIGURE 11.16. (a) Biasing of an n-p-n bipolar transistor. (b) Schematic representation of an n-p-n bipolar transistor. The dark areas are the contact pads.

be extremely thin and only lightly doped. As a consequence, most electrons diffuse through the base and reach the collector area, which is strongly reverse-biased with respect to the base. In other words, the strong positive charge on the collector terminal attracts the electrons and accelerates them towards the collector. This constitutes an amplification of the signal which was injected into the emitter/base section.

The electron flow from emitter to collector can be controlled by the bias voltage on the base: A *large* positive (forward-) bias on the base increases the electron injection into the p-area. In contrast, a *small*, but still positive base voltage results in a smaller electron injection from the emitter into the base area. As a consequence, the strong collector signal mimics the waveform of the input signal between emitter and base.

One may consider the amplification from a more quantitative point of view. The forward-biased emitter-base diode is made to have a small resistivity (approximately  $10^{-3} \Omega$  cm), whereas the reverse-biased base-collector diode has a much larger resistivity (about 10  $\Omega$  cm). Since the current flowing through the device is practically identical in both parts, the power ( $P = I^2 R$ ) is larger in the collector circuit. This results in a power gain.

In another application, a transistor is used as an electronic



FIGURE 11.17. Normally-off-type nchannel MOSFET. The dark areas symbolize the (aluminum) metallizations. The "oxide" layer consists of SiO<sub>2</sub> or Si<sub>3</sub>N<sub>4</sub>. This layer is about 10 nm thick. Quite often, the B and S terminals are interconnected.

switch. The electron flow from emitter to collector can be essentially terminated by applying only a small or even a zero emitter/base voltage which causes little or no electron injection into the base area. Conversely, a large emitter/base voltage causes a large emitter to collector current. Again, the size of the emitter/base voltage determines the magnitude of the collector current.

In a p–n–p transistor, the majority carriers are holes. Its function and features are similar to the above-discussed n–p–n transistor.

The metal-oxide-semiconductor field effect transistor (MOSFET) consists of highly doped  $(n^+)$  source and drain regions (as emitter and collector are called for this device); Figure 11.17. They are laid down (ion implanted) on a p-substrate, called the body. A thin oxide layer, on which a metal film has been deposited, electrically insulates the gate metal from the body. Now, consider a positive voltage on the drain with respect to the source. In essence, there is no electron flow from source to drain as long as the gate voltage is zero. (The device is therefore called a normallyoff MOSFET). If, however, a large enough positive voltage is applied to the gate (with respect to the body), most of the holes immediately below the gate oxide are repelled, that is, they are driven into the p-substrate, thus removing possible recombination sites. Concomitantly, negative charge carriers are attracted into the layer below the gate oxide (called the *channel*). This provides a path (or a bridge) for the electrons between source and drain. Thus, in this case, a current flows between source and drain.

The MOSFET dominates the integrated circuit industry at present. It is utilized in memories, microcomputers, logic circuits, amplifiers, analog switches, and operational amplifiers. One of the advantages is that no current flows between gate and body. Thus, only little power is expended for its operation, which is vital to prevent overheating of the device.

#### 11.5 • Conduction in Polymers

Materials that are electrical (and thermal) insulators are of great technical importance and are, therefore, used in large quantities in the electronics industry, for example, as handles for a variety of tools, as coatings of wires, and for casings of electrical equipment. Most polymeric materials are insulating and have been used for this purpose for decades. It came, therefore, as a surprise when it was discovered that some polymers and organic substances may have electrical properties which resemble those of conventional semiconductors, metals, or even superconductors. We shall focus our attention mainly on these materials. This does not imply that conducting polymers are of technical importance at this time. Indeed, they are not yet. This is due to the fact that many presently known conducting polymers seem to be unstable at or above room temperature. In addition, some dopants used to impart a greater conductivity are highly toxic, and doping often makes the polymers brittle. These problems have been partially overcome, however, in recent years. Historically, transoidal polyacetylene (see Figure 11.18) has been used as a conducting polymer. It represents what is called a *conjugated organic polymer*, that is, it has alternating single and double bonds between the carbon atoms. It is obtained as a silvery, flexible, and lightweight film which has a conductivity comparable to that of silicon. Its conductivity increases with increasing temperature, similarly as in semiconductors (Figure 11.13). The conductivity of trans-polyacetylene can be made to increase by up to seven orders of magnitude by doping it with arsenic pentafluoride, iodine, or bromine, which yields a p-type semiconductor, see Figure 11.19. Thus,  $\sigma$  approaches the lower end of the conductivity of metals, as shown in Figure 11.20. Among other (albeit non-toxic) dopants are n-dodecyl sulfonate (soap). However, the stability of this material is very poor; it deteriorates in hours or days. This very drawback, which it shares with many other conducting polymers, nevertheless can be profitably utilized

FIGURE 11.18. Transoidal isomer of polyacetylene (*trans*-(CH)<sub>x</sub>). For details of the molecular structure of polymers, see Chapter 3.3, in particular Figure 3.16.





FIGURE 11.19. Conductivity change of polyacetylene as a result of doping. In polymers the "doping" concentration varies between one tenth of a percent up to 20–40%.

in special devices such as remote gas sensors, biosensors, and other remotely readable indicators which detect changes in humidity, radiation dosage, mechanical abuse, or chemical release.

Other conducting polymers include polypyrrole and polyaniline. The latter has a reasonably good conductivity and a high environmental stability. It has been used for electronic devices such as field-effect transistors, electrochromic displays, as well as for rechargeable batteries. The complex consisting of *poly*-(2vinylpyridine) and iodine is used despite its relatively low conductivity ( $10^{-3}$  1/ $\Omega$  cm) for cathodes in lithium/iodine batteries for implantable pacemakers. These batteries have lifetimes of about 10 years and are relatively lightweight.

Arsenic pentafluoride–doped graphite has a conductivity which is about that of copper; see Figure 11.20. However, the high conductivity of graphite occurs only in the hexagonal plane of graphite (Figure 3.8). The conductivity is four orders of magnitude smaller perpendicular to this layer. Finally, and surprisingly, *poly*-sulfur nitride (SN)<sub>*x*</sub>, which consists of alternating sulfur and nitrogen atoms and which has a room temperature conductivity of about  $10^3 \Omega^{-1} \text{ cm}^{-1}$ along the chain direction, becomes superconducting close to 0 K!

In order to better understand the electronic properties of polymers by means of the electron theory and the band structure



concept, one needs to know the degree of order or the degree of periodicity of the atoms because only ordered and strongly interacting atoms or molecules lead, as we know, to distinct and wide electron bands (Figure 11.5). Now, it has been observed that the degree of order in polymers depends on the regularity of the molecular structure. Certain heat treatments may influence some structural parameters. For example, if a simple polymer is slowly cooled below its melting point, one might observe that some macromolecules align parallel to each other. Actually, slow cooling yields, for certain polymers, a highly crystalline structure. The individual chains are, however, separated by regions of supercooled liquid, that is, by amorphous material (Figure 3.17).

We need to pursue this somewhat further. Figure 11.21 shows two simplified band structures for *trans*-(CH)<sub>x</sub> assuming different distances between the carbon atoms. In Figure 11.21(a), all carbon bond lengths are taken to be equal. The resulting band structure is found to be characteristic for a metal, that is, the highest band is *partially* filled by electrons. Where are the free electrons in the conduction band of *trans*- $(CH)_x$  coming from? We realize that one of the electrons in the double bond of a conjugated polymer can be considered to be only loosely bound to the neighboring carbon atoms. Thus, this electron can be easily disassociated from its carbon atom by a relatively small energy, which may be provided by thermal energy. The delocalized electrons behave like free electrons and may be accelerated as usual in an electric field.

In reality, however, a uniform bond length between the carbon atoms does not exist in polyacetylene. Instead, the distances between the carbon atoms alternate because of the alternating single and double bonds. Band structure calculations for this case show, interestingly enough, a gap between the individual energy bands. The resulting band structure is typical for a semiconductor (or an insulator)! The width of the band gap near the Fermi level depends mainly on the degree of alternating bond lengths [Figure 11.21(b)].

It has been shown that the band structure in Figure 11.21(b) best represents the experimental observations. Specifically, one finds a band gap of about 1.5 eV between the valence band and the conduction band. This explains the semiconducting characteristics of *trans*-(CH)<sub>x</sub>. In order to improve the conductivity of  $(CH)_x$ , one would attempt to decrease the differences of the carbon–carbon bond lengths, thus eventually approaching the uniform bond length as shown in Figure 11.21(a). This has indeed been accomplished by synthesizing  $(CH)_x$  via a *non-conjugated* precursor polymer which is subsequently heat treated. Conductivities as high as  $10^2 1/(\Omega \text{ cm})$  have been obtained this way.

It should be noted in closing that the interpretation of conducting polymers is still in flux and future research needs to clarify certain points.





## 11.6 • Ionic Conductors

Electrical conduction in ionically bonded materials, such as the alkali-halides, is extremely small. The reason for this is that the atoms in these chemical compounds strive to assume the noble gas configuration for maximal stability and thus transfer electrons between each other to form positively charged cations and negatively charged anions. The binding forces between the ions are electrostatic in nature, that is, they are very strong, as explained in Section 3.2. Essentially no free electrons are therefore formed. As a consequence, the room temperature conductivity in ionic crystals is about 22 orders of magnitude smaller than that for typical metallic conductors (Figure 11.1). The wide band gap in insulators allows only extremely few electrons to become excited from the valence into the conduction band [Figure 11.6(d)].

The main contribution to the electrical conduction in ionic crystals (as little as it may be) is, however, due to a mechanism which we have not yet discussed, namely, ionic conduction. Ionic conduction is caused by the movement of some negatively (or positively) charged ions which *hop* from lattice site to lattice site under the influence of an electric field; see Figure 11.22(b). (This type of conduction is similar to that which is known to occur in aqueous electrolytes; see Chapter 9.) The ionic conductivity:

$$\sigma_{\rm ion} = N_{\rm ion} \ e \ \mu_{\rm ion} \tag{11.18}$$

is, as outlined before [Eq. (11.14)], the product of three quantities. In the present case,  $N_{\text{ion}}$  is the number of ions per unit volume which can change their position under the influence of an electric field whereas  $\mu_{\text{ion}}$  is the mobility of these ions.

In order for ions to move through a crystalline solid, they must have sufficient energy to pass over an *energy barrier* (Figure 11.22). Further, an equivalent lattice site next to a given ion must be empty in order for an ion to be able to change its position. Thus,  $N_{ion}$  in Eq. (11.18) depends on the vacancy concentration in the crystal (i.e., on the number of *Schottky defects*; see Section 6.1.1). In short, the theory of ionic conduction contains essential elements of diffusion theory, as introduced in Chapter 6.

Diffusion theory links the mobility of the ions, which is contained in Eq. (11.18) with the diffusion coefficient *D*, through the Einstein relation:

$$\mu_{\rm ion} = \frac{De}{k_B T}.$$
(11.19)



FIGURE 11.22.

Schematic representation of a potential barrier which an ion (•) has to overcome to exchange its site with a vacancy ( $\Box$ ): (a) without an external electric field; (b) with an external electric field. d = distance between two equivalent adjacent lattice sites; Q = activation energy. See Chapter 6. The diffusion coefficient varies with temperature by an Arrhenius equation, (6.8):

$$D = D_0 \exp\left(-\frac{Q}{k_B T}\right),\tag{11.20}$$

where *Q* is the activation energy for the process under consideration (Figure 11.22), and  $D_0$  is a pre-exponential factor which depends on the vibrational frequency of the atoms and some structural parameters. Combining Eqs. (11.18) through (11.20) yields:

$$\sigma_{\rm ion} = \frac{N_{\rm ion} e^2 D_0}{k_B T} \exp\left(-\frac{Q}{k_B T}\right).$$
(11.21)

Equation (11.21) is shortened by combining the pre-exponential constants into  $\sigma_0$ :

$$\sigma_{\rm ion} = \sigma_0 \exp\left(-\frac{Q}{k_B T}\right).$$
 (11.22)

In summary, the ionic conduction increases exponentially with increasing temperature (as semiconductors do; Figure 11.13). Further,  $\sigma_{ion}$  depends on a few other parameters, such as the number of ions that can change their position, the vacancy concentration, as well as on an activation energy.

# 11.7 • Thermoelectric Phenomena

Assume two different types of materials (e.g., a copper and an iron wire) which are connected at their ends to form a loop, as shown in Figure 11.23. One of the junctions is brought to a higher temperature than the other. Then a potential difference,  $\Delta V$ , be-



FIGURE 11.23. Schematic representation of two thermocouples made of copper and iron which are brought in contact with each other (Seebeck effect).

tween these two **thermocouples** is observed which is essentially proportional to the temperature difference,  $\Delta T$ , where:

$$\frac{\Delta V}{\Delta T} = S \tag{11.23}$$

is called the *thermoelectric power*, or the Seebeck coefficient (after its inventor, T.J. Seebeck, a German physicist who discovered, in 1821, that a thermoelectric circuit like the one just described, deflected a close-by compass needle). A thermoelectric power of several microvolts per degree is commonly observed. As an example, the frequently used copper/constantan (Cu–45% Ni) combination yields about 43  $\mu$ V/K. It has a useful range between –180 and +400°C. For higher temperatures, thermocouples of chromel (90%Ni–10%Cr) and alumel (95%Ni–2%Mn-2%Al) or platinum/Pt–13%Rh (up to 1700°C) are available. Some semiconductors have Seebeck coefficients which reach in the millivolt per degree range, that is, they are one or two orders of magnitude higher than for metals and alloys. Among them are bismuth telluride (Bi<sub>2</sub>Te<sub>3</sub>), lead telluride (PbTe), or silicon–30% germanium alloys.

*Thermocouples* made of metal wires are utilized as rigid, inexpensive, and fast probes for measuring temperatures even at otherwise not easily accessible places. *Thermoelectric power generators* (utilizing the above-mentioned semiconductors) are used particularly in remote locations of the earth (Siberia, Alaska, etc.). They contain, for example, a ring of thermoelements, arranged over the glass chimney of a kerosene lamp which is concomitantly used for lighting. The temperature difference of 300°C thus achieved yields electric power of a few watts or sometimes



FIGURE 11.24. Thermoelectric refrigeration devices which make use of the Peltier effect. (a) Principle arrangement. (b) Efficient device utilizing p- and n-type semiconductors (see Section 11.4) in conjunction with metals.

more, which can be used for radios or communication purposes. Other fuel-burning devices provide, for example, an emf for cathodic protection of pipe lines (see Chapter 9). Heat produced by the decay of radioisotopes or by small nuclear reactors yields thermoelectric power for scientific instruments on the moon (e.g., to record moon quakes) and for relaying the information back to earth. In solar thermoelectric generators sunlight is concentrated by concave mirrors on thermocouples. Most of the above-described devices have an efficiency between 5 and 10%.

A reversion of the Seebeck effect is the **Peltier effect**: A direct electric current that flows through junctions made of different materials causes one junction to be cooled and the other to heat up (depending on the direction of the current); see Figure 11.24(a). Lead telluride or bismuth telluride in combination with metals are frequently used. One particularly effective device for which temperature differences up to 70°C have been achieved is shown in Figure 11.24(b). It utilizes n- and p-type semiconductors (see Section 11.4) in conjunction with metals. Cooling occurs on those junctions that are connected to the upper metal plate (1 and 2), whereas heat develops on the lower junctions 3 and 4. The heat on the lower plate is removed by water or air cooling. The above-quoted temperature drop can even be enhanced by cascading several devices, that is, by joining multiple thermoelectric refrigerators for which each stage acts as the heat sink for the next.

The thermoelectric effects can be explained by applying elements of electron theory as described in the previous sections: When two different types of conducting materials are brought into contact, electrons are transferred from the material with higher Fermi energy ( $E_F$ ) "down" into the material having a lower  $E_F$  until both Fermi energies are equal. As a consequence, the material that had the smaller  $E_F$  assumes a negative charge with respect to the other. This results in the above-mentioned *contact* potential between the materials. The contact potential is temperature-dependent. Specifically, when a material is heated, a substantial amount of electrons is excited across the Fermi energy to higher energy levels. These extra electrons drift to the cold junction, which becomes negatively charged compared to the hot junction. The equivalent is true for the Peltier effect: The electrons having a larger energy (that is, those having a higher  $E_F$ ) are caused by the current to transfer their extra energy into the material having a lower  $E_F$ , which in turn heats up. Concomitantly, the material having a higher  $E_F$  is caused to lose energy and thus becomes colder.

#### 11.8 • Dielectric Properties

Dielectric materials, that is, insulators, possess a number of important electrical properties which make them useful in the electronics industry. This needs some explanation.

When a voltage is momentarily applied to two parallel metal plates which are separated by a distance, L, as shown in Figure 11.25, then the resulting electric charge essentially remains on these plates even after the voltage has been removed (at least as long as the air is dry). This ability to store an electric charge is called the *capacitance*, C, which is defined to be the charge, q, per applied voltage, V, that is:

$$C = \frac{q}{V},\tag{11.24}$$

where *C* is given in coulombs per volt or farad (SI units, see Appendix II). Understandably, the capacitance is higher, the larger



FIGURE 11.25. Two metal plates, separated by a distance, *L*, can store electric energy after having been charged momentarily by a battery.

the area, *A*, of the plates and the smaller the distance, *L*, between them. Further, the capacitance depends on the material that may have been inserted between the plates. The experimental observations lead to:

$$C = \epsilon \ \epsilon_0 \frac{A}{L} \tag{11.25}$$

where

$$\epsilon = \frac{C}{C_{\text{vac}}} \tag{11.26}$$

determines the magnitude of the added storage capability. It is called the (unitless) *dielectric constant* (or occasionally the *relative permittivity*,  $\epsilon_r$ ).  $\epsilon_0$  is a universal constant having the value of  $8.85 \times 10^{-12}$  farad per meter (F/m) or As/Vm and is known by the name *permittivity of empty space* (or of vacuum). Some values for the dielectric constant are given in Table 11.2. The dielectric constant of empty space is set to be 1 whereas  $\epsilon$  of air and many other gases is nearly 1.

We now need to explain why the capacitance increases when a piece of a dielectric material is inserted between two conductors [see Eq. (11.25)]. For this, one has to realize that, under the influence of an external electric field, the negatively charged electron cloud of an atom becomes displaced with respect to its pos-

Barium titanate	4000	Ferroelectric	
Water	81.1		
Acetone	20		
Silicon	11.8		
GaAs	10.9		
Marble	8.5		
Soda–lime–glass	6.9		
Porcelain	6.0		
Epoxy	4.0		
Fused silica	4.0	Dielectric	
Nylon 6,6	4.0		
PVC	3.5		
Ice	3.0		
Amber	2.8		
Polyethylene	2.3		
Paraffin	2.0		
Air	1.000576		

TABLE 11.2 DC dielectric constants of some materials

FIGURE 11.26. An atom is represented by a positively charged core and a surrounding, negatively charged electron cloud (a) in equilibrium and (b) in an external electric field. (c) Schematic representation of an electric dipole as, for example, created by separation of the negative and positive charges by an electric field, as seen in (b).



itively charged core; see Figure 11.26(b). As a result, a dipole is created which has an electric **dipole moment**:

$$p = q \cdot X, \tag{11.27}$$

where *X* is the separation between the positive and the negative charge as depicted in Figure 11.26(c). (The dipole moment is generally a vector pointing from the negative to the positive charge.) The process of dipole formation (or alignment of already existing dipoles) under the influence of an external electric field that has an electric field strength,  $\mathcal{E}$ , is called **polarization**. Dipole formation of all involved atoms within a dielectric material causes a charge redistribution so that the surface which is nearest to the positive capacitor plate is negatively charged (and vice versa), see Figure 11.27(a). As a consequence, electric field lines within a dielectric are created which are opposite in direction to the external field lines. Effectively, the electric field lines within a dielectric material are weakened due to polarization, as depicted in Figure 11.27(b). In other words, the electric field strength (11.6)

$$\mathscr{E} = \frac{V}{L} = \frac{\mathscr{E}_{\text{vac}}}{\epsilon} \tag{11.28}$$

is reduced by inserting a dielectric between two capacitor plates.

Within a dielectric material the electric field strength,  $\mathcal{E}$ , is replaced by the **dielectric displacement**, *D* (also called the *surface charge density*), that is:

$$D = \epsilon \ \epsilon_0 \ \mathscr{E} = \frac{q}{A}. \tag{11.29}$$

The dielectric displacement is the superposition of two terms:

$$D = \epsilon_0 \, \mathscr{E} + P, \tag{11.30}$$



FIGURE 11.27. Schematic representation of two capacitor plates between which a dielectric material is inserted. (a) Induction of electric dipoles of opposite charge. (b) Weakening of the electric field *within* the dielectric material [Eq. (11.28)]. (c) The direction of the polarization vector is from the negative induced charge to the positive induced charge. (d) The dielectric displacement, *D*, within the dielectric material is the sum of  $\epsilon_0$  and *P* [Eq. (11.30)].

where *P* is called the **dielectric polarization**, that is, the induced electric dipole moment per unit volume [Figures 11.27(c and d)]. The units for *D* and *P* are C m<sup>-2</sup>; see Eq. (11.29). (*D*,  $\mathcal{E}$ , and *P* are generally vectors.) In other words, the polarization is responsible for the increase in charge density (*q*/*A*) above that for vacuum.

The mechanism just described is known by the name **electronic polarization**. It occurs in all dielectric materials that are subjected to an electric field. In ionic materials, such as the alkali halides, an additional process may occur which is called **ionic polarization**. In short, cations and anions are somewhat displaced from their equilibrium positions under the influence of an external field and thus give rise to a net dipole moment. Finally, many materials already possess permanent dipoles which can be *aligned* in an external electric field. Among them are water, oils, organic liquids, waxes, amorphous polymers, polyvinylchloride, and certain ceramics such as barium titanate (BaTiO<sub>3</sub>). This mechanism is termed *orientation polarization* or



**molecular polarization**. All three polarization processes are additive if applicable; see Figure 11.28.

Most capacitors are used in electric circuits involving alternating currents. This requires the dipoles to reorient quickly under a rapidly changing electric field. Not all polarization mechanisms respond equally quick to an alternating electric field. For example, many molecules are relatively sluggish in reorientation. Thus, molecular polarization breaks down already at relatively low frequencies; see Figure 11.28. In contrast, electronic polarization responds quite rapidly to an alternating electric field even at frequencies up to 10<sup>16</sup> Hz.

At certain frequencies a substantial amount of the excitation energy is absorbed and transferred into heat. This process is called *dielectric loss*. It is imperative to know the frequency for dielectric losses for a given material so that the device is not operated in this range.

#### 11.9 • Ferroelectricity and Piezoelectricity

Ferroelectric materials, such as barium titanate, exhibit spontaneous polarization without the presence of an external electric field. Their dielectric constants are orders of magnitude larger than those of dielectrics (see Table 11.2). Thus, they are quite suitable for the manufacturing of small-sized, highly efficient capacitors. Most of all, however, ferroelectric materials retain their state of polarization even after an external electric field has been removed. Specifically, if a ferroelectric is exposed to a strong electric field,  $\mathcal{C}$ , its permanent dipoles become increasingly aligned



with the external field direction until eventually all dipoles are parallel to  $\mathscr{C}$  and saturation of the polarization,  $P_s$ , has been achieved, as depicted in Figure 11.29. Once the external field has been withdrawn, a **remanent polarization**,  $P_r$ , remains which can only be removed by inverting the electric field until a coercive field,  $\mathscr{C}_c$ , has been reached (Figure 11.29). By further increasing the reverse electric field, parallel orientation of the dipoles in the opposite direction is achieved. Finally, when reversing the field once more, a complete hysteresis loop is obtained, as depicted in Figure 11.29. All taken, ferroelectricity is the electric analogue to ferromagnetism, which will be discussed in Chapter 12. Therefore, ferroelectrics can be utilized for memory devices in computers, etc. The area within a hysteresis loop is proportional to the energy per unit volume that is dissipated once a full field cycle has been completed.

A critical temperature, called the *Curie temperature*, exists, above which the ferroelectric effects are destroyed and the material becomes dielectric. Typical Curie temperatures range from  $-200^{\circ}$ C for strontium titanate to at least 640°C for NaNbO<sub>3</sub>.

The question remains to be answered, why do certain materials such as BaTiO<sub>3</sub> possess spontaneous polarization? This can be explained by knowing that in the tetragonal crystal structure of BaTiO<sub>3</sub>, the negatively charged oxygen ions and the positively charged Ti<sup>4+</sup> ion are slightly displaced from their symmetrical positions, as depicted in Figure 11.30. This results in a permanent ionic dipole moment along the *c*-axis within the unit cell. A large number of such dipoles line up in clusters (also called *domains*). In the virgin state, the polarization directions of the individual domains are, however, randomly oriented, so that the

FIGURE 11.30. Tetragonal crystal structure of barium titanate at room temperature. Note the upward displacement of the Ti<sup>4+</sup> ion in the center compared to the downward displacement of all surrounding  $O^{2-}$  ions. a = 0.398 nm; c = 0.403 nm.



material has no net polarization (Figure 11.31). An external field eventually orients the dipoles of the favorably oriented domains parallel to  $\mathcal{C}$ . Specifically, those domains in which the dipoles are already nearly parallel to  $\mathcal{C}$  grow at the expense of unfavorably oriented domains.

By heating  $BaTiO_3$  above its Curie temperature (120°C), the tetragonal unit cell transforms to a cubic cell whereby the ions now assume symmetric positions. Thus, no spontaneous alignment of dipoles remains and  $BaTiO_3$  becomes dielectric.

If pressure is applied to a ferroelectric material, such as Ba-TiO<sub>3</sub>, a change in the just-mentioned polarization may occur which results in a small voltage across the sample. Specifically, the slight change in dimensions causes a variation in bond lengths between cations and anions. This effect is called **piezoelectricity**.<sup>3</sup> It is found in a number of materials such as quartz (however, much weaker than in BaTiO<sub>3</sub>), in ZnO, and in complicated ceramic compounds such as PbZrTiO<sub>6</sub>. Piezoelectricity is utilized in devices that are designed to convert mechanical strain into electricity. Those devices are called *transducers*. Applications include strain gages, microphones, sonar detectors, and phonograph pickups, to mention a few.

The inverse mechanism, in which an electric field produces a change in dimensions in a ferroelectric material, is called **elec**-**trostriction**. An earphone utilizes such a device. Probably the most important application, however, is the quartz crystal resonator which is used in electronic devices as a *frequency selec*-*tive element*. Specifically, a periodic strain is exerted to a quartz crystal by an alternating electric field which excites this crystal

<sup>&</sup>lt;sup>3</sup>*Piezo* (latin) = pressure.



FIGURE 11.31. Schematic representation of spontaneous alignments of electric dipoles within a domain and random alignment of the dipole moments of several domains in a ferroelectric material such as BaTiO<sub>3</sub>. Compare to Figure 12.8.

to vibrations. These vibrations are monitored in turn by piezoelectricity. If the applied frequency coincides with the natural resonance frequency of the molecules, then amplification occurs. In this way, very distinct frequencies are produced which are utilized for clocks or radio frequency signals.

## Problems

- 11.1. A current of 2 A flows through a slab of tin, 1 mm thick and 2 mm wide, whose conductivity is  $10^6$  1/ $\Omega$ m. Calculate the voltage drop between two potential probes that are 10 cm apart along the slab.
- 11.2. Calculate the number of free electrons per cubic centimeter for sodium from resistance data ( $\rho = 4.2 \times 10^{-8} \Omega m$ ; relaxation time  $3.1 \times 10^{-14}$ s).
- 11.3. Calculate the population density of electrons for a metal. (Take  $\sigma = 5 \times 10^5 \text{ 1/}\Omega\text{cm}$ ;  $v_F = 10^8 \text{ cm/s}$ , and  $\tau = 3 \times 10^{-14}\text{s.}$ )
- 11.4. Calculate the number of free electrons per cm<sup>3</sup> for gold using its density (19.3 g/cm<sup>3</sup>) and its atomic mass (196.967 g/mol). (*Hint:* Look in Chapter 3.)
- 11.5. Calculate the number of electrons in the conduction band for silicon at T = 300 K.
- 11.6. At what (hypothetical) temperature would all 10<sup>22</sup> cm<sup>-3</sup> valence electrons be excited to the conduction band in a

semiconductor with  $E_g = 1$  eV? (*Hint:* Use a programmable calculator.)

11.7. In the figure below,  $\sigma$  is plotted as a function of the reciprocal temperature for an intrinsic semiconductor. Calculate the gap energy. (Hint: Combine (11.12) and (11.15) and take the ln from the resulting equation assuming N<sub>e</sub>  $\equiv$  N<sub>h</sub> · Why?).)



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- 11.8. Calculate the conductivity at room temperature for germanium containing  $5 \times 10^{16}$  arsenic atoms per cubic centimeter. (*Hint:* Use the mobility of the electrons in the host material.)
- 11.9. What current flows through a p–n diode to which a voltage of 0.3V is applied and a saturation current of 1  $\mu$ A is assumed at 300 K?
- 11.10. Calculate the mobility of electrons in a metal when the time between

two electron/atom collisions is  $2.5 \times 10^{-12}$ s.

- 11.11. Show that  $\mathscr{C} = \mathscr{C}_{vac}/\epsilon$  [Eq. (11.28)] by combining Eqs. (11.6), (11.24), and (11.26) and their equivalents for vacuum.
- 11.12. Show that the dielectric polarization is  $P = (\epsilon - 1) \epsilon_0$ %. What values do *P* and *D* have for vacuum?
- 11.13. Show that  $\epsilon \epsilon_0 \mathscr{E} = q/A$  [Eq. (11.29)] by combining some pertinent equations.

## Suggestions for Further Study

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