

Figure 11.49

The microstructure of the tungsten carbide–cobalt chromium coating on the substrate.

[Courtesy of TWI Ltd. (The Welding Institute, Granta Park, Great Abington, Cambridge, UK)]

11.10 NANOTECHNOLOGY AND CERAMICS

Considering the range and variety of the applications for ceramic materials, one realizes that their potential can never be fully realized because of one major disadvantage, that is, their brittle nature and therefore low toughness. Nanocrystalline ceramics may improve on this inherent weakness of these materials. The following paragraphs are intended to describe the state-of-the-art in the production of bulk nanocrystalline ceramics.

Bulk nanocrystalline ceramics are produced using the standard powder metallurgy techniques described in Sec. 11.4. The difference is that the starting powder is in the nanosize range, being smaller than 100 nm. However, the nanocrystalline ceramic powders have a tendency to chemically or physically bond together to form bigger particles called *agglomerates* or *aggregates*. Agglomerated powders, even if their size is in the nanosize or near nanosize range, do not pack as well as non-agglomerated powders. In a nonagglomerated powder after compaction, the available pore sizes are between 20 to 50 percent of the size of the nanocrystal. Because of this small pore size, the sintering stage and densification proceed quickly and at lower temperatures. For instance, in the case of nonagglomerated TiO_2 (powder size less than 40 nm), the compact densifies to almost 98 percent of theoretical density at approximately 700°C with a sintering time of 120 min. Conversely for an agglomerated powder of average size 80 nm consisting of 10 to 20 nm crystallites, the compact densifies to 98 percent of theoretical density at about 900°C with a sintering time of 30 min. The major reason for the difference in sintering temperature is the existence of larger pores in the agglomerated compact. Because higher sintering temperatures are required, the compacted nanocrystallites eventually grow to a

microcrystalline range, which is undesirable. The grain growth is drastically influenced by sintering temperature and only modestly by sintering time. Thus, the main issue in successfully producing bulk nanocrystalline ceramics is to start with nonagglomerated powder and to optimize the sintering process. However, this is very difficult to achieve.

To remedy the difficulty in producing nanocrystalline bulk ceramics, engineers are utilizing pressure-assisted sintering, a sintering process with externally applied pressure that is similar to *hot isostatic pressing* (HIP), hot extrusion, and sinter forging (see Sec. 11.4). In these processes, the ceramic compact is deformed and densified simultaneously. The primary advantage of sinter forging in producing nanocrystalline ceramics is in its mechanism of pore shrinkage. As discussed in Sec. 11.4.3, in conventional microcrystalline ceramics the pore shrinkage process is based on atomic diffusion. Under sinter forging, pore shrinkage of the nanocrystalline compact is nondiffusional and is based on the plastic deformation of the crystals. Nanocrystalline ceramics are more ductile at elevated temperatures (around 50 percent of melt) than their microcrystalline counterparts. It is believed that nanocrystalline ceramics are more ductile as a result of superplastic deformation. As discussed in previous chapters, superplasticity occurs because of sliding and rotation of the grains under high load and temperature. Because they are able to deform plastically, the pores are squeezed shut by plastic flow as shown in Fig. 11.50 rather than by diffusion.

Because of this ability to close large pores, even agglomerated powders can be densified to near their theoretical values. Additionally, the application of pressure prevents the grains from growing to above the nanoscale region. For instance, sinter forging of agglomerated TiO_2 for 6 h at a pressure of 60 MPa and a temperature of 610°C produces a true strain of 0.27 (extremely high for ceramics), density of 91 percent of theoretical value, and an average grain size of 87 nm. The same powder when sintered without pressure requires a sintering temperature of 800°C to achieve the same density while producing an average grain size of 380 nm (not nanocrystalline). It is important to note that superplastic deformation in nanocrystalline ceramics occurs in a limited range of pressures and temperatures, and one must be aware of the range. If the treatment is outside this range, the diffusional mechanism of pore shrinkage may take over, which results in a microcrystalline product with low density.

In conclusion, advances in nanotechnology will potentially lead to the production of nanocrystalline ceramics with exceptional levels of strength and ductility, and therefore improved toughness. Specifically, the improvements in ductility allow for

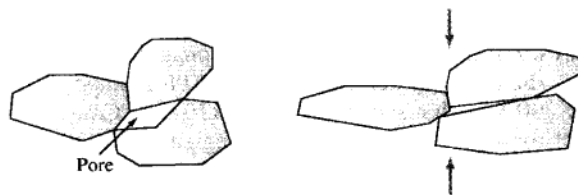


Figure 11.50

A schematic showing pore shrinkage through plastic flow (grain boundary sliding) in nanocrystalline ceramics.

better bonding of ceramics to metals in coating technologies, and the increased toughness allows for better resistance to wear. Such advances could revolutionize the use of ceramics in a wide variety of applications.

11.11 SUMMARY

Ceramic materials are inorganic, nonmetallic materials consisting of metallic and nonmetallic elements bonded together primarily by ionic and/or covalent bonds. As a result, the chemical compositions and structures of ceramic materials vary considerably. They may consist of a single compound such as, for example, pure aluminum oxide, or they may be composed of a mixture of many complex phases such as the mixture of clay, silica, and feldspar in electrical porcelain.

The properties of ceramic materials also vary greatly due to differences in bonding. In general, most ceramic materials are typically hard and brittle with low impact resistance and ductility. Consequently, in most engineering designs, high stresses in ceramic materials are usually avoided, especially if they are tensile stresses. Ceramic materials are usually good electrical and thermal insulators due to the absence of conduction electrons, and thus many ceramics are used for electrical insulation and refractories. Some ceramic materials can be highly polarized with electric charge and are used for dielectric materials for capacitors. Permanent polarization of some ceramic materials produces piezoelectric properties that permit these materials to be used as electromechanical transducers. Other ceramic materials, for example, Fe_3O_4 , are semiconductors and find application for thermistors for temperature measurement. Graphite, diamond, buckyballs, and buckytubes are all allotropes of carbon and are discussed in this chapter because graphite is sometimes considered a ceramic material. These allotropes have significantly different properties that are directly related to differences in atomic structure and positioning. Buckyballs and buckytubes are becoming more important in nanotechnology applications.

The processing of ceramic materials usually involves the agglomeration of small particles by a variety of methods in the dry, plastic, or liquid states. Cold-forming processes predominate in the ceramics industry, but hot-forming processes are also used. Pressing, slip casting, and extrusion are commonly used ceramic-forming processes. After forming, ceramic materials are usually given a thermal treatment such as sintering or vitrification. During sintering, the small particles of a formed article are bonded together by solid-state diffusion at high temperatures. In vitrification, a glass phase serves as a reaction medium to bond the unmelted particles together.

Glasses are inorganic ceramic products of fusion that are cooled to a rigid solid without crystallization. Most inorganic glasses are based on a network of ionically covalently bonded silica (SiO_2) tetrahedra. Additions of other oxides such as Na_2O and CaO modify the silica network to provide a more workable glass. Other additions to glasses create a spectrum of properties. Glasses have special properties such as transparency, hardness at room temperature, and excellent resistance to most environments that make them important for many engineering designs. One of the important applications of ceramics is in coating of component surface is to protect it from corrosion or wear. Glasses, oxides, and carbides are all used as coating materials for various applications. Nanotechnology research is promising to improve on the major drawback of ceramic materials: their brittleness. Early research shows that nanocrystalline ceramics possess higher ductility. This may allow for cheaper production of more complex ceramic parts.

11.12 DEFINITIONS

Sec. 11.1

Ceramic materials: inorganic, nonmetallic materials that consist of metallic and nonmetallic elements bonded together primarily by ionic and/or covalent bonds.

Sec. 11.2

Coordination number (CN): the number of equidistant nearest neighbors to an atom or ion in a unit cell of a crystal structure. For example, in NaCl, CN = 6 since six equidistant Cl^- anions surround a central Na^+ cation.

Radius ratio (for an ionic solid): the ratio of the radius of the central cation to that of the surrounding anions.

Critical (minimum) radius ratio: the ratio of the central cation to that of the surrounding anions when all the surrounding anions just touch each other and the central cation.

Octahedral interstitial site: the space enclosed when the nuclei of six surrounding atoms (ions) form an octahedron.

Tetrahedral interstitial site: the space enclosed when the nuclei of four surrounding atoms (ions) form a tetrahedron.

Graphite: a layered structure of carbon atoms covalently bonded to three others inside the layer. Various layers are the bonded through secondary bonds.

Buckyball: also called Buckminster fullerene is a soccer ball-shaped molecule of carbon atoms (C_{60}).

Buckytube: a tubular structure made of carbon atoms covalently bonded together.

Sec. 11.4

Firing (of a ceramic material): heating a ceramic material to a high enough temperature to cause a chemical bond to form between the particles.

Dry pressing: the simultaneous uniaxial compaction and shaping of ceramic granular particles (and binder) in a die.

Isostatic pressing: the simultaneous compaction and shaping of a ceramic powder (and binder) by pressure applied uniformly in all directions.

Slip casting: a ceramic shape-forming process in which a suspension of ceramic particles and water are poured into a porous mold and then some of the water from the cast material diffuses into the mold, leaving a solid shape in the mold. Sometimes excess liquid within the cast solid is poured from the mold, leaving a cast shell.

Sintering (of a ceramic material): the process in which fine particles of a ceramic material become chemically bonded together at a temperature high enough for atomic diffusion to occur between the particles.

Vitrification: melting or formation of a glass; the vitrification process is used to produce a viscous liquid glass in a ceramic mixture upon firing. Upon cooling, the liquid phase solidifies and forms a vitreous or glassy matrix that bonds the unmelted particles of the ceramic material together.

Sec. 11.7

Refractory (ceramic) material: a material that can withstand the action of a hot environment.

Sec. 11.8

Glass: a ceramic material that is made from inorganic materials at high temperatures and is distinguished from other ceramics in that its constituents are heated to fusion and then cooled to the rigid condition without crystallization.

Glass transition temperature: the center of the temperature range in which a noncrystalline solid changes from being glass-brittle to being viscous.

Glass-forming oxide: an oxide that forms a glass easily; also an oxide that contributes to the network of silica glass when added to it, such as B_2O_3 .

Network modifiers: an oxide that breaks up the silica network when added to silica glass; modifiers lower the viscosity of silica glass and promote crystallization. Examples are Na_2O , K_2O , CaO , and MgO .

Intermediate oxides: an oxide that may act either as a glass former or as a glass modifier, depending on the composition of the glass. Example, Al_2O_3 .

Glass reference points (temperatures)

Working point: at this temperature the glass can easily be worked.

Softening point: at this temperature the glass flows at an appreciable rate.

Annealing point: at this temperature stresses in the glass can be relieved.

Strain point: at this temperature the glass is rigid.

Float glass: flat glass that is produced by having a ribbon of molten glass cool to the glass-brittle state while floating on the top of a flat bath of molten tin and under a reducing atmosphere.

Thermally tempered glass: glass that has been reheated to near its softening temperature and then rapidly cooled in air to introduce compressive stresses near its surface.

Chemically tempered glass: glass that has been given a chemical treatment to introduce large ions into its surface to cause compressive stresses at its surface.

Sec. 11.9

Glaze: a glass coating applied to a ceramic substrate.

Porcelain enamel: a glass coating applied to a metal substrate.

Glass enamel: a glass coating applied to a glass substrate.

11.13 PROBLEMS

Answers to problems marked with an asterisk are given at the end of the book.

Knowledge and Comprehension Problems

- 11.1 Define a ceramic material.
- 11.2 What are some properties common to most ceramic materials?
- 11.3 Distinguish between traditional and engineering ceramic materials and give examples of each.
- 11.4 What two main factors affect the packing of ions in ionic solids?
- 11.5 Define (a) coordination number and (b) critical radius ratio for the packing of ions in ionic solids.
- 11.6 What is the spinel crystal structure?
- 11.7 Draw the unit cell for BaF_2 , which has the fluorite (CaF_2) crystal structure. If the Ba^{2+} ions occupy the FCC lattice sites, which sites do the F^- ions occupy?
- 11.8 What fraction of the octahedral interstitial sites are occupied in the CaF_2 structure?
- 11.9 What is the antifluorite structure? What ionic compounds have this structure? What fraction of the tetrahedral interstitial sites are occupied by cations?
- 11.10 Describe the perovskite structure. What fraction of the octahedral interstitial sites are occupied by the tetravalent cation?
- 11.11 Draw a section of the graphite structure. Why are the layers of graphite able to slide past each other easily?
- 11.12 Describe and illustrate the following silicate structures: (a) island, (b) chain, and (c) sheet.

- 11.13 Describe the structure of a sheet of kaolinite.
- 11.14 Describe the bonding arrangement in the cristobalite (silica) network structure.
- 11.15 Describe the feldspar network structure.
- 11.16 What are the basic steps in the processing of ceramic products by the agglomeration of particles?
- 11.17 What types of ingredients are added to ceramic particles in preparing ceramic raw materials for processing?
- 11.18 Describe two methods for preparing ceramic raw materials for processing.
- 11.19 Describe the dry-pressing method for producing such ceramic products as technical ceramic compounds and structural refractories. What are the advantages of dry-pressing ceramic materials?
- 11.20 Describe the isostatic-pressing method for producing ceramic products.
- 11.21 Describe the four stages in the manufacture of a spark plug insulator.
- 11.22 What are the advantages of hot-pressing ceramics materials?
- 11.23 Describe the steps in the slip-casting process for ceramic products.
- 11.24 What is the difference between (a) drain and (b) solid slip casting?
- 11.25 What are the advantages of slip casting?
- 11.26 What types of ceramic products are produced by extrusion? What are the advantages of this process? Limitations?
- 11.27 What are the purposes of drying ceramic products before firing?
- 11.28 What is the sintering process? What occurs to the ceramic particles during sintering?
- 11.29 What is the vitrification process? In what type of ceramic materials does vitrification take place?
- 11.30 What are the three basic components of traditional ceramics?
- 11.31 What is the approximate composition of kaolin clay?
- 11.32 What is the role of clay in traditional ceramics?
- 11.33 What is flint? What role does it have in traditional ceramics?
- 11.34 What is feldspar? What role does it have in traditional ceramics?
- 11.35 List some examples of whiteware ceramic products.
- 11.36 Why is the term *triaxial* used to describe some whitewares?
- 11.37 What are the two most important industrial abrasives?
- 11.38 What are important properties for industrial abrasives?
- 11.39 Why do most ceramic materials have low thermal conductivities?
- 11.40 What are refractories? What are some of their applications?
- 11.41 What are the two main types of ceramic refractory materials?
- 11.42 Give the composition and several applications for the following refractories: (a) silica, (b) fireclay, and (c) high-alumina.
- 11.43 What do most basic refractories consist of? What are some important properties of basic refractories? What is a main application for these materials?
- 11.44 What is the high-temperature reusable-surface insulation that can withstand temperatures as high as 1260°C made of?
- 11.45 Define a glass.
- 11.46 What are some of the properties of glasses that make them indispensable for many engineering designs?

- 11.47 How is a glass distinguished from other ceramic materials?
- 11.48 Define the glass transition temperature.
- 11.49 Name two glass-forming oxides. What are their fundamental subunits and their shape?
- 11.50 What is fused silica glass? What are some of its advantages and disadvantages?
- 11.51 What is the basic composition of soda-lime glass? What are some of its advantages and disadvantages? What are some applications for soda-lime glass?
- 11.52 Define the following viscosity reference points for glasses: working, softening, annealing, and strain.
- 11.53 Describe the float-glass process for the production of flat-glass products. What is its major advantage?
- 11.54 What is tempered glass? How is it produced? Why is tempered glass considerably stronger in tension than annealed glass? What are some applications for tempered glass?
- 11.55 What is chemically strengthened glass? Why is chemically strengthened glass stronger in tension than annealed glass?
- 11.56 What is an allotrope? Name as many carbon allotropes as you can.
- 11.57 What is a Buckminster fullerene? What are some of its properties? Draw a schematic.
- 11.58 What is a carbon nanotube? What are some of its properties? Name some applications for nanotubes.
- 11.59 Name five groups of ceramic coating materials.
- 11.60 Define the following terms: (a) glaze, (b) porcelain enamel, (c) glass enamel.
- 11.61 How are glass coatings applied to various components?
- 11.62 Define agglomerates or aggregates in nanoceramic production.

Application and Analysis Problems

- 11.63 Using Pauling's equation (Eq. 2.10), compare the percent covalent character of the following compounds: hafnium carbide, titanium carbide, tantalum carbide, boron carbide, and silicon carbide.
- *11.64 Using Fig. 11.51, calculate the critical radius ratio for octahedral coordination.

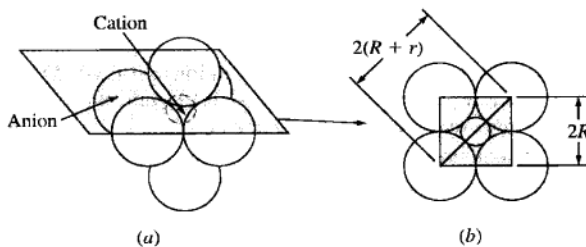


Figure 11.51

(a) Octahedral coordination of six anions (radii = R) around a central cation of radius r . (b) Horizontal section through center of (a).

- 11.65** Predict the coordination number for (a) BaO and (b) LiF. Ionic radii are $\text{Ba}^{2+} = 0.143 \text{ nm}$, $\text{O}^{2-} = 0.132 \text{ nm}$, $\text{Li}^{+} = 0.078 \text{ nm}$, and $\text{F}^{-} = 0.133 \text{ nm}$.
- *11.66** Calculate the density in grams per cubic centimeter of CsI, which has the CsCl structure. Ionic radii are $\text{Cs}^{+} = 0.165 \text{ nm}$ and $\text{I}^{-} = 0.220 \text{ nm}$.
- 11.67** Calculate the density in grams per cubic centimeter of CsBr, which has the CsCl structure. Ionic radii are $\text{Cs}^{+} = 0.165 \text{ nm}$ and $\text{Br}^{-} = 0.196 \text{ nm}$.
- 11.68** Calculate the linear densities in ions per nanometer in the [110] and [111] directions for (a) NiO and (b) CdO. Ionic radii are $\text{Ni}^{2+} = 0.078 \text{ nm}$, $\text{Cd}^{2+} = 0.103 \text{ nm}$, and $\text{O}^{2-} = 0.132 \text{ nm}$.
- *11.69** Calculate the planar densities in ions per square nanometer on the (111) and (110) planes for (a) CoO and (b) LiCl. Ionic radii are $\text{Co}^{2+} = 0.082 \text{ nm}$, $\text{O}^{2-} = 0.132 \text{ nm}$, $\text{Li}^{+} = 0.078 \text{ nm}$, and $\text{Cl}^{-} = 0.181 \text{ nm}$.
- 11.70** Calculate the density in grams per cubic centimeter of (a) SrO and (b) VO. Ionic radii are $\text{V}^{2+} = 0.065 \text{ nm}$, $\text{Co}^{2+} = 0.082 \text{ nm}$, and $\text{O}^{2-} = 0.132 \text{ nm}$.
- 11.71** Calculate the ionic packing factor for (a) MnO and (b) SrO. Ionic radii are $\text{Mn}^{2+} = 0.091 \text{ nm}$, $\text{Sr}^{2+} = 0.127 \text{ nm}$, and $\text{O}^{2-} = 0.132 \text{ nm}$.
- 11.72** ZnTe has the zinc blende crystal structure. Calculate the density of ZnTe. Ionic radii are $\text{Zn}^{2+} = 0.083 \text{ nm}$ and $\text{Te}^{2-} = 0.211 \text{ nm}$.
- 11.73** BeO has the zinc blende crystal structure. Calculate the density of BeO. Ionic radii are $\text{Be}^{2+} = 0.034 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.
- *11.74** Calculate the density in grams per cubic centimeter of ZrO_2 , which has the CaF_2 crystal structure. Ionic radii are $\text{Zr}^{4+} = 0.087 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.
- *11.75** Calculate the linear density in ions per nanometer in the [111] and [110] directions for CeO_2 , which has the fluorite structure. Ionic radii are $\text{Ce}^{4+} = 0.102 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.
- 11.76** Calculate the planar density in ions per square nanometer in the (111) and (110) planes of ThO_2 , which has the fluorite structure. Ionic radii are $\text{Th}^{4+} = 0.110 \text{ nm}$ and $\text{O}^{2-} = 0.132 \text{ nm}$.
- 11.77** Calculate the ionic packing factor for SrF_2 , which has the fluorite structure. Ionic radii are $\text{Sr}^{2+} = 0.127 \text{ nm}$ and $\text{F}^{-} = 0.133 \text{ nm}$.
- 11.78** Why are only two-thirds of the octahedral interstitial sites filled by Al^{3+} ions when the oxygen ions occupy the HCP lattice sites in Al_2O_3 ?
- 11.79** Calculate the ionic packing factor for CaTiO_3 , which has the perovskite structure. Ionic radii are $\text{Ca}^{2+} = 0.106 \text{ nm}$, $\text{Ti}^{4+} = 0.064 \text{ nm}$, and $\text{O}^{2-} = 0.132 \text{ nm}$. Assume the lattice constant $a = 2(r_{\text{Ti}^{4+}} + r_{\text{O}^{2-}})$.
- 11.80** Calculate the density in grams per cubic centimeter of SrSnO_3 , which has the perovskite structure. Ionic radii are $\text{Sr}^{2+} = 0.127 \text{ nm}$, $\text{Sn}^{4+} = 0.074 \text{ nm}$, and $\text{O}^{2-} = 0.132 \text{ nm}$. Assume $a = 2(r_{\text{Sr}^{2+}} + r_{\text{O}^{2-}})$.
- *11.81** Determine the composition of the ternary compound at point y in Fig. 11.30.
- 11.82** Why are triaxial porcelains not satisfactory for use at high frequencies?
- 11.83** What kinds of ions cause an increase in the conductivity of electrical porcelain?
- 11.84** What is the composition of most technical ceramics?
- 11.85** How are pure single-compound technical ceramic particles processed to produce a solid product? Give an example.
- 11.86** What causes the lack of plasticity in crystalline ceramics?

- 11.87** Explain the plastic deformation mechanism for some single-crystal ionic solids such as NaCl and MgO. What is the preferred slip system?
- 11.88** What structural defects are the main cause of failure of polycrystalline ceramic materials?
- 11.89** How do (a) porosity and (b) grain size affect the tensile strength of ceramic materials?
- 11.90** A reaction-bonded silicon nitride ceramic has a strength of 250 MPa and a fracture toughness of 3.4. What is the largest-sized internal flaw that this material can support without fracturing? (Use $Y = 1$ in the fracture-toughness equation.)
- *11.91** The maximum-sized internal flaw in a hot-pressed silicon carbide ceramic is 25 μm . If this material has a fracture toughness of $3.7 \text{ MPa} \cdot \sqrt{\text{m}}$, what is the maximum stress that this material can support? (Use $Y = \sqrt{\pi}$.)
- 11.92** A partially stabilized zirconia advanced ceramic has a strength of 352 MPa and a fracture toughness of $7.5 \text{ MPa} \cdot \sqrt{\text{m}}$. What is the largest-sized internal flaw (expressed in micrometers) that this material can support? (Use $Y = \sqrt{\pi}$.)
- 11.93** A fully stabilized, cubic polycrystalline ZrO_2 sample has a fracture toughness of $K_{\text{IC}} = 3.8 \text{ MPa} \cdot \sqrt{\text{m}}$ when tested on a four-point bend test.
- (a) If the sample fails at a stress of 450 MPa, what is the size of the largest surface flaw? Assume $Y = \sqrt{\pi}$.
- (b) The same test is performed with a partially stabilized ZrO_2 specimen. This material is transformation-toughened and has a $K_{\text{IC}} = 12.5 \text{ MPa} \cdot \sqrt{\text{m}}$. If this material has the same flaw distribution as the fully stabilized sample, what stress must be applied to cause failure?
- 11.94** How does the specific volume versus temperature plot for a glass differ from that for a crystalline material when these materials are cooled from the liquid state?
- 11.95** How does the silica network of a simple silica glass differ from crystalline (cristobalite) silica?
- 11.96** How is it possible for BO_3^{3-} triangles to be converted to BO_4^{4-} tetrahedral and still maintain neutrality in some borosilicate glasses?
- 11.97** What are glass network modifiers? How do they affect the silica-glass network? Why are they added to silica glass?
- 11.98** What are glass intermediate oxides? How do they affect the silica-glass network? Why are they added to silica glass?
- 11.99** What is the purpose of (a) MgO and (b) Al_2O_3 additions to soda-lime glass?
- 11.100** Distinguish between hard and soft glasses and long and short glasses.
- 11.101** A soda-lime plate glass between 500°C (strain point) and 700°C (softening point) has viscosities between $10^{14.2}$ and $10^{7.5}$ P, respectively. Calculate a value for the activation energy in this temperature region.
- *11.102** A soda-lime glass has a viscosity of $10^{14.6}$ P at 560°C. What will be its viscosity at 675°C if the activation energy for viscous flow is 430 kJ/mol?
- 11.103** A soda-lime glass has a viscosity of $10^{14.3}$ P at 570°C. At what temperature will its viscosity be $10^{9.9}$ P if the activation energy for the process is 430 kJ/mol?
- 11.104** A borosilicate glass between 600°C (annealing point) and 800°C (softening point) has viscosities of $10^{12.5}$ P and $10^{7.4}$ P, respectively. Calculate a value for the activation energy for viscous flow in this region, assuming the equation $\eta = \eta_0 e^{Q/RT}$ is valid.

- 11.105** Discuss mechanical, electrical, and thermal properties of diamond. In each case, explain the behavior in terms of its atomic structure.
- 11.106** Discuss the challenges in producing bulk nanocrystalline ceramics.
- 11.107** Why is the HIP process more suitable for synthesizing nanocrystalline ceramics?

Synthesis and Evaluation Problems

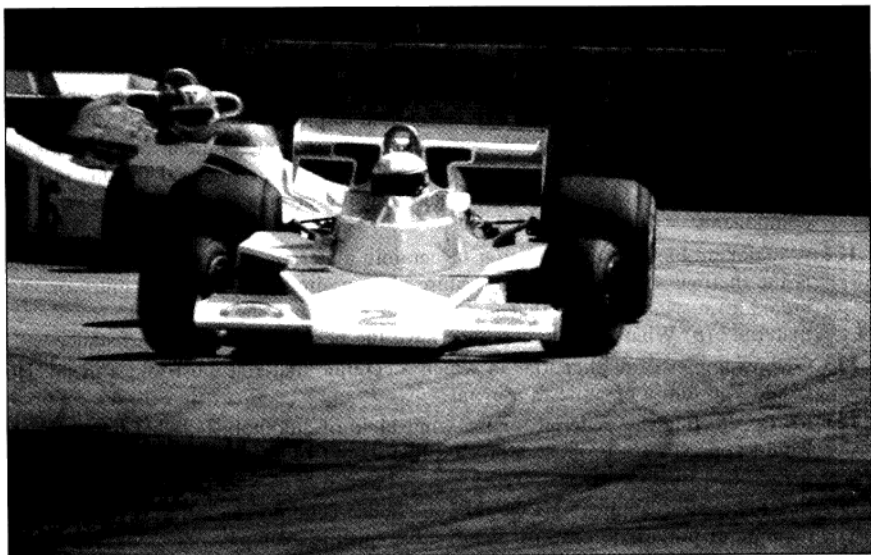
- 11.108** Tensile property data of ceramic materials show more scatter than metals. Can you explain why?
- 11.109** (a) Discuss the advantages and disadvantages of using advanced ceramics in the structure of internal combustion engines. (b) Propose some methods of overcoming the shortcomings of ceramics for this application.
- 11.110** Investigate the application of ceramics in the electronic industry. (a) What are these applications? (b) Why are ceramics selected?
- 11.111** For insulation purposes, you would like to cover the surface of a substrate with an extremely thin layer of Si_3N_4 . (a) Propose a process that could achieve this. (b) Can the proposed process be used to form large objects with complex shapes? Explain.
- 11.112** Explain, from an atomic structure point of view, why metals can be plastically deformed to form large and complex shapes while complex ceramic parts cannot be manufactured by this technique.
- 11.113** Alumina (Al_2O_3) and chromium oxide (Cr_2O_3) are ceramic materials that form an isomorphous phase diagram. (a) What does this tell you about the solubility limit of one component in the other? (b) What type of a solid solution is formed? (c) Explain what substitution takes place.
- 11.114** (a) How are the ceramic tiles used in the thermal protection system of the space shuttle attached to its frame? (b) Why is the thermal protection system of the space shuttle made from small tiles (15 to 20 cm width) and not larger, more contoured ones?
- 11.115** The nose cap and the wing leading edges of the space shuttle may reach temperatures of up to 1650°C . (a) Would the silica fiber compound (HRSI) be a suitable candidate for these sections of the shuttle? (b) If not, select a suitable material for this location. (c) Investigate the important properties of the selected material that satisfy the design needs.
- 11.116** Carbon/carbon composites have desirable properties at very high temperatures that make suitable materials for many aerospace applications. However, the carbon in the material can react with the oxygen in the atmosphere at temperatures above 450°C , and gaseous oxides form. Develop solutions for this problem.
- 11.117** Low toughness is the major problem for many structural ceramics. Many cutting tools are made of ceramics with improved toughness. For example, tungsten carbide particles (WC) are embedded in a metal matrix such as nickel or cobalt. (a) Explain how this improves the toughness of the tool. (b) How is the choice of matrix material important (i.e., would aluminum work as the matrix material)?
- 11.118** It is very difficult to machine ceramic components to a desired shape. This is because ceramics are strong and brittle. The stresses produced due to cutting forces could create surface cracks and other damages that, in turn, weaken the component. Propose a technique that will reduce the cutting forces and the possibility of cracking during machining of ceramics.

- 11.119** Concrete is an important construction material that is classified as a ceramic (or a ceramic composite) material. It has excellent strength characteristics in compression but is extremely weak in tension. (a) Propose ways of improving the tension bearing characteristics of concrete. (b) What problems do you anticipate in your process?
- 11.120** Refer to Fig. 11.48, in which glass plates are strengthened by inducing compressive stresses on the surfaces. Suggest a way of producing compressive stress on the surfaces of a concrete slab using mechanical means. Show schematically how this will help.
- 11.121** Conventional taps are prone to dripping because rubber washers are susceptible to wear and the metal seat (brass) is susceptible to pitting corrosion. (a) Which class of materials would be a suitable replacement for the rubber/metal combination that would reduce the dripping problem? (b) Select a specific material for this problem. (c) What problems would you anticipate in using or manufacturing of these components?
- 11.122** A major problem in the selection of ceramic materials for various applications is the thermal shock (rapid temperature change similar to during re-entry or breaking) resistance. (a) What factors control thermal shock resistance of a material? (b) What specific ceramics have the best thermal shock resistance?
- 11.123** Give examples of applications in which a ceramic material must join a metal. How would you join a ceramic to a metal?
- 11.124** (a) In selecting the material for the windshield of automobiles, what type of glass would you use? (b) Propose a process that would keep glass shards from dispersing if the glass fractures.
- 11.125** In what coating applications would you choose ceramic coating as opposed to metallic or polymeric coating? Why? Give specific examples.
- 11.126** Oxide coatings are usually used to protect against oxidation and damage at elevated temperatures, and carbides are used to protect against wear. Can you explain why? Give examples.
- 11.127** During inspection a small crack is found in the ceramic coating of a component. Would you be concerned about this small crack?
- 11.128** Due to impact of hail, there is a very small circular damage to the surface of your automobile windshield. (a) What happens if you ignore this small damage? (b) How would you fix this without changing the windshield?
- 11.129** If there is a 1-in. crack in your automobile windshield and you would like to slow down its propagation, what would you do?

12

CHAPTER

Composite Materials



(Corbis/RF)

Carbon-carbon composites have a combination of properties that renders them uniquely superior in operating temperatures as high as 2800°C. For example, unidirectional high-modulus surface-treated carbon-carbon composites (55 vol % fiber) have a tensile modulus of 180 GPa at room temperature to 175 GPa at 2000°C. The tensile strength is also remarkably constant, varying from 950 MPa at room temperature to 1100 MPa at 2000°C. In addition, properties such as high thermal conductivity and low coefficient of thermal expansion, in conjunction with high strength and modulus, indicate a material that is thermal-shock resistant. The combination of these properties makes this material suitable for re-entry applications, rocket motors, and aircraft brakes. The more commercial application of this material is in the brake pads of racing cars.¹ ■

¹"ASM Engineered Materials Handbook," *Composites*, vol. 1, ASM International, 1991.

LEARNING OBJECTIVES

By the end of this chapter, students will be able to . . .

1. Define a composite material, the major constituents, and various classifications.
2. Describe the role of the particulate (fiber) and the matrix (resin), and name various forms of each.
3. Define a multidirectional laminated composite and its advantages over unidirectional laminated composites.
4. Describe how one would estimate the material properties of a fiber-reinforced composite material based on material properties and volume fraction of the matrix and fiber constituents.
5. Describe various processes used to produce a component made of composite materials.
6. Describe the properties, characteristics, and classifications of concrete, asphalt, and wood, composite materials that are used extensively in structural and construction applications.
7. Define a sandwich structure.
8. Define Polymer Matrix, Metal Matrix, and Ceramic Matrix Composites, and name advantages and disadvantages for each.

12.1 INTRODUCTION

What is a composite material? Unfortunately there is no widely accepted definition of what a composite material is. A dictionary defines a composite as something made up of distinct parts (or constituents). At the atomic level, materials such as some metal alloys and polymeric materials could be called composite materials since they consist of different and distinct atomic groupings. At the microstructural level (about 10^{-4} to 10^{-2} cm), a metal alloy such as a plain-carbon steel containing ferrite and pearlite could be called a composite material since the ferrite and pearlite are distinctly visible constituents as observed in the optical microscope. At the macrostructural level (about 10^{-2} cm or greater), a glass-fiber-reinforced plastic, in which the glass fibers can be distinctly recognized by the naked eye, could be considered a composite material. Now we see that the difficulty in defining a composite material is the size limitations we impose on the constituents that make up the material. In engineering design, a composite material usually refers to a material consisting of constituents in the micro- to macroscale range, and even favors the macros. For the purposes of this book, the following is a definition of a composite material:

A **composite material** is a materials system composed of a suitably arranged mixture or combination of two or more micro- or macroconstituents with an interface separating them, that differ in form and chemical composition and are essentially insoluble in each other.

The engineering importance of a composite material is that two or more distinctly different materials combine to form a composite material that possesses

properties that are superior, or important in some other manner, to the properties of the individual components. A multitude of materials fit into this category, and thus a discussion of all these composite materials is far beyond the scope of this book. In this chapter, only some of the most important composite materials used in engineering will be discussed. These are fiber-reinforced plastics, concrete, asphalt, and wood, as well as several miscellaneous types of composite materials. Examples of the use of composite materials in engineering designs are shown in Fig. 12.1.

12.2 FIBERS FOR REINFORCED-PLASTIC COMPOSITE MATERIALS

Three main types of synthetic fibers are used in the United States to reinforce plastic materials: glass, aramid,² and carbon. Glass is by far the most widely used reinforcement fiber and is the lowest in cost. Aramid and carbon fibers have high strengths and low densities and so are used in many applications, particularly aerospace, in spite of their higher cost.

12.2.1 Glass Fibers for Reinforcing Plastic Resins

Glass fibers are used to reinforce plastic matrices to form structural composites and molding compounds. Glass-fiber-plastic composite materials have the following favorable characteristics: high strength-to-weight ratio; good dimensional stability; good resistance to heat, cold, moisture, and corrosion; good electrical insulation properties; ease of fabrication; and relatively low cost.

The two most important types of glass used to produce glass fibers for composites are *E* (electrical) and *S* (high-strength) glasses.

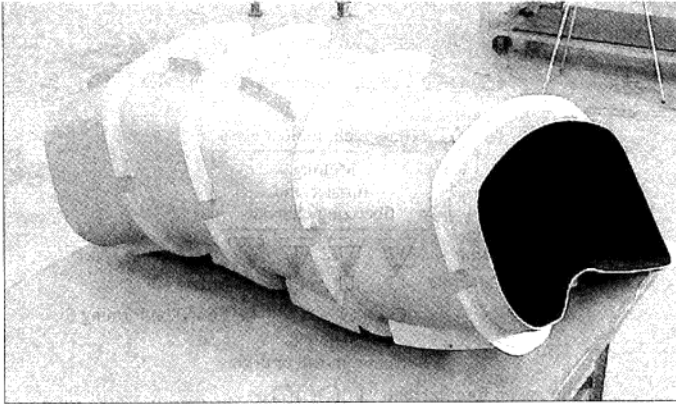
E glass is the most commonly used glass for continuous fibers. Basically, E glass is a lime-aluminum-borosilicate glass with zero or low sodium and potassium levels. The basic composition of E glass ranges from 52 to 56 percent SiO_2 , 12 to 16 percent Al_2O_3 , 16 to 25 percent CaO , and 8 to 13 percent B_2O_3 . E glass has a tensile strength of about 500 ksi (3.44 GPa) in the virgin condition and a modulus of elasticity of 10.5 Msi (72.3 GPa).

S glass has a higher strength-to-weight ratio, is more expensive than E glass, and is used primarily for military and aerospace applications. The tensile strength of S glass is over 650 ksi (4.48 GPa), and its modulus of elasticity is about 12.4 Msi (85.4 GPa). A typical composition for S glass is about 65 percent SiO_2 , 25 percent Al_2O_3 , and 10 percent MgO .

Production of Glass Fibers and Types of Fiberglass-Reinforcing Materials

Glass fibers are produced by drawing monofilaments of glass from a furnace containing molten glass and gathering a large number of these filaments to form a strand of glass fibers (Fig. 12.2). The strands then are used to make glass-fiber yarns or **rovings** that consist of a collection of bundles of continuous filaments. The

²Aramid fiber is an aromatic polyamide polymer fiber with a very rigid molecular structure.



(a)



(b)

Figure 12.1

(a) A finished duct test article, with cured flanges.

(After page 37 step 7 of *High-Performance Composites Magazine*, Jan. 2002.)

(b) A carbon-fiber placement won a key role on the joint-strike fighter of Lockheed-Martin's X-35. A carbon-fiber placed inlet duct is manufactured four times faster than the conventional part with significantly fewer fasteners required.

(From cover of *High-Performance Composites Magazine*, Jan. 2002.)

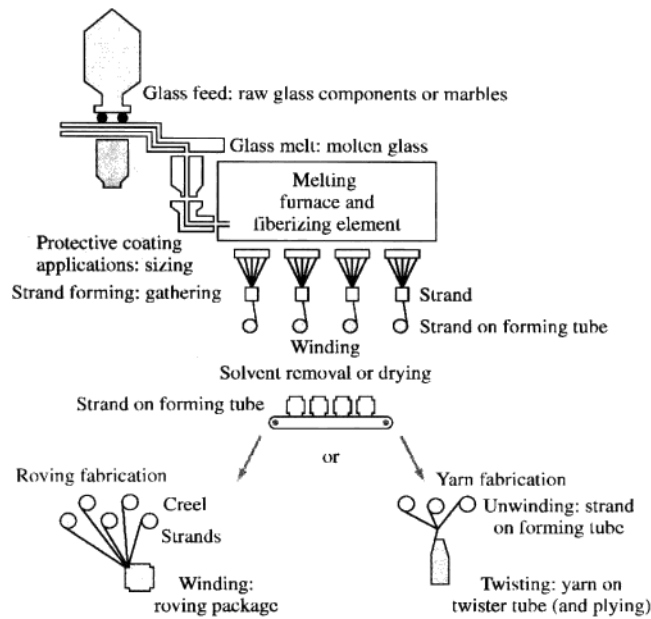


Figure 12.2
Glass-fiber manufacturing process.
(From M.M. Schwartz, "Composite Materials Handbook," McGraw-Hill, 1984, pp. 2–24.
Reproduced with permission of The McGraw-Hill Companies.)

Table 12.1 Comparative yarn properties for fiber reinforcements for plastics

Property	Glass (E)	Carbon (HT)	Aramid (Kevlar 49)
Tensile strength, ksi (MPa)	450 (3100)	500 (3450)	525 (3600)
Tensile modulus, Msi (GPa)	11.0 (76)	33 (228)	19 (131)
Elongation at break (%)	4.5	1.6	2.8
Density (g/cm ³)	2.54	1.8	1.44

rovings may be in continuous strands or woven to make woven roving. Glass-fiber reinforcing mats (Fig. 12.3) are made of continuous strands (Fig. 12.3a) or chopped strands (Fig. 12.3c). The strands are usually held together with a resinous binder. Combination mats are made with woven roving chemically bonded to chopped-strand mat (Fig. 12.3d).

Properties of Glass Fibers The tensile properties and density of E-glass fibers are compared to those of carbon and aramid fibers in Table 12.1. It is noted that glass fibers have a lower tensile strength and modulus than carbon and aramid fibers but

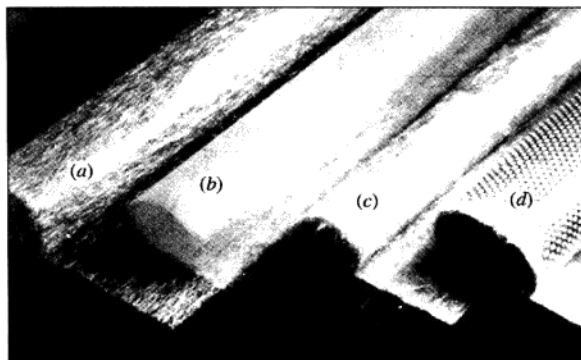


Figure 12.3

Fiberglass-reinforcing mats: (a) continuous-strand mat, (b) surfacing mat, (c) chopped-strand mat, and (d) combination of woven roving and chopped-strand mat. (Courtesy of Owens/Corning Fiberglass Co.)

a higher elongation. The density of glass fibers is also higher than that of carbon and aramid fibers. However, because of their low cost and versatility, glass fibers are by far the most commonly used reinforcing fibers for plastics (Table 12.1).

12.2.2 Carbon Fibers for Reinforced Plastics

Composite materials made by using carbon fibers for reinforcing plastic resin matrices such as epoxy are characterized by having a combination of light weight, very high strength, and high stiffness (modulus of elasticity). These properties make the use of carbon-fiber-plastic composite materials especially attractive for aerospace applications. Unfortunately, the relatively high cost of the carbon fibers restricts their use in many industries such as the automotive industry. **Carbon fibers** for these composites are produced mainly from two sources, *polyacrylonitrile* (PAN) (see Sec. 10.6) and pitch, which are called *precursors*.

In general, carbon fibers are produced from PAN precursor fibers by three processing stages: (1) *stabilization*, (2) *carbonization*, and (3) *graphitization* (Fig. 12.4). In the *stabilization stage*, the PAN fibers are first stretched to align the fibrillar networks within each fiber parallel to the fiber axis, and then they are oxidized in air at about 200°C to 220°C (392°F to 428°F) while held in tension.

The second stage in the production of high-strength carbon fibers is *carbonization*. In this process, the stabilized PAN-based fibers are pyrolyzed (heated) until they become transformed into carbon fibers by the elimination of O, H, and N from the precursor fiber. The carbonization heat treatment is usually carried out in an inert atmosphere in the 1000°C to 1500°C (1832°F to 2732°F) range. During the carbonization process,

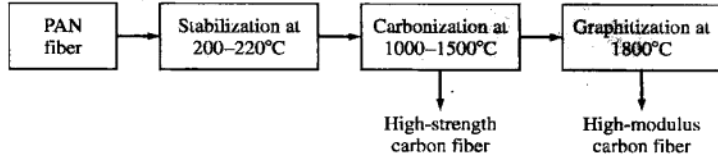


Figure 12.4

Processing steps for producing high-strength, high-modulus carbon fibers from polyacrylonitrile precursor material.

turbostratic graphite-like fibrils or ribbons are formed within each fiber that greatly increase the tensile strength of the material.

A third stage, or *graphitization treatment*, is used if an increase in the modulus of elasticity is desired at the expense of high tensile strength. During graphitization, which is carried out above about 1800°C (3272°F), the preferred orientation of the graphite-like crystallites within each fiber is increased.

The carbon fibers produced from PAN precursor material have a tensile strength that ranges from about 450 to 650 ksi (3.10 to 4.45 MPa) and a modulus of elasticity that ranges from about 28 to 35 Msi (193 to 241 GPa). In general the higher-moduli fibers have lower tensile strengths, and vice versa. The density of the carbonized and graphitized PAN fibers is usually about 1.7 to 2.1 g/cm³, while their final diameter is about 7 to 10 μm. Figure 12.5 shows a photograph of a group of about 6000 carbon fibers called a **tow**.

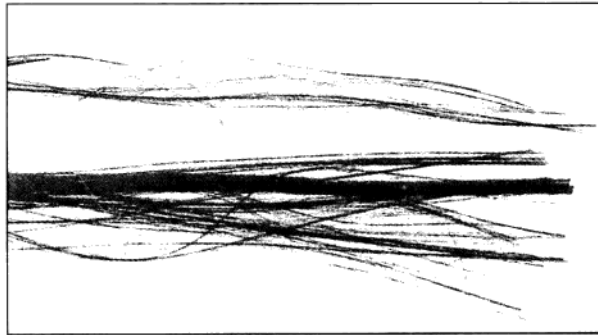


Figure 12.5

Photograph of a tow of about 6000 carbon fibers.
(Courtesy of the Fiberite Co., Winona, Minn.)

12.2.3 Aramid Fibers for Reinforcing Plastic Resins

Aramid fiber is the generic name for aromatic polyamide fibers. Aramid fibers were introduced commercially in 1972 by Du Pont under the trade name of Kevlar, and at the present time there are two commercial types: Kevlar 29 and 49. Kevlar 29 is a low-density, high-strength aramid fiber designed for such applications as ballistic protection, ropes, and cables. Kevlar 49 is characterized by a low density and high strength and modulus. The properties of Kevlar 49 make its fibers useful as reinforcement for plastics in composites for aerospace, marine, automotive, and other industrial applications.

The chemical repeating unit of the Kevlar polymer chain is that of an aromatic polyamide, shown in Fig. 12.6. Hydrogen bonding holds the polymer chains together in the transverse direction. Thus, collectively these fibers have high strength in the longitudinal direction and weak strength in the transverse direction. The aromatic ring structure gives high rigidity to the polymer chains, causing them to have a rodlike structure.

Kevlar aramid is used for high-performance composite applications where light weight, high strength and stiffness, damage resistance, and resistance to fatigue and stress rupture are important. Of special interest is that Kevlar-epoxy material is used for various parts of the space shuttle.

12.2.4 Comparison of Mechanical Properties of Carbon, Aramid, and Glass Fibers for Reinforced-Plastic Composite Materials

Figure 12.7 compares typical stress-strain diagrams for carbon, aramid, and glass fibers, and one can see that the fiber strength varies from about 250 to 500 ksi (1720 to 3440 MPa), while the fracture strain ranges from 0.4 to 4.0 percent. The tensile modulus of elasticity of these fibers ranges from 10×10^6 to 60×10^6 psi (68.9 to 413 GPa). The carbon fibers provide the best combination of high strength, high stiffness (high modulus), and low density, but have lower elongations. The aramid fiber Kevlar 49 has a combination of high strength, high modulus (but not as high as the carbon fibers), low density, and high elongation (impact resistance). The glass fibers have lower strengths and moduli and higher densities (Table 12.1). Of the glass fibers, the S-glass fibers have higher strengths and elongations than

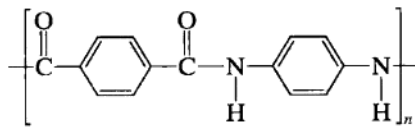


Figure 12.6
Repeating chemical structural unit for
Kevlar fibers.

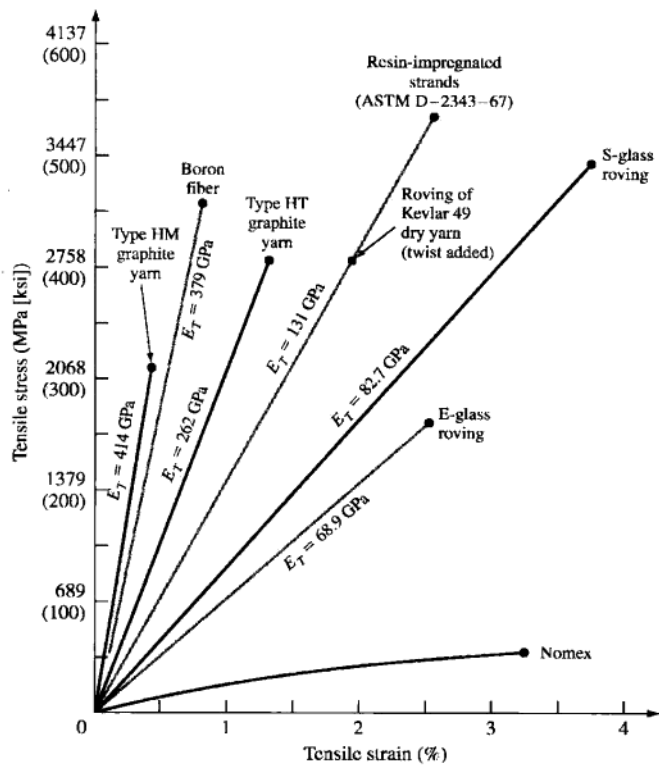


Figure 12.7
Stress-strain behavior of various types of reinforcing fibers.
(After "Kevlar 49 Data Manual," E. I. du Pont de Nemours & Co., 1974.)

the E-glass fibers. Because the glass fibers are much less costly, they are more widely used.

Figure 12.8 compares the strength to density and the stiffness (tensile modulus) to density of various reinforcing fibers. This comparison shows the outstanding strength-to-weight and stiffness-to-weight ratios of carbon and aramid (Kevlar 49) fibers as contrasted to those properties of steel and aluminum. Because of these favorable properties, carbon- and aramid-reinforced-fiber composites have replaced metals for many aerospace applications.

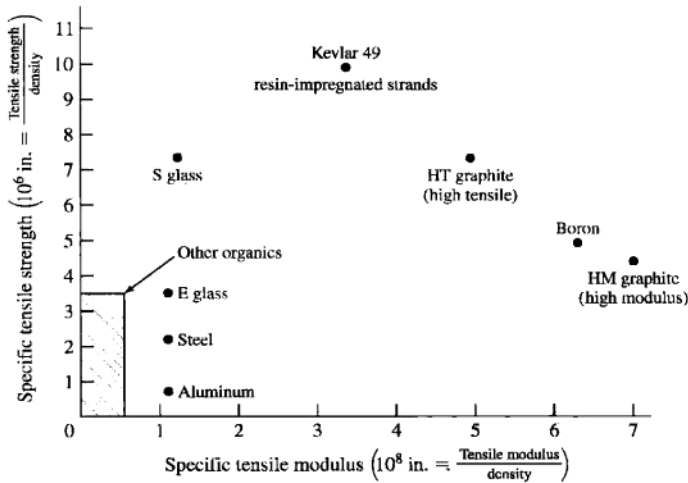


Figure 12.8

Specific tensile strength (tensile strength to density) and **specific tensile modulus** (tensile modulus to density) for various types of reinforcing fibers.

(Courtesy of E.I. du Pont de Nemours & Co., Wilmington, Del.)

12.3 FIBER-REINFORCED-PLASTIC COMPOSITE MATERIALS

12.3.1 Matrix Materials for Fiber-Reinforced-Plastic Composite Materials

Two of the most important matrix plastic resins for fiber-reinforced plastics are unsaturated polyester and epoxy resins. The chemical reactions responsible for the cross-linking of these thermosetting resins have already been described in Sec. 10.8.

Some of the properties of unfilled cast rigid polyester and epoxy resins are listed in Table 12.2. The polyester resins are lower in cost but are usually not as strong as the epoxy resins. Unsaturated polyesters are widely used for matrices of fiber-reinforced plastics. Applications for these materials include boat hulls, building panels, and structural panels for automobiles, aircraft, and appliances. Epoxy resins cost more but have special advantages such as good strength properties and lower shrinkage after curing than polyester resins. Epoxy resins are commonly used as matrix materials for carbon- and aramid-fiber composites.

Table 12.2 Some properties of unfilled cast polyester and epoxy resins

	Polyester	Epoxy
Tensile strength, ksi (MPa)	6–13 (40–90)	8–19 (55–130)
Tensile modulus of elasticity, Msi (GPa)	0.30–0.64 (2.0–4.4)	0.41–0.61 (2.8–4.2)
Flexural yield strength, ksi (MPa)	8.5–23 (60–160)	18.1 (125)
Impact strength (notched-bar Izod test), ft · lb/in. (J/m) of notch	0.2–0.4 (10.6–21.2)	0.1–1.0 (5.3–53)
Density (g/cm ³)	1.10–1.46	1.2–1.3

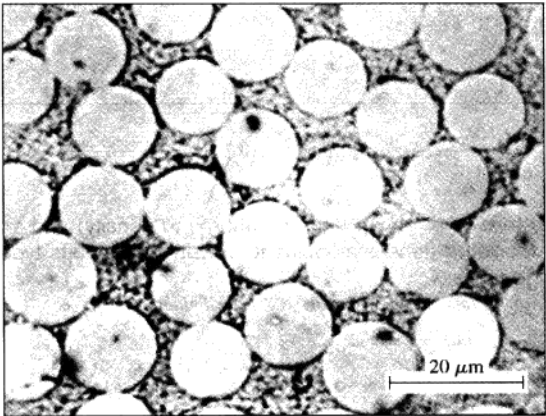


Figure 12.9
Photomicrograph of a cross section of a uni-
directional fiberglass-polyester composite material.
(After D. Hull, "An Introduction to Composite Materials,"
Cambridge, 1981, p. 63. Reprinted with the permission of
Cambridge University Press.)

12.3.2 Fiber-Reinforced-Plastic Composite Materials

Fiberglass-Reinforced Polyester Resins The strength of fiberglass-reinforced plastics is mainly related to the glass content of the material and the arrangement of the glass fibers. In general, the higher the weight percent glass in the composite, the stronger the reinforced plastic is. When there are parallel strands of glass, as may be the case for filament winding, the fiberglass content may be as high as 80 wt %, which leads to very high strengths for the composite material. Figure 12.9 shows a photomicrograph of a cross section of a fiberglass-polyester-resin composite material with unidirectional fibers.

Any deviation from the parallel alignment of the glass strands reduces the mechanical strength of the fiberglass composite. For example, composites made with

Table 12.3 Some mechanical properties of fiberglass-polyester composites

	Woven cloth	Chopped roving	Sheet-molding compound
Tensile strength, ksi (MPa)	30–50 (206–344)	15–30 (103–206)	8–20 (55–138)
Tensile modulus of elasticity, Msi (GPa)	1.5–4.5 (103–310)	0.80–2.0 (55–138)	
Impact strength	5.0–30	2.0–20.0	7.0–22.0
notched bar, Izod	(267–1600)	(107–1070)	(374–1175)
ft · lb/in. (J/m) of notch			
Density (g/cm ³)	1.5–2.1	1.35–2.30	1.65–2.0

Table 12.4 Some typical mechanical properties of a commercial unidirectional composite laminate of carbon fibers (62% by volume) and epoxy resin

Properties	Longitudinal (0°)	Transverse (90°)
Tensile strength, ksi (MPa)	270 (1860)	9.4 (65)
Tensile modulus of elasticity, Msi (GPa)	21 (145)	1.36 (9.4)
Ultimate tensile strain (%)	1.2	0.70

Source: Hercules, Inc.

woven fiberglass fabrics because of their interlacing have lower strengths than if all the glass strands were parallel (Table 12.3). If the roving is chopped, producing a random arrangement of glass fibers, the strength is lower for a specific direction but equal in all directions (Table 12.3).

Carbon-Fiber-Reinforced-Epoxy Resins In carbon-fiber composite materials, the fibers contribute the high tensile properties for rigidity and strength, while the matrix is the carrier for the alignment of the fibers and contributes some impact strength. Epoxy resins are by far the most commonly used matrixes for carbon fibers, but other resins such as polyimides, polyphenylene sulfides, or polysulfones may be used for certain applications.

The major advantage of carbon fibers is that they have very high strength and moduli of elasticity (Table 12.1) combined with low density. For this reason, carbon-fiber composites are replacing metals in some aerospace applications where weight saving is important (Fig. 12.1). Table 12.4 lists some typical mechanical properties of one type of carbon-fiber-epoxy composite material that contains 62 percent by volume of carbon fibers. Figure 12.10 shows the exceptional fatigue properties of unidirectional carbon (graphite)-epoxy composite material as compared to those of aluminum alloy 2024-T3.

In engineering-designed structures, the carbon-fiber-epoxy material is **laminated** so that different tailor-made strength requirements are met (Fig. 12.11). Figure 12.12 shows a photomicrograph of a five-layer bidirectional carbon-fiber-epoxy composite material after curing.

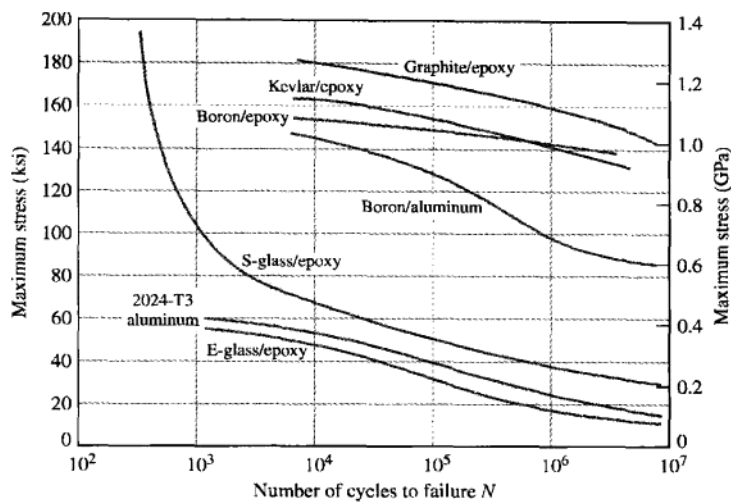


Figure 12.10
Fatigue properties (maximum stress versus number of cycles to failure) for carbon (graphite)–epoxy unidirectional composite material as compared to the fatigue properties of some other composite materials and aluminum alloy 2024-T3. R (the minimum stress–maximum stress for tension–tension cyclic test) = 0.1 at room temperature.
(Courtesy of Hercules, Inc.)

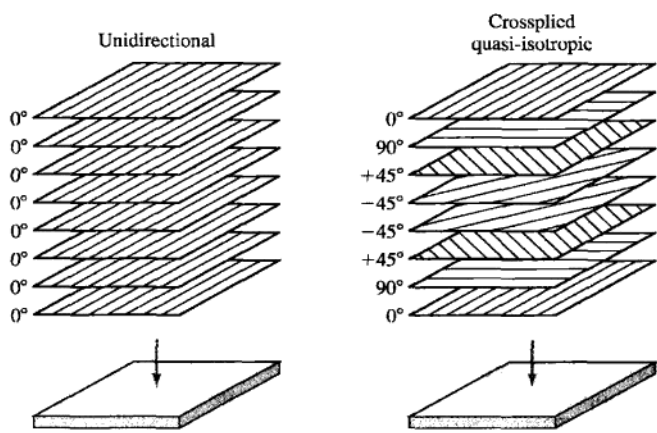
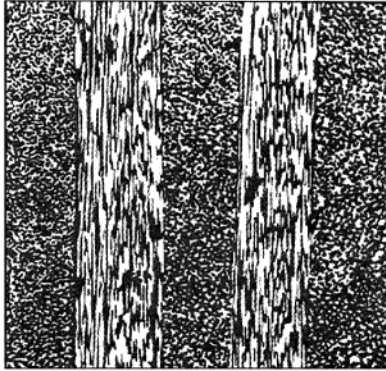


Figure 12.11
Unidirectional and multidirectional laminate plies for a composite laminate.
(Courtesy of Hercules, Inc.)

**Figure 12.12**

Photomicrograph of five-layer bidirectional carbon-fiber-epoxy composite material.

(After J.J. Dwyer, *Composites*, *Am. Mach.*, July 13, 1979, pp. 87–96.)

A unidirectional Kevlar 49 fiber-epoxy composite contains 60 percent by volume of Kevlar 49 fibers and 40 percent epoxy resin. The density of the Kevlar 49 fibers is 1.48 Mg/m^3 and that of the epoxy resin is 1.20 Mg/m^3 . (a) What are the weight percentages of Kevlar 49 and epoxy resin in the composite material, and (b) what is the average density of the composite?

**EXAMPLE
PROBLEM 12.1**
■ Solution

Basis is 1 m^3 of composite material. Therefore, we have 0.60 m^3 of Kevlar 49 and 0.40 m^3 of epoxy resin. Density = mass/volume, or

$$\rho = \frac{m}{V} \quad \text{and} \quad m = \rho V$$

- a. Mass of Kevlar 49 = $\rho V = (1.48 \text{ Mg/m}^3)(0.60 \text{ m}^3) = 0.888 \text{ Mg}$
 Mass of epoxy resin = $\rho V = (1.20 \text{ Mg/m}^3)(0.40 \text{ m}^3) = 0.480 \text{ Mg}$
 Total mass = 1.368 Mg

$$\text{Wt \% Kevlar 49} = \frac{0.888 \text{ Mg}}{1.368 \text{ Mg}} \times 100\% = 64.9\%$$

$$\text{Wt \% epoxy resin} = \frac{0.480 \text{ Mg}}{1.368 \text{ Mg}} \times 100\% = 35.1\%$$

- b. Average density of composite is

$$\rho_c = \frac{m}{V} = \frac{1.368 \text{ Mg}}{1 \text{ m}^3} = 1.37 \text{ Mg/m}^3 \quad \blacktriangleleft$$

12.3.3 Equations for Elastic Modulus of a Lamellar Continuous-Fiber-Plastic Matrix Composite for Isostrain and Isostress Conditions

Isostrain Conditions Let us consider an idealized lamellar composite test sample with alternate layers of continuous fibers and matrix materials, as shown in Fig. 12.13. In this case, the stress on the material causes uniform strain on all the composite layers. We shall assume that the bonding between the layers remains intact during the stressing. This type of loading on the composite sample is called the *isostrain condition*.

Let us now derive an equation relating the elastic modulus of the composite in terms of the elastic moduli of the fiber and matrix and their volume percentages. First, the load on the composite structure is equal to the sum of the load on the fiber layers plus the load on the matrix layers, or

$$P_c = P_f + P_m \tag{12.1}$$

Since $\sigma = P/A$, or $P = \sigma A$,

$$\sigma_c A_c = \sigma_f A_f + \sigma_m A_m \tag{12.2}$$

where σ_c , σ_f , and σ_m are the stresses and A_c , A_f , and A_m are the fractional areas of the composite, fiber, and matrix, respectively. Since the lengths of the layers of matrix and fiber are equal, the areas A_c , A_f , and A_m in Eq. 12.2 can be replaced by the volume fractions V_c , V_f , and V_m , respectively:

$$\sigma_c V_c = \sigma_f V_f + \sigma_m V_m \tag{12.3}$$

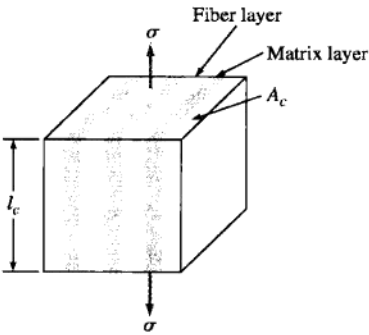


Figure 12.13
Composite structure consisting of layers of fiber and matrix under isostrain conditions of loading. (Volume of composite V_c = area A_c \times length l_c .)

Since the volume fraction of the total composite is 1, then $V_c = 1$, and Eq. 12.3 becomes

$$\sigma_c = \sigma_f V_f + \sigma_m V_m \quad (12.4)$$

For isostrain conditions and assuming a good bond between the composite layers,

$$\epsilon_c = \epsilon_f = \epsilon_m \quad (12.5)$$

Dividing Eq. 12.4 by Eq. 12.5, since all the strains are equal, gives

$$\frac{\sigma_c}{\epsilon_c} = \frac{\sigma_f V_f}{\epsilon_f} + \frac{\sigma_m V_m}{\epsilon_m} \quad (12.6)$$

Now we can substitute the modulus of elasticity E_c for σ_c/ϵ_c , E_f for σ_f/ϵ_f , and E_m for σ_m/ϵ_m , giving

$$E_c = E_f V_f + E_m V_m \quad (12.7)$$

This equation is known as the *rule of mixtures for binary composites* and enables a value for the elastic modulus of a composite to be calculated knowing the elastic moduli of the fiber and matrix and their volume percentages.

Equations for the Loads on the Fiber and Matrix Regions of a Lamellar Composite Structure Loaded Under Isostrain Conditions The ratio of the loads on the fiber and matrix regions of a binary composite material stressed under isostrain conditions can be obtained from their $P = \sigma A$ ratios. Thus, since $\sigma = E\epsilon$ and $\epsilon_f = \epsilon_m$,

$$\frac{P_f}{P_m} = \frac{\sigma_f A_f}{\sigma_m A_m} = \frac{E_f \epsilon_f A_f}{E_m \epsilon_m A_m} = \frac{E_f A_f}{E_m A_m} = \frac{E_f V_f}{E_m V_m} \quad (12.8)$$

If the total load on a specimen stressed under isostrain conditions is known, then the following equation applies:

$$P_c = P_f + P_m \quad (12.9)$$

where P_c , P_f , and P_m are the loads on the total composite, fiber region, and matrix region, respectively. By combining Eq. 12.9 with Eq. 12.8, the load on each of the fiber and matrix regions can be determined if values for E_f , E_m , V_f , V_m , and P_c are known.

Calculate (a) the modulus of elasticity, (b) the tensile strength, and (c) the fraction of the load carried by the fiber for the following composite material stressed under isostrain conditions. The composite consists of a continuous glass-fiber-reinforced-epoxy resin produced by using 60 percent by volume of E-glass fibers having a modulus of elasticity of $E_f = 10.5 \times 10^6$ psi and a tensile strength of 350,000 psi and a hardened epoxy resin with a modulus of $E_m = 0.45 \times 10^6$ and a tensile strength of 9000 psi.

EXAMPLE PROBLEM 12.2

■ **Solution**

a. Modulus of elasticity of the composite is

$$\begin{aligned} E_c &= E_f V_f + E_m V_m \\ &= (10.5 \times 10^6 \text{ psi})(0.60) + (0.45 \times 10^6 \text{ psi})(0.40) \\ &= 6.30 \times 10^6 \text{ psi} + 0.18 \times 10^6 \text{ psi} \\ &= 6.48 \times 10^6 \text{ psi (44.6 GPa)} \quad \blacktriangleleft \end{aligned} \tag{12.7}$$

b. Tensile strength of the composite is

$$\begin{aligned} \sigma_c &= \sigma_f V_f + \sigma_m V_m \\ &= (350,000 \text{ psi})(0.60) + (9000 \text{ psi})(0.40) \\ &= 210,000 + 3600 \text{ psi} \\ &= 214,000 \text{ psi or 214 ksi (1.47 GPa)} \quad \blacktriangleleft \end{aligned} \tag{12.4}$$

c. Fraction of load carried by fiber is

$$\begin{aligned} \frac{P_f}{P_c} &= \frac{E_f V_f}{E_f V_f + E_m V_m} \\ &= \frac{(10.5 \times 10^6 \text{ psi})(0.60)}{(10.5 \times 10^6 \text{ psi})(0.60) + (0.45 \times 10^6 \text{ psi})(0.40)} \\ &= \frac{6.30}{6.30 + 0.18} = 0.97 \quad \blacktriangleleft \end{aligned}$$

Isostress Conditions Let us now consider the case of an idealized lamellar composite structure consisting of layers of fiber and matrix in which the layers are perpendicular to the applied stress, as shown in Fig. 12.14. In this case, the stress on

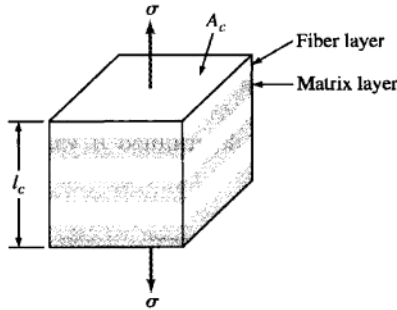


Figure 12.14

Composite structure consisting of layers of fiber and matrix under isostress conditions of loading. (Volume of composite $V_c = \text{area } A_c \times \text{length } l_c$.)

the composite structure produces an equal stress condition on all the layers and so is called the *isostress condition*.

To derive an equation for the elastic modulus for the layered composite for this type of loading, we shall begin with an equation that states that the stress on the total composite structure is equal to the stress on the fiber layers and the stress on the matrix layers. Thus,

$$\sigma_c = \sigma_f = \sigma_m \quad (12.10)$$

The total strain for the composite in the directions of the stresses is thus equal to the sum of the strains in the fiber and matrix layers,

$$\epsilon_c = \epsilon_f + \epsilon_m \quad (12.11)$$

Assuming that the area perpendicular to the stress does not change after the stress is applied and assuming unit length for the composite after being stressed, then

$$\epsilon_c = \epsilon_f V_f + \epsilon_m V_m \quad (12.12)$$

where V_f and V_m are the volume fractions of the fiber and matrix laminates, respectively.

Assuming Hooke's law is valid under loading, then

$$\epsilon_c = \frac{\sigma}{E_c} \quad \epsilon_f = \frac{\sigma}{E_f} \quad \epsilon_m = \frac{\sigma}{E_m} \quad (12.13)$$

Substituting the equations of Eq. 12.13 into Eq. 12.12 gives

$$\frac{\sigma}{E_c} = \frac{\sigma V_f}{E_f} = \frac{\sigma V_m}{E_m} \quad (12.14)$$

Dividing each term of Eq. 12.14 by σ gives

$$\frac{1}{E_c} = \frac{V_f}{E_f} + \frac{V_m}{E_m} \quad (12.15)$$

Obtaining a common denominator yields

$$\frac{1}{E_c} = \frac{V_f E_m}{E_f E_m} + \frac{V_m E_f}{E_m E_f} \quad (12.16)$$

Rearranging,

$$\frac{1}{E_c} = \frac{V_f E_m + V_m E_f}{E_f E_m}$$

or

$$E_c = \frac{E_f E_m}{V_f E_m + V_m E_f} \quad (12.17)$$

**EXAMPLE
PROBLEM 12.3**

Calculate the modulus of elasticity for a composite material consisting of 60 percent by volume of continuous E-glass fiber and 40 percent epoxy resin for the matrix when stressed under *isostress conditions* (i.e., the material is stressed perpendicular to the continuous fiber). The modulus of elasticity of the E glass is 10.5×10^6 psi and that of the epoxy resin is 0.45×10^6 psi.

■ Solution

$$\begin{aligned}
 E_c &= \frac{E_f E_m}{V_f E_m + V_m E_f} \\
 &= \frac{(10.5 \times 10^6 \text{ psi})(0.45 \times 10^6 \text{ psi})}{(0.60)(0.45 \times 10^6) + (0.40)(10.5 \times 10^6)} \\
 &= \frac{4.72 \times 10^{12} \text{ psi}^2}{0.27 \times 10^6 \text{ psi} + 4.20 \times 10^6 \text{ psi}} \\
 &= 1.06 \times 10^6 \text{ psi (7.30 GPa)} \quad \blacktriangleleft
 \end{aligned} \tag{12.17}$$

Note that the isostress condition of stressing the composite material results in a modulus of elasticity for the 60 percent E-glass fiber–40 percent epoxy composite material that is about six times lower than that obtained by stressing under the isostrain condition.

A schematic representation comparing isostrain loading to isostress loading of a composite layered structure (Fig. 12.15) shows that higher-modulus values are obtained with isostrain loading for equal volumes of fibers.

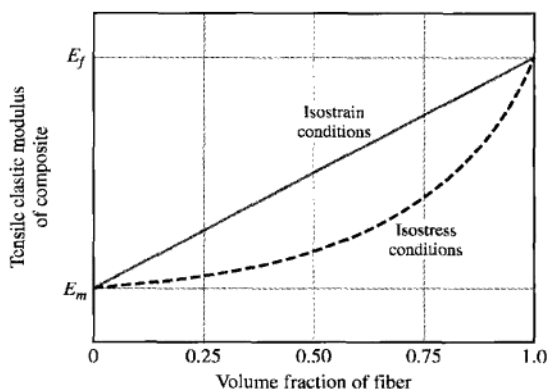


Figure 12.15

Schematic representation of the tensile elastic modulus as a function of the volume fraction of fiber in a reinforced-fiber–plastic matrix unidirectional composite laminate loaded under isostrain and isostress conditions. For a given volume fraction of fiber in the composite, the material loaded under isostrain conditions has a higher modulus.

12.4 OPEN-MOLD PROCESSES FOR FIBER-REINFORCED-PLASTIC COMPOSITE MATERIALS

There are many open-mold methods used for producing fiber-reinforced plastics. Some of the most important of these will now be discussed briefly.

12.4.1 Hand Lay-Up Process

This is the simplest method of producing a fiber-reinforced part. To produce a part with the **hand lay-up** process by using fiberglass and a polyester, a gel coat is first applied to the open mold (Fig. 12.16). Fiberglass reinforcement that is normally in the form of a cloth or mat is manually placed in the mold. The base resin mixed with catalysts and accelerators is then applied by pouring, brushing, or spraying. Rollers or squeegees are used to thoroughly wet the reinforcement with the resin and to remove entrapped air. To increase the wall thickness of the part being produced, layers of fiberglass mat or woven roving and resin are added. Applications for this method include boat hulls, tanks, housings, and building panels.

12.4.2 Spray Lay-Up Process

The **spray lay-up method** of producing fiber-reinforced-plastic shells is similar to the hand lay-up method and can be used to make boat hulls, tub-shower units, and

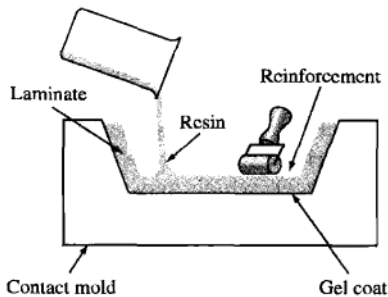
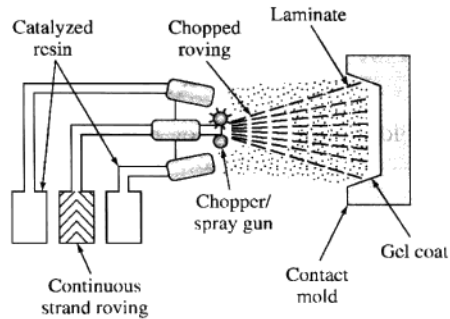


Figure 12.16

Hand lay-up method for molding fiber-reinforced-plastic composite materials. Pouring the resin over the reinforcement in the mold.

(Courtesy of Owens/Corning Fiberglass Co.)

**Figure 12.17**

Spray lay-up method for molding fiber-reinforced-plastic composite materials; advantages of this method include greater shape complexity for the molded part and an ability to automate the process.

(Courtesy of Owens Corning.)

other medium- to large-size shapes. In this process, if fiberglass is used, continuous-strand roving is fed through a combination chopper and spray gun (Fig. 12.17) that simultaneously deposits chopped roving and catalyzed resin into the mold. The deposited laminate is then densified with a roller or squeegee to remove air and to make sure the resin impregnates the reinforcing fibers. Multiple layers may be added to produce the desired thickness. Curing is usually at room temperature, or it may be accelerated by the application of a moderate amount of heat.

12.4.3 Vacuum Bag–Autoclave Process

The **vacuum bag molding** process is used to produce high-performance laminates usually of fiber-reinforced-epoxy systems. Composite materials produced by this method are particularly important for aircraft and aerospace applications.

We shall now look at the various steps of this process required to produce a finished part. First, a long, thin sheet, which may be about 60 in. (152 cm) wide, of **prepreg** carbon-fiber-epoxy material is laid out on a large table (Fig. 12.18). The prepreg material consists of unidirectional long carbon fibers in a partially cured epoxy matrix. Next, pieces of the prepreg sheet are cut out and placed on top of each other on a shaped tool to form a laminate. The layers, or *plies* as they are called, may be placed in different directions to produce the desired strength pattern since the highest strength of each ply is in the direction parallel to the fibers (Fig. 12.11).

After the laminate is constructed, the tooling and attached laminate are vacuum-bagged, with a vacuum being applied to remove entrapped air from the laminated part. Finally, the vacuum bag enclosing the laminate and the tooling is put into an

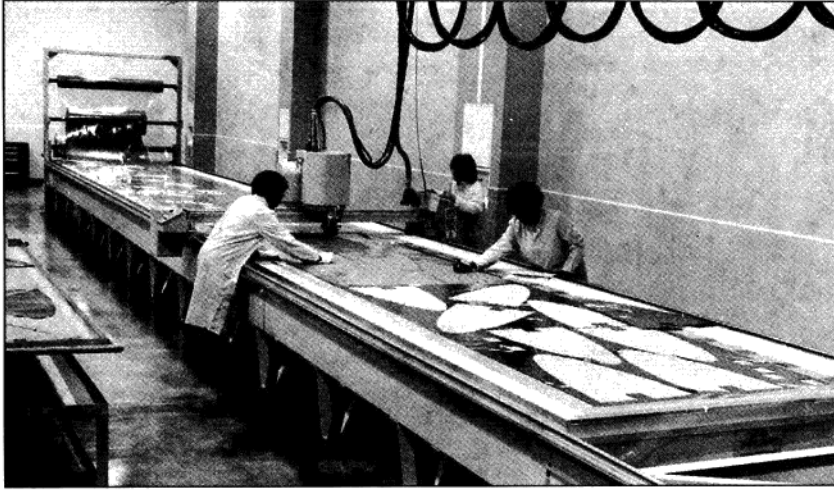


Figure 12.18

Carbon-fiber-epoxy prepreg sheet being cut with computerized cutter at McDonnell Douglas composite facility.

(Courtesy of McDonnell Douglas Corp.)

autoclave for the final curing of the epoxy resin (Fig. 12.19). The conditions for curing vary depending on the material, but the carbon-fiber-epoxy composite material is usually heated at about 190°C (375°F) at a pressure of about 100 psi. After being removed from the autoclave, the composite part is stripped from its tooling and is ready for further finishing operations.

Carbon-fiber-epoxy composite materials are used mainly in the aerospace industry where the high strength, stiffness, and lightness of the material can be fully utilized. For example, this material is used for airplane wings, elevator and rudder parts, and the cargo bay doors of the space shuttle. Cost considerations have prevented the widespread use of this material in the auto industry.

12.4.4 Filament-Winding Process

Another important open-mold process to produce high-strength hollow cylinders is the **filament-winding** process. In this process, the fiber reinforcement is fed through a resin bath and then wound on a suitable mandrel (Fig. 12.20). When sufficient layers have been applied, the wound mandrel is cured either at room temperature or at an elevated temperature in an oven. The molded part is then stripped from the mandrel.

The high degree of fiber orientation and high fiber loading with this method produce extremely high tensile strengths in hollow cylinders. Applications for this process include chemical and fuel storage tanks, pressure vessels, and rocket motor cases.

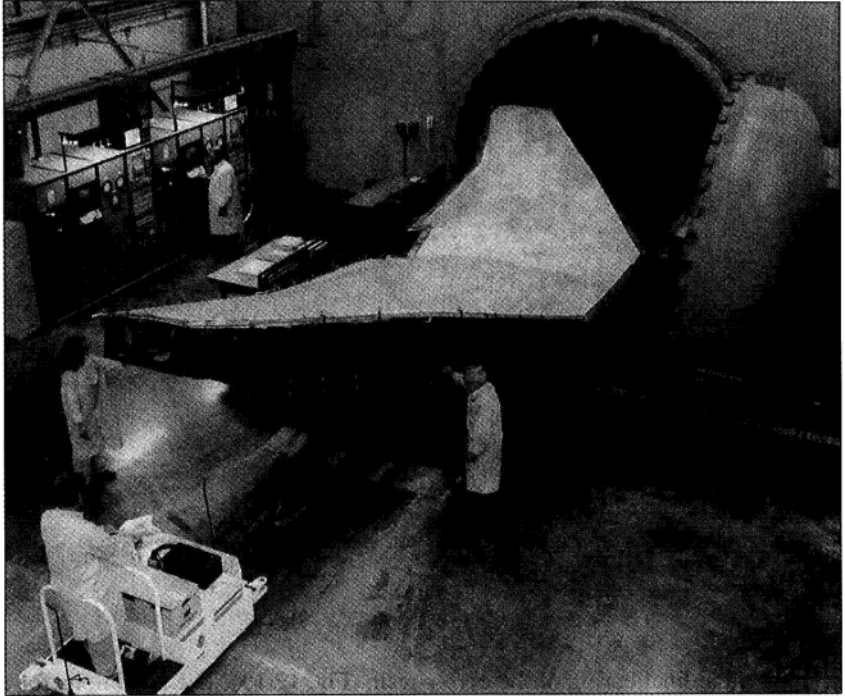


Figure 12.19

Carbon-fiber-epoxy laminate of AV-8B wing section and tooling being put into autoclave for curing at McDonnell Aircraft Co. plant.

(Courtesy of McDonnell Douglas Corp.)

12.5 CLOSED-MOLD PROCESSES FOR FIBER-REINFORCED-PLASTIC COMPOSITE MATERIALS

There are many closed-mold methods used for producing fiber-reinforced-plastic materials. Some of the most important of these will now be discussed briefly.

12.5.1 Compression and Injection Molding

These are two of the most important high-volume processes used for producing fiber-reinforced plastics with closed molds. These processes are essentially the same as those discussed in Sec. 10.5 for plastic materials except that the fiber reinforcement is mixed with the resin before processing.

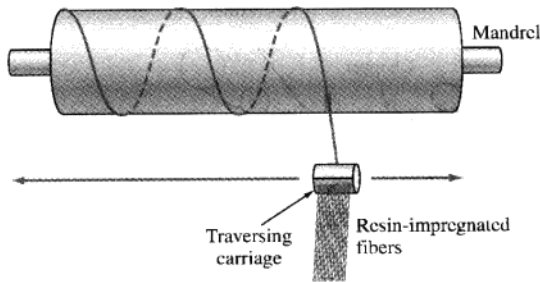


Figure 12.20

Filament-winding process for producing fiber-reinforced-plastic composite materials. The fibers are first impregnated with plastic resin and then wound around a rotating mandrel (drum). The carriage containing the resin-impregnated fibers traverses during the winding, laying down the impregnated fibers.

(From H.G. De Young, "Plastic Composites Fight for Status," *High Technol*, October 1983, p. 63.)

12.5.2 The Sheet-Molding Compound (SMC) Process

The **sheet-molding compound** process is one of the newer closed-mold processes used to produce fiber-reinforced-plastic parts, particularly in the automotive industry. This process allows excellent resin control and good mechanical strength properties (Table 12.3) to be obtained while producing high-volume, large-size, highly uniform products.

The sheet-molding compound is usually manufactured by a highly automated continuous-flow process. Continuous-strand fiberglass roving is chopped in lengths of about 2 in. (5.0 cm) and deposited on a layer of resin-filler paste that is traveling on a polyethylene film (Fig. 12.21). Another layer of resin-filler paste is deposited later over the first layer to form a continuous sandwich of fiberglass and resin filler. The sandwich with top and bottom covers of polyethylene is compacted and rolled into package-sized rolls (Fig. 12.21).

The rolled-up SMC is next stored in a maturation room for about one to four days so that the sheet can carry the glass. The SMC rolls are then moved to near the press and cut into the proper charge pattern for the specific part and placed in a matched metal mold that is hot (300°F [149°C]). The hydraulic press then is closed, and the SMC flows uniformly under pressure (1000 psi) throughout the mold to form the final product. Sometimes an in-mold coating may be injected in the middle of the pressing operation to improve the surface quality of the SMC part.

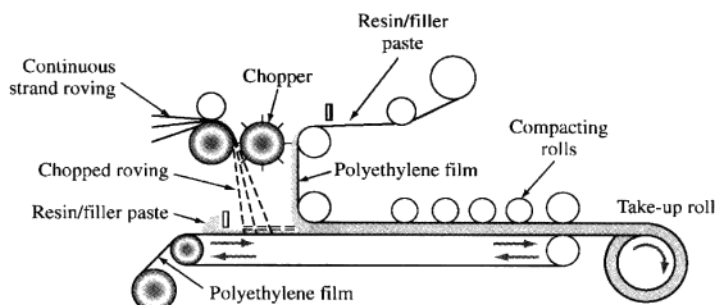


Figure 12.21

Manufacturing process for sheet-molding compound. The machine shown produces a sandwich of fiberglass and resin-filler paste between two thin-film sheets of polyethylene. The sheet-molding compound produced must be aged before being pressed into a finished product.

(Courtesy of Owens Corning.)

The advantages of the SMC process over the hand lay-up or spray lay-up processes are more-efficient high-volume production, improved surface quality, and uniformity of product. The use of SMC is particularly advantageous in the automotive industry for the production of front-end and grille-opening panels, body panels, and hoods. For example, the front hood of the 1984 Chevrolet Corvette was made of SMC. This clamshell hood was made by adhesively bonding a 0.080-in. (0.20-cm) inner panel to an outer mold-coated 0.10-in. (0.25-cm) panel.

12.5.3 Continuous-Pultrusion Process

Continuous **pultrusion** is used for the manufacturing of fiber-reinforced plastics of constant cross section such as structural shapes, beams, channels, pipe, and tubing. In this process, continuous-strand fibers are impregnated in a resin bath and then are drawn through a heated steel die that determines the shape of the finished stock (Fig. 12.22). Very high strengths are possible with this material because of the high fiber concentration and orientation parallel to the length of the stock being drawn.

12.6 METAL-MATRIX AND CERAMIC-MATRIX COMPOSITES

12.6.1 Metal-Matrix Composites (MMCs)

Metal-matrix composite materials have been so intensely researched over the past years that many new high-strength-to-weight materials have been produced. Most of these materials have been developed for the aerospace industries, but some are being used in other applications such as automobile engines. In general, according to rein-

forcement, the three main types of MMCs are continuous-fiber, discontinuous-fiber, and particulate reinforced.

Continuous-Fiber-Reinforced MMCs Continuous filaments provide the greatest improvement in stiffness (tensile modulus) and strength for MMCs. One of the first developed continuous-fiber MMCs was the aluminum alloy matrix–boron fiber

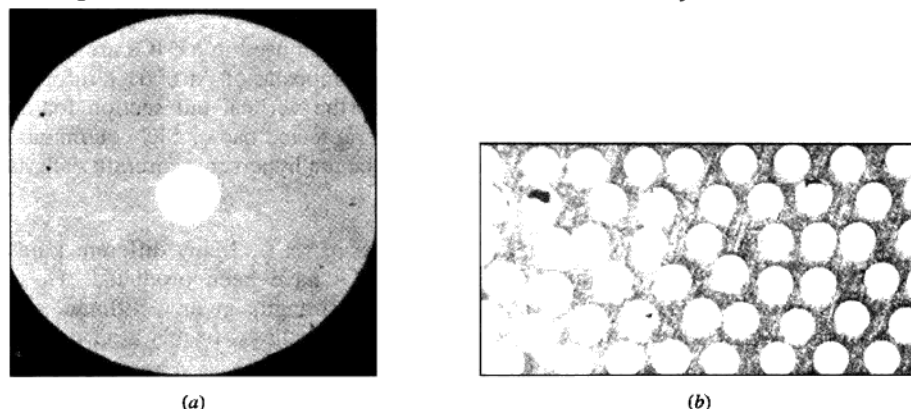


Figure 12.22

(a) 100- μm -diameter boron filament surrounding a 12.5- μm diameter tungsten-wire core. (b) Micrograph of a cross section of an aluminum alloy–boron composite (magnification 40 \times).

(After "Engineered Materials Handbook" vol. 1, ASM International, 1987, p. 852. Reprinted with permission of ASM International. All rights reserved. www.asminternational.org.)

Table 12.5 Mechanical properties of metal-matrix composite materials

	Tensile strength		Elastic modulus		Strain to failure (%)
	MPa	ksi	GPa	Msi	
Continuous-fiber MMCs:					
Al 2024-T6 (45% B) (axial)	1458	211	220	32	0.810
Al 6061-T6 (51% B) (axial)	1417	205	231	33.6	0.735
Al 6061-T6 (47% SiC) (axial)	1462	212	204	29.6	0.89
Discontinuous-fiber MMCs:					
Al 2124-T6 (20% SiC)	650	94	127	18.4	2.4
Al 6061-T6 (20% SiC)	480	70	115	17.7	5
Particulate MMCs:					
Al 2124 (20% SiC)	552	80	103	15	7.0
Al 6061 (20% SiC)	496	72	103	15	5.5
No reinforcement:					
Al 2124-F	455	66	71	10.3	9
Al 6061-F	310	45	68.9	10	12

reinforced system. The boron fiber for this composite is made by chemically vapor depositing boron on a tungsten-wire substrate (Fig. 12.22a). The Al-B composite is made by hot pressing layers of B fibers between aluminum foils so that the foils

deform around the fibers and bond to each other. Figure 12.22*b* shows a cross section of a continuous-B-fiber–aluminum alloy matrix composite. Table 12.5 lists some mechanical properties for some B fiber-reinforced–aluminum alloy composites. With the addition of 51 vol % B, the axial tensile strength of aluminum alloy 6061 was increased from 310 to 1417 MPa, while its tensile modulus was increased from 69 to 231 GPa. Applications for Al-B composites include some of the structural members in the midfuselage of the space shuttle orbiter.

Other continuous-fiber reinforcements that have been used in MMCs are silicon carbide, graphite, alumina, and tungsten fibers. A composite of Al 6061 reinforced with SiC continuous fibers is being evaluated for the vertical tail section for an advanced fighter aircraft. Of special interest is the projected use of SiC continuous-fiber reinforcements in a titanium aluminide matrix for hypersonic aircraft such as the National Aerospace plane (Fig. 1.1).

Discontinuous-Fiber- and Particulate-Reinforced MMCs Many different kinds of discontinuous and particulate reinforced MMCs have been produced. These materials have the engineering advantage of higher strength, greater stiffness, and better dimensional stability than the unreinforced metal alloys. In this brief discussion of MMCs, we will focus on aluminum alloy MMCs.

Particulate-reinforced MMCs are low-cost aluminum alloy MMCs made by using irregular-shaped particles of alumina and silicon carbide in the range of about 3 to 200 μm in diameter. The particulate, which is sometimes given a proprietary coating, can be mixed with the molten aluminum alloy and cast into remelt ingots or extrusion billets for further fabrication. Table 12.5 indicates that the ultimate tensile strength of Al alloy 6061 can be increased from 310 to 496 MPa with a 20 percent SiC addition, while the tensile modulus can be increased from 69 to 103 GPa. Applications for this material include sporting equipment and automobile engine parts.

Discontinuous-fiber-reinforced MMCs are produced mainly by powder metallurgy and melt infiltration processes. In the powder metallurgy process, needlelike silicon carbide whiskers about 1 to 3 μm in diameter and 50 to 200 μm long (Fig. 12.23) are mixed with metal powders, consolidated by hot pressing, and then extruded or forged into the desired shape. Table 12.5 shows that the ultimate tensile strength of Al alloy 6061 can be increased from 310 to 480 MPa with a 20 percent SiC whisker addition, while the tensile modulus can be raised from 69 to 115 GPa. Although greater increases in strength and stiffness can be achieved with the whisker additions than with the particulate material, the powder metallurgy and melt infiltration processes are more costly. Applications for discontinuous-fiber-reinforced aluminum alloy MMCs include missile guidance parts and high-performance automobile pistons.

12.6.2 Ceramic-Matrix Composites (CMCs)

Ceramic-matrix composites have been developed recently with improved mechanical properties such as strength and toughness over the unreinforced ceramic matrix. Again, the three main types according to reinforcement are continuous-fiber, discontinuous-fiber, and particulate reinforced.

Continuous-Fiber-Reinforced CMCs Two kinds of continuous fibers that have been used for CMCs are silicon carbide and aluminum oxide. In one process to make a ceramic-matrix composite, SiC fibers are woven into a mat and then chemical vapor

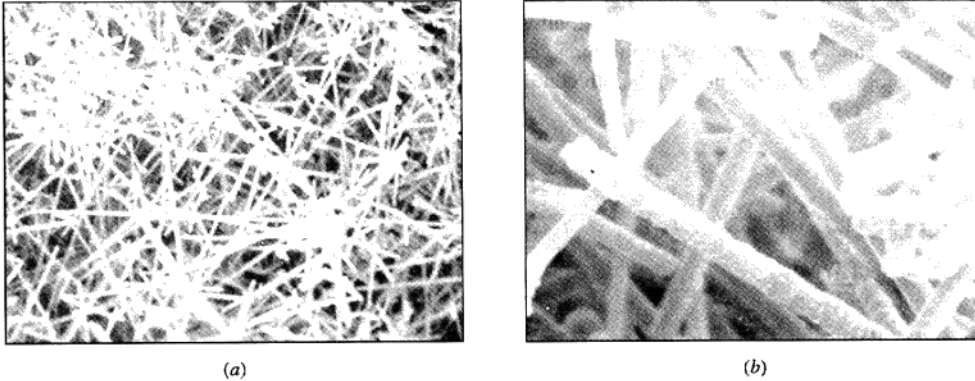


Figure 12.23

Micrographs of single-crystal silicon carbide whiskers used to reinforce metal-matrix composites. The whiskers are 1 to 3 μm in diameter and 50 to 200 μm long.

(Courtesy of American Matrix Corp.)

deposition is used to impregnate SiC into the fibrous mat. In another process, SiC fibers are encapsulated by a glass-ceramic material (see Example Problem 12.8). Applications for these materials include heat-exchanger tubes, thermal protection systems, and materials for corrosion-erosion environments.

Discontinuous (Whisker)- and Particulate-Reinforced CMCs Ceramic whiskers (Fig. 12.23) can significantly increase the fracture toughness of monolithic ceramics (Table 12.6). A 20 vol % SiC whisker addition to alumina can increase the fracture toughness of the alumina ceramic from about 4.5 to 8.5 $\text{MPa}\sqrt{\text{m}}$. Short-fiber and particulate reinforced ceramic-matrix materials have the advantage of being able to be fabricated by common ceramic processes such as hot isostatic pressing (HIPing).

Table 12.6 Mechanical properties of SiC whisker reinforced ceramic-matrix composites at room temperature

Matrix	SiC whisker content (vol %)	Flexural strength		Fracture toughness	
		MPa	ksi	$\text{MPa}\sqrt{\text{m}}$	$\text{ksi}\sqrt{\text{in.}}$
Si_3N_4	0	400–650	60–95	5–7	4.6–6.4
	10	400–500	60–75	6.5–9.5	5.9–8.6
	30	350–450	50–65	7.5–10	6.8–9.1
Al_2O_3	0	4.5	4.1
	10	400–510	57–73	7.1	6.5
	20	520–790	75–115	7.5–9.0	6.8–8.2

Source: "Engineered Materials Handbook," vol. 1, Composites, ASM International, 1987, p. 942.

**EXAMPLE
PROBLEM 12.4**

A metal-matrix composite is made from a boron (B) fiber-reinforced aluminum alloy (Fig. EP12.6). To form the boron fiber, a tungsten (W) wire ($r = 10 \mu\text{m}$) is coated with boron, giving a final radius of $75 \mu\text{m}$. The aluminum alloy is then bonded around the boron fibers, giving a volume fraction of 0.65 for the aluminum alloy. Assuming that the rule of binary mixtures (Eq. 12.7) applies also to ternary mixtures, calculate the effective tensile elastic modulus of the composite material under isostrain conditions. Data: $E_W = 410 \text{ GPa}$; $E_B = 379 \text{ GPa}$; $E_{Al} = 68.9 \text{ GPa}$.

■ Solution

$$E_{\text{comp}} = f_W E_W + f_B E_B + f_{Al} E_{Al} \quad f_{W+B} = 0.35$$

$$f_W = \frac{\text{area of W wire}}{\text{area of B fiber}} \times f_{W+B}$$

$$f_W = \frac{\pi (10 \mu\text{m})^2}{\pi (75 \mu\text{m})^2} \times 0.35 = 6.22 \times 10^{-3} \quad f_{Al} = 0.65$$

$$f_B = \frac{\text{area of B fiber} - \text{area of W wire}}{\text{area of B fiber}} \times f_{W+B}$$

$$= \frac{\pi (75 \mu\text{m})^2 - \pi (10 \mu\text{m})^2}{\pi (75 \mu\text{m})^2} \times 0.35 = 0.344$$

$$E_{\text{comp}} = f_W E_W + f_B E_B + f_{Al} E_{Al}$$

$$= (6.22 \times 10^{-3})(410 \text{ GPa}) + (0.344)(379 \text{ GPa}) + (0.65)(68.9 \text{ GPa})$$

$$= 178 \text{ GPa} \blacktriangleleft$$

Note that the tensile modulus (stiffness) of the composite is about 2.5 times that of the unreinforced aluminum alloy.

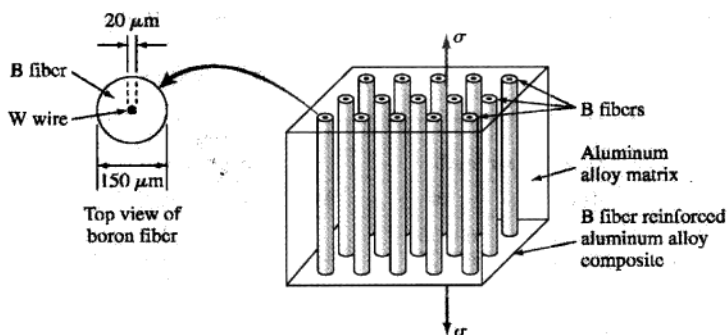


Figure EP12.4

**EXAMPLE
PROBLEM 12.5**

A metal-matrix composite is made with 80 percent by volume of aluminum alloy 2124-T6 and 20 percent by volume of SiC whiskers. The density of the 2124-T6 alloy is 2.77 g/cm^3 and that of the whiskers is 3.10 g/cm^3 . Calculate the average density of the composite material.

■ Solution

Basis is 1 m^3 of material; thus, we have 0.80 m^3 of 2124 alloy and 0.20 m^3 of SiC fiber in 1 m^3 of material.

$$\text{Mass of 2124 alloy in } 1 \text{ m}^3 = (0.80 \text{ m}^3)(2.77 \text{ Mg/m}^3) = 2.22 \text{ Mg}$$

$$\text{Mass of SiC whiskers in } 1 \text{ m}^3 = (0.20 \text{ m}^3)(3.10 \text{ Mg/m}^3) = 0.62 \text{ Mg}$$

$$\text{Total mass in } 1 \text{ m}^3 \text{ of composite} = 2.84 \text{ Mg}$$

$$\text{Ave. density} = \frac{\text{mass}}{\text{unit volume}} = \frac{\text{total mass of material in } 1 \text{ m}^3}{1 \text{ m}^3} = 2.84 \text{ Mg/m}^3 \blacktriangleleft$$

Ceramic-matrix composites are believed to be toughened by three main mechanisms, all of which result from the reinforcing fibers interfering with crack propagation in the ceramic. These mechanisms are:

1. *Crack deflection.* Upon encountering the reinforcement, the crack is deflected, making its propagating path more meandering. Thus, higher stresses are required to propagate the crack.
2. *Crack bridging.* Fibers or whiskers can bridge the crack and help keep the material together, thus increasing the stress level needed to cause further cracking (Fig. 12.24).
3. *Fiber pullout.* The friction caused by fibers or whiskers being pulled out of the cracking matrix absorbs energy, and thus higher stresses must be applied to produce further cracking. Therefore, a good interfacial bond is required between the fibers and the matrix for higher strengths. There also should be a good match of coefficient of expansion between the matrix and fibers if the material is to be used at high temperatures.

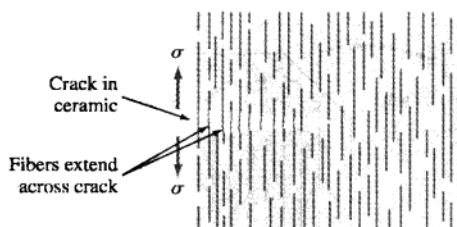


Figure 12.24

Schematic diagram showing how reinforcing fibers can inhibit crack propagation in ceramic-matrix materials by crack bridging and fiber pullout energy absorption.

EXAMPLE
PROBLEM 12.6

A ceramic-matrix composite is made with continuous SiC fibers embedded in a glass-ceramic matrix (Fig. EP12.6). (a) Calculate the tensile elastic modulus of the composite under isostrain conditions, and (b) calculate the stress σ at which the cracks start to grow. Data are as follows:

Glass-ceramic matrix:

$$E = 94 \text{ GPa}$$
$$K_{IC} = 2.4 \text{ MPa } \sqrt{\text{m}}$$

Largest preexisting flaw is $10 \mu\text{m}$
in diameter

SiC fibers:

$$E = 350 \text{ GPa}$$
$$K_{IC} = 4.8 \text{ MPa } \sqrt{\text{m}}$$

Largest surface notches are $5 \mu\text{m}$
deep

■ Solution

a. Calculation of E for the composite. Assuming Eq. 12.5 for isostrain conditions is valid,

$$E_{\text{comp}} = f_{GC}E_{GC} + f_{SiC}E_{SiC}$$

Since the length of the fibers is the same, we can calculate the volume fraction of the SiC fibers by calculating the area fraction occupied by the fibers on the surface at the ends of the fibers. From Fig. EP12.8, each $50\text{-}\mu\text{m}$ -diameter fiber is enclosed by an $80 \mu\text{m} \times 80 \mu\text{m}$ area. Thus,

$$f_{SiC} = \frac{\text{area of fiber}}{\text{selected tot. area}} = \frac{\pi (25 \mu\text{m})^2}{(80 \mu\text{m})(80 \mu\text{m})} = 0.307$$

$$f_{GC} = 1 - 0.307 = 0.693$$

$$E_{\text{comp}} = (0.693)(94 \text{ GPa}) + (0.307)(350 \text{ GPa}) = 172 \text{ GPa} \blacktriangleleft$$

b. Stress at which cracks first start to form in the composite. For isostrain conditions,

$\epsilon_{\text{comp}} = \epsilon_{GC} = \epsilon_{SiC}$. Since $\sigma = E\epsilon$ and $\epsilon = \sigma/E$,

$$\frac{\sigma_{\text{comp}}}{E_{\text{comp}}} = \frac{\sigma_{GC}}{E_{GC}} = \frac{\sigma_{SiC}}{E_{SiC}}$$

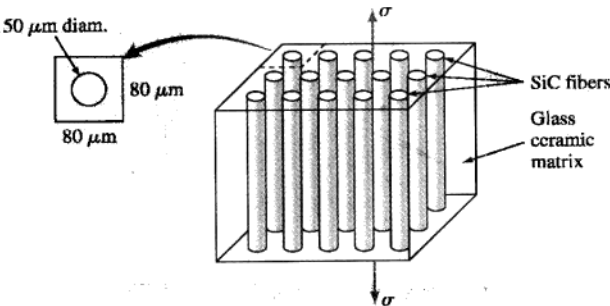


Figure EP12.6

Fracture begins in a given component when $\sigma = K_{IC}/\sqrt{\pi a}$ (Eq. 11.1), assuming $Y = 1$. We shall calculate the minimum stress to cause crack formation in both materials and then compare our results. The component that cracks with the lower stress will determine at what stress the composite will begin to crack.

- (i) Glass ceramic. For this material, the largest preexisting flaw is $10\ \mu\text{m}$ in diameter.

This value is $2a$ for Eq. 11.1, and thus $a = 10\ \mu\text{m}/2$ or $a = 5\ \mu\text{m}$.

$$\frac{\sigma_{\text{comp}}}{E_{\text{comp}}} = \frac{\sigma_{GC}}{E_{GC}} = \left(\frac{K_{IC,GC}}{\sqrt{\pi a}} \right) \left(\frac{1}{E_{GC}} \right)$$

$$\sigma_{\text{comp}} = \left(\frac{E_{\text{comp}}}{E_{GC}} \right) \left(\frac{K_{IC,GC}}{\sqrt{\pi a}} \right) = \left(\frac{172\ \text{GPa}}{94\ \text{GPa}} \right) \left[\frac{2.4\ \text{MPa}\sqrt{\text{m}}}{\sqrt{\pi(5 \times 10^{-6}\ \text{m})}} \right] = 1109\ \text{MPa}$$

- (ii) SiC fibers. For this material, $a = 5\ \mu\text{m}$ for surface cracks.

$$\sigma_{\text{comp}} = \left(\frac{E_{\text{comp}}}{E_{\text{SiC}}} \right) \left(\frac{K_{IC,\text{SiC}}}{\sqrt{\pi a}} \right) = \left(\frac{172\ \text{GPa}}{350\ \text{GPa}} \right) \left[\frac{4.8\ \text{MPa}\sqrt{\text{m}}}{\sqrt{\pi(5 \times 10^{-6}\ \text{m})}} \right] = 596\ \text{MPa}$$

Thus, the SiC fibers in the ceramic composite will begin to crack first at an applied stress of 596 MPa. ◀

12.6.3 Ceramic Composites and Nanotechnology

Recently, nanotechnology researchers have developed ceramics matrix composites with improved mechanical, chemical, and electrical properties by integrating carbon nanotubes in the microstructure of conventional alumina. This is an exciting new development that further increases the importance of nanotechnology in materials science. Researchers have been able to create a ceramic composite made of alumina, 5 to 10 percent carbon nanotubes, and 5 percent finely milled niobium. The compact was sintered and densified to produce a solid that possesses a fracture toughness up to five times greater than pure alumina. The new material is also able to conduct electricity at a rate ten trillion times higher than pure alumina. Finally, it can either conduct heat (if the nanotubes are aligned parallel to the direction of heat flow) or act as a thermal protection barrier (if the nanotubes are aligned perpendicular to the direction of heat flow). This makes the new ceramic an outstanding candidate for thermal protection-coating applications.

12.7 SUMMARY

A composite material with respect to materials science and engineering can be defined as a materials system composed of a mixture or combination of two or more micro- or macro-constituents that differ in form and chemical composition and are essentially insoluble in each other.

Some fiber-reinforced-plastic composite materials are made with synthetic fibers of glass, carbon, and aramid. Of these three fibers, glass fibers are the lowest in cost and

have intermediate strength and highest density when compared to the others. Carbon fibers have high strength, high modulus, and low density but are expensive and so are used only for applications requiring their especially high strength-to-weight ratio. Aramid fibers have high strength and low density but are not as stiff as carbon fibers. Aramid fibers are also relatively expensive and so are used for applications where a high strength-to-weight ratio is required along with better flexibility than carbon fibers. The most commonly used matrices for glass fibers for fiber-reinforced-plastic composites are the polyesters, whereas the most commonly used matrices for carbon-fiber-reinforced plastics are the epoxies. Carbon-fiber-reinforced-epoxy composite materials are used extensively for aircraft and aerospace applications. Glass-fiber-reinforced-polyester composite materials have a much wider usage and find application in the building, transportation, marine, and aircraft industries, for example.

Concrete is a ceramic composite material consisting of aggregate particles (i.e., sand and gravel) in a hardened cement paste matrix usually made with portland cement. Concrete as a construction material has advantages that include usable compressive strength, economy, castability on the job, durability, fire resistance, and aesthetic appearance. The low tensile strength of concrete can be increased significantly by reinforcement with steel rods. A further improvement in the tensile strength of concrete is attainable by introducing residual compressive stresses in the concrete at positions of high tensile loading by prestressing with steel reinforcements.

Wood is a natural composite material consisting essentially of cellulose fibers bonded together by a matrix of polymeric material made up mainly of lignin. The macrostructure of wood consists of sapwood, which is made up primarily of living cells and which carries the nutrients, and heartwood, which is composed of dead cells. The two main types of woods are softwoods and hardwoods. Softwoods have exposed seeds and narrow (needlelike) leaves, whereas hardwoods have covered seeds and broad leaves. The microstructure of wood consists of arrays of cells mainly in the longitudinal direction of the tree stem. Softwoods have long, thin-walled tubular cells called *tracheids*, whereas hardwoods have a dense cell structure that contains large vessels for the conduction of fluids. Wood as a construction material has advantages that include usable strength, economy, ease of workability, and durability if properly protected.

12.8 DEFINITIONS

Sec. 12.1

Composite material: a materials system composed of a mixture or combination of two or more micro- or macroconstituents that differ in form and chemical composition and are essentially insoluble in each other.

Sec. 12.2

Fiber-reinforced plastics: composite materials consisting of a mixture of a matrix of a plastic material such as a polyester or epoxy strengthened by fibers of high strength such as glass, carbon, or aramid. The fibers provide the high strength and stiffness, and the plastic matrix bonds the fibers together and supports them.

E-glass fibers: fibers made from E (electrical) glass, which is a borosilicate glass and which is the most commonly used glass for fibers for fiberglass-reinforced plastics.

S-glass fibers: fibers made from S glass, which is a magnesia-alumina-silicate glass and which is used for fibers for fiberglass-reinforced plastics when extra-high-strength fibers are required.

Roving: a collection of bundles of continuous fibers twisted or untwisted.

Carbon fibers (for a composite material): carbon fibers produced mainly from polyacrylonitrile (PAN) or pitch that are stretched to align the fibrillar network structure within each carbon fiber and which are heated to remove oxygen, nitrogen, and hydrogen from the starting or precursor fibers.

Tow (of fibers): a collection of numerous fibers in a straight-laid bundle, specified according to the number of fibers it contains—e.g., 6000 fibers/tow.

Aramid fibers: fibers produced by chemical synthesis and used for fiber-reinforced plastics. Aramid fibers have an aromatic (benzene ring type) polyamide linear structure and are produced commercially by the Du Pont Co. under the trade name of Kevlar.

Specific tensile strength: the tensile strength of a material divided by its density.

Specific tensile modulus: the tensile modulus of a material divided by its density.

Sec. 12.3

Laminate: a product made by bonding sheets of a material together, usually with heat and pressure.

Unidirectional laminate: a fiber-reinforced–plastic laminate produced by bonding together layers of fiber-reinforced sheets that all have continuous fibers in the same direction in the laminate.

Multidirectional laminate: a fiber-reinforced–plastic laminate produced by bonding together layers of fiber-reinforced sheets with some of the directions of the continuous fibers of the sheets being at different angles.

Laminate ply (lamina): one layer of a multilayer laminate.

Sec. 12.4

Hand lay-up: the process of placing (and working) successive layers of reinforcing material in a mold by hand to produce a fiber-reinforced composite material.

Spray lay-up: a process in which a spray gun is used to produce a fiber-reinforced product. In one type of spray-up process, chopped fibers are mixed with plastic resin and sprayed into a mold to form a composite material part.

Vacuum bag molding: a process of molding a fiber-reinforced–plastic part in which sheets of transparent flexible material are placed over a laminated part that has not been cured. The sheets and the part are sealed, and a vacuum is then applied between the cover sheets and the laminated part so that entrapped air is mechanically worked out of the laminate. Then the vacuum-bagged part is cured.

Prepreg: a ready-to-mold plastic resin-impregnated cloth or mat that may contain reinforcing fibers. The resin is partially cured to a “B” stage and is supplied to a fabricator who uses the material as the layers for a laminated product. After the layers are laid up to produce a final shape, the layers are bonded together, usually with heat and pressure, by the curing of the laminate.

Filament winding: a process for producing fiber-reinforced plastics by winding continuous reinforcement previously impregnated with a plastic resin on a rotating mandrel. When a sufficient number of layers have been applied, the wound form is cured and the mandrel removed.

Sec. 12.5

Sheet-molding compound (SMC): a compound of plastic resin, filler, and reinforcing fiber used to make fiber-reinforced–plastic composite materials. SMC is usually made with about 25 to 30 percent fibers about 1 in. (2.54 cm) long, of which fiberglass is the most commonly used fiber. SMC material is usually preaged to a state so that it can support itself and then cut to size and placed in a compression mold. Upon hot pressing, the SMC cures to produce a rigid part.

Pultrusion: a process for producing a fiber-reinforced-plastic part of constant cross section continuously. The pultruded part is made by drawing a collection of resin-dipped fibers through a heated die.

12.9 PROBLEMS

Answers to the problems marked with an asterisk are given at the end of the book.

Knowledge and Comprehension Problems

- 12.1 Define a composite material with respect to a materials system.
- 12.2 What are the three main types of synthetic fibers used to produce fiber-reinforced-plastic composite materials?
- 12.3 What are some of the advantages of glass-fiber-reinforced plastics?
- 12.4 What are the differences in the compositions of E and S glasses? Which is the strongest and the most costly?
- 12.5 How are glass fibers produced? What is a glass-fiber roving?
- 12.6 What properties make carbon fibers important for reinforced plastics?
- 12.7 What are two materials used as precursors for carbon fibers?
- 12.8 What are the processing steps for the production of carbon fibers from polyacrylonitrile (PAN)? What reactions take place at each step?
- 12.9 What is a tow of carbon fibers?
- 12.10 What processing steps are carried out if a very-high-strength type of carbon fiber is desired? If a very-high-modulus type of carbon fiber is desired, what processing steps are carried out?
- 12.11 What is an aramid fiber? What are two types of commercially available aramid fibers?
- 12.12 Describe the hand lay-up process for producing a fiberglass-reinforced part. What are some advantages and disadvantages of this method?
- 12.13 Describe the spray lay-up process for producing a fiberglass-reinforced part. What are some advantages and disadvantages of this method?
- 12.14 Describe the vacuum bag-autoclave process for producing a carbon-fiber-reinforced epoxy part for an aircraft.
- 12.15 Describe the filament-winding process. What is a distinct advantage of this process from an engineering design standpoint?
- 12.16 Describe the sheet-molding compound manufacturing process. What are some of the advantages and disadvantages of this process?
- 12.17 Describe the pultrusion process for the manufacture of fiber-reinforced plastics. What are some advantages of this process?
- 12.18 What are the principal components of most concretes?
- 12.19 What are the basic raw materials for portland cement? Why is it called portland cement?
- 12.20 What are the names, chemical formulas, and abbreviations for the four principal compounds of portland cement?
- 12.21 List the five main ASTM types of portland cement and give the general conditions for which each is used and their applications.

- 12.22 What is asphalt? Where is asphalt obtained?
- 12.23 What are chemical composition ranges for asphalts?
- 12.24 What does an asphalt mix consist of? What is the asphalt content of a type IV road-paving asphalt?
- 12.25 Describe the different layers in the cross section of a tree stem. Also, give the functions of each layer.
- 12.26 What are the subrings of the annual growth rings of trees?
- 12.27 What axis is parallel to the annual rings? What axis is perpendicular to the annual ring?
- 12.28 Describe the microstructure of a softwood tree.
- 12.29 Describe the microstructure of a hardwood tree. What is the difference between ring-porous and diffuse-porous tree microstructures?
- 12.30 Describe the cell-wall ultrastructure of a wood cell.
- 12.31 Describe the constituents of a wood cell.

Application and Analysis Problems

- 12.32 What type of chemical bonding takes place within the aramid fibers? What type of chemical bonding takes place between the aramid fibers?
- 12.33 How does the chemical bonding within and between the aramid fibers affect their mechanical strength properties?
- 12.34 Compare the tensile strength, tensile modulus of elasticity, elongation, and density properties of glass, carbon, and aramid fibers (Table 12.1 and Fig. 12.8).
- 12.35 What are some carbon-fiber-epoxy composite laminates designed with the carbon fibers of different layers oriented at different angles to each other?
- 12.36 Define specific tensile strength and specific tensile modulus. What type of reinforcing fibers of those shown in Fig. 12.8 has the highest specific modulus and what type has the highest specific tensile strength?
- 12.37 What are two of the most important matrix plastics for fiber-reinforced plastics? What are some advantages of each type?
- 12.38 How does the amount and arrangement of the glass fibers in fiberglass-reinforced plastics affect their strength?
- 12.39 What are the main property contributions of the carbon fibers in carbon-fiber-reinforced plastics? What are the main property contributions of the matrix plastic?
- *12.40 A unidirectional carbon-fiber-epoxy resin composite contains 68 percent by volume of carbon fiber and 32 percent epoxy resin. The density of the carbon fiber is 1.79 g/cm^3 and that of the epoxy resin is 1.20 g/cm^3 . (a) What are the weight percentages of carbon fibers and epoxy resin in the composite? (b) What is the average density of the composite?
- 12.41 The average density of a carbon-fiber-epoxy composite is 1.615 g/cm^3 . The density of the epoxy resin is 1.21 g/cm^3 and that of the carbon fibers is 1.74 g/cm^3 . (a) What is the volume percentage of carbon fibers in the composite? (b) What are the weight percentages of epoxy resin and carbon fibers in the composite?
- 12.42 Derive an equation relating the elastic modulus of a layered composite of unidirectional fibers and a plastic matrix that is loaded under isostrain conditions.
- *12.43 Calculate the tensile modulus of elasticity of a unidirectional carbon-fiber-reinforced-plastic composite material that contains 64 percent by volume of

carbon fibers and is stressed under isostrain conditions. The carbon fibers have a tensile modulus of elasticity of 54.0×10^6 psi and the epoxy matrix a tensile modulus of elasticity of 0.530×10^6 psi.

- 12.44 If the tensile strength of the carbon fibers of the 64 percent carbon-fiber-epoxy composite material of Prob. 12.43 is 0.31×10^6 psi and that of the epoxy resin is 9.20×10^3 psi, calculate the strength of the composite material in psi. What fraction of the load is carried by the carbon fibers?
- 12.45 Calculate the tensile modulus of elasticity of a unidirectional Kevlar 49-fiber-epoxy composite material that contains 63 percent by volume of Kevlar 49 fibers and is stressed under isostrain conditions. The Kevlar 49 fibers have a tensile modulus of elasticity of 27.5×10^6 psi and the epoxy matrix a tensile modulus of elasticity of 0.550×10^6 psi.
- 12.46 If the tensile strength of the Kevlar 49 fibers is 0.550×10^6 psi and that of the epoxy resin is 11.0×10^3 psi, calculate the strength of the composite material of Prob. 12.45. What fraction of the load is carried by the Kevlar 49 fibers?
- 12.47 Derive an equation relating the elastic modulus of a layered composite of unidirectional fibers and a plastic matrix that is stressed under isostress conditions.
- *12.48 Calculate the tensile modulus of elasticity for a laminated composite consisting of 62 percent by volume of unidirectional carbon fibers and an epoxy matrix under isostress conditions. The tensile modulus of elasticity of the carbon fibers is 340 GPa and that of the epoxy is 4.50×10^3 MPa.
- 12.49 Calculate the tensile modulus of elasticity of a laminate composite consisting of 62 percent by volume of unidirectional Kevlar 49 fibers and an epoxy matrix stressed under isostress conditions. The tensile modulus of elasticity of the Kevlar 49 fibers is 170 GPa and that of the epoxy is 3.70×10^3 MPa.
- 12.50 What advantages and disadvantages does concrete offer as a composite material?
- 12.51 How is portland cement made? Why is a small amount of gypsum added to portland cement?
- 12.52 What type of chemical reactions occur during the hardening of portland cement?
- 12.53 Write the chemical reactions for C_3S and C_2S with water.
- 12.54 Which component of portland cement hardens rapidly and is mostly responsible for early strength?
- 12.55 Which component of portland cement reacts slowly and is mainly responsible for the strengthening after about 1 week?
- 12.56 Which compound is kept to a low level for sulfate-resisting portland cements?
- 12.57 Why is C_4AF added to portland cement?
- 12.58 Why is it important that during the first few days of the curing of concrete the evaporation of water from its surface be prevented or reduced?
- 12.59 What method is used to make air-entrained concrete? What volume percent of air is used in the concrete for frost protection?
- 12.60 How does the water-cement ratio (by weight) affect the compressive strength of concrete? What ratio gives a compressive strength of about 5500 psi to normal concrete? What is the disadvantage of too high a water-cement ratio? Of too low a water-cement ratio?
- 12.61 What major factors should be taken into account in the design of concrete mixtures?
- 12.62 What are the absolute volume percent ranges for the major components of normal concrete?

- *12.63** We want to produce 100 ft^3 of concrete with a ratio of 1:1.9:3.8 (by weight) of cement, sand, and gravel, respectively. What are the required amounts of the components if 5.5 gal of water per sack of cement is to be used? Assume the free moisture contents of the sand and gravel are 3 and 0 percent, respectively. The specific gravities of the cement, sand, and gravel are 3.15, 2.65, and 2.65, respectively. (One sack of cement weighs 94 lb and 1 ft^3 water = 7.48 gal.) Give answers for the cement in sacks, the sand and gravel in pounds, and the water in gallons.
- 12.64** We want to produce 50 ft^3 of concrete with a ratio of 1:1.9:3.2 (by weight) of cement, sand, and gravel, respectively. What are the required amounts of the components if 5.5 gal of water per sack of cement is to be used? Assume the free moisture contents of the sand and gravel are 4 and 0.5 percent, respectively. The specific gravities of the cement, sand, and gravel are 3.15, 2.65, and 2.65, respectively. (One sack of cement weighs 94 lb and 1 ft^3 water = 7.48 gal.) Give answers for the cement in sacks, the sand and gravel in pounds, and the water in gallons.
- 12.65** Why is concrete mainly used in compression in engineering designs?
- 12.66** What is reinforced concrete? How is it made?
- 12.67** What is the main advantage of prestressed concrete?
- 12.68** Describe how compressive stresses are introduced in pretensioned prestressed concrete.
- 12.69** Describe how compressive stresses are introduced in posttensioned prestressed concrete.
- 12.70** What characteristics are desirable for the aggregate for a road-paving asphalt?
- 12.71** What is the difference between softwoods and hardwoods? Give several examples of both. Are all hardwoods physically hard?
- 12.72** What are the functions of the wood rays of a tree?
- 12.73** A piece of wood containing moisture weighs 210 g, and after oven drying to a constant weight, it weighs 125 g. What is its percent moisture content?
- 12.74** A piece of wood contains 15 percent moisture. What must its weight have been before oven drying if it has a constant weight of 125 g after drying?
- 12.75** A piece of wood contains 45 percent moisture. What must its final weight be after oven drying if it weighed 165 g before drying?
- 12.76** What is the reason for the relatively high strength of wood in the longitudinal direction of the tree stem as compared to the transverse direction?
- 12.77** What is the green condition for wood? Why is wood much weaker in the green condition than in the kiln-dried condition?
- 12.78** Why does wood shrink much more in the transverse direction than in the longitudinal direction?
- *12.79** A metal-matrix composite (MMC) is made of a 6061-Al alloy matrix and continuous boron fibers. The boron fibers are produced with an $12.5 \text{ }\mu\text{m}$ diameter tungsten-wire core that is coated with boron to make a final $107 \text{ }\mu\text{m}$ diameter fiber. A unidirectional composite is made with 51 vol % of the boron fibers in the Al 2024 matrix. Assuming the law of mixtures applies to isostrain conditions, calculate the tensile modulus of the composite in the direction of the fibers. Data are $E_B = 370 \text{ GPa}$, $E_W = 410 \text{ GPa}$, and $E_{Al} = 70.4 \text{ GPa}$.
- 12.80** A newly developed metal-matrix composite is made for the National Aerospace

plane with a matrix of the intermetallic compound titanium aluminide (Ti_3Al) and continuous silicon carbide fibers. A unidirectional composite is made with the SiC continuous fibers all in one direction. If the modulus of the composite is 220 GPa and assuming isostrain conditions, what must the volume percent of SiC fibers in the composite be if $E_{\text{SiC}} = 390$ GPa and $E_{\text{TiAl}} = 145$ GPa?

- 12.81** A metal-matrix composite is made with a matrix of Al 6061 alloy and 47 vol % Al_2O_3 continuous fibers all in one direction. If isostrain conditions prevail, what is the tensile modulus of the composite in the direction of the fibers? Data are $E_{\text{Al}_2\text{O}_3} = 395$ GPa and $E_{\text{Al 6061}} = 68.9$ GPa.
- 12.82** An MMC is made with an Al 2024 alloy with 20 vol percent SiC whiskers. If the density of the composite is 2.90 g/cm^3 and that of the SiC fibers is 3.10 g/cm^3 , what must the density of the Al 2024 alloy be?
- *12.83** A ceramic-matrix composite (CMC) is made with continuous SiC fibers embedded in a reaction-bonded silicon nitride (RBSN) matrix with all the SiC fibers aligned in one direction. Assuming isostrain conditions, what is the volume fraction of the SiC fibers in the composite if the composite has a tensile modulus of 250 GPa? Data are $E_{\text{SiC}} = 395$ GPa and $E_{\text{RBSN}} = 155$ GPa.
- 12.84** The largest preexisting flaw in the reaction-bonded silicon nitride matrix of Prob. 12.84 is $6.0 \mu\text{m}$ in diameter, and the largest surface notch on the SiC fibers is $3.5 \mu\text{m}$ deep. Calculate the stress at which cracks first form in the composite when stress is slowly applied under isostrain conditions and in the direction of the fibers. Data are $K_{\text{IC RBSN}} = 3.5 \text{ MPa} \cdot \sqrt{\text{m}}$ and $K_{\text{IC SiC}} = 4.8 \text{ MPa} \cdot \sqrt{\text{m}}$.
- 12.85** A ceramic-matrix composite is made with an aluminum oxide (Al_2O_3) matrix and continuous silicon-carbide-fiber reinforcement with all the SiC fibers in one direction. The composite consists of 30 vol% of SiC fibers. If isostrain conditions exist, calculate the tensile modulus of the composite in the direction of the fibers. If a load of 8 MN is applied to the composite in the direction of the fibers, what is the elastic strain in the composite if the surface area over which the load is applied is 55 cm^2 ? Data are $E_{\text{Al}_2\text{O}_3} = 350$ GPa and $E_{\text{SiC}} = 340$ GPa.
- *12.86** For Prob. 12.85, the Al_2O_3 matrix has flaws up to $10 \mu\text{m}$ in diameter and the largest surface notch of the SiC fibers is $4.5 \mu\text{m}$. (a) Will the matrix or the fibers crack first? (b) What stress on the composite in the direction of the fibers will cause the first crack to form? Data are $K_{\text{IC Al}_2\text{O}_3} = 3.8 \text{ MPa} \cdot \sqrt{\text{m}}$ and $K_{\text{IC SiC}} = 4.6 \text{ MPa} \cdot \sqrt{\text{m}}$.

Synthesis and Evaluation Problems

- 12.87** Using Fig. 12.7, estimate the amount of energy required to fail each fiber. Rank your results for increasing toughness. Discuss your findings.
- 12.88** If the majority of strength and stiffness of a fiber-reinforced composite comes from the fiber, what role(s) does the matrix material play?
- 12.89** The original tennis rackets were made of natural wood. Would you orient the wood's fiber direction (grain direction) parallel to the axis of the shaft of the racket or perpendicular to it? Explain.
- 12.90** Nowadays, composite materials such as carbon-fiber-reinforced-epoxy are the material of choice for tennis rackets. Explain what material properties are important in the design of a tennis racket frame. What are the advantages of the current materials used in the frame of the tennis racket?

- 12.91** The tensile strength of bulk borosilicate glass is 57 MPa. The tensile strength for the corresponding glass fiber (with diameters ranging from 3–20 μm) is 3.4 GPa. Can you explain why?
- 12.92** Which do you think has a higher tensile strength, cold drawn 1040 steel or a E-glass fiber? Verify your answer. Discuss possible reasons.
- 12.93** Determine the specific tensile strength (tensile strength/density) and specific tensile modulus (modulus of elasticity/density) for steel alloy 4340, aluminum alloy 2024-T6, as rolled titanium alloy, and carbon-fiber-reinforced-epoxy (Table 12.4). Make a plot similar to Fig. 12.9 and analyze your results.
- 12.94** A beam of rectangular cross-section ($b = 0.3$ in, $h = 0.6$ in) is made of 1040 annealed steel. (a) Calculate the product EI called the flexural rigidity of the beam, where E is the modulus of elasticity and I is the cross-sectional moment of inertia ($I = bh^3/12$ for rectangular cross-sections). (b) If you were to make this beam from aluminum 6061-T6 with the same flexural rigidity EI , given that b cannot change, what value of h would you choose? (c) If you were to make this beam from unidirectional carbon fiber composites (use Table 12.4), what would the value of h be? (d) In all three cases, calculate the weight of the beam if the length is given to be 6 ft (analyze your results).
- 12.95** (a) In Prob. 12.89 (given the same restriction on width, b), if the beam is under pure bending, M , of 400 lb · in and the normal stress, σ , acting on the cross section is not to exceed 30 ksi, design the cross-section for the given loading ($\sigma = 6M/bh^2$). (b) Determine the weight of the beam for each candidate material. (c) Determine the material cost of each beam. Analyze your results.
- 12.96** (a) In Prob. 12.89, if all three beams are to have the same cross-sectional area, compare their flexural rigidities. (b) Which material gives you the highest EI ?
- 12.97** A stress-bearing component is made of aluminum 2024-T4. The company would like to reduce the weight of this component by manufacturing it from unidirectional carbon-fiber-composite laminate (without changing its dimensions). (a) Design the fiber and matrix volume fraction of this laminate such that its modulus of elasticity is comparable to that of aluminum. (b) How much weight will you save? (Assume isostrain conditions and no voids will exist in your material)
- 12.98** If you use the same exact fiber volume fraction found in Prob. 12.93, what will the modulus of elasticity of the composite be, assuming isostress conditions? Compare the results with Prob. 12.93. How do you explain this discrepancy?
- 12.99** When designing a tubular fishing rod, one should consider the hoop strength (to prevent the collapsing-straw effect) and the axial stiffness of the rod (to prevent excessive elastic deformation in the rod). (a) Propose a process to make a tubular section of the fishing rods from fiber-reinforced composites. (b) What steps would you take to assure that (i) hoop stresses are properly supported and (ii) the axial stiffness is sufficient? (c) Suggest suitable materials for this application.
- 12.100** (a) When designing the shaft of a golf club (a driver), what mechanical loading conditions should we consider? (b) How can fiber-reinforced composites support these loading conditions (propose a process)? (c) Identify the advantages of replacing stainless-steel shafts with composite shafts.
- 12.101** (a) Compare and contrast the properties of the following fiber-reinforced composite materials: Kevlar 49–epoxy, S glass–epoxy, SiC–tungsten, carbon–carbon composites. (b) Give one general application for each material.
- 12.102** How are concrete and carbon fiber reinforced epoxy similar? How are they different?

- 12.103** Referring to Table 12.4, explain why the tensile strength and tensile modulus of the composite is considerably lower in the transverse direction when compared to the longitudinal direction. What do we call this behavior of such materials? Draw a schematic to explain.
- 12.104** You are provided with 0° plies of a light weight, fiber-reinforced composite for a manufacturing of a cylindrical pressure vessel. Suggest ways of using the 0° plies to withstand the stresses in the pressure vessel. Recall that in a pressurized vessel, both axial and hoop (circumferential) stresses will be developed. Draw a schematic to explain.
- 12.105** In total hip replacement, most surgeons prefer a ceramic femoral head on a polymer cup as opposed to a titanium alloy head on a polymer cup. Speculate on the reasons for this. Perform a web search and find out the reason. Does the answer surprise you?

Electrical Properties of Materials



(© Peidong Yang/UC Berkeley.)

Researchers are constantly trying to find ways to manufacture computer chips with smaller dimensions and more devices. Today's industry focus is on developing the nanotechnology required to manufacture electronic devices on a nanowire with a diameter of approximately 100 nm.

The chapter-opening photo is the transmission electron microscope image of two heterogeneous nanowires with alternating layers of dark (silicon/germanium) and light (silicon) regions.¹

In this chapter, electrical conduction in metals is considered first. The effects of impurities, alloy additions, and temperature on the electrical conductivity of metals are discussed. The energy-band model for electrical conduction in metals is then considered. Following this, the effects of impurities and temperature on the electrical conductivity of semiconducting materials are considered. Finally, the principles of operation of some basic semiconducting devices are examined, and some of the fabrication processes used to produce modern microelectronic circuitry are presented. An example of the complexity of recent microelectronic integrated circuitry is shown in Fig. 13.1. ■

¹http://www.berkeley.edu/news/media/releases/2002/02/05_wires.html

LEARNING OBJECTIVES

By the end of this chapter, students will be able to . . .

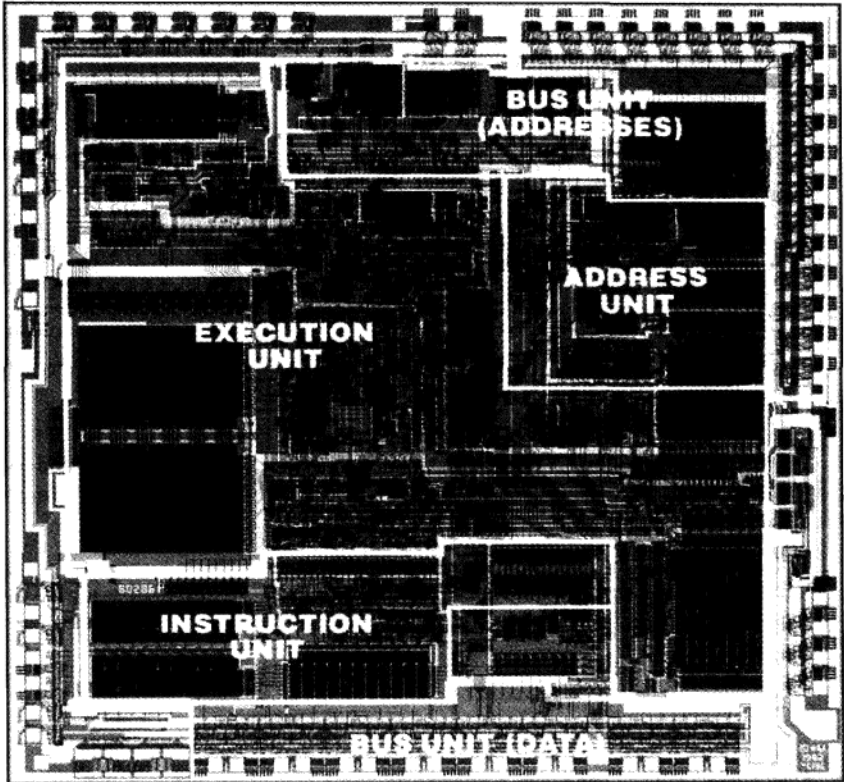
1. Define conductivity, semiconductivity, and insulative properties of materials and be able to classify, in a general manner, how each class of materials (i.e., metals, ceramics, polymers) is rated according to their electrical properties.
2. Explain the concept of electrical conductivity, resistivity, drift velocity, and mean free path in metals. Describe the effect of increasing or decreasing temperature on each.
3. Describe the energy band model and be able to define electrical properties of metals, polymers, ceramics, and electronic materials based on it.
4. Define intrinsic and extrinsic semiconductors, and describe how charge is transported in such materials.
5. Define n- and p-type semiconductors and the effect of temperature on their electrical behavior.
6. Name as many semiconducting devices as possible (i.e., LEDs, rectifiers, transistors) and in each case explain how the device functions.
7. Define microelectronics and explain various steps in the manufacturing of integrated circuits.
8. Explain in detail the electrical properties of ceramics as related to dielectrics, insulators, capacitors, ferroelectricity, and the piezoelectric effect.
9. Project the future trends in the area of chip and computer manufacturing.

13.1 ELECTRICAL CONDUCTION IN METALS

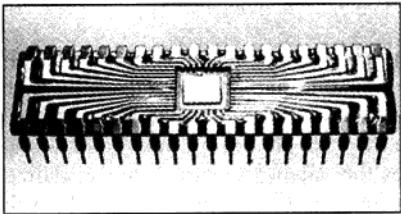
13.1.1 The Classic Model for Electrical Conduction in Metals

In metallic solids, the atoms are arranged in a crystal structure (for example, FCC, BCC, and HCP) and are bound together by their outer valence electrons by metallic bonding (see Sec. 2.5.3). The metallic bonds in solid metals make the free movement of the valence electrons possible since they are shared by many atoms and are not bound to any particular atom. Sometimes the valence electrons are visualized as forming an electron charge cloud, as shown in Fig. 13.2a. Other times the valence electrons are considered to be individual free electrons not associated with any particular atom, as shown in Fig. 13.2b.

In the classic model for electrical conduction in metallic solids, the outer valence electrons are assumed to be completely free to move between the positive-ion cores (atoms without valence electrons) in the metal lattice. At room temperature, the positive-ion cores have kinetic energy and vibrate about their lattice positions. With increasing temperature, these ions vibrate with increasing amplitudes, and there is a continuous interchange of energy between the ion cores and their valence electrons. In the absence of an electric potential, the motion of the valence electrons is random and restricted, so there is no net electron flow in any direction and thus no current



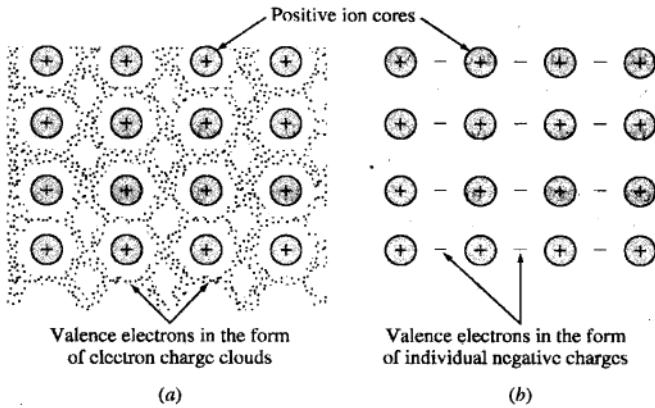
(a)



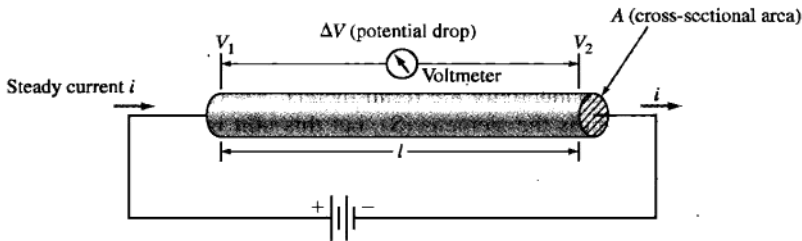
(b)

Figure 13.1

(a) The microprocessor or “computer on a chip” shown is magnified about six times on a side and incorporates about 3.1 million transistors on a single chip of silicon that is actually about 17.2 mm on each side. This microprocessor is the Intel Pentium and uses BICMOS technology with minimum design features of 0.8 μm . (b) One-half actual size microprocessor mounted in a package with connecting wire passages shown. (Courtesy of Intel Corporation, Santa Clara, CA.)

**Figure 13.2**

Schematic arrangements of the atoms in one plane of a monovalent metal such as copper, silver, or sodium. In (a) the valence electrons are pictured as an "electron gas," and in (b) the valence electrons are visualized as free electrons of unit charge.

**Figure 13.3**

Potential difference ΔV applied to metal wire specimen of cross-sectional area A .

flow. In the presence of an applied electric potential, the electrons attain a directed *drift velocity* that is proportional to the applied field but in the opposite direction.

13.1.2 Ohm's Law

Consider a length of copper wire whose ends are connected to a battery, as shown in Fig. 13.3. If a potential difference V is applied to the wire, a current i will flow that is proportional to the resistance R of the wire. According to *Ohm's law*, the **electric current** flow i is proportional to the applied voltage V and inversely proportional to the resistance of the wire, or

$$i = \frac{V}{R} \quad (13.1)$$

where i = electric current, A (amperes)

V = potential difference, V (volts)

R = resistance of wire, Ω (ohms)

The **electrical resistance** R of an electrical conductor such as the metal wire specimen of Fig. 13.3 is directly proportional to its length l and inversely proportional to its cross-sectional area A . These quantities are related by a material constant called the **electrical resistivity** ρ , as

$$R = \rho \frac{l}{A} \quad \text{or} \quad \rho = R \frac{A}{l} \quad (13.2)$$

The units for electrical resistivity, which is a constant for a material at a particular temperature, are

$$\rho = R \frac{A}{l} = \Omega \frac{\text{m}^2}{\text{m}} = \text{ohm-meter} = \Omega \cdot \text{m}$$

Often it is more convenient to think in terms of the passage of electric current instead of resistance, and so the quantity **electrical conductivity** σ^* is defined as the reciprocal of electrical resistivity:

$$\sigma = \frac{1}{\rho} \quad (13.3)$$

The units for electrical conductivity are $(\text{ohm-meter})^{-1} = (\Omega \cdot \text{m})^{-1}$. The SI unit for the reciprocal of the ohm is the siemens (S), but this unit is rarely used and so will not be used in this book.

Table 13.1 lists the electrical conductivities of some selected metals and non-metals. From this table, it is seen that **electrical conductors** such as pure metals silver, copper, and gold have the highest conductivities, about $10^7 (\Omega \cdot \text{m})^{-1}$. **Electrical insulators** such as polyethylene and polystyrene, on the other hand, have very low electrical conductivities, about $10^{-14} (\Omega \cdot \text{m})^{-1}$, which are about 10^{20} times less than those of the highly conductive metals. Silicon and germanium have conductivities in between those of metals and insulators and are thus classified as **semiconductors**.

* σ = Greek letter sigma

Table 13.1 Electrical conductivities of some metals and nonmetals at room temperature

Metals and alloys	$\sigma (\Omega \cdot \text{m})^{-1}$	Nonmetals	$\sigma (\Omega \cdot \text{m})^{-1}$
Silver	6.3×10^7	Graphite	10^5 (average)
Copper, commercial purity	5.8×10^7	Germanium	2.2
Gold	4.2×10^7	Silicon	4.3×10^{-4}
Aluminum, commercial purity	3.4×10^7	Polyethylene	10^{-14}
		Polystyrene	10^{-14}
		Diamond	10^{-14}

A wire whose diameter is 0.20 cm must carry a 20 A current. The maximum power dissipation along the wire is 4 W/m (watts per meter). Calculate the minimum allowable conductivity of the wire in $(\text{ohm-meters})^{-1}$ for this application.

**EXAMPLE
PROBLEM 13.1**

■ **Solution**

$$\text{Power } P = iV = i^2R \quad \text{where } i = \text{current, A} \quad R = \text{resistance, } \Omega$$

$$V = \text{voltage, V} \quad P = \text{power, W (watts)}$$

$$R = \rho \frac{l}{A} \quad \text{where } \rho = \text{resistivity, } \Omega \cdot \text{m}$$

$$l = \text{length, m}$$

$$A = \text{cross-sectional area of wire, m}^2$$

Combining these two equations gives

$$P = i^2 \rho \frac{l}{A} = \frac{i^2 l}{\sigma A} \quad \text{since } \rho = \frac{1}{\sigma}$$

Rearranging gives $\sigma = \frac{i^2 l}{PA}$

Given that $P = 4 \text{ W (in 1 m)} \quad i = 20 \text{ A} \quad l = 1 \text{ m}$

and $A = \frac{\pi}{4} (0.0020 \text{ m})^2 = 3.14 \times 10^{-6} \text{ m}^2$

thus

$$\sigma = \frac{i^2 l}{PA} = \frac{(20 \text{ A})^2 (1 \text{ m})}{(4 \text{ W})(3.14 \times 10^{-6} \text{ m}^2)} = 3.18 \times 10^7 (\Omega \cdot \text{m})^{-1} \blacktriangleleft$$

Therefore, for this application, the conductivity σ of the wire must be equal to or greater than $3.18 \times 10^7 (\Omega \cdot \text{m})^{-1}$.

If a copper wire of commercial purity is to conduct 10 A of current with a maximum voltage drop of 0.4 V/m, what must be its minimum diameter? [σ (commercially pure Cu) = $5.85 \times 10^7 (\Omega \cdot \text{m})^{-1}$.]

**EXAMPLE
PROBLEM 13.2**

■ **Solution**

Ohm's law: $V = iR$ and $R = \rho \frac{l}{A}$

Combining the two equations gives

$$V = i \rho \frac{l}{A}$$

and rearranging gives

$$A = i \rho \frac{l}{V}$$

Substituting $(\pi/4)d^2 = A$ and $\rho = 1/\sigma$ yields

$$\frac{\pi}{4}d^2 = \frac{il}{\sigma V}$$

and solving for d gives

$$d = \sqrt{\frac{4il}{\pi\sigma V}}$$

Given that $i = 10$ A, $V = 0.4$ V for 1 m of wire, $l = 1.0$ m (chosen length of wire), and conductivity of Cu wire $\sigma = 5.85 \times 10^7$ ($\Omega \cdot \text{m}$)⁻¹, thus

$$d = \sqrt{\frac{4il}{\pi\sigma V}} = \sqrt{\frac{4(10 \text{ A})(1.0 \text{ m})}{\pi[5.85 \times 10^7 (\Omega \cdot \text{m})^{-1}](0.4 \text{ V})}} = 7.37 \times 10^{-4} \text{ m} \blacktriangleleft$$

Therefore, for this application, the Cu wire must have a diameter of 7.37×10^{-4} m or greater.

Equation 13.1 is called the *macroscopic form* of Ohm's law since the values of i , V , and R are dependent on the geometrical shape of a particular electrical conductor. Ohm's law can also be expressed in a *microscopic form*, which is independent of the shape of the electrical conductor, as

$$\mathbf{J} = \frac{\mathbf{E}}{\rho} \quad \text{or} \quad \mathbf{J} = \sigma \mathbf{E} \quad (13.4)$$

where \mathbf{J} = current density, A/m² ρ = electrical resistivity, $\Omega \cdot \text{m}$
 \mathbf{E} = electric field, V/m σ = electrical conductivity ($\Omega \cdot \text{m}$)⁻¹

The **current density \mathbf{J}** and electric field \mathbf{E} are vector quantities with magnitude and direction. Both macroscopic and microscopic forms of Ohm's law are compared in Table 13.2.

Table 13.2 Comparison of the macroscopic and microscopic forms of Ohm's law

Macroscopic form of Ohm's law	Microscopic form of Ohm's law
$i = \frac{V}{R}$	$\mathbf{J} = \frac{\mathbf{E}}{\rho}$
where i = current, A V = voltage, V R = resistance, Ω	where \mathbf{J} = current density, A/m ² \mathbf{E} = electric field, V/m ρ = electrical resistivity, $\Omega \cdot \text{m}$

13.1.3 Drift Velocity of Electrons in a Conducting Metal

At room temperature, the positive-ion cores in a metallic conductor crystal lattice vibrate about neutral positions and therefore possess kinetic energy. The free electrons continually exchange energy with the lattice ions by elastic and inelastic collisions. Since there is no external electric field, the electron motion is random, and since there is no net electron motion in any direction, there is no net current flow.

If a uniform electric field of intensity \mathbf{E} is applied to the conductor, the electrons are accelerated with a definite velocity in the direction opposite to the applied field. The electrons periodically collide with the ion cores in the lattice and lose their kinetic energy. After a collision, the electrons are free to accelerate again in the applied field, and as a result the electron velocity varies with time in a "sawtooth manner," as shown in Fig. 13.4. The average time between collisions is 2τ , where τ is the *relaxation time*.

The electrons thus acquire an average drift velocity \mathbf{v}_d that is directly proportional to the applied electric field \mathbf{E} . The relationship between the drift velocity and the applied field is

$$\mathbf{v}_d = \mu \mathbf{E} \quad (13.5)$$

where μ (mu), the electron mobility, $\text{m}^2/(\text{V} \cdot \text{s})$, is the proportionality constant.

Consider the wire shown in Fig. 13.5 as having a current density \mathbf{J} flowing in the direction shown. Current density by definition is equal to the rate at which charges cross any plane that is perpendicular to \mathbf{J} , i.e., a certain number of amperes per square meter or coulombs per second per square meter flow past the plane.

The electron flow in a metal wire subjected to a potential difference depends on the number of electrons per unit volume, the electronic charge $-e$ ($-1.60 \times 10^{-19} \text{ C}$), and the drift velocity of the electrons, \mathbf{v}_d . The rate of charge flow per unit area

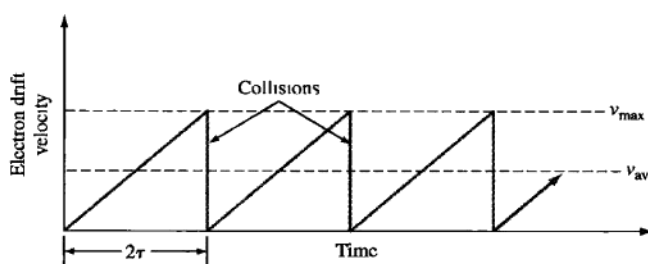
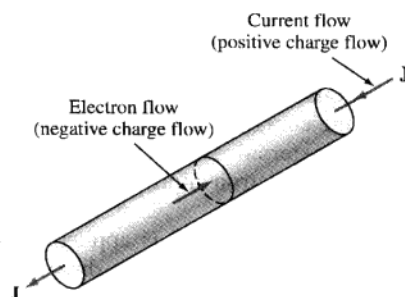


Figure 13.4

Electron drift velocity versus time for classical model for electrical conductivity of a free electron in a metal.

**Figure 13.5**

A potential difference along a copper wire causes electron flow, as indicated in the drawing. Because of the negative charge on the electron, the direction of electron flow is opposite that of conventional current flow, which assumes positive charge flow.

is $-nev_d$. However, by convention, electric current is considered to be positive charge flow, and thus the current density \mathbf{J} is given a positive sign. In equation form then,

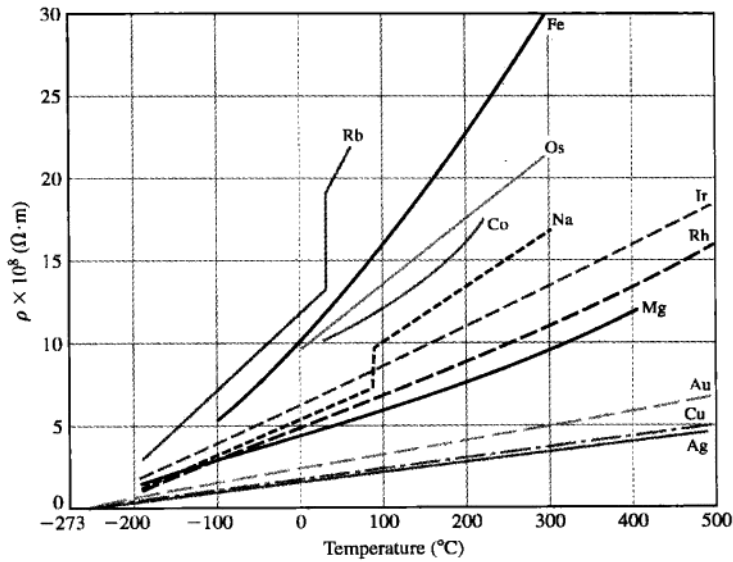
$$\mathbf{J} = nev_d \quad (13.6)$$

13.1.4 Electrical Resistivity of Metals

The electrical resistivity of a pure metal can be approximated by the sum of two terms, a thermal component ρ_T and a residual component ρ_r :

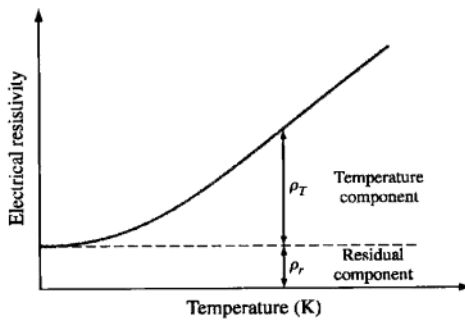
$$\rho_{\text{total}} = \rho_T + \rho_r \quad (13.7)$$

The thermal component arises from the vibrations of the positive-ion cores about their equilibrium positions in the metallic crystal lattice. As the temperature is increased, the ion cores vibrate more and more, and a large number of thermally excited elastic waves (called *phonons*) scatter conduction electrons and decrease the mean free paths and relaxation times between collisions. Thus as the temperature is increased, the electrical resistivities of pure metals increase, as shown in Fig. 13.6. The residual component of the electrical resistivity of pure metals is small and is caused by structural imperfections such as dislocations, grain boundaries, and impurity atoms that scatter electrons. The residual component is almost independent of temperature and becomes significant only at low temperatures (Fig. 13.7).

**Figure 13.6**

The effect of temperature on the electrical resistivity of selected metals. Note that there is almost a linear relationship between resistivity and temperature ($^{\circ}C$).

(From Zwikker, "Physical Properties of Solid Materials," Pergamon, 1954, pp. 247, 249.)

**Figure 13.7**

Schematic variation of electrical resistivity of a metal with absolute temperature. Note that at higher temperatures the electrical resistivity is the sum of a residual component ρ_r and a thermal component ρ_T .

Table 13.3 Temperature resistivity coefficients

Metal	Electrical resistivity at 0°C ($\mu\Omega \cdot \text{cm}$)	Temperature resistivity coefficient α_T ($^{\circ}\text{C}^{-1}$)
Aluminum	2.7	0.0039
Copper	1.6	0.0039
Gold	2.3	0.0034
Iron	9	0.0045
Silver	1.47	0.0038

For most metals at temperatures above about -200°C , the electrical resistivity varies almost linearly with temperature, as shown in Fig. 13.6. Thus, the electrical resistivities of many metals may be approximated by the equation

$$\rho_T = \rho_{0^{\circ}\text{C}}(1 + \alpha_T T) \quad (13.8)$$

where $\rho_{0^{\circ}\text{C}}$ = electrical resistivity at 0°C

α_T = temperature coefficient of resistivity, $^{\circ}\text{C}^{-1}$

T = temperature of metal, $^{\circ}\text{C}$

Table 13.3 lists the temperature resistivity coefficients for selected metals. For these metals α_T ranges from 0.0034 to 0.0045 ($^{\circ}\text{C}^{-1}$).

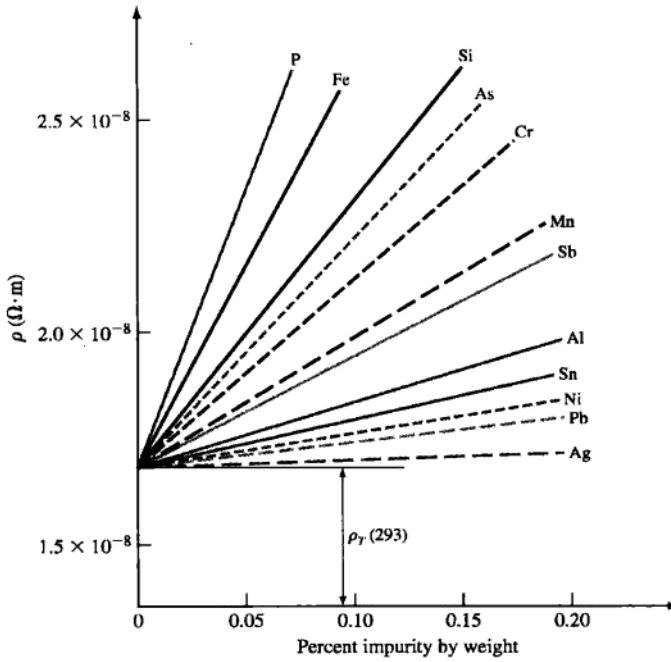
EXAMPLE PROBLEM 13.3

Calculate the electrical resistivity of pure copper at 132°C , using the temperature resistivity coefficient for copper from Table 14.3.

■ Solution

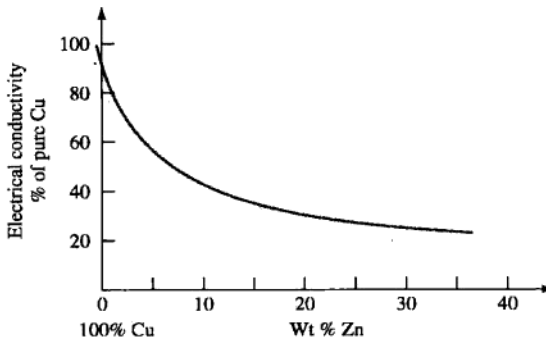
$$\begin{aligned}
 \rho_T &= \rho_{0^{\circ}\text{C}}(1 + \alpha_T T) & (13.8) \\
 &= 1.6 \times 10^{-6} \Omega \cdot \text{cm} \left(1 + \frac{0.0039}{^{\circ}\text{C}} \times 132^{\circ}\text{C} \right) \\
 &= 2.42 \times 10^{-6} \Omega \cdot \text{cm} \\
 &= 2.42 \times 10^{-8} \Omega \cdot \text{m} \blacktriangleleft
 \end{aligned}$$

Alloying elements added to pure metals cause additional scattering of the conduction electrons and thus increase the electrical resistivity of pure metals. The effect of small additions of various elements on the room temperature electrical resistivity of pure copper is shown in Fig. 13.8. Note that the effect of each element varies considerably. For the elements shown, silver increases the resistivity the least and phosphorus the most for the same amount added. The addition of larger amounts of alloying elements such as 5 to 35 percent zinc to copper to make the copper-zinc brasses increase the electrical resistivity and thus decrease the electrical conductivity of pure copper greatly, as shown in Fig. 13.9.

**Figure 13.8**

The effect of small additions of various elements on the room temperature electrical resistivity of copper.

[From F. Pawlek and K. Reichel, *Z. Metallkd.*, 47:347 (1956). Used by permission.]

**Figure 13.9**

The effect of zinc additions to pure copper in reducing the electrical conductivity of the copper.
(After ASM data.)

13.2 ENERGY-BAND MODEL FOR ELECTRICAL CONDUCTION

13.2.1 Energy-Band Model for Metals

Let us now consider the **energy-band model** for electrons in solid metals since it helps us to understand the mechanism of electrical conduction in metals. We use the metal sodium to explain the energy-band model since the sodium atom has a relatively simple electronic structure.

Electrons of isolated atoms are bound to their nuclei and can only have energy levels that are *sharply defined* such as the $1s^1$, $1s^2$, $2s^1$, $2s^2$, . . . states as necessitated by the Pauli principle. Otherwise, it would be possible for all electrons in an atom to descend to the lowest energy state, $1s^1$! Thus, the 11 electrons in the neutral sodium atom occupy two $1s$ states, two $2s$ states, six $2p$ states, and one $3s$ state, as illustrated in Fig. 13.10a. The electrons in the lower levels ($1s^2$, $2s^2$, $2p^6$) are tightly bound and constitute the *core electrons* of the sodium atom (Fig. 13.10b). The outer $3s^1$ electron can be involved in bonding with other atoms and is called the *valence electron*.

In a solid block of metal, the atoms are close together and touch each other. The valence electrons that are delocalized (Fig. 13.11a) interact and interpenetrate each other so that their original sharp atomic energy levels are broadened into wider regions called *energy bands* (Fig. 13.11b). The inner electrons, since they are shielded from the valence electrons, do not form bands.

Each valence electron in a block of sodium metal, for example, must have a slightly different energy level according to the Pauli exclusion principle. Thus, if there are N sodium atoms in a block of sodium, where N can be very large, there will be N distinct but only slightly different $3s^1$ energy levels in the $3s$ energy band.

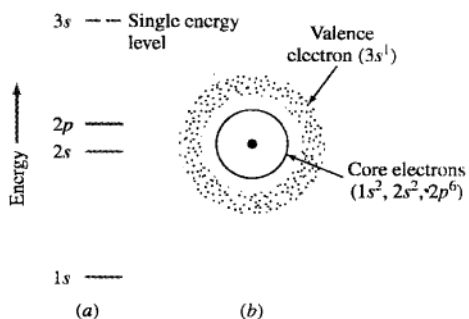


Figure 13.10

(a) Energy levels in a single sodium atom.
(b) Arrangement of electrons in a sodium atom. The outer $3s^1$ valence electron is loosely bound and is free to be involved in metallic bonding.

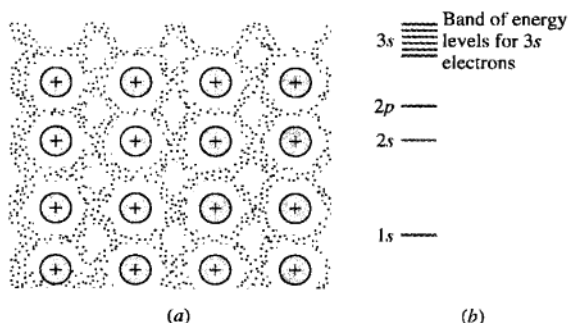


Figure 13.11

(a) Delocalized valence electrons in a block of sodium metal. (b) Energy levels in a block of sodium metal; note the expansion of the $3s$ level into an energy band and that the $3s$ band is shown closer to the $2p$ level since bonding has caused a lowering of the $3s$ levels of the isolated sodium atoms.

Each energy level is called a *state*. In the valence energy band, the energy levels are so close that they form a continuous energy band.

Figure 13.12 shows part of the energy-band diagram for metallic sodium as a function of interatomic spacing. In solid metallic sodium the $3s$ and $3p$ energy bands overlap (Fig. 13.12). However, since there is only one $3s$ electron in the sodium atom, the $3s$ band is only half-filled (Fig. 13.13a). As a result, very little energy is required to excite electrons in sodium from the highest filled states to the lowest empty ones. Sodium is, therefore, a good conductor since very little energy is required to produce electron flow in it. Copper, silver, and gold also have half-filled outer s bands.

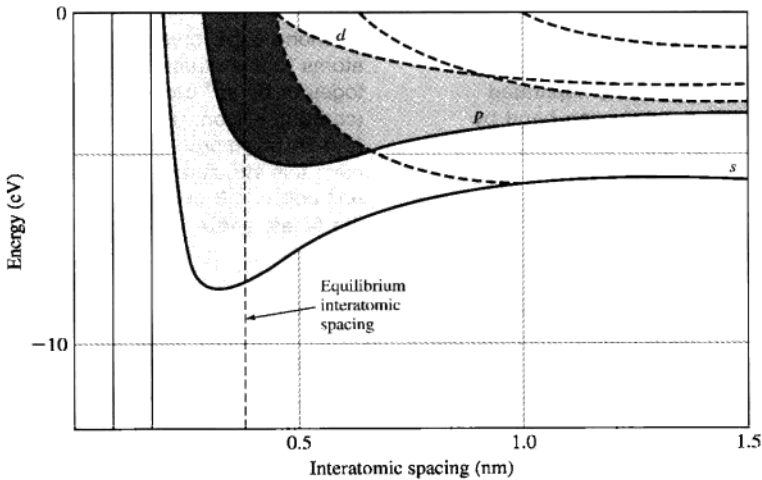


Figure 13.12

Valence energy bands in sodium metal. Note the splitting of the s , p , and d levels.

[Reprinted with permission from J.C. Slater, *Phys. Rev.*, **45**:794 (1934). Copyright 1934 by the American Physical Society.]

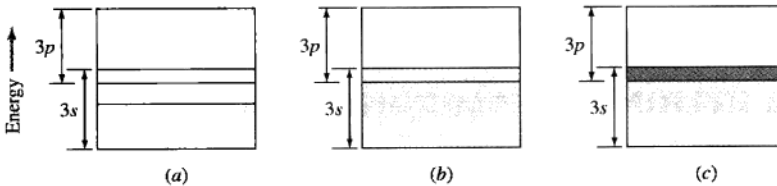
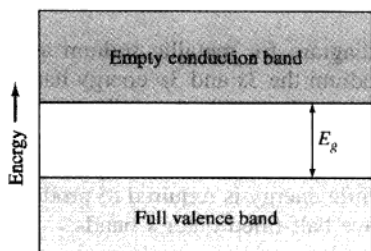


Figure 13.13

Schematic energy-band diagrams for several metallic conductors.

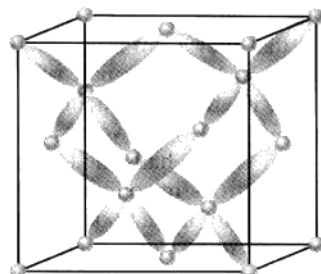
(a) Sodium, $3s^1$: the $3s$ band is half-filled since there is only one $3s^1$ electron. (b) Magnesium, $3s^2$: the $3s$ band is filled and overlaps the empty $3p$ band. (c) Aluminum, $3s^2 3p^1$: the $3s$ band is filled and overlaps the partially filled $3p$ band.

**Figure 13.14**

Energy-band diagram for an insulator. The valence band is completely filled and is separated from an empty conduction band by a large energy gap E_g .



MatVis

**Figure 13.15**

Diamond cubic crystal structure. The atoms in this structure are bonded together by sp^3 covalent bonds. Diamond (carbon), silicon, germanium, and gray tin (the tin polymorph stable below 13°C) all have this structure. There are 8 atoms per unit cell: $\frac{1}{8} \times 8$ at the corners, $\frac{1}{2} \times 6$ at the faces, and 4 inside the unit cube.

In metallic magnesium, both $3s$ states are filled. However, the $3s$ band overlaps the $3p$ band and allows some electrons into it, creating a partially filled $3sp$ combined band (Fig. 13.13b). Thus, in spite of the filled $3s$ band, magnesium is a good conductor. Similarly, aluminum, which has both $3s$ states and one $3p$ state filled, is also a good conductor because the partially filled $3p$ band overlaps the filled $3s$ band (Fig. 13.13c).

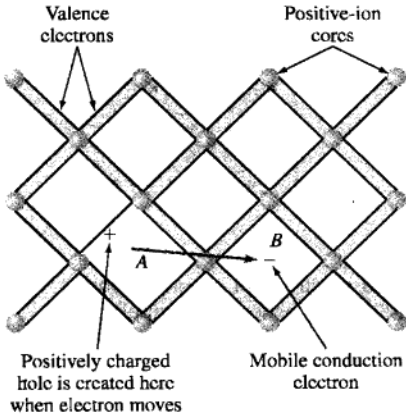
13.2.2 Energy-Band Model for Insulators

In insulators, electrons are tightly bound to their bonding atoms by ionic or covalent bonding and are not “free” to conduct electricity unless highly energized. The energy-band model for insulators consists of a lower filled **valence band** and an upper empty **conduction band**. These bands are separated by a relatively large energy gap E_g (Fig. 13.14). To free an electron for conduction, the electron must be energized to “jump” the gap, which may be as much as 6 to 7 eV as, for example, in pure diamond. In diamond, the electrons are tightly held by sp^3 tetrahedral covalent bonding (Fig. 13.15).

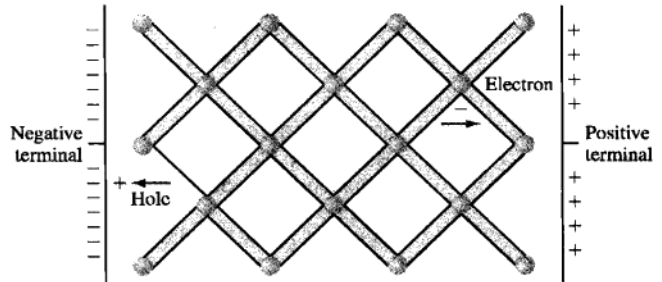
13.3 INTRINSIC SEMICONDUCTORS

13.3.1 The Mechanism of Electrical Conduction in Intrinsic Semiconductors

Semiconductors are materials whose electrical conductivities are between those of highly conducting metals and poorly conducting insulators. **Intrinsic semiconductors** are pure semiconductors whose electrical conductivity is determined by their inherent conductive properties. Pure elemental silicon and germanium are intrinsic

**Figure 13.16**

Two-dimensional representation of the diamond cubic lattice of silicon or germanium showing positive-ion cores and valence electrons. Electron has been excited from a bond at *A* and has moved to point *B*.

**Figure 13.17**

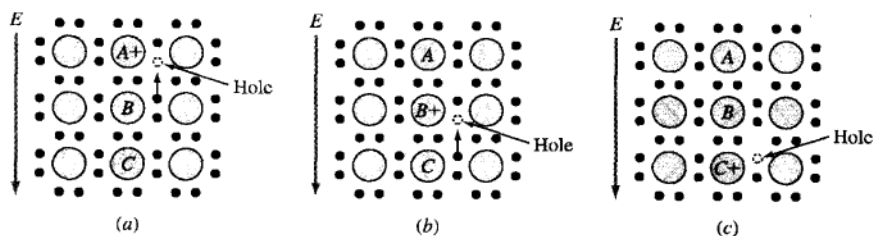
Electrical conduction in a semiconductor such as silicon showing the migration of electrons and holes in an applied electric field.

semiconducting materials. These elements, which are in group IVA in the periodic table, have the diamond cubic structure with highly directional covalent bonds (Fig. 13.15). Tetrahedral sp^3 hybrid bonding orbitals consisting of electron pairs bond the atoms together in the crystal lattice. In this structure, each silicon or germanium atom contributes four valence electrons.

Electrical conductivity in pure semiconductors such as Si and Ge can be described qualitatively by considering the two-dimensional pictorial representation of the diamond cubic crystal lattice shown in Fig. 13.16. The circles in this illustration represent the *positive-ion cores* of the Si or Ge atoms, and the joining pairs of lines indicate bonding *valence electrons*. The bonding electrons are unable to move through the crystal lattice and hence to conduct electricity unless sufficient energy is provided to excite them from their bonding positions. When a critical amount of energy is supplied to a valence electron to excite it away from its bonding position, it becomes a free conduction electron and leaves behind a positively charged “hole” in the crystal lattice (Fig. 13.16).

13.3.2 Electrical Charge Transport in the Crystal Lattice of Pure Silicon

In the electrical conduction process in a semiconductor such as pure silicon or germanium, both electrons and holes are charge carriers and move in an applied electric field. Conduction **electrons** have a negative charge and are attracted to the positive terminal of an electrical circuit (Fig. 13.17). **Holes**, on the other hand,

**Figure 13.18**

Schematic illustration of the movement of holes and electrons in a pure silicon semiconductor during electrical conduction caused by the action of an applied electric field.

(After S.N. Levine, "Principles of Solid State Microelectronics," Holt, 1963.)

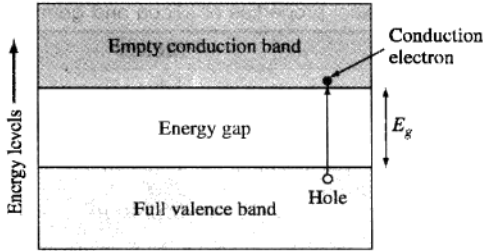
behave like positive charges and are attracted to the negative terminal of an electrical circuit (Fig. 13.17). A hole has a positive charge equal in magnitude to the electron charge.

The motion of a "hole" in an electric field can be visualized by referring to Fig. 13.18. Let a hole exist at atom A where a valence electron is missing, as shown in Fig. 13.18a. When an electric field is applied in the direction shown in Fig. 13.18a, a force is exerted on the valence electrons of atom B, and one of the electrons associated with atom B will break loose from its bonding orbital and move to the vacancy in the bonding orbital of atom A. The hole will now appear at atom B and in effect will have moved from A to B in the direction of the applied field (Fig. 13.18b). By a similar mechanism, the hole is transported from atom B to C by an electron moving from C to B (Fig. 13.18c). The net result of this process is that an electron is transported from C to A, which is in the direction opposite to the applied field, and a hole is transported from A to C, which is in the direction of the applied field. Thus, during electrical conduction in a pure semiconductor such as silicon, negatively charged electrons move in the direction opposite to the applied field (conventional current flow) and toward the positive terminal and positively charged holes move in the direction of the applied field toward the negative terminal.

13.3.3 Energy-Band Diagram for Intrinsic Elemental Semiconductors

Energy-band diagrams are another method of describing the excitation of valence electrons to become conduction electrons in semiconductors. For this representation only the energy required for the process is involved, and no physical picture of the electrons moving in the crystal lattice is given. In the energy-band diagram for intrinsic elemental semiconductors (for example, Si or Ge), the bound valence electrons of the covalently bonded crystal occupy the energy levels in the lower valence band, which is almost filled at 20°C (Fig. 13.19).

Above the valence band there is a forbidden energy gap in which no energy states are allowed and which is 1.1 eV for silicon at 20°C. Above the energy gap

**Figure 13.19**

Energy-band diagram for an intrinsic elemental semiconductor such as pure silicon. When an electron is excited across the energy gap, an electron-hole pair is created. Thus, for each electron that jumps the gap, two charge carriers, an electron and a hole, are produced.

there is an almost empty (at 20°C) conduction band. At room temperature thermal energy is sufficient to excite some electrons from the valence band to the conduction band, leaving vacant sites or holes in the valence band. Thus, when an electron is excited across the energy gap into the conduction band, two charge carriers are created, a negatively charged electron and a positively charged hole. Both electrons and holes carry electric current.

13.3.4 Quantitative Relationships for Electrical Conduction in Elemental Intrinsic Semiconductors

During electrical conduction in intrinsic semiconductors, the current density \mathbf{J} is equal to the sum of the conduction due to *both* electrons and holes. Using Eq. 13.6,

$$\mathbf{J} = nq\mathbf{v}_n^* + pq\mathbf{v}_p^* \quad (13.9)$$

where n = number of conduction electrons per unit volume

p = number of conduction holes per unit volume

q = absolute value of electron or hole charge, 1.60×10^{-19} C

$\mathbf{v}_n, \mathbf{v}_p$ = drift velocities of electrons and holes, respectively.

Dividing both sides of Eq. 13.9 by the electric field \mathbf{E} and using Eq. 13.4, $\mathbf{J} = \sigma\mathbf{E}$,

$$\sigma = \frac{\mathbf{J}}{\mathbf{E}} = \frac{nq\mathbf{v}_n}{\mathbf{E}} + \frac{pq\mathbf{v}_p}{\mathbf{E}} \quad (13.10)$$

The quantities \mathbf{v}_n/\mathbf{E} and \mathbf{v}_p/\mathbf{E} are called the *electron* and *hole mobilities*, respectively, since they measure how fast the electrons and holes in semiconductors drift in an applied electric field. The symbols μ_n and μ_p are used for the mobilities of

*The subscript n (for negative) refers to electrons, and the subscript p (for positive) refers to holes.

Table 13.4 Some physical properties of silicon and germanium at 300 K

	Silicon	Germanium
Energy gap, eV	1.1	0.67
Electron mobility μ_n , $\text{m}^2/(\text{V} \cdot \text{s})$	0.135	0.39
Hole mobility μ_p , $\text{m}^2/(\text{V} \cdot \text{s})$	0.048	0.19
Intrinsic carrier density n_i , carriers/ m^3	1.5×10^{16}	2.4×10^{19}
Intrinsic resistivity ρ , $\Omega \cdot \text{m}$	2300	0.46
Density, g/m^3	2.33×10^6	5.32×10^6

Source: After E.M. Conwell, "Properties of Silicon and Germanium II," *Proc. IRE*, June 1958, p. 1281.

electrons and holes, respectively. Substituting electron and hole mobilities for v_n/E and v_p/E in Eq. 13.10 enables the electrical conductivity of a semiconductor to be expressed as

$$\sigma = nq\mu_n + pq\mu_p \quad (13.11)$$

The units for mobility μ are

$$\frac{v}{E} = \frac{\text{m/s}}{\text{V/m}} = \frac{\text{m}^2}{\text{V} \cdot \text{s}}$$

In intrinsic elemental semiconductors, electrons and holes are created in pairs; thus, the number of conduction electrons equals the number of holes produced, so that

$$n = p = n_i \quad (13.12)$$

where n = intrinsic carrier concentration, carriers/unit volume.

Equation 13.11 now becomes

$$\sigma = n_i q (\mu_n + \mu_p) \quad (13.13)$$

Table 13.4 lists some of the important properties of intrinsic silicon and germanium at 300 K.

The mobilities of electrons are always greater than those of holes. For intrinsic silicon the electron mobility of $0.135 \text{ m}^2/(\text{V} \cdot \text{s})$ is 2.81 times greater than the hole mobility of $0.048 \text{ m}^2/(\text{V} \cdot \text{s})$ at 300 K (Table 13.4). The ratio of electron-to-hole mobility for intrinsic germanium is 2.05 at 300 K.

EXAMPLE PROBLEM 13.4

Calculate the number of silicon atoms per cubic meter. The density of silicon is $2.33 \text{ Mg}/\text{m}^3$ ($2.33 \text{ g}/\text{cm}^3$), and its atomic mass is $28.08 \text{ g}/\text{mol}$.

■ Solution

$$\begin{aligned} \frac{\text{Si atoms}}{\text{m}^3} &= \left(\frac{6.023 \times 10^{23} \text{ atoms}}{\text{mol}} \right) \left(\frac{1}{28.08 \text{ g/mol}} \right) \left(\frac{2.33 \times 10^6 \text{ g}}{\text{m}^3} \right) \\ &= 5.00 \times 10^{28} \text{ atoms}/\text{m}^3 \quad \blacktriangleleft \end{aligned}$$

Calculate the electrical resistivity of intrinsic silicon at 300 K. For Si at 300 K, $n_i = 1.5 \times 10^{16}$ carriers/m³, $q = 1.60 \times 10^{-19}$ C, $\mu_n = 0.135$ m²/(V · s), and $\mu_p = 0.048$ m²/(V · s).

**EXAMPLE
PROBLEM 13.5**

■ **Solution**

$$\begin{aligned}\rho &= \frac{1}{\sigma} = \frac{1}{n_i q (\mu_n + \mu_p)} \quad (\text{reciprocal of Eq. 13.13}) \\ &= \frac{1}{\left(\frac{1.5 \times 10^{16}}{\text{m}^3}\right)(1.60 \times 10^{-19} \text{ C})\left(\frac{0.135 \text{ m}^2}{\text{V} \cdot \text{s}} + \frac{0.048 \text{ m}^2}{\text{V} \cdot \text{s}}\right)} \\ &= 2.28 \times 10^3 \Omega \cdot \text{m} \quad \blacktriangleleft\end{aligned}$$

The units for the reciprocal of Eq. 13.13 are ohm-meters as is shown by the following unit conversion:

$$\rho = \frac{1}{n_i q (\mu_n + \mu_p)} = \frac{1}{\left(\frac{1}{\text{m}^3}\right)(\text{C})\left(\frac{1 \text{ A} \cdot \text{s}}{1 \text{ C}}\right)\left(\frac{\text{m}^2}{\text{V} \cdot \text{s}}\right)\left(\frac{1 \text{ V}}{1 \text{ A} \cdot \Omega}\right)} = \Omega \cdot \text{m}$$

13.3.5 Effect of Temperature on Intrinsic Semiconductivity

At 0 K, the valence bands of intrinsic semiconductors such as silicon and germanium are completely filled and their conduction bands completely empty. At temperatures above 0 K, some of the valence electrons are thermally activated and excited across the energy gap into the conduction band, creating electron-hole pairs. Thus, in contrast to metals, whose conductivities decrease with increasing temperatures, the conductivities of semiconductors *increase* with increasing temperatures for the temperature range over which this process predominates.

Since electrons are thermally activated into the conduction band of semiconductors, the concentration of thermally activated electrons in semiconductors shows a temperature dependence similar to that of many other thermally activated processes. By analogy with Eq. 5.1, the concentration of electrons with sufficient thermal energy to enter the conduction band (and thus creating the same concentration of holes in the valence band), n_i , varies according to

$$n_i \propto e^{-(E_g - E_{av})/kT} \quad (13.14)$$

where E_g = band energy gap

E_{av} = average energy across band gap

k = Boltzmann's constant

T = temperature, K

For intrinsic semiconductors such as pure silicon and germanium, E_{av} is halfway across the gap, or $E_g/2$. Thus Eq. 13.14 becomes

$$n_i \propto e^{-(E_g - E_g/2)/kT} \quad (13.15a)$$

or

$$n_i \propto e^{-E_g/2kT} \quad (13.15b)$$

Since the electrical conductivity σ of an intrinsic semiconductor is proportional to the concentration of electrical charge carriers, n_i , Eq. 13.15b can be expressed as

$$\sigma = \sigma_0 e^{-E_g/2kT} \quad (13.16a)$$

or in natural logarithmic form,

$$\ln \sigma = \ln \sigma_0 - \frac{E_g}{2kT} \quad (13.16b)$$

where σ_0 is an overall constant that depends mainly on the mobilities of electrons and holes. The slight temperature dependence of σ_0 on temperature will be neglected in this text.

Since Eq. 13.16b is the equation of a straight line, the value of $E_g/2k$ and hence E_g can be determined from the slope of the plot of $\ln \sigma$ versus $1/T$, K^{-1} . Figure 13.20 shows an experimental plot of $\ln \sigma$ versus $1/T$, K^{-1} , for intrinsic silicon.

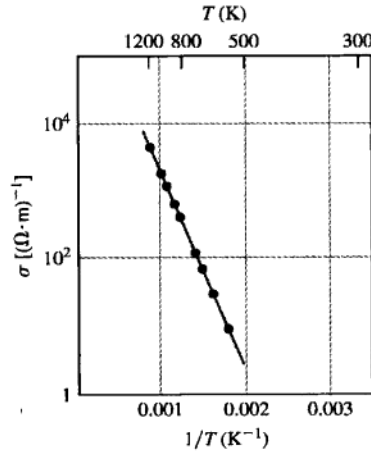


Figure 13.20

Electrical conductivity as a function of reciprocal absolute temperature for intrinsic silicon.

(From C.A. Wert and R.M. Thomson, "Physics of Solids," 2d ed., McGraw-Hill, 1970, p. 282. Reproduced with permission of The McGraw-Hill Companies.)

The electrical resistivity of pure silicon is $2.3 \times 10^3 \Omega \cdot \text{m}$ at room temperature, 27°C (300 K). Calculate its electrical conductivity at 200°C (473 K). Assume that the E_g of silicon is 1.1 eV; $k = 8.62 \times 10^{-5} \text{ eV/K}$.

**EXAMPLE
PROBLEM 13.6**

■ **Solution**

For this problem, we use Eq. 14.16a and set up two simultaneous equations. We then eliminate σ_0 by dividing the first equation by the second.

$$\begin{aligned}\sigma &= \sigma_0 \exp \frac{-E_g}{2kT} \\ \sigma_{473} &= \sigma_0 \exp \frac{-E_g}{2kT_{473}} \\ \sigma_{300} &= \sigma_0 \exp \frac{-E_g}{2kT_{300}}\end{aligned}\quad (13.16a)$$

Dividing the first equation by the second to eliminate σ_0 gives

$$\begin{aligned}\frac{\sigma_{473}}{\sigma_{300}} &= \exp \left(\frac{-E_g}{2kT_{473}} + \frac{E_g}{2kT_{300}} \right) \\ \frac{\sigma_{473}}{\sigma_{300}} &= \exp \left[\frac{-1.1 \text{ eV}}{2(8.62 \times 10^{-5} \text{ eV/K})} \left(\frac{1}{473 \text{ K}} - \frac{1}{300 \text{ K}} \right) \right] \\ \ln \frac{\sigma_{473}}{\sigma_{300}} &= 7.777 \\ \sigma_{473} &= \sigma_{300}(2385) \\ &= \frac{1}{2.3 \times 10^3 \Omega \cdot \text{m}}(2385) = 1.04 (\Omega \cdot \text{m})^{-1} \blacktriangleleft\end{aligned}$$

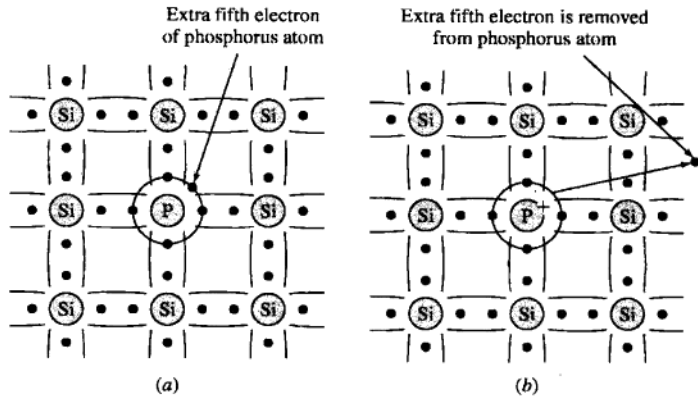
The electrical conductivity of the silicon increased by about 2400 times when the temperature was raised from 27 to 200°C .

13.4 EXTRINSIC SEMICONDUCTORS

Extrinsic semiconductors are very dilute substitutional solid solutions in which the solute impurity atoms have different valence characteristics from the solvent atomic lattice. The concentrations of the added impurity atoms in these semiconductors are usually in the range of 100 to 1000 parts per million (ppm).

13.4.1 n-Type (Negative-Type) Extrinsic Semiconductors

Consider the two-dimensional covalent bonding model for the silicon crystal lattice shown in Fig. 13.21a. If an impurity atom of a group VA element, such as phosphorus, replaces a silicon atom, which is a group IVA element, there will be one excess electron above the four needed for the tetrahedral covalent bonding in

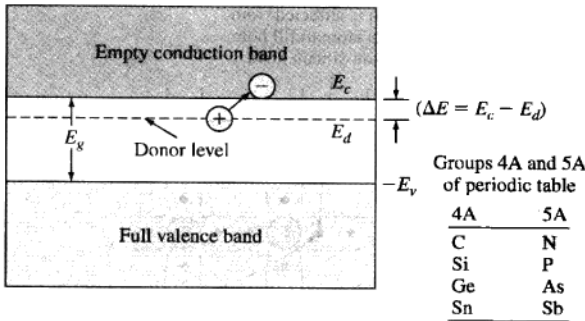
**Figure 13.21**

(a) The addition of a pentavalent phosphorus impurity atom to the tetravalent silicon lattice provides a fifth electron that is weakly attached to the parent phosphorus atom. Only a small amount of energy (0.044 eV) makes this electron mobile and conductive. (b) Under an applied electric field the excess electron becomes conductive and is attracted to the positive terminal of the electrical circuit. With the loss of the extra electron, the phosphorus atom is ionized and acquires a +1 charge.

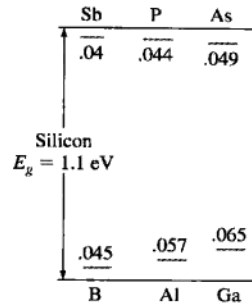
the silicon lattice. This extra electron is only loosely bonded to the positively charged phosphorus nucleus and has a binding energy of 0.044 eV at 27°C. This energy is about 5 percent of that required for a conduction electron to jump the energy gap of 1.1 eV of pure silicon. That is, only 0.044 eV of energy is required to remove the excess electron from its parent nucleus so that it can participate in electrical conduction. When under the action of an electrical field, the extra electron becomes a free electron available for conduction and the remaining phosphorus atom becomes ionized and acquires a positive charge (Fig. 13.21b).

Group VA impurity atoms such as P, As, and Sb when added to silicon or germanium provide easily ionized electrons for electrical conduction. Since these group VA impurity atoms donate conduction electrons when present in silicon or germanium crystals, they are called *donor impurity atoms*. Silicon or germanium semiconductors containing group V impurity atoms are called **n-type (negative-type) extrinsic semiconductors** since the majority charge carriers are electrons.

In terms of the energy-band diagram for silicon, the extra electron of a group VA impurity atom occupies an energy level in the forbidden energy gap just slightly below the empty conduction band, as shown in Fig. 13.22. Such an energy level is called a **donor level** since it is provided by a donor impurity atom. A donor group VA impurity atom, upon losing its extra electron, becomes ionized and acquires a positive charge. Energy levels for the group VA impurity donor atoms Sb, P and As in silicon are shown in Fig. 13.23.

**Figure 13.22**

Energy-band diagram for an n-type extrinsic semiconductor showing the position of the donor level for the extra electron of a group VA element such as P, As, and Sb that is contained in the silicon crystal lattice (Fig. 13.21a). Electrons at the donor energy level require only a small amount of energy ($\Delta E = E_c - E_d$) to be excited into the conduction band. When the extra electron at the donor level jumps to the conduction band, a positive immobile ion is left behind.

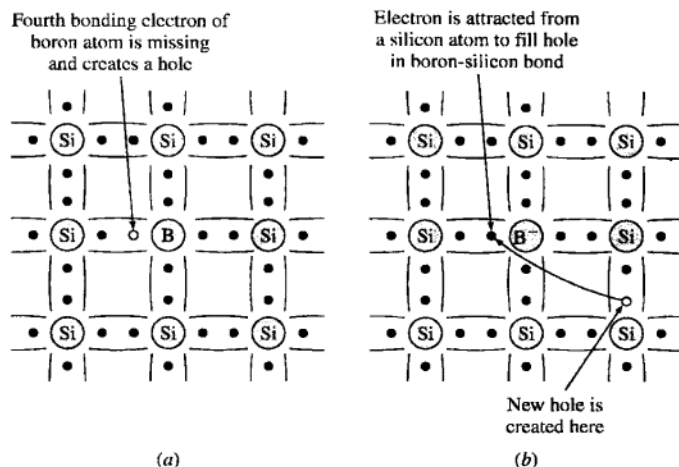
**Figure 13.23**

Ionization energies (in electron volts) for various impurities in silicon.

13.4.2 p-Type (Positive-Type) Extrinsic Semiconductors

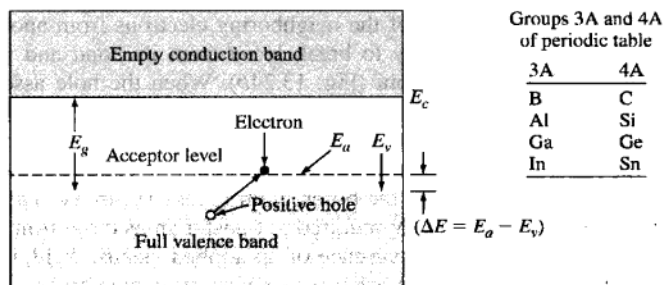
When a trivalent group IIIA element such as boron is substitutionally introduced in the silicon tetrahedrally bonded lattice, one of the bonding orbitals is missing, and a hole exists in the bonding structure of the silicon (Fig. 13.24a). If an external electric field is applied to the silicon crystal, one of the neighboring electrons from another tetrahedral bond can attain sufficient energy to break loose from its bond and move to the missing bond (hole) of the boron atom (Fig. 13.24b). When the hole associated with the boron atom is filled by an electron from a neighboring silicon atom, the boron atom becomes ionized and acquires a negative charge of -1 . The binding energy associated with the removal of an electron from a silicon atom, thereby creating a hole, and the subsequent transfer of the electron to the boron atom is only 0.045 eV. This amount of energy is small compared to the 1.1 eV required to transfer an electron from the valence band to the conduction band. In the presence of an applied electric field, the hole created by the ionization of a boron atom behaves as a positive charge carrier and migrates in the silicon lattice toward the negative terminal, as described in Fig. 13.17.

In terms of the energy-band diagram, the boron atom provides an energy level called an **acceptor level** that is slightly higher (≈ 0.045 eV) than the uppermost level of the full valence band of silicon (Fig. 13.25). When a valence electron of a silicon atom near a boron atom fills a missing electron hole in a boron-silicon valence bond (Fig. 13.24b), this electron is elevated to the acceptor level and creates a negative boron ion. In this process, an electron hole is created in the silicon lattice that acts

**Figure 13.24**

(a) The addition of a trivalent boron impurity atom into the tetravalent lattice creates a hole in one of the boron-silicon bonds since one electron is missing.

(b) Under an applied electric field, only a small amount of energy (0.045 eV) attracts an electron from a nearby silicon atom to fill this hole, thereby creating an immobile boron ion with a -1 charge. The new hole created in the silicon lattice acts as a positive charge carrier and is attracted to the negative terminal of an electrical circuit.

**Figure 13.25**

Energy-band diagram for a p-type extrinsic semiconductor showing the position of the acceptor level created by the addition of an atom of a group IIIA element such as Al, B, or Ga to replace a silicon atom in the silicon lattice (Fig. 13.24). Only a small amount of energy ($\Delta E = E_a - E_v$) is necessary to excite an electron from the valence band to the acceptor level, thereby creating an electron hole (charge carrier) in the valence band.

as a positive charge carrier. Atoms of group IIIA elements such as B, Al, and Ga provide acceptor levels in silicon semiconductors and are called *acceptor atoms*. Since the majority carriers in these extrinsic semiconductors are holes in the valence bond structure, they are called **p-type (positive-carrier-type) extrinsic semiconductors**.

13.4.3 Doping of Extrinsic Silicon Semiconductor Material

The process of adding small amounts of substitutional impurity atoms to silicon to produce extrinsic silicon semiconducting material is called *doping*, while impurity atoms themselves are called *dopants*. The most commonly used method of doping silicon semiconductors is the *planar process*. In this process, dopant atoms are introduced into selected areas of the silicon from one surface in order to form regions of p- or n-type material. The wafers are usually about 4 in. (10 cm) in diameter and about a few hundred micrometers² thick.

In the diffusion process for doping silicon wafers, the dopant atoms are typically deposited on or near the surface of the wafer by a gaseous deposition step, followed by a drive-in diffusion that moves the dopant atoms farther into the wafer. A high temperature of about 1100°C is required for this diffusion process. More details of this process will be described in Sec. 13.6 on microelectronics.

13.4.4 Effect of Doping on Carrier Concentrations in Extrinsic Semiconductors

The Mass Action Law In semiconductors such as silicon and germanium, mobile electrons and holes are constantly being generated and recombined. At constant temperature under equilibrium conditions the product of the negative free electron and positive hole concentrations is a constant. The general relation is

$$np = n_i^2 \quad (13.17)$$

where n_i is the intrinsic concentration of carriers in a semiconductor and is a constant at a given temperature. This relation is valid for both intrinsic and extrinsic semiconductors. In an extrinsic semiconductor the increase in one type of carrier (n or p) reduces the concentration of the other through recombination so that the product of the two (n and p) is a constant at any given temperature.

The carriers whose concentration in extrinsic semiconductors is the larger are designated the **majority carriers**, and those whose concentration is the smaller are called the **minority carriers** (see Table 13.5). The concentration of electrons in an n-type semiconductor is denoted by n_n and that of holes in n-type material by p_n . Similarly, the concentration of holes in a p-type semiconductor is given by p_p and that of electrons in p-type material by n_p .

Charge Densities in Extrinsic Semiconductors A second fundamental relationship for extrinsic semiconductors is obtained from the fact that the total crystal must

²¹ micrometer (μm) = 10^{-4} cm = 10^4 Å.

Table 13.5 Summary of the carrier concentrations in extrinsic semiconductors

Semiconductor	Majority-carrier concentrations	Minority-carrier concentrations
n-type	n_n (concentration of electrons in n-type material)	p_n (concentration of holes in n-type material)
p-type	p_p (concentration of holes in p-type material)	n_p (concentration of electrons in p-type material)

be electrically neutral. This means that the charge density in each volume element must be zero. There are two types of charged particles in extrinsic semiconductors such as Si and Ge: immobile ions and mobile charge carriers. The immobile ions originate from the ionization of donor or acceptor impurity atoms in the Si or Ge. The concentration of the positive donor ions is denoted by N_d and that of the negative acceptor ions by N_a . The mobile charge carriers originate mainly from the ionization of the impurity atoms in the Si or Ge, and their concentrations are designated by n for the negatively charged electrons and p for the positively charged holes.

Since the semiconductor must be electrically neutral, the magnitude of the total negative charge density must equal the total positive charge density. The total negative charge density is equal to the sum of the negative acceptor ions N_a and the electrons, or $N_a + n$. The total positive charge density is equal to the sum of the positive donor ions N_d and the holes, or $N_d + p$. Thus,

$$N_a + n = N_d + p \tag{13.18}$$

In an n-type semiconductor created by adding donor impurity atoms to intrinsic silicon, $N_a = 0$. Since the number of electrons is much greater than the number of holes in an n-type semiconductor (that is, $n \gg p$), then Eq. 13.18 reduces to

$$n_n \approx N_d \tag{13.19}$$

Thus, in an n-type semiconductor the free-electron concentration is approximately equal to the concentration of donor atoms. The concentration of holes in an n-type semiconductor is obtained from Eq. 13.17. Thus,

$$p_n = \frac{n_i^2}{n_n} \approx \frac{n_i^2}{N_d} \tag{13.20}$$

The corresponding equations for p-type semiconductors of silicon and germanium are

$$p_p \approx N_a \tag{13.21}$$

and

$$n_p = \frac{n_i^2}{p_p} \approx \frac{n_i^2}{N_a} \tag{13.22}$$

Typical Carrier Concentrations in Intrinsic and Extrinsic Semiconductors For silicon at 300 K, the intrinsic carrier concentration n_i is equal to 1.5×10^{16} carriers/m³. For extrinsic silicon doped with arsenic at a typical concentration of 10^{21} impurity atoms/m³,

$$\text{Concentration of major carriers } n_n = 10^{21} \text{ electrons/m}^3$$

$$\text{Concentration of minority carriers } p_n = 2.25 \times 10^{11} \text{ holes/m}^3$$

Thus, for extrinsic semiconductors the concentration of the majority carriers is normally much larger than that of the minority carriers. Example Problem 14.7 shows how the concentrations of majority and minority carriers can be calculated for an extrinsic silicon semiconductor.

A silicon wafer is doped with 10^{21} phosphorus atoms/m³. Calculate (a) the majority-carrier concentration, (b) the minority-carrier concentration, and (c) the electrical resistivity of the doped silicon at room temperature (300 K). Assume complete ionization of the dopant atoms; $n_i(\text{Si}) = 1.5 \times 10^{16} \text{ m}^{-3}$, $\mu_n = 0.135 \text{ m}^2/(\text{V} \cdot \text{s})$, and $\mu_p = 0.048 \text{ m}^2/(\text{V} \cdot \text{s})$.

EXAMPLE PROBLEM 13.7

■ Solution

Since the silicon is doped with phosphorus, a group V element, the doped silicon is *n-type*.

a. $n_n = N_d = 10^{21} \text{ electrons/m}^3 \blacktriangleleft$

b. $p_n = \frac{n_i^2}{N_d} = \frac{(1.5 \times 10^{16} \text{ m}^{-3})^2}{10^{21} \text{ m}^{-3}} = 2.25 \times 10^{11} \text{ holes/m}^3 \blacktriangleleft$

c.
$$\rho = \frac{1}{q\mu_n n_n} = \frac{1}{(1.60 \times 10^{-19} \text{ C}) \left(0.135 \frac{\text{m}^2}{\text{V} \cdot \text{s}}\right) \left(\frac{10^{21}}{\text{m}^3}\right)}$$

$$= 0.0463 \Omega \cdot \text{m} \blacktriangleleft$$

*See Example Problem 13.5 for the conversion of units.

A phosphorus-doped silicon wafer has an electrical resistivity of $8.33 \times 10^{-5} \Omega \cdot \text{m}$ at 27°C. Assume mobilities of charge carriers to be the constants $0.135 \text{ m}^2/(\text{V} \cdot \text{s})$ for electrons and $0.048 \text{ m}^2/(\text{V} \cdot \text{s})$ for holes.

EXAMPLE PROBLEM 13.8

- What is its majority-carrier concentration (carriers per cubic meter) if complete ionization is assumed?
- What is the ratio of phosphorus to silicon atoms in this material?

■ Solution

- Phosphorus produces an *n-type* silicon semiconductor. Therefore, the mobility of the charge carriers will be assumed to be that of electrons in silicon at 300 K,

which is $0.1350 \text{ m}^2/(\text{V} \cdot \text{s})$. Thus,

$$\rho = \frac{1}{n_n q \mu_n}$$

$$\text{or } n_n = \frac{1}{\rho q \mu_n} = \frac{1}{(8.33 \times 10^{-5} \Omega \cdot \text{m})(1.60 \times 10^{-19} \text{ C})(0.1350 \text{ m}^2/(\text{V} \cdot \text{s}))} \\ = 5.56 \times 10^{23} \text{ electrons/m}^3 \blacktriangleleft$$

- b. Assuming each phosphorus atom provides one electron charge carrier, there will be 5.56×10^{23} phosphorus atoms/ m^3 in the material. Pure silicon contains 5.00×10^{28} atoms/ m^3 (Example Problem 13.4). Thus, the ratio of phosphorus to silicon atoms will be

$$\frac{5.56 \times 10^{23} \text{ P atoms/m}^3}{5.00 \times 10^{28} \text{ Si atoms/m}^3} = 1.11 \times 10^{-5} \text{ P to Si atoms} \blacktriangleleft$$

13.4.5 Effect of Total Ionized Impurity Concentration on the Mobility of Charge Carriers in Silicon at Room Temperature

Figure 13.26 shows that the mobilities of electrons and holes in silicon at room temperature are at a maximum at low impurity concentrations and then decrease with impurity concentration, reaching a minimum value at high concentrations. Example Problem 13.9 shows how neutralizing one type of charge carrier with another leads to a lower mobility for the majority carriers.

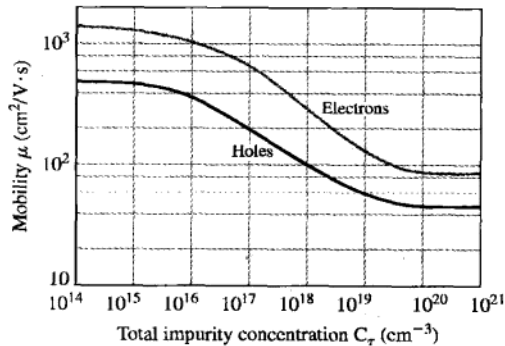


Figure 13.26

The effect of total ionized impurity concentration on the mobility of charge carriers in silicon at room temperature.

(From A.S. Grove, "Physics and Technology of Semiconductor Devices", Wiley, 1967, p. 110. Reprinted with permission of John Wiley & Sons, Inc.)

**EXAMPLE
PROBLEM 13.9**

A silicon semiconductor at 27°C is doped with 1.4×10^{16} boron atoms/cm³ plus 1.0×10^{16} phosphorus atoms/cm³. Calculate (a) the equilibrium electron and hole concentrations, (b) the mobilities of electrons and holes, and (c) the electrical resistivity. Assume complete ionization of the dopant atoms. $n_i(\text{Si}) = 1.50 \times 10^{10}$ cm⁻³.

■ Solution

- a. *Majority-carrier concentration:* The net concentration of immobile ions is equal to the acceptor ion concentration minus the donor ion concentration. Thus,

$$\begin{aligned} p_p &\approx N_a - N_d = 1.4 \times 10^{16} \text{ B atoms/cm}^3 - 1.0 \times 10^{16} \text{ P atoms/cm}^3 \\ &\approx N_a \approx 4.0 \times 10^{15} \text{ holes/cm}^3 \quad \blacktriangleleft \end{aligned}$$

Minority-carrier concentration: Electrons are the minority carriers. Thus,

$$n_p = \frac{n_i^2}{N_a} = \frac{(1.50 \times 10^{10} \text{ cm}^{-3})^2}{4 \times 10^{15} \text{ cm}^{-3}} = 5.6 \times 10^4 \text{ electrons/cm}^3 \quad \blacktriangleleft$$

- b. *Mobilities of electrons and holes:* For electrons, using the total impurity concentration $C_T = 2.4 \times 10^{16}$ ions/cm³ and Fig. 13.26,

$$\mu_n = 900 \text{ cm}^2/(\text{V} \cdot \text{s}) \quad \blacktriangleleft$$

For holes, using $C_T = 2.4 \times 10^{16}$ ions/cm³ and Fig. 13.26,

$$\mu_p = 300 \text{ cm}^2/(\text{V} \cdot \text{s}) \quad \blacktriangleleft$$

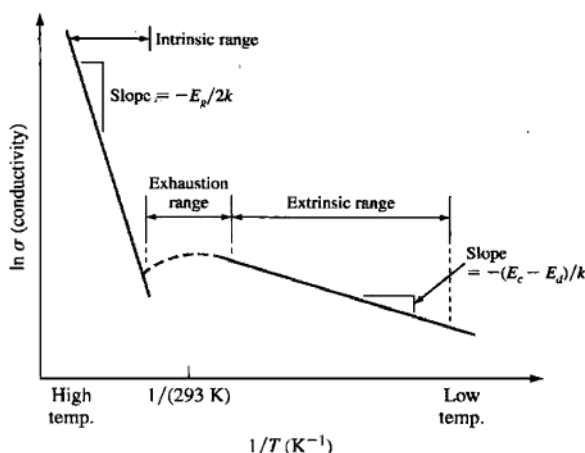
- c. *Electrical resistivity:* The doped semiconductor is p-type:

$$\begin{aligned} \rho &= \frac{1}{q\mu_p p_p} \\ &= \frac{1}{(1.60 \times 10^{-19} \text{ C})[300 \text{ cm}^2/(\text{V} \cdot \text{s})](4.0 \times 10^{15}/\text{cm}^3)} \\ &= 5.2 \Omega \cdot \text{cm} \quad \blacktriangleleft \end{aligned}$$

13.4.6 Effect of Temperature on the Electrical Conductivity of Extrinsic Semiconductors

The electrical conductivity of an extrinsic semiconductor such as silicon that contains doped impurity atoms is affected by temperature, as shown schematically in Fig. 13.27. At lower temperatures, the number of impurity atoms per unit volume activated (ionized) determines the electrical conductivity of the silicon. As the temperature is increased, more and more impurity atoms are ionized, and thus the electrical conductivity of extrinsic silicon increases with increasing temperature in the extrinsic range (Fig. 13.27).

In this extrinsic range, only a relatively small amount of energy (≈ 0.04 eV) is required to ionize the impurity atoms. The amount of energy required to excite a donor electron into the conduction band in n-type silicon is $E_c - E_d$ (Fig. 13.22).

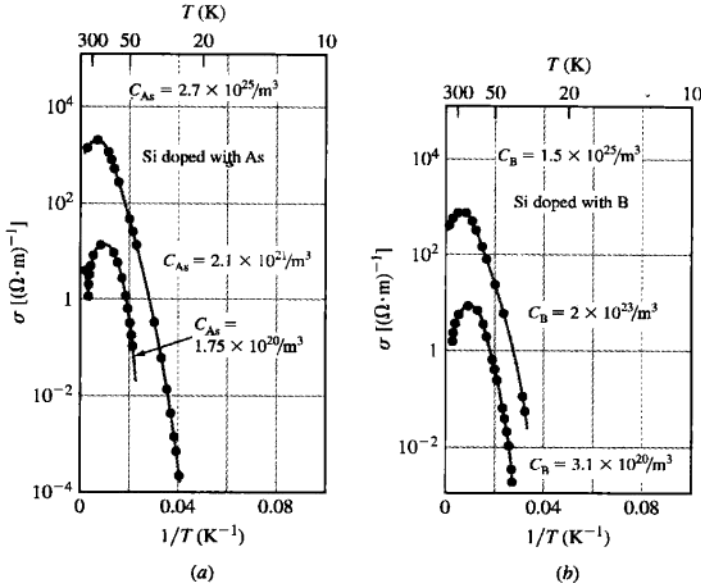
**Figure 13.27**

Schematic plot of $\ln \sigma$ (conductivity) versus $1/T$ (K^{-1}) for an n-type extrinsic semiconductor.

Thus, the slope of $\ln \sigma$ versus $1/T$ (K^{-1}) for n-type silicon is $-(E_c - E_d)/k$. Correspondingly, the amount of energy required to excite an electron in p-type silicon into an acceptor level and thereby create a hole in the valence band is $E_a - E_v$. Thus, the slope of $\ln \sigma$ versus $1/T$ (K^{-1}) for p-type silicon is $-(E_a - E_v)/k$ (Fig. 13.27).

For a certain temperature range above that required for complete ionization, an increase in temperature does not substantially change the electrical conductivity of an extrinsic semiconductor. For an n-type semiconductor, this temperature range is referred to as the *exhaustion range* since donor atoms become completely ionized after the loss of their donor electrons (Fig. 13.27). For p-type semiconductors, this range is referred to as the *saturation range* since acceptor atoms become completely ionized with acceptor electrons. To provide an exhaustion range at about room temperature (300 K), silicon doped with arsenic requires about 10^{21} carriers/ m^3 (Fig. 13.28a). Donor exhaustion and acceptor saturation temperature ranges are important for semiconductor devices since they provide temperature ranges that have essentially constant electrical conductivities for operation.

As the temperature is increased beyond that of the exhaustion range, the intrinsic range is entered upon. The higher temperatures provide sufficient activation energies for electrons to jump the semiconductor gap (1.1 eV for silicon) so that intrinsic conduction becomes dominant. The slope of the $\ln \sigma$ versus $1/T$ (K^{-1}) plot becomes much steeper and is $-E_g/2k$. For silicon-based semiconductors with an energy gap of 1.1 eV, extrinsic conduction can be used up to about 200°C. The upper limit for the use of extrinsic conduction is determined by the temperature at which intrinsic conductivity becomes important.

**Figure 13.28**

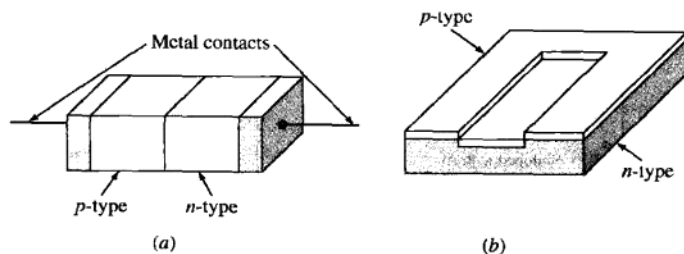
(a) Plot of $\ln \sigma$ versus $1/T$ (K^{-1}) for As-doped Si. At the lowest level of impurity the intrinsic contribution is slightly visible at the highest temperatures; slope of the line at 40 K gives $E_i = 0.048$ eV. (b) Plot of $\ln \sigma$ versus $1/T$ (K^{-1}) for B-doped Si. Slope of the line below 50 K gives $E_i = 0.043$ eV.

(From C.A. Wert and R.M. Thomson, "Physics of Solids," 2d ed., McGraw-Hill, 1970, p. 282. Reproduced with permission of The McGraw-Hill Companies.)

13.5 SEMICONDUCTOR DEVICES

The use of semiconductors in the electronics industry has become increasingly important. The ability of semiconductor manufacturers to put extremely complex electrical circuits on a single chip of silicon of about 1 cm square or less and about $200 \mu\text{m}$ thick has revolutionized the design and manufacture of countless products. An example of the complex electronic circuitry able to be put on a silicon chip is shown in Fig. 13.1 of an advanced microprocessor or "computer on a chip." The microprocessor forms the basis for many of the latest products that use the progressive miniaturization of silicon-based semiconductor technology.

In this section, we will first study the electron-hole interactions at a pn junction and then examine the operation of the pn junction diode. We shall then look at some applications of pn junction diodes. Finally, we shall briefly examine the operation of the bipolar junction transistor.

**Figure 13.29**

(a) pn junction diode grown in the form of a single crystal bar.

(b) Planar pn junction formed by selectively diffusing a p-type impurity into an n-type semiconductor crystal.

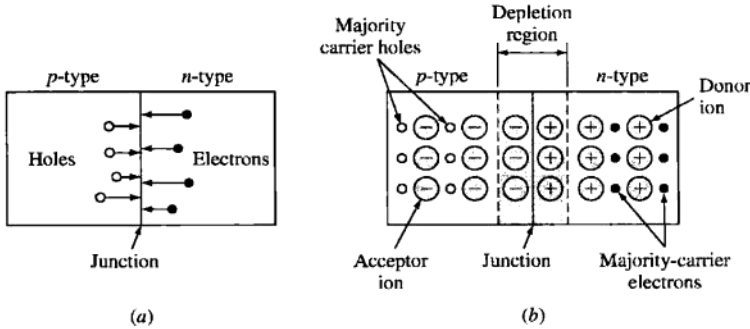
13.5.1 The pn Junction

Most common semiconductor devices depend on the properties of the boundary between p-type and n-type materials, and therefore we shall examine some of the characteristics of this boundary. A pn junction diode can be produced by growing a single crystal of intrinsic silicon and doping it first with n-type material and then with p-type material (Fig. 13.29a). More commonly, however, the pn junction is produced by solid-state diffusion of one type of impurity (for example, p-type) into existing n-type material (Fig. 13.29b).

The pn Junction Diode at Equilibrium Let us consider an ideal case in which p-type and n-type silicon semiconductors are joined together to form a junction. Before joining, both types of semiconductors are electrically neutral. In the p-type material, holes are the majority carriers and electrons are the minority carriers. In the n-type material, electrons are the majority carriers and holes are the minority carriers.

After joining the p- and n-type materials (i.e., after a **pn junction** is formed in actual fabrication), the majority carriers near or at the junction diffuse across the junction and recombine (Fig. 13.30a). Since the remaining ions near or at the junction are physically larger and heavier than the electrons and holes, they remain in their positions in the silicon lattice (Fig. 13.30b). After a few recombinations of majority carriers at the junction, the process stops because the electrons crossing over the junction into the p-type material are repelled by the large negative ions. Similarly, holes crossing over the junction are repelled by the large positive ions in the n-type material. The immobile ions at the junction create a zone depleted of majority carriers called a *depletion region*. Under equilibrium conditions (i.e., open-circuit conditions) there exists a potential difference or barrier to majority-carrier flow. Thus, there is no net current flow under open-circuit conditions.

The pn Junction Diode Reverse-Biased When an external voltage is applied to a pn junction, it is said to be **biased**. Let us consider the effect of applying an external voltage from a battery to the pn junction. The pn junction is said to be **reverse-biased** if the n-type material of the junction is connected to the positive

**Figure 13.30**

(a) pn junction diode showing majority carriers (holes in p-type material and electrons in n-type material) diffusing toward junction. (b) Formation of depletion region at and near pn junction due to loss of majority carriers in this region by recombination. Only ions remain in this region in their positions in the crystal structure.

terminal of the battery and if the p-type material is connected to the negative terminal (Fig. 13.31). With this arrangement, the electrons (majority carriers) of the n-type material are attracted to the positive terminal of the battery away from the junction and the holes (majority carriers) of the p-type material are attracted to the negative terminal of the battery away from the junction (Fig. 13.31). The movement of the majority-carrier electrons and holes away from the junction increases its barrier width, and as a result current resulting from majority carriers will not flow. However, thermally generated minority carriers (holes in n-type material and electrons in p-type material) will be driven toward the junction so that they can combine and create a very small current flow under reverse-bias conditions. This minority or *leakage current* is usually of the order of microamperes (μA) (Fig. 13.32).

The pn Junction Diode Forward-Biased The pn junction diode is said to be **forward-biased** if the n-type material of the junction is connected to the negative terminal of an external battery (or other electrical source) and if the p-type material is connected to the positive terminal (Fig. 13.33). In this arrangement, the majority carriers are repelled toward the junction and can combine, that is, electrons are repelled away from the negative terminal of the battery toward the junction and holes are repelled away from the positive terminal toward the junction.

Under forward bias—that is, forward bias with respect to majority carriers—the energy barrier at the junction is reduced so that some electrons and holes can cross the junction and subsequently recombine. During the forward biasing of a pn junction, electrons from the battery enter the negative material of the diode (Fig. 13.33). For every electron that crosses the junction and recombines with a hole, another electron enters from the battery. Also, for every hole that recombines with

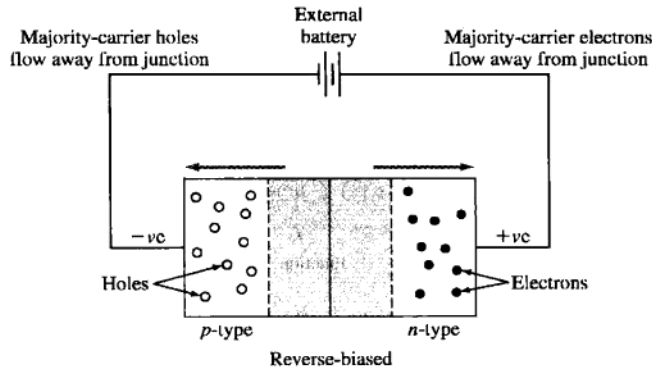


Figure 13.31
Reverse-biased pn junction diode. Majority carriers are attracted away from the junction, creating a wider depletion region than when the junction is at equilibrium. Current flow due to majority carriers is reduced to near zero. However, minority carriers are biased forward, creating a small leakage current, as shown in Fig. 13.32.

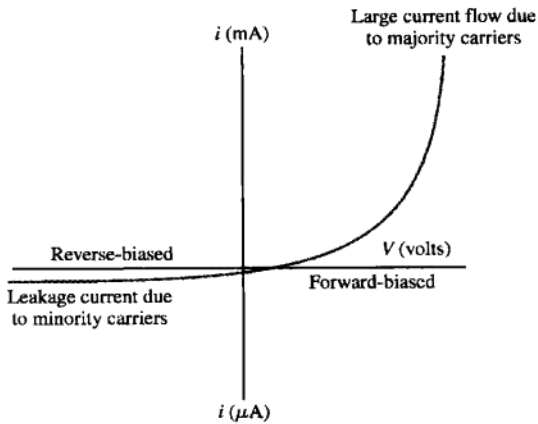


Figure 13.32
Schematic of current-voltage characteristics of a pn junction diode. When the pn junction diode is reverse-biased, a leakage current due to minority carriers combining exists. When the pn junction diode is forward-biased, a large current flows because of recombination of majority carriers.

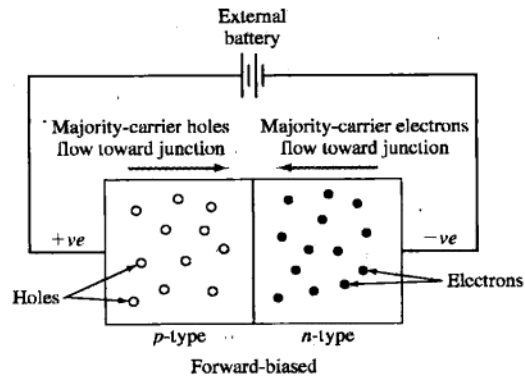
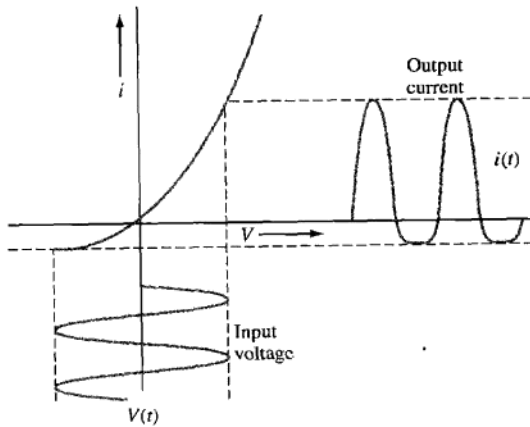


Figure 13.33
Forward-biased pn junction diode. Majority carriers are repelled toward the junction and cross over it to recombine so that a large current flows.

**Figure 13.34**

Voltage-current diagram illustrating the rectifying action of a pn junction diode that converts alternating current (ac) to direct current (dc). The output current is not completely direct current but is mostly positive. This dc signal can be smoothed out by using other electronic devices.

an electron in the n-type material, a new hole is formed whenever an electron leaves the p-type material and flows toward the positive terminal of the battery. Since the energy barrier to electron flow is reduced when the pn junction is forward-biased, considerable current can flow, as indicated in Fig. 13.32. Electron flow (and hence current flow) can continue as long as the pn junction is forward-biased and the battery provides an electron source.

13.5.2 Some Applications for pn Junction Diodes

Rectifier Diodes One of the most important uses of pn junction diodes is to convert alternating voltage into direct voltage, a process known as *rectification*. Diodes used for this process are called **rectifier diodes**. When an AC signal is applied to a pn junction diode, the diode will conduct only when the p region has a positive voltage applied to it relative to the n region. As a result, half-wave rectification will be produced, as shown in Fig. 13.34. This output signal can be smoothed out with other electronic devices and circuits so that a steady DC signal can be produced. Solid-state silicon rectifiers are used in a wide range of applications that require from tenths of an ampere to several hundred amperes or more. Voltages, too, can be as high as 1000 V or more.

Breakdown Diodes Breakdown diodes, or *zener diodes* as they are sometimes called, are silicon rectifiers in which the reverse current (leakage current) is small, and then with only slightly more reverse-bias voltage, a breakdown voltage is reached upon

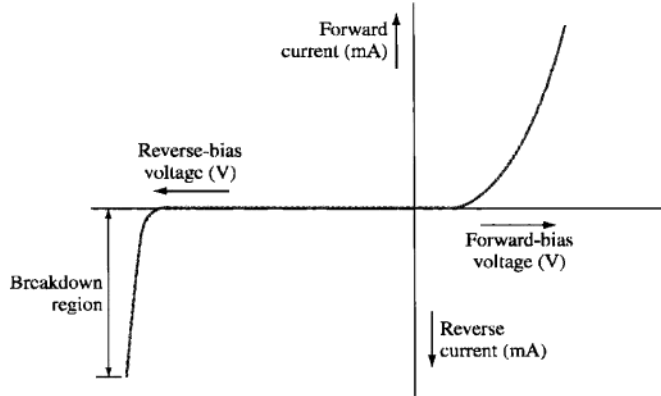


Figure 13.35

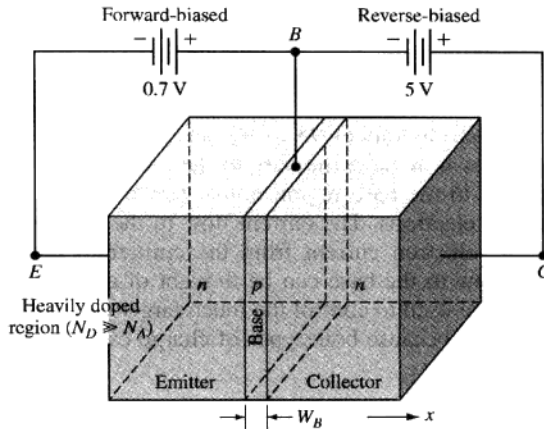
Zener (avalanche) diode characteristic curve. A large reverse current is produced at the breakdown-voltage region.

which the reverse current increases very rapidly (Fig. 13.35). In the so-called zener breakdown, the electric field in the diode becomes strong enough to attract electrons directly out of the covalently bonded crystal lattice. The electron-hole pairs created then produce a high reverse current. At higher reverse-bias voltages than the zener breakdown voltages, an avalanche effect occurs, and the reverse current is very large. One theory to explain the avalanche effect is that electrons gain sufficient energy between collisions to knock more electrons from covalent bonds, which can then reach high enough energies to conduct electricity. Breakdown diodes can be made with breakdown voltages from a few to several hundred volts and are used for voltage-limiting applications and for voltage stabilizing under conditions of widely varying current.

13.5.3 The Bipolar Junction Transistor

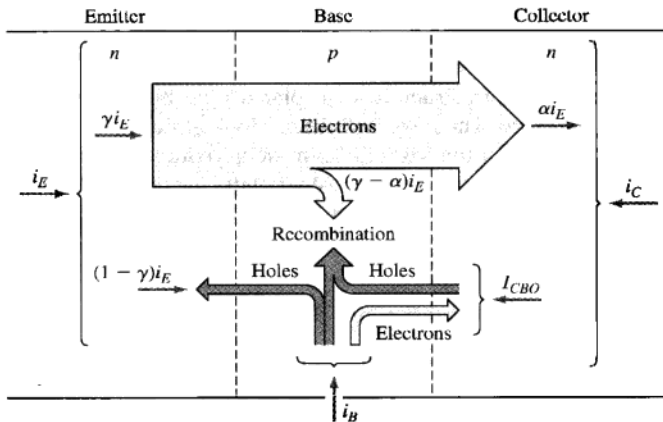
A **bipolar junction transistor (BJT)** is an electronic device that can serve as a current amplifier. This device consists of two pn junctions that occur sequentially in a single crystal of a semiconducting material such as silicon. Figure 13.36 shows schematically an npn-type bipolar junction transistor and identifies the three main parts of the transistor: *emitter*, *base*, and *collector*. The emitter of the transistor emits charge carriers. Since the emitter of the npn transistor is n-type, it emits electrons. The base of the transistor controls the flow of charge carriers and is p-type for the npn transistor. The base is made very thin (about 10^{-3} cm thick) and is lightly doped so that only a small fraction of the charge carriers from the emitter will recombine with the oppositely charged majority carriers of the base. The collector of the BJT collects charge carriers mainly from the emitter. Since the collector section of the npn transistor is n-type, it collects mainly electrons from the emitter.

Under normal operation of the npn transistor, the emitter-base junction is forward-biased and the collector-base junction is reverse-biased (Fig. 13.36). The forward bias on the emitter-base junction causes an injection of electrons from the emitter into the base (Fig. 13.37). Some of the electrons injected into the base are lost

**Figure 13.36**

Schematic illustration of an npn bipolar junction transistor. The n region on the left is the emitter, the thin p region in the middle is the base, and the n region on the right is the collector. For normal operation, the emitter-base junction is forward-biased and the collector-base junction is reverse-biased.

(From C.A. Holt, "Electronic Circuits," Wiley, 1978, p. 49. Reprinted with permission of John Wiley & Sons, Inc.)

**Figure 13.37**

Charge carrier motion during the normal operation of an npn transistor. Most of the current consists of electrons from the emitter that go right through the base to the collector. Some of the electrons, about 1 to 5 percent, recombine with holes from the base current flow. Small reverse currents due to thermally generated carriers are also present, as indicated.

(From R.J. Smith, "Circuits, Devices and Systems," 3rd ed., Wiley, 1976, p. 343. Reprinted with permission of John Wiley & Sons, Inc.)

by recombination with holes in the p-type base. However, most of the electrons from the emitter pass right through the thin base into the collector, where they are attracted by the positive terminal of the collector. Heavy doping of the emitter with electrons, light doping of the base with holes, and a very thin base are all factors that cause most of the emitter electrons (about 95 to 99 percent) to pass right through to the collector. Very few holes flow from the base to the emitter. Most of the current flow from the base terminal to the base region is the flow of holes to replace those lost by recombination with electrons. The current flow to the base is small and is about 1 to 5 percent of the electron current from the emitter to the collector. In some respects, the current flow to the base can be thought of as a control valve since the small base current can be used to control the much larger collector current. The bipolar transistor is so named because both types of charge carriers (electrons and holes) are involved in its operation.

13.6 MICROELECTRONICS

Modern semiconductor technology has made it possible to put thousands of transistors on a "chip" of silicon about 5 mm square and 0.2 mm thick. This ability to incorporate very large numbers of electronic elements on silicon chips has greatly increased the capability of electronic device systems (Fig. 13.1).

Large-scale integrated (LSI) microelectronic circuits are manufactured by starting with a silicon single-crystal wafer (n- or p-type) about 100 to 125 mm in diameter and 0.2 mm thick. The surface of the wafer must be highly polished and free from defects on one side since the semiconductor devices are fabricated into the polished surface of the wafer. Figure 13.38 shows a silicon wafer after the microelectronic circuits have been fabricated into its surface. About 100 to 1000 chips (depending on their size) can be produced from one wafer.

First, let us examine the structure of a planar-type bipolar transistor fabricated into a silicon wafer surface. Then, we will briefly look at the structure of a more compact type of transistor called the MOSFET, or *metal oxide semiconductor field-effect transistor*, which is used in many modern semiconductor device systems. Finally, we will outline some of the basic procedures used in the manufacturing of modern microelectronic circuits.

13.6.1 Microelectronic Planar Bipolar Transistors

Microelectronic planar bipolar transistors are fabricated into the surface of a silicon single-crystal wafer by a series of operations that require access to only one surface of the silicon wafer. Figure 13.39 shows a schematic diagram of the cross section of an npn planar bipolar transistor. In its fabrication, a relatively large island of n-type silicon is formed first in a p-type silicon base or substrate. Then smaller islands of p- and n-type silicon are created in the larger n-type island (Fig. 13.39). In this way, the three fundamental parts of the npn bipolar transistor, the emitter, base, and collector, are formed in a planar configuration. As in the case of the individual npn bipolar transistor described in Sec. 13.5 (see Fig. 13.36), the emitter-base junction is forward-biased and the base-collector junction is reverse-biased. Thus, when elec-

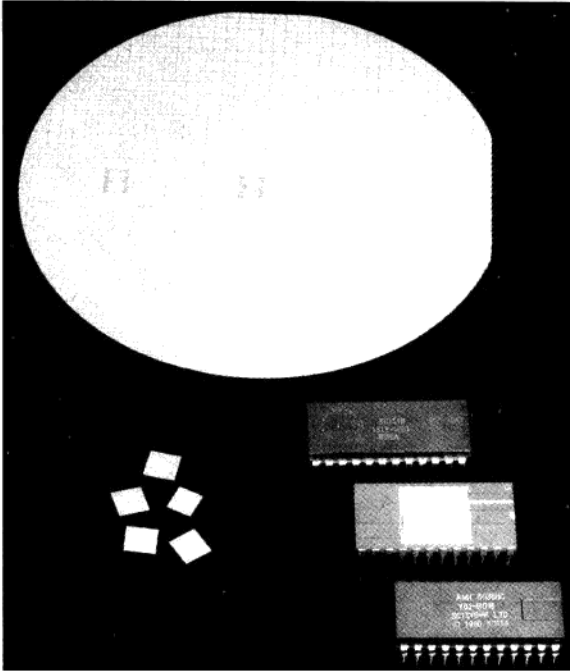


Figure 13.38

This photograph shows a wafer, individual integrated circuits, and three chip packages (the middle package is ceramic and the other two are plastic). The three larger devices along the middle of this wafer are *process control monitors* (PCMs) to monitor the technical quality of the dice on the wafer.

(Courtesy of ON semiconductor.)

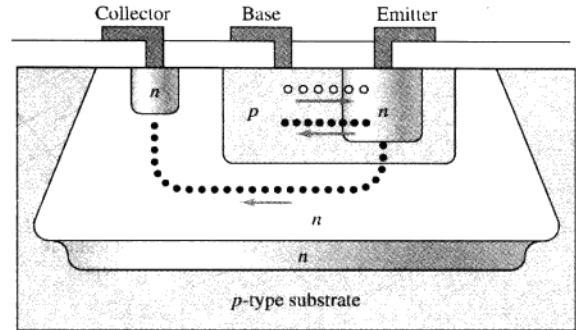


Figure 13.39

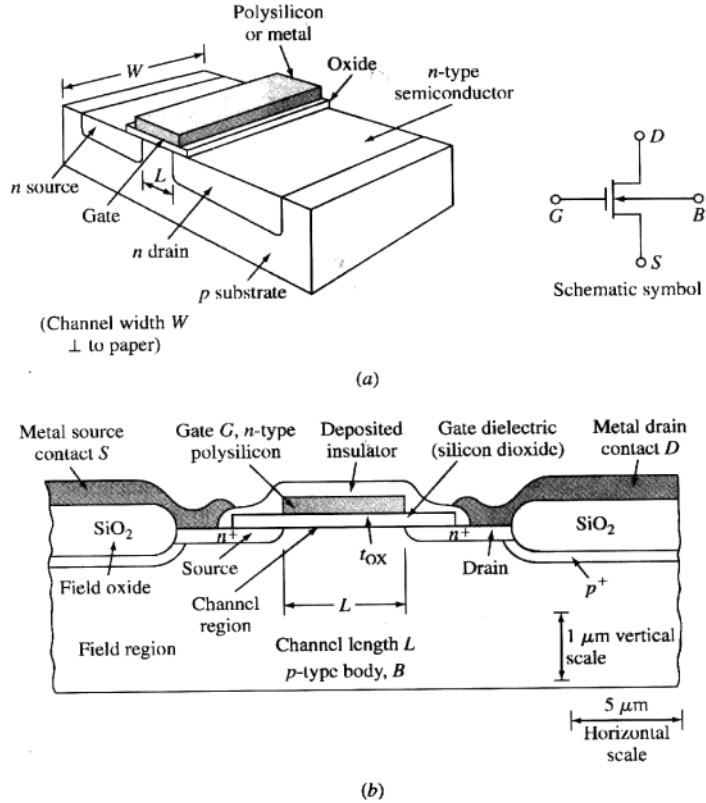
Microelectronic planar bipolar npn transistor fabricated in a single crystal of silicon by a series of operations that require access to only one surface of the silicon chip. The entire chip is doped with p-type impurities, and then islands of n-type silicon are formed. Smaller p- and n-type areas are next created within these islands in order to define the three fundamental elements of the transistor: the emitter, the base, and the collector. In this microelectronic bipolar transistor, the emitter-base junction is forward-biased and the collector-base junction is reverse-biased, as in the case of the isolated npn transistor of Fig. 13.36. The device exhibits gain because a small signal applied to the base can control a large one at the collector.

(From J.D. Meindl, "Microelectronic Circuit Elements," *Scientific American*, September 1977, p. 75. Illustration © Gabor Kiss. Reprinted by permission of Gabor Kiss.)

trons from the emitter are injected into the base, most of them go into the collector and only a small percentage (~ 1 to 5 percent) recombine with holes from the base terminal (see Fig. 13.37). The microelectronic planar bipolar transistor can therefore function as a current amplifier in the same way as the individual macroelectronic bipolar transistor.

13.6.2 Microelectronic Planar Field-Effect Transistors

In many of today's modern microelectronic systems, another type of transistor, called the *field-effect transistor*, is used because of its low cost and compactness. The most common field-effect transistor used in the United States is the n-type metal oxide semiconductor field-effect transistor. In the n-type MOSFET, or NMOS, two islands of n-type silicon are created in a substrate of p-type silicon,

**Figure 13.40**

Schematic diagram of an NMOS field-effect transistor: (a) overall structure and (b) cross-sectional view.

(From D.A. Hodges and H.G. Jackson, "Analysis and Design of Digital Integrated Circuits," McGraw-Hill, 1983, p. 40. Reproduced with permission of The McGraw-Hill Companies)

as shown in Fig. 13.40. In the NMOS device, the contact where the electrons enter is called the *source*, and the contact where they leave is called the *drain*. Between the n-type silicon of the source and the drain, there is a p-type region on whose surface a thin layer of silicon dioxide is formed that acts as an insulator. On top of the silicon dioxide another layer of polysilicon (or metal) is deposited to form the third contact for the transistor, called the *gate*. Since silicon dioxide is an excellent insulator, the gate connection is not in direct electrical contact with the p-type material below the oxide.

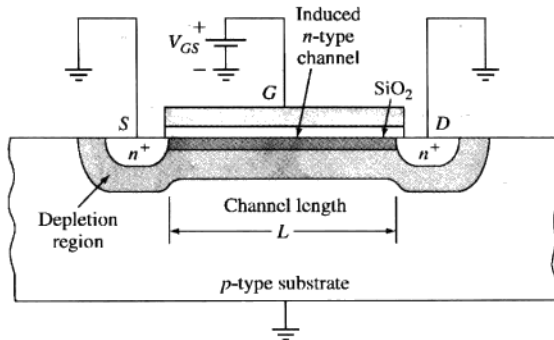


Figure 13.41

Idealized NMOS device cross section with positive gate-source voltage (V_{GS}) applied, showing depletion regions and the induced channel.

(From D.A. Hodges and H.G. Jackson, "Analysis and Design of Digital Integrated Circuits," McGraw-Hill, 1983, p. 43.

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For a simplified type of NMOS when no voltage is applied to the gate, the p-type material under the gate contains majority carriers that are holes, and only a few electrons are attracted to the drain. However, when a positive voltage is applied to the gate, its electric field attracts electrons from the nearby n^+ source and drain regions to the thin layer beneath the surface of the silicon dioxide just under the gate so that this region becomes n-type silicon, with electrons being the majority carriers (Fig. 13.41). When electrons are present in this channel, a conducting path exists between the source and the drain. Thus, electrons will flow between the source and the drain if there is a positive voltage difference between them.

The MOSFET, like the bipolar transistor, is also capable of current amplification. The gain in MOSFET devices is usually measured in terms of a voltage ratio instead of a current ratio as for the bipolar transistor. p-type MOSFETs with holes for majority carriers can be made in a similar way, using p-type islands for the source and drain in an n-type substrate. Since the current carriers are electrons in NMOS devices and holes in PMOS ones, they are known as *majority-carrier devices*.

MOSFET technology is the basis for most large-scale integrated digital memory circuits, mainly because individual MOSFET take up less silicon chip area than the bipolar transistor and hence greater densities of transistors can be obtained. Also, the cost of fabrication of the MOSFET LSIs is less than that for the bipolar transistor types. However, there are some applications for which bipolar transistors are necessary.



Figure 13.42

Engineer laying out an integrated circuit network.

(Courtesy of Harris Corporation.)

13.6.3 Fabrication of Microelectronic Integrated Circuits

The design of a microelectronic integrated circuit is first laid out on a large scale, usually with computer assistance so that the most space-conserving design can be made (Fig. 13.42). In the most common fabrication process, the layout is used to prepare a set of photomasks, each of which contains the pattern for a single layer of the multiple-layer finished integrated circuit (Fig. 13.43).

Photolithography The process by which a microscopic pattern is transferred from a photomask to the silicon wafer surface of the integrated circuit is called *photolithography*. Figure 13.44 shows the steps necessary to form an insulating layer of silicon dioxide on the silicon surface, which contains a pattern of regions of exposed silicon substrate. In one type of photolithographic process shown in step 2 of Fig. 13.44, an oxidized wafer is first coated with a layer of *photoresist*, a light-sensitive polymeric material. The important property of photoresist is that its solubility in certain solvents is greatly affected by its exposure to *ultraviolet*

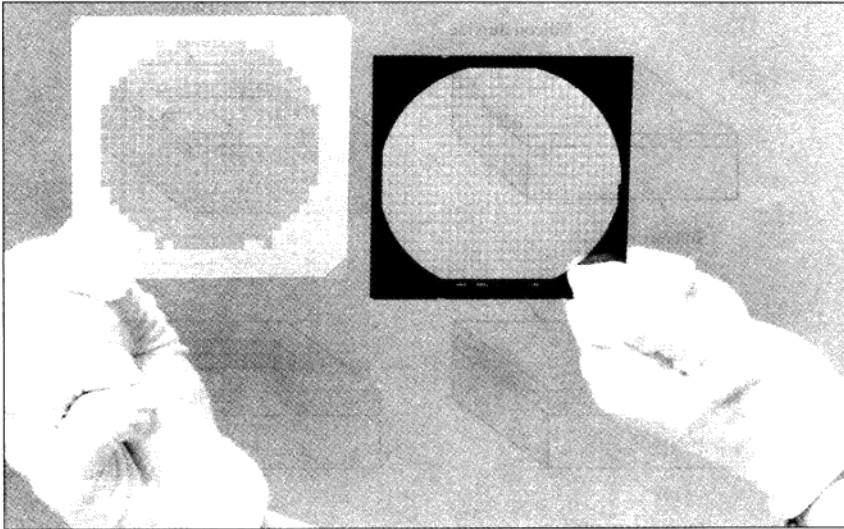


Figure 13.43

This photograph depicts two types of photolithographic masks used in the fabrication of integrated circuits. At the left is the more durable chrome mask, which is used for long production runs and can be used to produce emulsion masks like the one shown on the right. Emulsion masks are less expensive and tend to be used for shorter production runs, such as the fabrication of prototypes.

(Courtesy of ON semiconductor.)

(UV) radiation. After exposure to UV radiation (step 3 of Fig. 13.44) and subsequent development, a pattern of photoresist is left wherever the mask was transparent to the UV radiation (step 4 of Fig. 13.44). The silicon wafer is then immersed in a solution of hydrofluoric acid, which attacks only the exposed silicon dioxide and not the photoresist (step 5 of Fig. 13.44). In the final step of the process the photoresist pattern is removed by another chemical treatment (step 6 of Fig. 13.44). The photolithographic process has improved so that it is now possible to reproduce surface dimensions to about $0.5\ \mu\text{m}$.

Diffusion and Ion Implantation of Dopants into the Surface of Silicon Wafers

To form active circuit elements such as bipolar and MOS transistors in integrated circuits, it is necessary to selectively introduce impurities (dopants) into the silicon substrate to create localized n- and p-type regions. There are two main techniques for introducing dopants into the silicon wafers: (1) *diffusion* and (2) *ion implantation*.

The Diffusion Technique As previously described in Sec. 5.3, the impurity atoms are diffused into the silicon wafers at high temperatures, that is, about 1000°C to 1100°C . Important dopant atoms such as boron and phosphorus move much more

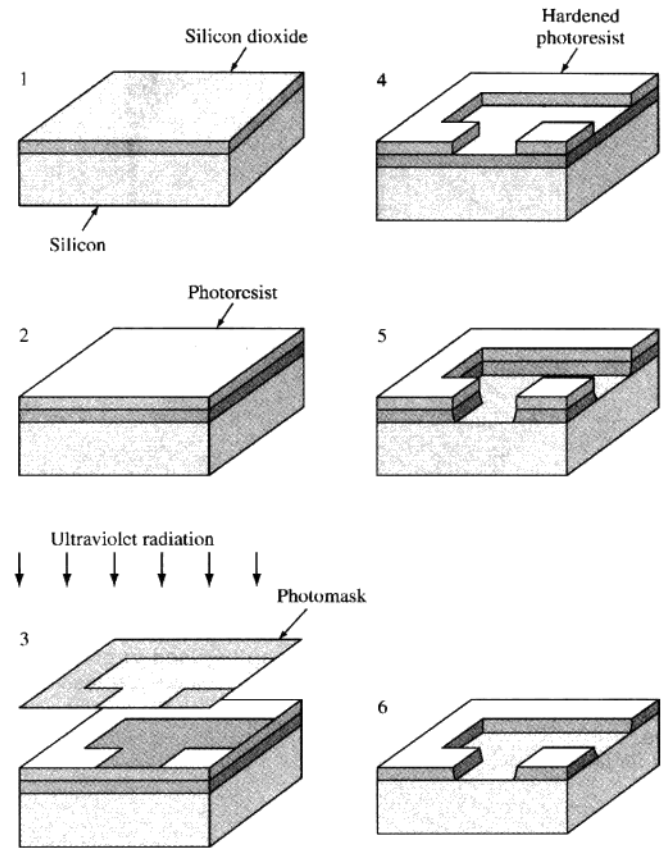
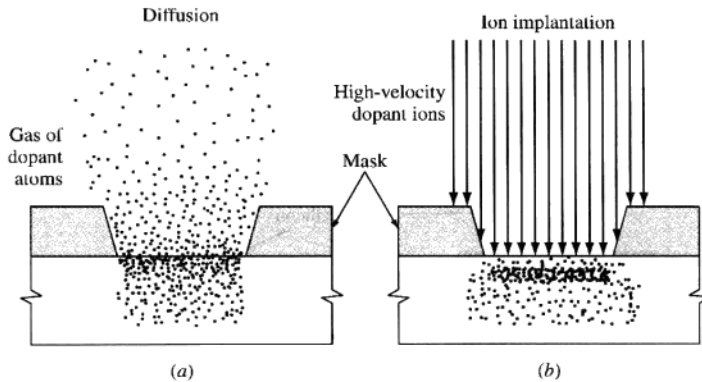


Figure 13.44

The steps for the photolithographic process. In this process, a microscopic pattern can be transferred from a photomask to a material layer in an actual circuit. In this illustration, a pattern is shown being etched into a silicon dioxide layer on the surface of a silicon wafer. The oxidized wafer (1) is first coated with a layer of a light-sensitive material called *photoresist* and (2) then exposed to ultraviolet light through the photomask. (3) The exposure renders the photomask insoluble in a developer solution; hence a pattern of photoresist is left wherever the mask is transparent (4). The wafer is next immersed in a solution of hydrofluoric acid, which selectively attacks the silicon dioxide, (5) leaving the photoresist pattern and the silicon substrate unaffected.

(6) In the final step, the photoresist pattern is removed by another chemical treatment. (© George V. Kelvin. Reprinted by permission.)

slowly through silicon dioxide than through the silicon crystal lattice. Thin silicon dioxide patterns can serve as masks to prevent the dopant atoms from penetrating into the silicon (Fig. 13.45*a*). Thus, a rack of silicon wafers can be placed into a diffusion furnace at 1000°C to 1100°C in an atmosphere containing phosphorus (or

**Figure 13.45**

Selective doping processes for exposed silicon surfaces: (a) high-temperature diffusion of impurity atoms; and (b) ion implantation.

(From S. Triebwasser, "Today and Tomorrow in Microelectronics," from the Proceedings of an NSF workshop held at Arlie, VA., Nov. 19–22, 1978.)

boron), for example. The phosphorus atoms will enter the unprotected surface of the silicon and slowly diffuse into the bulk of the wafer, as shown in Fig. 13.45a.

The important variables that control the concentration and depth of penetration are *temperature* and *time*. To achieve the maximum control of concentration, most diffusion operations are carried out in two steps. In the first, or *predeposits*, step, a relatively high concentration of dopant atoms is deposited near the surface of the wafer. After the predeposits step, the wafers are placed in another furnace, usually at a higher temperature, for the *drive-in diffusion* step, which achieves the necessary concentration of dopant atoms at a particular depth below the surface of the silicon wafer.

The Ion Implantation Technique Another selective doping process for silicon wafers for integrated circuits is the ion implantation technique (Fig. 13.45b), which has the advantage that the dopant impurities can be embedded at room temperature. In this process, the dopant atoms are ionized (electrons are removed from atoms to form ions) and the ions are accelerated to high energies through a high potential difference of 50 to 100 kV. When the ions strike the silicon wafer, they are embedded to varying depths, depending on their mass and energy and the type of surface protection of the silicon surface. A photoresist or silicon dioxide pattern can mask regions of the surface where ion implantation is not desired. The accelerated ions cause some damage to the crystal lattice of the silicon, but most of the damage can be healed by annealing at a moderate temperature. Ion implantation is useful wherever the doping level must be accurately controlled. Another important advantage of ion implantation is its ability to introduce dopant impurities through a thin oxide layer. This technique makes it possible to adjust the threshold voltages of MOS transistors. By means of ion implantation, both NMOS and PMOS transistors can be fabricated on the same wafer.

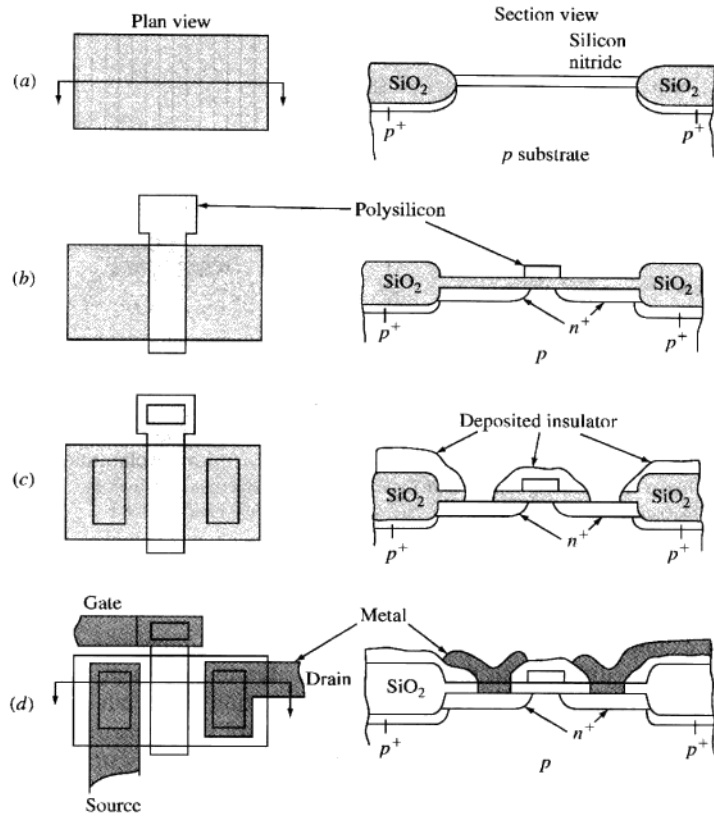


Figure 13.46
Steps in NMOS field-effect transistor fabrication: (a) first mask; (b) second mask: polysilicon gate and source-drain diffusion; (c) third mask: contact areas; and (d) fourth mask: metal pattern.
(From D.A. Hodges and H.G. Jackson, "Analysis and Design of Digital Integrated Circuits," McGraw-Hill, 1983, p. 17. Reproduced with permission of The McGraw-Hill Companies.)

MOS Integrated Circuit Fabrication Technology There are many different procedures used in the fabrication of MOS integrated circuits. New innovations and discoveries for improving the equipment design and processing of integrated circuits (ICs) are constantly being made in this rapidly progressing technology. The general processing sequence for one method of producing NMOS integrated circuits is described in the following steps³ and illustrated in Figs. 13.46 and 13.47.

³After D.A. Hodges and H.G. Jackson, "Analysis and Design of Digital Integrated Circuits," McGraw-Hill, 1983, pp. 16–18.