Engineering materials are classified into five classes: metals, ceramics, semiconductors, polymers, and composites. These categories are defined according to the distinctly different natures of bonding, structure and properties of the materials, as outlined below.

- 1. *Metals* can be considered to be held together by mutually shared free-electron bonding, and they are generally electrical and thermal conductors. Their high mechanical tensile strength and ductility are of frequent use.
- 2. The strong ionic bonding in *ceramics* results in generally high melting point, brittleness, good corrosion resistance, low thermal conductivity, and high compressive strength. Variation in the chemical bonding and crystal structure results in a large variety of electronic and magnetic properties of ceramics.
- 3. Semiconductors are dominated by covalent bonds. The importance of semiconductors in electronics has made them a unique class of materials, processed to have precisely controlled composition and structure. Microelectronic devices based on silicon technology are the basis of modern electric and electronic engineering. Compound semiconductors have important applications in laser and quantum devices.
- 4. Bonding in *polymers* basically consists of covalent bonds within hydrocarbon chains and cross-linking between chains. Common elements within the chains are C, O, N, H, and Si. The chain is extremely strong because of the covalent bonding, while the interchain interaction

is rather weak. Polymers are attractive for practical applications because they are relatively easy to synthesize or exist in nature, and thus are inexpensive. Polymers have profound applications in electronics and our daily life.

5. *Composites* are structures in which two or more materials are combined to produce a new material whose properties would not be attainable with a single material. A composite of metal and ceramic, for example, combines the heat resistance of the ceramic with the ductility of the metal. The most important applications for fiber-reinforced composites are as structural materials where rigidity, strength, and low density are required.

Materials constitute an extremely broad topic, in view of the range of structural, functional, and smart materials that are the backbones of modern technology. This article introduces a framework for advanced materials with an emphasis on functional materials.

### METALLIC MATERIALS

#### Metals and Alloys

Metals and alloys are the most important structural materials (1). The best-known single-element metals are Al, Cu, Mg, Ag, Co, Au, and Pt. The crystal structures of these materials are mostly simple face-centered cubic (fcc), body-centered cubic (bcc), and hexagonal close-packed (hcp). Most of them are good electrical and thermal conductors. The classification of metals is based on their physical properties; we refer to hightemperature materials (e.g., Ti, Ni, W, Mo, Nb, and Zr), magnetic materials (e.g., Fe, Co, and Ni), and low-cost electric conductors (e.g., Al, Cu, and sometimes Ag).

Alloys and steels cover the majority of metallic materials used in engineering. By adding specific elements into an alloy, various properties of the system can be enhanced. If one component is dissolved one or more others without changing the structure of the host component(s), the resulting alloy is called a *solid solution*. Solid solutions are phases of variable composition, and in principle any number of components can be alloyed together to form a series of solid solutions. The range of compositions of solid solutions can be determined from a phase diagram. The replacement of copper atoms by nickel on the lattice of pure copper yields an example of a *substitutional solid solution*. The compositions of commercial alloys are quite complex, and they are usually identified by numbers, such as Al–Cu alloy 2014 and 6061, and steel 4140 and 4340.

### **Intermetallics and Superalloys**

Metals are dominated by metallic bonds, which means that the free electrons are contributed by all of the atoms and they are shared by all of the atoms; thus, the metal atoms are embedded in the sea of free electrons. On the other hand, metal atoms can share local electrons, partially forming valence bonds, thus, intermetallic compounds are formed. An *intermetallic compound* is a phase that crystallizes with a structure other than those of its components. Typical intermetallic compounds are NiAl, Ni<sub>3</sub>Al, TiAl<sub>3</sub>, MoSi<sub>2</sub>, and Ni<sub>3</sub>Sn. Taking Ni<sub>3</sub>Al as an example, the two components Al and Ni have

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face-centered cubic (fcc) structure, while  $Ni_3Al$  has the ordered  $Cu_3Au$  structure. Intermetallic compounds offer potential applications in high-temperature materials (2), metallurgy and chemistry (3), magnetoresistance and magnetostrictance (4), shape memory alloys, and diffusion barriers (5).

Superalloys are special combinations of metals that maintain high strength during prolonged exposure to elevated temperatures, as in turbine blades in jet engines. Superalloys consist mostly of nickel, with smaller amounts of Al, Ti, Cr, etc. The essential idea is to create small precipitates such as  $Ni_3Al$  and  $Ni_3Ti$  in the nickel matrix to obstruct the motion of dislocations, the atomic-scale cause of undesirable deformation. The initiation of fracture is also greatly reduced by growing single-crystal blades that have no grain boundaries.

# **Functional Metallic Materials**

Magnetic Metallic Materials. Magnetic properties arise from the atomic magnetic moments due to the alignment of electron spins (6,7). The electron configuration of the constituents and the structure of the compounds determine the orientation and arrangement of atomic magnetic moments, resulting in different types of magnetism. Two electrons are termed *paired* if they coincide in all of their quantum numbers except the spin quantum number; then, the magnetic moments of the two cancel each other. Substances having only paired electrons are *diamagnetic*. When they are introduced into an external magnetic field, a force acts on the electrons and an electric current is induced; the magnetic field of this current is opposed to the external field (Lenz's rule), thus, the substance is repelled by the external magnetic field. Typical diamagnetic materials are Al<sub>2</sub>O<sub>3</sub>, CaF<sub>2</sub>, Cu, MgO, and Au.

In a paramagnetic material unpaired electrons are present. When an external magnetic field acts on a paramagnetic substance, the magnetic moments of the electrons adopt the orientation of this field, the sample is magnetized, and the force pulls the substance into the field. Typical examples of paramagnetic materials are Al, CeO<sub>2</sub>,  $(\alpha,\beta)$ -Mn, and TiO<sub>2</sub>. Ferromagnetism refers to a state in which the spins of all the unpaired electrons are aligned even in the absence of a magnetic field if the temperature is below a critical temperature. A ferromagnetic material has a nonvanishing magnetic moment, or spontaneous magnetization. In antiferromagnetism, although there is no net total moment in the absence of a field, there is an ordered spatial pattern of the individual magnetic moments, due to the antiparallel orientation of neighboring moments.

Fe, Co, and Ni are the most common ferromagnetic materials. Magnetic domains are characteristic of ferromagnetic materials. All of the atomic magnetic moments are aligned or nearly aligned within one domain, but the alignment varies from domain to domain. When the spins of all domains have been oriented in parallel, *saturation* is reached. To achieve this state a magnetic field with some minimum field strength is required. A *hysteresis curve* is an important characteristic of ferromagnetic materials (Fig. 1). Starting from an unmagnetized sample, an increasing applied magnetic field causes increasing magnetization until saturation is reached. After switching off the external field, there is some loss of magnetization, but a *remanent magnetization*  $M_r$  is retained. On reversing the magnetic field, the spins experience a reorienta-



**Figure 1.** A schematic diagram showing the hysteresis loop of a ferromagnetic material. The magnetization M is plotted against the applied field H.

tion. The minimum magnetic field required to bring the magnetization to zero is the *coercive force*  $H_c$ . The remanent magnetization depends on the magnetic domain alignment, and the coercive force is related to the movability of the magnetic domain boundaries. The area enclosed by the hysteresis loop is related to the energy consumption during the magnetization circle, and it is a frequently used quantity for characterizing permanent magnets.

Typical *soft* magnetic materials (displaying little hysteresis) with ordered structures are FeCo, Ni<sub>3</sub>Fe, Fe<sub>3</sub>Al, and FeAl. Other common soft magnetic materials include Fe–Si, Fe–Ni, Fe–Al, and Fe–Co. *Hard* magnetic material systems (useful for permanent magnets) include Fe–Ni–Al, Al–Ni–Co, Fe– Cr–Co, Nd–Fe–B, ferrites, M–Co, and M–Fe (where M stands for a rare earth element).

**Shape Memory Alloys.** The *shape memory alloy* NiTi is based on the transformation from the austenitic body-centered cubic (bcc) structure into the martensitic monoclinic structure (8,9). The former is a high-temperature phase, and the latter is a low-temperature phase. When the austenitic phase transforms into the martensitic phase, a deformation is created. If the phase transition reverses, the deformation will disappear. Therefore, the alloy is easily deformed in the martensitic state, but recovers its original shape when reheated to austenite. The shape memory alloy, a so-called *smart material*, has wide applications in sensors and transducers.

Elastic and Other Alloys. *Elastic alloys* are a group of materials with high, stable Young's modulus, nearly unaffected by temperature and frequency. Most elastic alloys are used in precision instruments and measurements. Typical examples are  $Ni_{36}CrTiAl$ ,  $Co_{40}NiCrMo$ , and niobium-based alloys.

Thermocouple alloys are popular materials for measuring temperature. Alloys with low and fixed thermal expansion coefficients have applications in metal-ceramic joining, precision instruments, temperature measurement, and instruments that operate at highly variable temperature. Alloys with high thermal expansion coefficients have applications in temperature control and sensing. Alloys with high thermal coefficients of resistance have been used as temperature sensors. Magnetic refrigeration is based on the *magnetocaloric effect*, the ability of some metals to heat up when they are magnetized and cool down when removed from the magnetic field. A new alloy  $Gd_5Si_2Ge_2$ , has been found to be an efficient material for magnetic refrigeration.

### **Multilayered Magnetic Materials**

Recent research has led to artificially grown multilayered metallic thin films. One of the most interesting and useful properties of metallic multilayers is the giant magnetoresistance (GMR) effect, observed in certain multilayers composed of alternating ferromagnetic and nonmagnetic layers such as Fe-Cr and Co-Cu (10,11): a large change in the electrical resistance experienced by current flowing parallel to the layers when an external magnetic field H is applied. This effect occurs in a multilayer where the magnetic moments of the alternating ferromagnetic layers display an antiparallel alignment when H = 0. If a sufficiently strong magnetic field is applied, the magnetic moments of the ferromagnetic layers assume a parallel alignment. This change in orientation causes a change in resistance, the largest resistance occurring when the moments are antiparallel and the smallest resistance occurring when they are parallel. GMR has applications in sensors, magnetoresistive random access memories, and magnetic reading heads.

#### Nanostructured Metallic Materials

Nanostructured metallic materials are usually classified into two types: dispersed nanoparticles and densified nanophase materials. Nanoparticles are the intermediate in structure between single atoms and solid materials; thus, their properties are quite different from that of the bulk because a large percentage of atoms are on the surface. Nanoparticles are widely used in catalysis because of their large surface contact areas. The commonly used metallic particles are Au (12), Fe, Co, Ni, Ag (13), Cu, and Pt (14). Size- and shape-selected nanocrystals can form self-assembled nanocrystal superlattices with long-range translational and even orientational order (15). The tunable interparticle distance can introduce very interesting electrical and optical properties.

Densified nanophase materials have a large percentage of atoms distributed in interfacial regions. Point defects and high-density interface dislocations are usually present. This type of material is expected to have enhanced mechanical properties because of the grain size effect. However, grain sliding is possible if the grain size is too small.

A very interesting structure observed in metallic alloys is the *quasicrystal*, which exhibits 5- or 10-fold symmetry axes. This type of structure is possible because the sizes of quasicrystals are usually small. Quasicrystals were first discovered in an Al–Mn alloy system (16). This discovery has had a large impact on conventional understanding of symmetry in crystal structures.

## CERAMICS

## **Structural Ceramics**

*Structural ceramics* are the commonly known ceramics which are used in building structures (17). They are mostly dominated by covalent and ionic bonding. Structural ceramics present high mechanical hardness and strength, and resistance to high temperature and abrasion. Typical examples are  $Al_2O_3$ , SiC,  $Si_3N_4$ , and  $ZrO_2$ . They are useful for applications in heat engines, cutting tools, high-temperature insulation, and abrasion resistors.  $Y_2O_3$ -stabilized  $ZrO_2$ , for example, has excellent mechanical properties at room temperature, but it quickly degrades at higher temperatures. Introduction of secondary phase particles, such as SiC, TiB<sub>2</sub> or MoSi<sub>2</sub>, can dramatically enhance its performance at high temperatures.  $Al_2O_3$ , SiC, and  $Si_3N_4$  are excellent high-temperature materials.

#### **Functional Ceramics**

Ferroelectric Materials. BaTiO<sub>3</sub> is a typical ferroelectric material, which will serve to illustrate ferroelectricity (Fig. 2). The Ti ions are surrounded by six oxygen ions in an octahedral configuration. BaTiO<sub>3</sub> has a cubic structure at  $T > 120^{\circ}$ C. For  $5^{\circ} < T < 120^{\circ}$ C, it is tetragonal. In the low temperature range of  $-90^{\circ} < T < 5^{\circ}$ C it has a orthorhombic structure, and for  $T < -90^{\circ}$ C it is rhombohedral. Thus, a structural transformation from centrosymmetric to noncentrosymmetric occurs at 120°C, and ferroelectricity occurs for T < 120°C. The oxygen and titanium ions are displaced to new positions [Fig. 2(b)], forming a tetragonal structure with c/a = 1.01 (18). A unilateral displacement of  $Ti^{4+}$  ion against  $O^{2-}$  results in a dipole moment. If the dipoles cancel each other through random orientation of ferroelectric domains, the material does not exhibit a macroscopic dipole moment. We call it paraelec*tric.* If the dipoles do not completely cancel each other, they form a macroscopic dipole, and the material is *ferroelectric*.



**Figure 2.** (a) Atomic structure of the perovskite cubic  $BaTiO_3$ . (b) [100]-projected ion positions in tetragonal  $BaTiO_3$ , where the relative displacements of the ions are indicated in reference to the cubic structure. (c) Schematic diagram of the hysteresis loop for a ferroelectric material.

The spontaneous alignment of dipoles that occurs at the onset of ferroelectricity is often associated with a crystallographic phase change from a centrosymmetric, nonpolar lattice to a noncentrosymmetric, polar lattice. If an external electric field is applied to the crystal, the population of the domains whose polarizations are parallel to the field will increase, while those whose polarizations are not parallel to the field will decrease. If the external electric field is removed, the domains cannot spontaneously compensate each other again; a remanent polarization  $P_r$  remains. In order to remove the remanent polarization an oppositely oriented electric field with the field strength  $E_c$ , called the *coercive field*, has to be applied to the crystal. The polarization hysteresis loop [Fig. 2(c)] is the basic characteristic of ferroelectric materials.

An increasing number of materials have been found to undergo spontaneous polarization. Lead titanate (PbTiO<sub>3</sub>), which has the same perovskite structure as BaTiO<sub>3</sub>, is ferroelectric. Other examples includes Rochelle salt (potassium sodium tartrate tetrahydrate); KH<sub>2</sub>PO<sub>4</sub>; KH<sub>2</sub>AsO<sub>4</sub>; perovskite NaNbO<sub>3</sub>, KNbO<sub>3</sub>, NaTaO<sub>3</sub>, and KTaO<sub>3</sub>; the ilmenite structures LiTaO<sub>3</sub> and LiNbO<sub>3</sub>; and tungsten oxide, WO<sub>3</sub>.

Ferromagnetic Materials. Magnetic ceramics are subdivided into three classes based on their crystal structures: spinels (or cubic ferrites), garnets (or rare earth ferrites), and magnetoplumbites (or hexagonal ferrites). Spinel ferrites are iron-containing spinels, such as MgFe<sub>2</sub>O<sub>4</sub>, which is generally written as 1MeO:1Fe<sub>2</sub>O<sub>3</sub>, where MeO stands for a transition metal oxide, e.g. Me = Ni, Co, Mn, or Zn. Spinel ferrites are used as pigments in data storage materials, especially  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (diskettes, recording tapes) and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> with additives of  $CoFe_2O_4$  (video cassettes).  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> has a spinel structure with point defects. The garnets, expressed as 3Me<sub>2</sub>O<sub>3</sub>:5Fe<sub>2</sub>O<sub>3</sub> (where  $Me_2O_3$  stands for a rare earth metal oxide, e.g.  $Y_2O_3$ , Gd<sub>2</sub>O<sub>3</sub>), are medium-hard ferrites and serve in microwave devices. Magnetoplumbites have the form 1MeO:6Fe<sub>2</sub>O<sub>3</sub>, where MeO stands for a divalent metal oxide from group II A, e.g., BaO, CaO, or SrO. Hexagonal ferrites, such as  $BaFe_{12}O_{19}$  and Ba<sub>2</sub>Zn<sub>2</sub>Fe<sub>12</sub>O<sub>22</sub>, are usually used as hard magnets. BaFe<sub>12</sub>O<sub>19</sub> also has important application in high-capacity diskettes.

Piezoelectric Materials. Piezoelectricity is the property of a crystal whereby it exhibits electric polarization when subjected to a stress; that is, when a compressive stress is applied, a charge will flow in one direction in a measuring circuit. Reversibly, if an electric field is applied, a piezoelectric crystal will stretch or compress depending on the direction of the field with the polarization in the crystal. Crystals can only be piezoelectric if they are noncentrosymmetric, to ensure noncompensation among the dipoles created by tetrahedra. To illustrate piezoelectricity, consider an atom with a positive charge that is surrounded tetrahedrally by anions (Fig. 3). The center of the negative charges is at the center of the tetrahedron. By exerting a pressure on the crystal along the vertex direction of the tetrahedron, the tetrahedron will experience a distortion and the center of the negative charges will no longer coincide with the position of the positive central atom: an electric dipole is generated. If all of the tetrahedra in the crystal have the same orientation or some other mutual orientation that does not allow for a cancellation among the dipoles, the crystal will have a macroscopic dipole moment.



**Figure 3.** Mechanism of the piezoelectric effect. An external pressure causes the deformation of a coordination tetrahedron, resulting in a shift of the gravity centers of the electric charges, creating a local polarization dipole.

Two opposite faces of the crystal have opposite electric charges.

The piezoelectric effect can convert a mechanical vibration into an electric signal or vice versa. It is widely used in quartz resonators, controlling tip movement in scanning probe microscopy, sensors for vibration waves in air and under sea, and so on. The most common piezoelectric materials are BaTiO<sub>3</sub>, Pb(Zn<sub>x</sub>Nb<sub>1-x</sub>)O<sub>3</sub> and Pb(Zr<sub>x</sub>Ti<sub>1-x</sub>)O<sub>3</sub> (PZT). Pb(Sc<sub>0.5</sub>Ta<sub>0.5</sub>)O<sub>3</sub>, Pb(Sc<sub>0.5</sub>Nb<sub>0.5</sub>)O<sub>3</sub>, and Pb(Mg<sub>0.33</sub>Nb<sub>0.67</sub>)O<sub>3</sub> are also ferroelectric compounds. These materials show a broad dielectric permittivity peak versus temperature, and dielectric dispersion at low frequencies (19).

From the phase diagram of the PbZrO<sub>3</sub>-PbTiO<sub>3</sub> system (20), only 7% of solid solution of Ti in the PZT system is required for the dominant phase to be ferroelectric (F) rather than antiferroelectric (A). The additional energy associated with applied pressure favors formation of antiferroelectric phases. Consequently, when PZT compositions are close to a phase boundary such as 7% solid solution of Ti, hydrostatic pressure can induce a transition between phases. Such pressure-induced transitions are technologically important, since they can be used in explosively driven power supplies, which operate by generating a shock wave that releases the bound surface charge on a polarized ferroelectric material. Since the F phase has a larger volume than the A phase, a suitable compressive stress produces an  $F \rightarrow A$  phase transition. When the ferroelectric has been poled (by cooling through the paraelectric $\rightarrow$ F transition under an electric field), virtually all the bound charge is released during the pressure induced  $F \rightarrow A$  transition. When the transition occurs very rapidly, power is generated and a substantial voltage appears across the ferroelectrics. Ferroelectric materials are among the most important smart materials (21).

**Electrostrictive and Magnetostrictive Materials.** The *electrostrictive (magnetostrictive)* effect is a phenomenon in which the strain created in a film is a linear or close to linear function of the externally applied electric (magnetic) field and stress. Electrostrictive (magnetostrictive) materials can con-

vert an electric (magnetic) signal into a mechanical displacement or vice versa. Electrostrictive  $Pb(Mg,Nb)O_3$  (PMN) and magnetostrictive (Tb,Dy)Fe<sub>2</sub> are typical examples. PZT and PMN have perovskite-type structure. Electrostrictive and magnetostrictive materials are electric and magnetic shape memory materials, and they can also be high-energy-density transducers.

PMN is not ferroelectric at room temperature, since its Curie temperature is below 0°C; but it exhibits very large electrostrictive effect. The piezoelectric coefficient  $d_{33}$  is the slope of the strain–electric-field curve when strain is measured in the same direction as the applied field. Its value for Pb(Mg<sub>0.3</sub>Nb<sub>0.6</sub>Ti<sub>0.1</sub>)O<sub>3</sub> is zero at zero field, but increases to a maximum of 1300 pC/N, three times larger than that of PZT, under a bias field of 3.7 kV/cm. This means that the electromechanical coupling coefficient can be tuned over a wide range to switch the transducer from inactive to extremely active.

**Pyroelectric Materials.** Among the piezoelectric crystals, some have a unique polar axis, an axis that shows properties at one end different from the other end. These crystals are called *polar crystals* because they are spontaneously polarized. The magnitude of the spontaneous polarization depends upon the temperature. Consequently, if a temperature gradient is imposed on the crystal along the polar axis, an electric charge is induced on the crystal surfaces perpendicular to the polar axis. This is the *pyroelectric effect*. Crystals having polar axes can exhibit piezoelectricity, pyroelectricity, and ferroelectricity.

Ferroelectric crystals are also pyroelectric. However, ferroelectric crystals are only those crystals for which the spontaneous polarization can be reversed by applying an electric field. Thus, a ferroelectric crystal is a spontaneously polarized material with reversible polarization.

Electro-optic, Magneto-optic, and Accousto-optic Materials. Electro-optic materials are a group of electroceramics the dielectric properties of which are tunable by applying an external field, which can be static, microwave, or even optical. The refractive index of the materials depends on the electric field, and they can be used in optical oscillators, frequency amplifiers, laser resonators, and so on. Typical electro-optic materials are LiNbO<sub>3</sub>, LiTaO<sub>3</sub>, Ca<sub>2</sub>Nb<sub>2</sub>O<sub>7</sub>, Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub>, KH<sub>2</sub>PO<sub>4</sub>, K(Ta<sub>x</sub>Nb<sub>1-x</sub>)O<sub>3</sub>, and BaNaNb<sub>5</sub>O<sub>15</sub>. Similarly, magneto-optic materials have the property that their dielectric properties can be tuned by applying a magnetic field. This is the basis of magneto-optic data storage, known as CD-ROM (compact disk read-only memory), in which the information is stored magnetically and read out optically.

Noncentrosymmetric ferroelectric ceramics are used in electro-optical applications. The key requirement is that the materials be optically transparent in the visible light wavelengths. Hot pressing of PZT powder (22) eliminates optical scattering due to porosity, grain boundaries, and internal refraction at domain walls. The solid solution dopants Ba, Sn, and La (La being most effective) and an oxygen atmosphere during hot pressing are used to achieve density and optical transparency of PLZT materials,  $Pb_{1-x}La_x(Zr_vTi_{1-v})_{1-x/4}O_3$ . The

applications of electro-optic materials are summarized in Table 1.

Similarly, the refractive index of a crystal can be modified by strain; this is known as the *acousto-optic effect*. The applied strain causes a change in inner binding potential, resulting in a modulation in the shape and size of the electron orbitals and leading to a change in polarization and refraction. The effect of strain on the crystal lattice strongly depends on the strain direction and the direction of the optical polarization. Typical acoustic-optic materials are LiNbO<sub>3</sub>, LiTaO<sub>3</sub>, PbMoO<sub>4</sub>, and PbMoO<sub>5</sub>. These crystals have refractive indices of  $\approx 2.2$ , and they are highly transparent to visible light frequencies.

Superconductive Materials. Superconductivity is the phenomenon of vanishing electrical resistance below the superconducting transition temperature  $T_{c}$ . Superconductors were first discovered in metal phases, such as Nb and Hg. The current research focuses on high-temperature superconductors, such as  $YBa_2Cu_3O_7$ ,  $Bi_2Sr_2CaCu_2O_{8+\delta}$ , and  $Tl_2Ba_2Ca_2Cu_3O_x$ . A superconductor is characterized by three physical quantities. First is the *critical transition temperature*  $T_{c}$ , below which the superconductivity appears. Second is the critical magnetic *field*  $H_{\rm c}$ , below which a superconducting body exhibits perfect diamagnetism and excludes a magnetic field. If the applied magnetic field is higher than  $H_c$ , the material reverts to the normal state.  $H_c$  is temperature-dependent. Finally, there is a critical current density  $J_{c}$ , above which the superconductivity is destroyed and the superconductor reverts to the normal state. Improving  $J_c$  is the essential task of current research in superconductivity.

Superconductors are classified into two types. Type I (soft) superconductors are found mainly among pure metals. A type I superconductor exhibits perfect diamagnetism and excludes a magnetic field up to  $H_c$ , higher than which it reverts to the normal state. In a type II (hard) superconductor total exclusion of the magnetic field does not take place above a value  $H_{c1}$ , where the superconductor exhibits new equilibrium conditions. In parts it is still superconducting; in other parts it does not exclude the magnetic field. Superconductivity is destroyed when the magnetic field reaches a higher value  $H_{c2}$ , the upper critical magnetic field, where upon the superconductor reverts to the normal state. Hg and Nb belong to the type I superconductors, and the ceramic superconductors belong to type II.

Superconductivity has important application in power transmission, nuclear magnetic resonance, extremely strong magnets, and high-speed computing.

High-Dielectric-Constant Materials. Ferroelectric materials have high permanent polarization; thus, they are also good

**Table 1. Electro-Optical Effects and Their Applications** 

Electro-Optical Effect	Applications
Birefringence	Shutters
Depolarization	Modulators, color filters, goggles, displays, memories
Scattering	Image storage, modulators, displays
Diffraction	Image storage
Photoferroelectric	Holographic recording
Photoelastic	Optical waveguides, modulators

candidates for high-dielectric-constant materials. The dielectric constant of  $BaTiO_3$  is 1600 (23). The dielectric constant of  $PbTiO_3$  varies from 100 at room temperature to 1000 at 490°C. These materials are needed for fabricating small-size capacitors to be used in dynamic random-access memories (DRAMs) (24).

**Ionic Conductors and Sensors.** Electric conductivity of a material is due to the flow of electrons and/or the migration of ions. *Ionic conductivity* involves the long-range migration of mobile ions through the material under the driving force of an applied electric field. The mobility of an ion in the crystal depends on three conditions. First, point vacancies must exist in the crystal for the exchange of ions. Second, the moving ions need to be small. Finally, the activation energy for the ion diffusion needs to be low.

Many compounds show exceptionally high ionic conductivity, and they fall into three groups: (1) halides and chalcogenides of silver and copper, where the metal atoms are bonded to different sites in a relatively random fashion; (2) oxides with the  $\beta$ -alumina structure, which have highly mobile monovalent cations; and (3) oxides of the CaF<sub>2</sub> fluorite structure, which have large concentrations of defects caused by either a variable-valence cation or a solid solution with a second cation of lower valence (e.g., CaO · ZrO<sub>2</sub> and Y<sub>2</sub>O<sub>3</sub> · ZrO<sub>2</sub>). Ionic conductors have wide applications in fuel cells, battery materials, and sensors. We now take ZrO<sub>2</sub> as an example to show its sensitivity to oxygen.

Pure ZrO<sub>2</sub> has multiphase transformations of

Monoclinic (M) 
$$\xleftarrow{1000^{\circ}C}$$
 Tetragonal (T)  $\xleftarrow{2370^{\circ}C}$  Cubic (C)

A volume change of  $\approx 9\%$  occurs in the  $M \leftrightarrow T$  transformation. Therefore, stable phases of  $ZrO_2$  can be obtained by doping  $Y_2O_3$ . An introduction of trivalent  $Y^{3+}$  into  $ZrO_2$  produces charged oxygen vacancies  $V_0$ , thus,  $O^{2-}$  can migrate easily at higher temperatures. Figure 4 shows an oxygen sensor using  $ZrO_2$  sandwiched between two multi-hole Pt electrodes. If there is a difference in oxygen partial pressure, say  $P_{O_2}(C) > P_{O_2}(A)$ , then  $O^{2-}$  will move from the higher-pressure side towards the lower-pressure side, resulting in a buildup of positive charges at the higher pressure side and negative charges



Figure 4. Ionic transport process in  $ZrO_2$  with a difference in oxygen partial pressures on the two sides.

at the lower-pressure side. Therefore, at the cathode side,

$$\frac{1}{2}O_2(P_{O_2}(C)) + 2e^- \rightarrow O^{2-}$$

and at the anode side,

$$O^{2-} \rightarrow \frac{1}{2}O_2(P_{O_2}(A)) + 2e^{-}$$

The potential produced is

$$V = \frac{RT}{4F} \ln \left( \frac{P_{O_2}(C)}{P_{O_2}(A)} \right)$$

where R is the gas constant, F the Faraday constant, and T the temperature. If the oxygen partial pressure is known at one side, the partial pressure at the other side can be calculated using the measured potential. This sensor has a wide range of applications in industry and in daily life.

Semiconductive Ceramics. On account of their complex grain boundary structure and charge barriers built up at the boundaries, some ceramics behave as semiconductors. We use two examples to illustrate this group of materials and their physical effects. The *varistor effect* consists in a highly sensitive nonlinear resistance change as a function of the applied voltage [Fig. 5(a)]. The resistance is extremely high when the applied voltage is below a critical voltage  $V_c$ , and there is almost no current flow; when the voltage exceeds  $V_c$ , the resistance drops dramatically, and a large current flows through. ZnO is a typical example, and it can be used for diode varistors and varistor rectifiers. Doping with Bi<sub>2</sub>O<sub>3</sub> and Pr<sub>6</sub>O<sub>11</sub> can improve the rectifying effect of ZnO.

A positive temperature coefficient (PTC) means that the resistance increases sharply as a function of the temperature around the Curie point [Fig. 5(b)]. This effect can be obtained in BaTiO<sub>3</sub> by substitution of divalent Ba<sup>2+</sup> with trivalent ions such as La<sup>3+</sup>, Pr<sup>3+</sup>, Nd<sup>3+</sup>, Gd<sup>3+</sup>, or Y<sup>3+</sup>, of Ti<sup>4+</sup> with Nb<sup>5+</sup>, Sb<sup>5+</sup>, or Ta<sup>5+</sup>. Semiconductive ceramics can also be formed by sintering in oxygen atmosphere. BaTiO<sub>3</sub> semiconductors can be synthesized by combining the two methods of valence mixing and reduction:

$$\begin{split} &\text{BaTiO}_3 + x\text{La} \to \text{Ba}_{1-x}^{2+}\text{La}_x^{3+}(\text{Ti}_x^{3+}\text{Ti}_{1-x}^{4+})\text{O}_3^{2-} \\ &\text{BaTiO}_3 + y\text{Nb} \to \text{Ba}^{2+}[\text{Nb}_y^{5+}(\text{Ti}_y^{3+}\text{Ti}_{1-2y}^{4+})]\text{O}_3^{2-} \\ &\text{BaTiO}_3 - z\text{O} \to \text{Ba}^{2+}(\text{Ti}_{2z}^{3+}\text{Ti}_{1-2z}^{4+})\text{O}_{3-z}^{2-} \end{split}$$

The PTC effect is believed to be due to the strong dependence of the height of the interface Schottky barrier on the dielectric constant. In the ferroelectric phase, the larger dielectric constant results in a lower grain boundary potential barrier. When the temperature is higher than the Curie point, a decrease in dielectric constant reduces the barrier height, leading to an abrupt increase in resistivity. PTC is mainly used in isothermal and temperature-sensitive devices.

### **Magnetic Nanocrystals and Ferrofluids**

Magnetic nanocrystals have important applications in information storage (25), color imaging (26), bioprocessing (27), magnetic refrigeration (28), and ferrofluids (29). On a scale of



**Figure 5.** (a) Schematic diagram showing the I-V characteristics of a varistor material. (b) Schematic illustration of the resistivity–temperature relationship for PTC material.

a few nanometers, the interactions between individual atomic spins cause their magnetic moments to align in the ordered pattern of a single domain. If the particle sizes are equal to or smaller than the domain size, many theoretical models of dynamical behavior predict simple, stable magnets with controllable classical properties, and many fascinating new classical and quantum phenomena are expected (30). Among the most extensively studied magnetic nanocrystals, metallic Fe, Co, and Ni and the oxides Fe<sub>3</sub>O<sub>4</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and MnFe<sub>2</sub>O<sub>4</sub> are typical examples (for a review see Ref. 31). Ferromagnetism transforms to *superparamagnetism* when the particle sizes are smaller than ~10 nm. In superparamagnetic materials each particle is a single magnetic domain.

### **Glass and Amorphous Materials**

A *glass* is a material that lacks long-range order and is below the temperature at which atomic or molecular rearrangements can occur on the time scale of the experiment. A large group of oxides, sulfides, selenides, tellurides, halides, nitrides, metallic alloys, and polymers can form glass structures (32). The criteria for forming an oxide glass structure are: (1) oxide glass networks should be formed by oxygen polyhedra; (2) the coordination number of each oxygen atom in the glass network should be 2; (3) the coordination number of each metal atom in the glass network should be 3 or 4; (4) oxide polyhedra must share corners, not edges or faces; (5) each polyhedron must share at least three corners.

Amorphous materials usually do not satisfy the criteria listed above. The atomic arrangement in an amorphous material can be considered as random, although the radial distribution of the atoms around a center atom may show some correlation. Typical examples are carbon, germanium, and  $SiO_2$ .

# **Optical Materials**

Electromagnetic radiation causes a variety of electronic processes in solids. These processes can be loosely characterized as either emission or absorption. *Luminescence, phosphorescence,* and *laser* action are three most important properties of the materials. Luminescence is defined as light emission in the visible spectrum that results from the collision of incident radiation with atomic electrons. ZnS doped with Mn is an example of electroluminescence.

If the electron transition in luminescence occurs slowly because the electron is temporarily trapped by impurities just below the conduction band, the light emission is delayed and occurs over a period of time. This is *phosphorescence*, an important application of which is found in the materials used in television screens, such as  $Y_2O_3$  doped with Eu. The coating on the cathode-ray tube is selected to give red, green, and blue light emission. The relaxation time is controlled to be short enough to preclude image overlap but long enough for the human eye to register the image.

A variety of oxides can be used to make lasers; single-crystal  $Al_2O_3$  doped with Cr is an example. The Cr doping creates a metastable state below the conduction band. The transition of an electron from this state to the empty valence state also triggers the other electrons in the metastable state, resulting in the emission of coherent photons.

In optical communication, the materials with high refraction index, high optical transparency, and low losses are needed (33). The most abundant and inexpensive materials for making optical fibers is  $SiO_2$ . This amorphous material has strong Si-O bonds. Some minority metal ions in the form of metallic oxides may be included in the  $SiO_2$  to decrease the binding between Si and O so as to control the physical properties, such as refraction index and thermal expansion coefficient, of the glass. Adding germanium or phosphorus increases the refraction index, while adding boron reduces it. Optical fibers must possess high mechanical strength and flexibility to withstand the rough handing incurred during installation and the varying environmental conditions. The current optical fibers are mainly silica, but more advanced materials are under development.

## **SEMICONDUCTORS**

## **Single-Element Semiconductors**

The most common single-element semiconducting materials are Si and Ge, with bandgaps of 1.107 eV and 0.67 eV, respectively. All of these materials have the diamond-type crystal structure, and they are dominated by covalent bonds. Silicon is the backbone of modern electronics. It is unique in that its oxide,  $SiO_2$ , is an insulator with high resistance to doping diffusion and is easy to etch, offering a large advantage for processing semiconductor devices.

### **Compound Semiconductors**

**Materials.** Semiconductive alloys cover a wide range of materials, and each of which is characterized by the band gap and the electron/hole mobility. Group III and V elements can be combined to form III–V compound semiconductors, such as GaAs, GaP and InP. Group II and VI elements can form II–VI semiconductors, such as CdTe and ZnTe. Table 2 summarizes the commonly known semiconductors.

Light-Emitting Diodes. Compound semiconductors, such as dopant GaAs, GaP, SiC, GaN, AlN, and InN, are potentially important materials for blue *light-emitting diodes* (LEDs). GaN has opened up new applications in short-wavelength (visible and ultraviolet) photonic devices for display and datastorage applications, solar-blind UV detectors, and hightemperature/high-power electronics. These materials and their ternary and quaternary alloys cover an energy bandgap range of 1.9 eV to 6.2 eV, suitable for band-to-band light generation with colors ranging from red to ultraviolet (for a review see Ref. 34).

Photoconductive Semiconductors. Both CdS and CdSe are used as visible-radiation sensors. Light meters for cameras and optical sensors for parts sensing in automation rely on these inexpensive semiconductors. The typical response time is  $\approx 50$  ms. PbS is sensitive to radiation in the near infrared. Its response is good for 1  $\mu$ m to 3.5  $\mu$ m wavelengths.

### Semiconductor Quantum Wells

Artificially structured materials composed of layers of different phases/composition are known as *heterostructures*. Multilayered materials are heterostructures composed of many alternating layers. In semiconductor heterostructures with layer thickness smaller than the electron mean free path of three-dimensional semiconductors, the motion of electrons and their interactions with photons are modified (35,36). Such modifications may result in novel electronic behavior that can be exploited to produce new electronic and photonic devices. The principal characteristic of multilayers is composition

Table 2. Bandgaps of Some Semiconductors

Material	Bandgap (eV)	Material	Bandgap (eV)
AIP	2.5	β-SiC	2.3
AIAs	2.16	$\alpha$ -SiC	2.9
AISb	1.60	ZnO	3.2
GaP	2.24	CdS	2.42
GaAs	1.35	CdSe	1.74
GaSb	0.67	PbS	0.37
InP	1.27	CdO	2.5
CdTe	1.44	$BaTiO_3$	2.8
InAs	0.36	Polyacetylene	1.4
ZnS	3.54	Poly( <i>p</i> -phenylene sulfide)	4.0
ZnSe	2.58	Polypyrrole	3.0

 Table 3. Heterostructured Semiconductor Quantum Wells

 and Emission Energies

Heterostructure System	Emission Wavelength <sup>a</sup> (eV)
$\overline{\mathrm{In}_{x}\mathrm{Ga}_{1-x}\mathrm{As}\mathrm{-}\mathrm{Ga}\mathrm{As}\;(0.2 < x < 1)}$	$1.3 \rightarrow 1.14$
$Al_x In_{1-x} As - Ga_y Al_{1-y} As$	1.89  ightarrow 1.42
(0 < x < 0.7, 0 < y < 1)	
$\operatorname{Ge}_{x}\operatorname{Si}_{1-x}-\operatorname{Si}\left(x=0.5\right)$	0.82, 0.92
$InP-In_xGa_{1-x}P (x = 0.61)$	1.655
GaSb-GaAs	1.07

<sup>*a*</sup> Low temperature.

modulation, and its effect on emission wavelength is given in Table 3 (see Ref. 37 for a review).

Figure 6 shows a transmission electron microscopy (TEM) image of a GaAs–AlAs multilayered heterostructure with a periodicity of 8 nm. The difference in bandgap energies for AlAs ( $E_g = 2.16 \text{ eV}$ ) and GaAs ( $E_g = 1.35 \text{ eV}$ ) creates *quantum* 



**Figure 6.** A cross-section high-resolution transmission electron microscopy image of a GaAs–AlAs multilayered semiconductive quantum well structure, where the white dots correspond to the atom dumbbells in the material. The electron beam direction is [110].

wells. Figure 7 schematically shows the energy band diagram for a GaAs–AlAs heterostructure. An electron in the GaAs layer can be considered to be partially confined in a quantum well of barrier height  $\Delta E$  equal to the difference in the energies of the bottoms of the conduction bands,  $E_c$ , for the two materials. For a particle in a one-dimensional potential well, the energy levels of the electron in the well are quantized, and the separation between the energy levels depends on the width of the well. The interaction between wells will broaden the energy levels, resulting in *minibands*. Adjusting the width of the layers can result in interesting light-emitting characteristics (37). Semiconductor multilayer structures have important technological applications in the area of highspeed microelectronics (38) and the quantum Hall effect (39,40).

### Semiconductor Quantum Dots

Heterostructured quantum wells are one-dimensional quantum structures. Semiconductor wires are two-dimensional quantum structures. Nanoparticle structures of semiconductors are three-dimensional quantum dots. CdS, CdSe, InP, GaP, and GaAs are examples. The properties of nanocrystals appear to be much different from bulk crystal if their size approaches the atomic or ionic diffusion lengths, the electronic elastic and inelastic mean free path lengths, or the correlation and screening lengths. Synthesis and studies of semiconductor nanocrystals have practical importance for many applications in optoelectronics. The most interesting phenomena associated with semiconductors are the quantum-dot effect, surface states, and electrical transport properties.

Quantum confinement in nanocrystals results in discrete energy levels. If the specimen is placed in an electric field, the energy levels of the dots will be affected by the field, according to what is known as the *Stark effect* in atomic physics. This effect has interesting applications in electro-optical devices (41,42). The optical properties of the semiconductor nanocrystals can be controlled by the particle size, since the energy



**Figure 7.** Quantum wells composed of GaAs–AlAs layers.  $E_c$  is the energy of the bottom of the conduction band,  $E_v$  is the energy of the top of the valence band, and  $E_g$  is the bandgap energy. The barrier height  $\Delta E$  is the difference between the values of  $E_c$  for AlAs and GaAs.

levels depend sensitively on the size of the nanocrystals (for a review see Ref. 43). Devices made of a single nanocrystal can also be fabricated (for a review see Ref. 44).

Alternatively, quantum dots can be formed in heterogeneously grown semiconductor layered structures by controlling the growth thermodynamics and kinetics to direct the atoms to specific regions, such as steps and high-strain regions on the substrate, during epitaxy of quantum wires (45). This technique uses the advantage offered by the lattice mismatch of material combinations such as (In,Ga)As-GaAs, InP-InGaP, and Ge-Si (see Ref. 46 for a review). Typically a thin wetting layer forms when the amount of deposited material does not exceed a critical value of a few lattice constants. Deposition of additional material results in the formation of locally coherent islands that allow for greater relaxation of elastic energy than does a two-dimensional flat layer. By controlling the growth condition, the size and shape of the islands can be controlled. The islands are known as the selfassembled quantum dots.

Another important application of semiconductors is in *non-linear optics*. Nonlinear optical interactions occur when the electric fields associated with optical beams propagating through a medium are strong enough to produce polarization fields proportional to the square or higher powers of the incident field. The second-order nonlinearity, for example, gives a polarization of  $E^2$  if the incident field is *E*. For a sinusoidal wave of frequency  $\omega$ ,  $E = E_0 \sin \omega t$ , the nonlinear polarization is

$$P_{(2)} = \chi_{(2)} E^2 = \chi_{(2)} E_0^2 \sin^2 \omega t = \frac{1}{2} \chi_{(2)} E_0^2 (1 - \cos 2\omega t)$$

with a frequency of  $2\omega$ . The second nonlinearity can thus be used in frequency mixing  $(\omega_1 \pm \omega_2 \rightarrow \omega_3)$  and parametric amplification  $(\omega_3 \rightarrow \omega_1 \pm \omega_2)$ . Optical nonlinearity property is important in electro-optics and optical communication.

#### **Porous Silicon**

Porous Si offers much technological promise due to its visible photoluminescence (47) (for a review see Ref. 48). Improvements in electronics require increased speed, decreased dimension, and increased functionality. As dimensions decrease, the device interconnects have become two or three times larger than the actual device. Because it may solve this problem, optoelectronics may represent the next generation in device structures. Porous Si has a spongelike structure, with particle sizes on the nanometer scale. It is formed by chemically etching silicon to achieve a large volume of porosity. The high quantum efficiency of 1% to 10% for porous Si (49) for visible light emission (1.6 eV to 2.1 eV) has made it attractive for optical interconnects.

### **Luminescent Materials**

Semiconductors are also used in electroluminescent (EL) displays (50). ZnS doped with Mn is an important monochrome EL phosphor. Efficient red emission can be obtained from the broad ZnS: Mn emission using a red filter of  $CdS_xSe_{1-x}$ . Terbium-doped ZnS is an efficient green phosphor. Cerium-doped SrS can give blue emission. Powder materials of  $Y_2O_3$ : Eu,  $SrGa_2S_4$ : Eu, and  $SrGa_2S_4$ : Ce are candidates, respectively, for red, green, and blue phosphors in cathodeluminescence and field-emission displays.

## POLYMERS

Polymers have been widely used in commercial as well as advanced technology because of their unique combination of easy synthesis and low cost. A polymer molecule consists of a large number of identical units, called *mers*. Polyethylene, for example, is made of  $CH_2=CH_2$  monomers, forming a linear molecule as shown in Fig. 8. The chains are linked to one another by secondary bonds. Polymer molecules can be oriented randomly, semicrystalline, or crystalline, depending on the structure of the polymer as well as the temperature. This section focuses on some engineering polymers, with an emphasis on their applications in electronics and electrical engineering.

### **Engineering Polymers**

Polymers include many important materials such as plastics, rubber, fibers, coatings and adhesives (51,52). *Plastics* are a large group of polymers that can be shaped. Polymers that can be formed repeatedly by application of heat and pressure are called *thermoplastics*. Those that can be formed only once are called *thermosets*. *Rubber* can be synthesized or taken from nature. Most rubber is used in tires. The long-chain molecular structure of polymers makes them ideal choices for fabrication of fibers. Their flexibility and strong adhesion make them suitable for surface coating and decoration as well as for adhesives.

Vinyls and related polymers are the fundamental materials for manufacturing clear films, flexible bottles, pipes, containers, fibers, and lenses. Typical examples are polyethylene, polyvinyl chloride, polystyrene, polytetrafluoroethylene (PTFE), and polymethyl methacrylate (PMMA). Polybutadiene, polyisoprene, and polychloroprene are examples of rubbers, which have important applications in manufacturing tires, belts, and molded parts. Polysters are the materials for fabricating fibers, clothes, and boat and auto body parts. Polyamides are used for making carpets, rope, and bulletproof vests. Polyacetal is useful for gears and machine parts. Polycarbonate is used for optical lenses, and epoxy for adhesives and composites.

Although a polymer is characterized by covalent bonds within the molecules, the molecules are bridged by either primary or secondary bonds. If polymer molecules are packed periodically, crystalline polymers are formed. The crystallinity of polymers is affected by the size of the side groups, the extent of chain branching, tacticity, the complexity of the repeat unit, and the degree of secondary bonding between parallel chain segments. Rubbers, for example, are noncrystal-



Figure 8. Schematic of the structure of polyethylene.

line materials because their glass transition temperatures  $(T_{\rm g})$  are below the ambient temperature. The glass transition temperature is a critical temperature through which the mechanical properties of the polymers change from brittle and glasslike to flexible and rubbery. The molecules in a rubber can be visualized as entangled and coiled upon one another. Upon stretching, the molecules become aligned with the direction of the applied load, resulting in one-dimensional ordered polymer. Polyethylene, for example, can form an orthorhombic crystalline structure.

#### **Polymers for Electronic Applications**

The major applications of polymers in electronics are: (1) radiation-sensitive stencils to define devices and interconnect wiring on the chip and package, (2) dielectric materials for use as chip carriers and as insulators to reduce shorts between multilevel metal interconnects, (3) encapsulation materials for corrosion and mechanical protection, (4) conducting polymers to conduct current for electronic packaging, and (5) nonlinear optical materials to transmit or switch light for photonic applications.

Radiation-Sensitive Polymers for Lithography. Lithography is a technique for fabricating patterned devices on chips and circuit boards. Radiation-sensitive polymers are used as stencils to transmit the circuit pattern to underlying layers. The polymers crosslink, degrade, or undergo molecular rearrangement when irradiated, and the area that is exposed can become either soluble (positive resist) or insoluble (negative resist) relative to the unexposed area. After the images are exposed and developed, a stencil is formed that will be resistant to the acids and bases used to pattern underlying oxide or metal layers. Lithography can be performed with photons, electrons, X rays, or ions, depending on the required resolution and applications (53). The positive photoresist belongs to the diazonaphthoquinone chemical family and is a novolac resin. Epoxy, vinyl, and halogen are the general radiation-sensitive groups used in negative crosslinking resists (54).

**Polymers for Electronic Packaging.** Circuit boards are the largest users of polymers in the semiconductor industry. The most widely used polymers are epoxy systems because of their excellent adhesion to many types of surfaces and low cost. For chip packaging, polymers are used as molding materials, as encapsulants, and as thin-film carriers for the chip itself. Plastics were first introduced as encapsulation materials to protect the chip from environmental corrosion or degradation. Epoxies are used to join the metal or ceramic caps to encapsulate the chip. The most common polymers for dielectric materials are polytetrafluoroethylene and polyimides (such as pyrometallic dianhydride and 4,4-oxidianiline).

Polymers for Interconnect Dielectrics. Integrated circuits require multilayer packaging of electronic devices. The multilayering of electronics and the formation of interconnections between the layers have become possible as a result of polymer dielectrics. Polymer dielectrics offer the following advantages for integrated circuits: ease of processing, good adhesion, low stress, high reliability, thermal stability and low cost. The most widely used polymers for dielectrics are polyimides, parylene, benzocyclobutene, polybenzoxazole, and polybenzothiazole (55).

# **Polymers for Optical Applications**

Nonlinear optics (NLO) is based on the anharmonic oscillation of atoms in a solid in response to the stimulation of an external light source, resulting in the emission of light signals with frequencies different from that of the incident light. Materials exhibiting nonlinear optical properties are usually noncentrosymmetric. To produce this type of structure using a polymer, the NLO molecules are aligned using a dc electric field. The alignment is frozen in by altering the polymer in some way to physically constrain the NLO dipoles while the field is applied. This is known as *polymer poling* (56).

Polymers can also be used for waveguides. This type of optical interconnect gives flexibility for integration with the polymer-interconnected electronics. Polymer waveguides can be fabricated by the techniques of etching, external diffusion, localized reaction and poling, and polymerization-induced internal diffusion (57). A polymer-integrated optical system can be made compatible with other electro-optic systems and processes.

## **Conducting Polymers**

Polymers have been widely chosen as insulators because of their inability to carry charge. In the past decades, however, new materials have been developed that exhibit the electronic and magnetic properties of metals while retaining physical and mechanical characteristics of polymers. Soluble polyacetylene precursors have been used to fabricate metalinsulator-semiconductor structures and light-emitting diodes (58). More stable materials with metal-like conductivities, such as polyaniline (59), polypyrrole (60), polythiophene (61), and poly(phenylenevinylene) (62), have potential applications in the semiconductor industry as materials for batteries, electromagnetic shielding, electrostatic discharge layers, and conducting radiation-sensitive polymers.

Acid doping is a fundamental mechanism for changing the conductivity of polymers. The conductivity of polyaniline, for example, can extend over 10 orders of magnitude when it is protonated with acids, where the base is the insulator and the salt is the conductor. All such conducting materials are doped after the polymer film has been formed by exposing the film to a doping gas or solution. The conductivity of polyacetylene and polypyrrole films can be enhanced by dipping them in a solution of an onium salt. It has also been found that this external doping can be replaced by incorporating onium salts into soluble conducting polymers, casting films, and subsequently exposing them to light, generating an acid *in situ* (63).

## Ferroelectric, Piezoelectric, and Pyroelectric Polymers

In contrast with inorganic PZT materials, *polyvinylidene fluoride* (PVDF) is a ferroelectric and piezoelectric organic polymer with low acoustical impedance, low density, and low permittivity (64). The low acoustic impedance enables good acoustical matching of the transducer to body tissues and water. The low density reduces the loading of an input acoustic wave, allowing fabrication of low-distortion microphones and hydrophones. The low permittivity of PVDF enables electrical matching of the transducers at higher frequencies, resulting in better image resolution.

The piezoelectric crystal structure of PVDF is created by mechanical drawing (65). This difficult fabrication is obviated by using the copolymer of PVDF with trifluoroethylene (PVDF-TrFE), which crystallizes directly into the piezoelectric state without drawing, so that the process of incorporating this polymer into sensors and transducers is greatly simplified. PVDF-TrFE is also a piezoelectric and pyroelectric material (66).

The piezoelectric property is directly related to the net electrical polarization of the structure. The monomer of PVDF is CH<sub>2</sub>=CF<sub>2</sub>, vinylidene fluoride (difluoroethylene), and that of PVDF-TrFE is a mixture of trifluoroethylene (CHF=CF<sub>2</sub>) and difluoroethylene. PVDF and PVDF-TrFE are incoherently polar. The hydrogen atoms are positively charged and the fluorine atoms negatively charged with respect to carbon atoms in the polymer (Fig. 9). Polymer molecules are usually in the form of long chains of monomers bonded together. Although many polymers with regularly repeating structures can crystallize, the crystals are usually microscopic in size:  $\sim 10$  nm in thickness (about an order of magnitude smaller than the length of the chain) and a few micrometers in width, and as a result, the molecules are folded and embedded in an amorphous matrix of the molecular chains oriented randomly. In order to increase the piezoelectricity, the individual moments of the molecules need to be aligned.

Crystalline PVDF has four basic structures:  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$  (67), among which the  $\beta$  phase is the most piezoelectrically active. Its structure is given in Fig. 9: all of the fluorine atoms line up in one direction, giving a polar crystalline unit cell.

PVDF has lower electromechanical coupling coefficient than the piezoelectric PZT ceramics, but it has several advantages, including low Young's modulus and large yield strain. However, the low melting point of PVDF ( $\approx 150^{\circ}$ C) and its sensitivity to chemicals, including most solvents and bases, bring in new difficulties in integrating the material with other components. On the other hand, it is the optimum choice as a sensor and transducer material for biosensors and biodevices.



**Figure 9.** [100] projected unit-cell structure of  $\beta$ -PVDF, exhibiting permanent polarization. For clarity, only one CH<sub>2</sub>=CF<sub>2</sub> mer is shown in ball-and-stick form, and the others are sketched using lines.

To produce a piezoelectic and pyroelectric material from a polar amorphous polymer, orientation polarization is introduced by applying a high electric field at temperatures above  $T_{\rm g}$ , where the dipoles are mobile. Some candidate materials are vinyl acetate, vinyl benzoate, vinyl isopropionate, and vinyl pivalate. In order for a semicrystalline polymer to be piezoelectic and pyroelectric, the crystalline phase must possess a net dipole moment, and the dipoles must be amenable to orientation, usually by electric field poling. Some typical examples are PVDF, polyvinyl fluoride (PVF), vinylidene fluoride-trifluoroethylene copolymers, and odd-numbered nylons (68).

### **Liquid Crystals**

Polymer dispersed liquid crystals (PDLCs) have some important electro-optical properties, including light scattering, diachronic absorbance, reflection of circularly polarized light by chiral materials, polarization and depolarization of light, and nonlinear optical effects. Liquid-crystal displays (LCDs) are the most widely used choice for portable display devices (69,70). Liquid-crystal molecules tend to align parallel to each other due to their chemical structure and orient themselves uniformly on a mechanically rubbed substrate. Their molecular orientation is very sensitive to an applied electric field. Thus, a liquid-crystal cell works as a tiny, optically tunable shutter that is controlled by a locally applied electric field. Each pixel is addressed by the top- and bottom-line electrodes of the cell according to information signals, producing a light image. With the use of the electric-field-driven alignment of liquid-crystal molecules, the optical properties of the materials can be manipulated, thus, they can be used for image display (71).

Scattering-based polarizers for image projection work on the principle of redirecting light rather than absorbing it. In the transparent state, a collimated beam of light passes through the light valve and into the projection optics, so that the screen appears bright. In the scattering state, the scattered light is directed into an aperture stop, which prevents the light from reaching the projection optical system. Thus the screen appears black. A gray scale is possible by using a weakly scattering state, which allows a portion of the light into the projection system. The LCD is mainly limited by two factors: the brightness and the response time.

### Low-Dielectric-Constant Polymers

With the shrinkage of device sizes, the wiring density and pitch increase dramatically. The propagation delay, crosstalk noise, and power dissipation due to resistance-capacitance coupling become significant as a result of increased wiring capacitance and interline capacitance. Low-dielectric-constant materials are potential candidates for interconnects to reduce power dissipation. Polymers such as parylene, polynaphthalene and polytetrafluoronaphthalene, polytetrafluoroethylene-AF, and poly[octafluorobis(benzocyclo)butene] are useful for this purpose (72). Nanoporous silica (73), phaseseparated inorganic-organic hybrids (74), and amorphous carbon (75) are also candidates.

### **COMPOSITE MATERIALS**

The engineering demands on materials for ever better performance are so great and diverse that no one material is able to satisfy them. This naturally leads to a resurgence of the ancient technique of combining different materials in a composite. A composite is a combination of two materials in which one material, called the reinforcing phase, in the form of fibers, sheets, or particles, is embedded in the other material, called the matrix phase. The reinforcing material and the matrix material can be metal, ceramic, or polymer. The most important advantage offered by composite materials is the enhancement of their mechanical properties. Figure 10 makes a comparison, for illustrative purposes only, between conventional monolithic materials such as aluminum and steel and composite materials (76). The high mechanical performance and light weight of composites make them attractive for space shuttles and aircraft.

The fibers constituting the reinforcing phase can be glass, boron carbides, carbon, organics such as oriented polyethylene fibers and aramid fibers, ceramics such as alumina and silicon carbide, or metallic glasses (77). The choice of fibers depends on the requirements for fiber flexibility as determined by the Young's modulus and the fiber diameter, for anisotropic bonding characteristics, and for operating temperature.

The matrix materials are polymers such as epoxy, polyimide, polysulfone, and polyphenylene sulfide, metals such as Ni, Cu, and Al, and ceramics such as  $Al_2O_3$ , BeO, MgO, MgAl<sub>2</sub>O<sub>4</sub>, SiC, Si<sub>3</sub>N<sub>4</sub>, borosilicate glass, and magnesium aluminosilicate glass ceramics. The performance of a composite depends strongly on the bonding at the interfaces between the fibers and the matrix, because that is the means of transferring the mechanical loading. *Mechanical bonding* results from the contraction of the matrix onto a central fiber, producing a gripping of the latter by the former. Chemical bonding includes *dissolution and wettability bonding*, due to atomic-scale contact, and *reaction bonding*, due to atomic diffusion.



**Figure 10.** Comparison of mechanical properties between conventional monolithic materials and composite materials.

## **Polymer Matrix Composites**

Polymer matrix composites (PMCs) have established themselves as engineering structural materials. Glass-fiber-reinforced polymer composites represent the largest class among PMCs. Various techniques are used for making glass fiber PMCs, among which hand lay-up is the simplest. Glass fibers are laid onto a mold by hand, and the resin is sprayed on or brushed on. Frequently, resin and fibers are spread together onto the mold and the deposited layers are densified with rollers. PMCs have a wide range of application in aerospace engineering.

## **Metal Matrix Composites**

Metal matrix composites (MMCs) offer high specific strength and specific modulus plus service temperature capability much higher than that of polymer matrix composites. Typical MMCs are boron-aluminum, carbon-aluminum,  $Al_2O_3/Al$ ,  $Al_2O_3/Mg$ , and SiC/Al. MMCs are fabricated by three types of techniques: solid-state, liquid-state, and *in situ*.

In solid-state fabrication, alternate layers of properly spaced boron fibers and aluminum foils are stacked to produce the desired fiber volume fraction and fiber orientation. A resin-based fugitive binder is used to keep the boron fibers in place. A combination of heat and pressure, in vacuum, causes the matrix to flow around the fibers and make a bond with the next matrix layer, enclosing and gripping the fibers in between.

Liquid-state fabrication uses liquid-metal (matrix) infiltration of fibers or fiber preforms. The infiltration may be carried out under atmospheric or inert-gas pressure or under vacuum. The long continuous fibers must be properly aligned and distributed before infiltration by the matrix. The application of high pressure to the liquid metal during solidification (e.g., squeeze casting) is required.

In situ fabrication is a process in which controlled unidirectional solidification of a eutectic alloy can result in a twophase microstructure with one of the phases, present in lamella or fiber form, distributed in the matrix. Ni–TiC, Co– NbC, and Ni–HfC are typical examples.

## **Ceramic Matrix Composites**

Fiber-reinforced ceramic matrix composites (CMCs) can greatly improve the ductility and toughness of ceramics. CMCs are usually manufactured in a two-stage process: incorporation of a reinforcing phase into a unconsolidated matrix followed by matrix consolidation (78,79). The fiber incorporation stage also involves some kind of fiber alignment. By far, the most common technique of fiber incorporation is *slurry infiltration*. A fiber tow is passed through a slurry tank (containing the matrix powder, a carrier liquid, and an organic binder) and wound on a drum. This is followed by cutting, stacking the tows, and consolidation. Hot pressing is the most common technique used to consolidate CMCs. Hot-pressed SiC-(Si, Al, O, N) and SiC whiskers in alumina are typical examples of CMCs.

## **Carbon Fiber Composites**

Carbon fiber composites are perhaps the most important composite materials because of their important applications in the aerospace industry. Carbon fibers have high axial

### FUNCTIONAL AND SMART MATERIALS 23

strength because of the in-plane covalent bonding of the graphitic layers. Carbon fibers can be made into close sheets and can be coated with epoxy for forming high-strength composites. SiC and pyrocarbon have been deposited on carbon fibers by chemical vapor deposition to form laminar structure. Growing SiC whiskers on the carbon fiber surface can result in a two- to threefold increase in interlaminar shear strength due to the increased surface area. Treating carbon fibers with several surface-oxidation agents leads to significant increases in the interlaminar shear strength of the composites.

# **OTHER MATERIALS**

## **Fullerenes and Related Carbon Materials**

Carbon is probably the most versatile element; it can form various structures. Amorphous carbon, partially disordered carbon black, graphite, and diamond are the commonest forms of carbon. The discovery of carbon fullerene  $C_{60}$  (80) and particularly carbon nanotubes (81) has raised a lot of technological interest. A carbon nanotube is composed of nearly concentric cylindrical graphitic sheets (82,83). The carbon tubes usually have a diameter of 3 nm to 20 nm, and their length can be more than 10  $\mu$ m. The aligned carbon tubes exhibit high dielectric anisotropy. The electronic and mechanical properties of the tubes are strongly affected by the size of the tube as well as the number of the graphitic layers. Graphitic structured carbon spheres (84,85) are candidates for surface coating, catalysis support, and high-strength composites.

## **Biomaterials**

Many living creatures have structures that exhibit far better properties than conventional materials can offer. The growing importance of bioengineering is raising a challenge to materials synthesis and processing. Biomaterials are actually composite materials of organic and inorganic, ceramic/metal and polymer. These materials are the foundation of drug delivery and tissue engineering (86). The materials used in medical applications, as for filling teeth and replacement of bones and joints, are required to stick to bone, mimic color, flex like natural tissues, and keep their form under extremes of heat and cold. Plastic polymer materials have fundamental importance for these purposes.

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