

CHAPTER 10

Semiconducting Materials

10.1 Introduction

Semiconductors are materials which have resistivities between the extremes of metallic conductors and insulators. A typical scale of conductivity of materials is depicted in Figure 10.1.

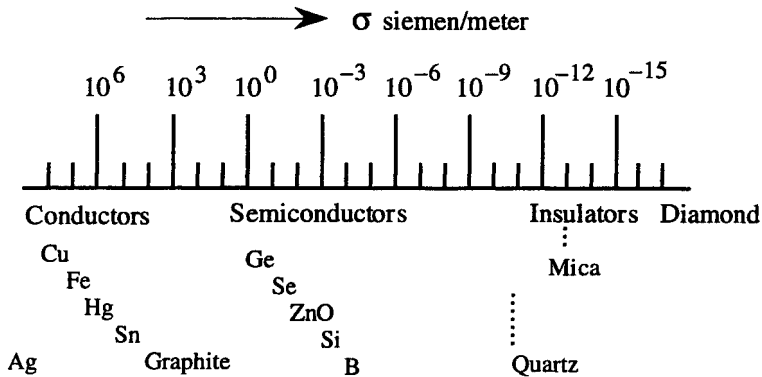


Figure 10.1 Range of conductivities of conducting, semiconducting, and insulating materials.

Semiconductors lie approximately between conductors (with $\sigma > 10^5$ siemen/meter) and insulators (with $\sigma < 10^{-10}$ siemen/meter). Semiconductors are materials with filled valence bands and have a small *forbidden energy gap* between the upper-filled band and the overlapping vacant energy band.

The electric conduction in semiconductors is effected by two types of charge carriers namely, *electrons* (negative charge carriers) and *holes* (positive charge carriers). Descriptions of energy bands and the concepts of free electrons and bound electrons are presented in Chapter 1.

Materials which are intrinsically semiconductors (with no impurities added) are known as *intrinsic semiconductors*. These are group IV elements namely, carbon (C), silicon (Si), germanium (Ge), and tin (Sn). These elements along with their neighbors are presented in Figure 10.2.

II	III	IV	V	VI
Be	B	C	N	O
Mg	Al	Si	P	S
Ca	Ga	Ge	As	Se
Sr	In	Sn	Sb	Te

Figure 10.2 Group IV elements and their neighbors in the periodic table.

Group IV elements have four valence electrons and are chemically similar. They also have similar crystalline structure. An atom of a group IV element shares its four valence electrons with its neighboring atoms forming a *covalent bonding*. The covalent bonding

specifies an *octave saturation* of the orbit which corresponds to a saturation of the outermost orbit of the eighth group element with $2n^2$ (n being the orbital number, 1, 2, 3, ...) law of saturation. As such a covalent bonded pure semiconductor prefers to be chemically inactive (as in the case of eighth group inert gases). The covalent bonding is represented in Figure 10.3, where the connecting parentheses indicate the shared covalence state of the electrons in each atom.

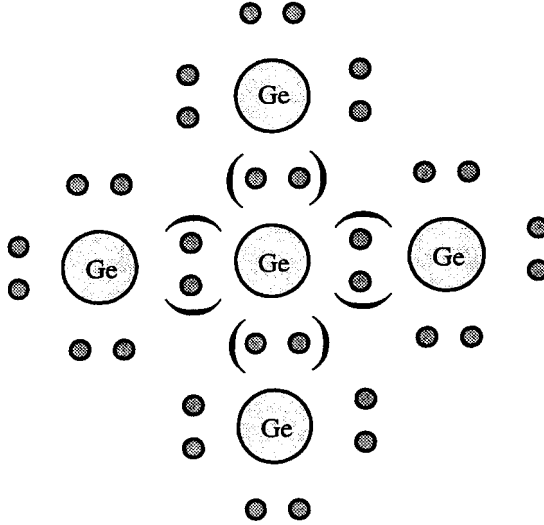


Figure 10.3 Covalent bonding.

In the absence of thermal energy, that is at 0 K, the valence band of a semiconductor is fully occupied and the conduction band has no electrons. As the temperature is raised, a small fraction of electrons in the valence band would acquire enough thermal energy so as to jump the forbidden energy gap E_g . The absence of electrons in the valence band corresponds to "holes". In reference to covalent bonding depicted in Figure 10.3, the movement of a covalently bonded electron away from a parent atom (due to acquiring thermal energy) creates a hole in the covalent structure which would be eventually occupied by an electron. Thus the migration of the electrons from atom-to-atom would necessitate filling and creation of holes. That is, the flow of electrons means a concurrent movement of holes as well. Inasmuch as holes attract the electrons, they can be regarded as positive charges with a value $+e$ ($= 1.6 \times 10^{-19}$) coulombs.

10.2 Properties of Intrinsic Semiconductors

The properties of group IV intrinsic semiconductors are presented in Table 10.1.

Among the four intrinsic semiconductors indicated in Table 10.1, Si and Ge are the materials largely used in the semiconducting devices. Their other physical properties (pertinent to semiconductor technology) are presented in Table 10.2.

Table 10.1 Properties of Group IV Intrinsic Semiconductors

Elements	Forbidden Energy Gap (E_g) (eV)	At 20 °C			Lattice Constant (a) nm
		Conductivity (σ) siemen/meter	Mobility $m^2/volt\text{-sec}$		
			Electron (μ_n)	Hole (μ_p)	
C (Diamond)	~ 6.0	$<10^{-6}$	0.1700	0.1200	0.3570
Si (Silicon)	1.1	5×10^{-6}	0.1900	0.0425	0.5430
Ge (Germanium)	0.7	2	0.3600	0.2300	0.5660
Sn (Tin)	0.1	10^6	0.2000	0.1000	0.6490

Table 10.2 Properties of Intrinsic Si and Ge

Properties	Ge	Si	Remarks
• Physical			
Density (d gm/cm ³)	5.360	2.400	
Atomic number (Z)	32.000	14.000	
Energy gap (E _g), eV	0.700	1.100	at 20°C
Effective mass of electrons (m_e^*/m)	0.082	0.190	m: mass of electron (1.6×10^{-31} kg)
Effective mass of holes (m_p^*/m)	0.280	0.490	
Electron mobility (μ_e) m ² /volt-sec	0.360	0.190	at 20°C
Hole mobility (μ_p) m ² /volt-sec	0.230	0.043	at 20°C
			(continued...)

Properties	Ge	Si	Remarks
Electron diffusion constant D_e (m^2/sec)	9.9×10^{-3}	3.8×10^{-3}	300K
Hole diffusion constant D_p (m^2/sec)	4.9×10^{-3}	1.3×10^{-3}	300K
Effective intrinsic electron concentration (n_i/m^3)	2.5×10^{13}	1.4×10^{10}	300K (measured)
• Electrical			
Conductivity (σ) siemen/meter	2.0	5×10^{-6}	at 20°C
Dielectric constant	16.0	11.8	
• Thermal			
Melting point °C	958.5	1420	
Thermal conductivity watt/cm°C	0.06×10^{-4}	0.024×10^{-4}	at 20°C
Coefficient of linear expansion per °C			

10.3 Conductivity of Intrinsic Semiconductors

Since both electrons and holes contribute to the conduction current in a semiconductor, the net conductivity (σ) is decided by the sum of the conductivity components due to electrons and holes. It is given by:

$$\sigma = n_n e \mu_n + n_p e \mu_p \quad (10.1a)$$

where n_n and n_p are the intrinsic electrons and holes per unit volume, respectively, and μ_n and μ_p represent, respectively, the electronic mobility and the hole mobility parameters. The electrons and the hole concentrations in the intrinsic state of the semiconductors at a given temperature are the same. That is, $n_n = n_p \cong 10^{16}$ per meter³ at 20°C and they increase exponentially with temperature. Theoretical and experimental studies indicate that the conductivity (σ) of an intrinsic semiconductor can be explicitly stipulated by:

$$\ln(\sigma) = A - E_g / (1.7 \times 10^{-4} \times T) \quad (10.1b)$$

where E_g is the forbidden gap energy in electron volt (eV), T is the temperature in K, and A is a constant for a material. The change in conductivity σ_1 to σ_2 as the temperature changes from T_1 to T_2 can be written as:

$$\ln (\sigma_1/\sigma_2) = (E_g/1.7 \times 10^{-4}) (1/T_1 - 1/T_2) \quad (10.2)$$

10.4 Germanium and Silicon

Among the group IV elements presented in Figure 10.2, Ge and Si became the natural choice for implementing solid-state devices due to their inherent semiconducting properties and their technological match in fabricating such devices.

In the beginning of semiconductor technology, Ge was the front candidate inasmuch as it could be produced in large quantities with sufficient purity (with the technological process then available).

Ge has higher mobility than Si which permits Ge devices to operate at high frequencies. However, Ge has a relatively low band gap energy ($E_g = 0.67$ eV) which makes the Ge devices more sensitive to temperature changes.

Si is one of the most widely used semiconductors in modern times. It has a high gap energy ($E_g = 1.12$ eV) as well as an abundance of SiO_2 in nature from which Si is extracted, and the superior thermal characteristics of silicon have made this element as the primary choice in semiconductor technology. In addition, SiO_2 allows oxide coating in the planar and IC technology facilitating the photolithographic-based monolithic and miniaturized device fabrication.

10.5 Extrinsic Semiconductors

These are semiconducting materials with deliberately added impurities (*dopants*) so that the electrical conductivity is dominantly dictated by the dopants. The level of impurity concentration ranges from one part per hundred to ten parts per million in typical commercial semiconductors. The maximum level of impurity concentration is so chosen as not to alter the crystalline structure of the host intrinsic medium; that is, a *phase change* is not introduced at this *solid solubility limit* of the impurity-host complex.

The impurity-atom sites in the intrinsic materials are of two types, namely:

- Substitutional impurities.
- Interstitial impurities.

The substitutional impurities occupy the atomic sites in the host lattice and the interstitial impurities fit between regular lattice sites.

Primarily, the doping materials used in semiconductor technology correspond to the adjacent groups, namely, group III and V elements of the intrinsic group IV semiconductors (Figure 10.2). When a group IV semiconductor is so doped, it is known as an *extrinsic semiconductor* since its electrical behavior is more predominantly dictated by the added impurities than by the intrinsic characteristics of the group IV element.

The doping material depending on its origin (group III or V) decides the nature of the extrinsic atoms as *acceptors* or *donors*, respectively. That is, addition of group V impurities, render the extrinsic semiconductor to have a set of easily activatable electrons into the conduction band (as free electrons). Hence, such an extrinsic material has acquired *donor atoms* by virtue of the added group V impurities. Likewise, addition of group III impurities would render the extrinsic material with excess of holes in the valence band, or the material is rich in *acceptor atoms* due to the presence of group III impurity.

The donor type semiconductors are also known as *N-type semiconductors*. As an example, consider a silicon material doped with group V impurity atoms, say P atoms. The pentavalent atom has five valence electrons unlike the tetravalent Si atoms which have only four valence electrons in their outermost orbit. Relevant covalent bonding is illustrated in Figure 10.4. The extra electron at the P atom can be seen independently present unlike the other electron pairs shared to constitute the covalent bonding. This loosely bound electron can be pulled away from the parent P atom with the small energy imparted to the material.

When this electron is detached, the P atom remains in the covalent bonded state in a positively charged ionic form. The detached electron would no longer remain in the already saturated valence band but would be located near the top of the energy gap. From this position, called the *donor level* (E_d), this extra electron can be activated into the conduction band to become a *charge carrier*. Thus, donor impurities add to the free-electron population in the conduction band facilitating an increased conductivity of the material.

Thus atoms from group V elements used as dopant atoms supply a negative or N-type excess charge carrier to the semiconducting material.

The P-type semiconductors are constituted by the addition of a group III element as the impurity to an intrinsic semiconductor. Say, for example, if Al atoms (with valency three) are added to silicon, the resulting covalent structure is illustrated in Figure 10.5.

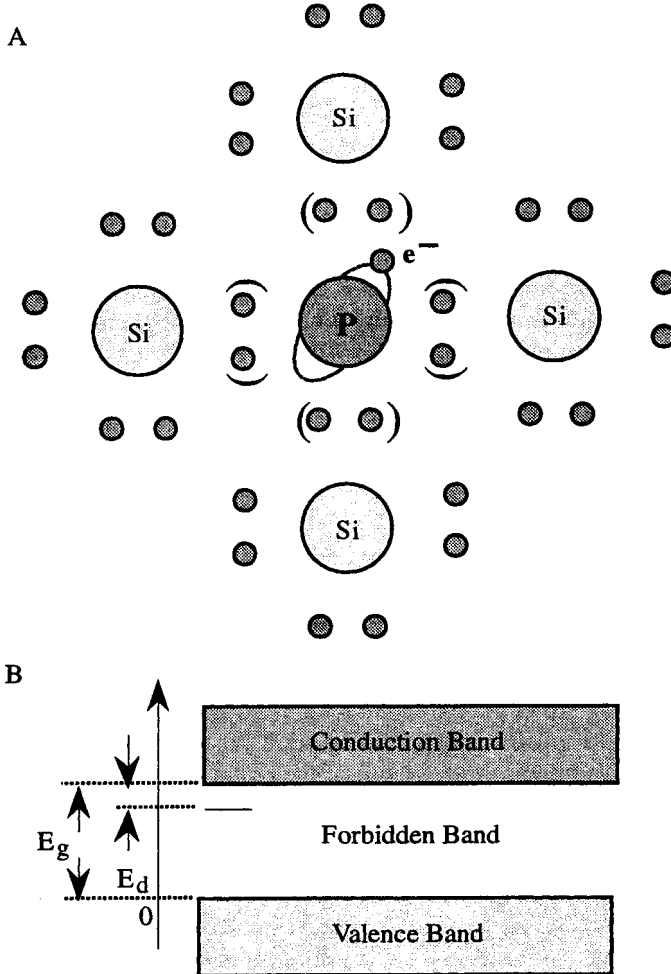


Figure 10.4 N-type semiconducting material.
 A. Modified covalent bonding with an excess electron at P atom;
 B. Energy-band diagram.

The aluminum atom when forming the covalent sharing with the neighboring Si atoms poses a deficiency in the bonding. This deficient location is ready to accept or attract an electron to form a valence band saturation and therefore could be considered as a positive carrier. Thus the presence of the third group atoms or an acceptor atom presumptuously

provides an excess positive carrier at its location. When the hole is filled by an electron, the group III atom becomes negatively ionized, but offers a complete covalent bonding.

The presence of a hole can be attributed with an energy level (known as *acceptor level*) E_a close to the uppermost part of the valence band. E_a depicts the small energy required to accept an electron from the valence band. The resulting deficiency of the electron at the valence band amounts to the inculcation of a positive carrier (hole) in the valence band.

10.6 Conductivity of Extrinsic Semiconductors

Suppose N_d and N_a represent the donor and acceptor impurity concentrations (per meter³). Then the conductivities of N-type and P-type materials can be defined as follows.

For an N-type material, the charge neutrality condition stipulates that, $n = p + N_D$ where n and p are electron and hole densities, respectively. Further, at equilibrium $np = n_i^2$ where n_i represents the intrinsic state electron (or hole) concentration. Therefore, n can be specified by $[N_D + (N_D^2 + 4n_i^2)^{1/2}]/2$. Normally, $N_D \gg n_i$. Hence $n = N_D$.

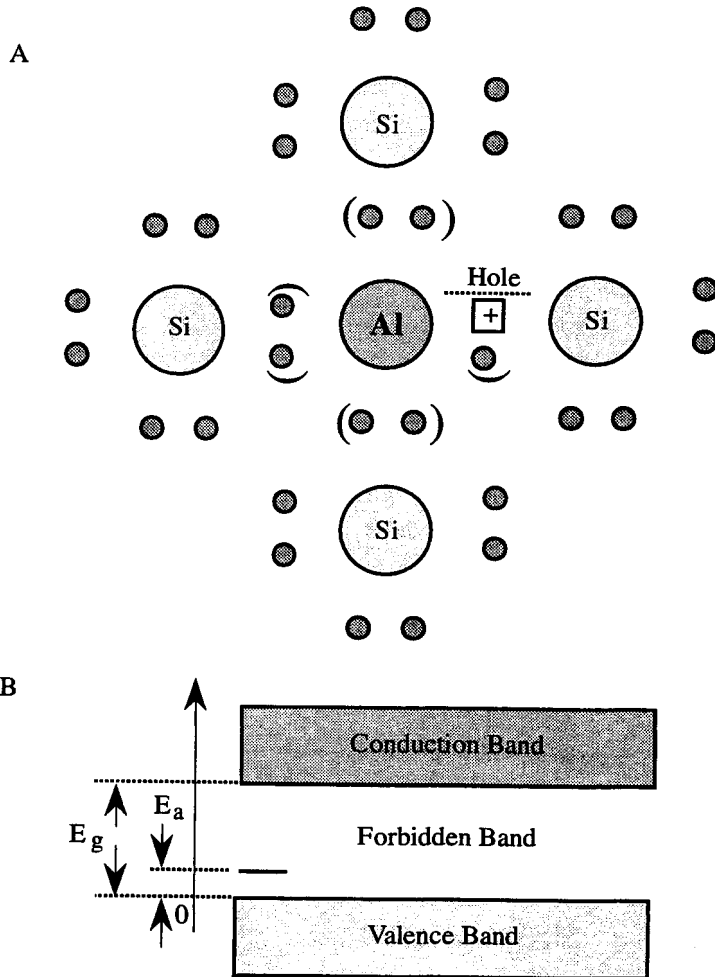


Figure 10.5 P-type semiconducting material.
A. Modified covalent-bonding with a hole created due to the deficiency of electron at Al atom;
B. Energy-band diagram.

Therefore, it follows that:

$$(\sigma)_{N\text{-type}} \equiv \mu_e N_D e \quad \text{siemen/meter} \quad (10.3a)$$

Likewise, for a P-type material,

$$(\sigma)_{P\text{-type}} = \mu_p N_A e \quad \text{siemen/meter} \quad (10.3b)$$

The donor level energy E_d and the acceptor level energy E_a represent the minimum energy required for the excess electron to be activated into the conduction band and the excess hole to be activated into the valence band, respectively. These are also designated as *ionization energies*. Representative values of E_d and E_a are presented in Table 10.3.

Table 10.3 Typical Impurity Atoms and Their Ionization Energy Levels

Type of Impurity	Element	Ionization Energy			
		E_d (eV)		E_a (eV)	
		Ge	Si	Ge	Si
Donor	P	0.0120	0.0440		
	As	0.0127	0.0490		
	Sb	0.0096	0.0390		
Acceptor	B			0.0104	0.0450
	Al			0.0102	0.0570
	Ga			0.0108	0.0650
	In			0.0112	0.1600

10.7 Majority and Minority Carriers

Table 10.4 Charge Carrier Species in N and P Materials

Type of Extrinsic Semiconductor	Temperature-Induced Charge Carriers (per meter ³)		Dopant Contribution of Charge Carriers (per meter ³)		Remarks
N-type	n_i	p_i	N_D		
P-type	n_i	p_i	N_A		<ul style="list-style-type: none"> • $n_i = p_i$. • Majority carrier: $(n_i + N_D)$. • Minority carrier: p_i. • $n_i = p_i$. • Majority carrier: $(p_i + N_A)$. • Minority carrier: n_i.

When a semiconductor is doped, this extrinsic state material has the charge carrier at a finite temperature $T > 0$ K, given in Table 10.4.

10.8 Compound Semiconductors

Semiconducting materials can also be constituted by compounding the elements of groups III–V and II–VI. These materials have the same structures as group IV semiconductors except that alternate atoms are different in their dispositions across the crystal. Typical compound semiconductors and their properties are presented in Table 10.5.

10.9 Alloys of Compound Semiconductors

In certain electronic devices, materials formed by the alloys of compound materials are used. For example, a solid solution of InAs and GaAs provides an alloy designated as (In, Ga)As. Similarly, InP and InAs solid solutions give rise to In(As, P) alloys. Further (In, Ga) (As, P) alloys are also feasible.

Table 10.5 Properties of Compound Semiconductors

Compound	Forbidden Energy Gap (E_g) (eV)	At 20 °C			
		Conductivity (σ) siemen/meter	Mobility $m^2/volt\text{-}sec$		Lattice Constant (a) in nm
			Electron (μ_n)	Hole (μ_p)	
AlSb	1.60	–	0.020	–	0.613
GaP	2.30	–	0.019	0.012	0.545
GaAs	1.40	10^{-6}	0.880	0.040	0.565
GaSb	0.70	–	0.600	0.080	0.612
InP	1.30	500	0.470	0.015	0.587
InAs	0.36	10^4	2.260	0.026	0.604
InSb	0.18	–	8.200	0.170	0.648
ZnS	3.70	–	0.014	0.0005	–
SiC	3.00	–	0.010	0.002	–

10.10 Amorphous Semiconductors

These are noncrystalline (or polycrystalline) materials (usually in thin/thick film forms) which consist of randomly oriented clusters of crystallites. The structure within the crystallites leads to an energy gap. Also the crystallites offer a covalent structure with broken bonds wherever the crystalline orientation changes. This gives rise to *dangling bonds* where unpaired electrons can act as traps for both itinerant electrons and holes. The result is that the mobility is greatly reduced. Also, the doping becomes less effective (in contributing to the

conductivity) as the carriers from the dopants are rendered immobile at the traps. However, if hydrogen atoms are introduced in the amorphous material, they neutralize the unpaired electrons, thereby dramatically reducing the dangling bond effects.

Amorphous semiconducting properties are less controllable than those of single crystalline intrinsic and/or extrinsic semiconductors. Still, amorphous structure can be very easily fabricated especially over a large area such as in solar panels or in xerographic applications. Therefore, amorphous semiconductors find potentials in upcoming technological trends.

10.11 Effective Masses of Electrons and Holes in Semiconductors

The charge carrier present in a semiconductor faces interactive force fields; as a result their effective masses are different from their actual masses. Shown in Table 10.6 are the typical values of the effective masses pertinent to various semiconducting materials.

Table 10.6 Effective Masses of Electrons and Holes in Various Semiconductors at Room Temperature

Semiconductor	Effective mass	
	Electrons m_e^*/m_0	Holes m_a^*/m_0
	(m ₀ : free electronic mass)	
Ge	0.082–0.120	0.280
Si	0.190–0.260	0.500
GaAs	0.067	0.650
GaP	0.350	0.500
InP	0.080	0.200
InSb	0.013	0.180
AlAs	–	–
InAs	0.019	0.410
GaSb	0.047	0.400
CdSe	0.140	0.370
CdS	0.270	0.070

10.12 Thermal Properties of Semiconductors

Much like metals (see Chapter 9), the electrical conductivity (σ) of semiconductors varies in direct proportion to the thermal conductivity (*Wiedemann–Fraz law* for metal). The thermal conductivity of semiconductors is given by:

$$K_{SC} = A_S T\sigma + K_V \quad (10.4)$$

where A_S is a constant, T is the temperature, and K_V is the contribution to thermal conductivity resulting from lattice vibrations.

In the intrinsic state, the electrical conductivity of semiconductors is given by:

$$\sigma_i = e(\mu_n + \mu_p) (A_c A_v)^{1/2} T^{3/2} \exp(-E_g/2k_B T) \tag{10.5}$$

where k_B is the Boltzmann constant and (A_c, A_v) are constants independent of temperature given by:

$$A_c = 2(2\pi m_e^* k_B/h^2)^{3/2} \tag{10.6a}$$

and

$$A_v = 2(2\pi m_n^* k_B/h^2)^{3/2} \tag{10.6b}$$

where h is the Planck constant and m_e^* and m_n^* are effective masses of electrons and holes, respectively.

10.13 Hall-Effect Properties of Semiconductors

When a semiconductor is subjected to cross-fields of magnetic force (H) and electric field (E), constituting a conduction current flow, $J_c = \sigma E$, the Lorentz force acting on the moving charge carriers would induce the Hall potential field (E_H) orthogonal to H and J_c as shown in Figure 10.6.

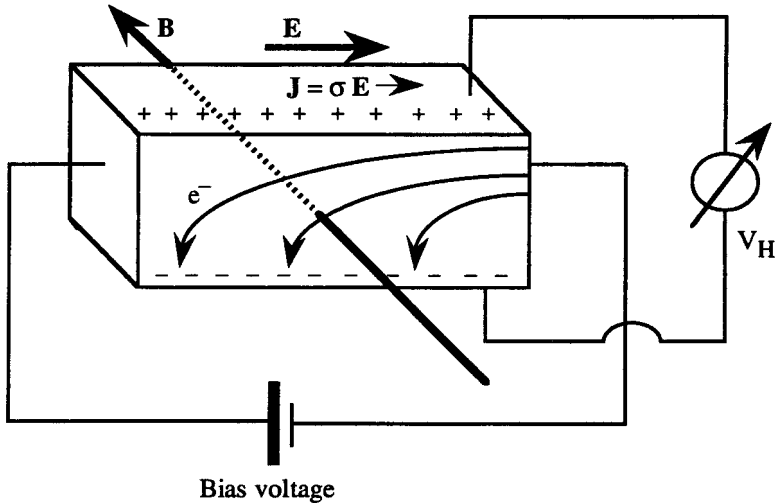


Figure 10.6 Hall-effect in semiconducting materials.
 V_H : Hall voltage.

The corresponding Hall voltage is given by $|E_H|/|B|$ and Hall coefficient (R_H) is defined as $R_H = |E_H|/|J B|$. Typical Hall coefficients of semiconducting materials are given in Table 10.7.

Table 10.7 Hall Coefficients of Typical Semiconductors

Material	R_H ($\text{cm}^3 \times 10^{-5} / \text{coulomb}$)
Si	-10^3
Ge	-10^4
InAs	0.5
InSb	10^3

10.14 Optical Properties of Semiconductors

AB-type binary compounds which crystallize in either the cubic zincblende or hexagonal wurtzite structure are typically semiconductors and are useful as *optical semiconductors*, *phosphors*, *photodetectors*, and *injection laser materials*. Typical examples of these materials are: ZnO, ZnS, ZnSe, ZnTe, CuCl, CuBr, GaP, GaAs, and CdS. Properties of these materials are listed in [2].

10.15 Miscellaneous Semiconductors

1. Ternary and quaternary compound semiconductors: These materials, though not in widespread use, are potentially considered in upcoming technologies such as nonlinear optics. They also offer certain distinct luminescence and lasing properties. Typically CdGeAs₂, CdSnP₂, ZnGeP₂, AgInSe₂, AgGaS₂ and CuAlS₂, have been considered as candidate materials.

2. Oxide semiconductors: These are semiconductors with a large forbidden gap. Cu₂O, NiO, and ZnO are typical oxide semiconductors which have been studied. Oxides like VO₂ and V₂O₃ exhibit high conductivity at high temperatures but they behave more like dielectrics at room temperature. Other oxides like SrTiO₃ and BaTiO₃ which are normally dielectrics could, however, be changed into semiconductors with appropriate doping.

3. Refractory semiconductors: These operate at high temperature and have very large energy gaps. They can be doped to form N- or P-type materials. Examples are: AlP, AlAs, InP, AlN, GaN, InN, BN, Bp, and BAs.

4. Superconducting semiconductors: Several semiconductors go into the superconducting state at temperatures less than 1 K. Typical such materials are: PbS, PbSe, PbTe, GeTe, SnTe, and SrTiO₂.

Interestingly, materials like InSb and InTe and the element Te become superconductors under high pressures.

5. Magnetic semiconductors: Some oxide-type and chalcogenide semiconductors exhibit magnetic properties. NiO, CoO, and FeO are antiferromagnetic materials, whereas, europium chalcogenides like EuO, EuS and EuSe, and CdCr₂Se₄ are semiconducting ferromagnetic materials. The spinels M²⁺OFe₂³⁺O₃ and garnets Y₃Fe₅O₁₂ are also semiconducting ferrimagnetic materials.

6. Organic semiconductors: Organic compounds such as anthracene ($C_{14}H_{10}$) and phthalocyanines have been observed to exhibit semiconducting properties. Single component aromatic compounds such as $C_{10}H_8$, $C_{14}H_{10}$, $C_{18}H_{12}$, and $C_{12}H_{14}$ which are insulators become photoconductive with sufficient photoexcitation. Their energy gap ranges from 2 to 5 eV. Impurities play a dominant role in the electrical conductivity of organic semiconductors.

Two component semiconductors consist of pairs of complementary molecules with large differences in their redox properties.

Low mobility and tendency for carrier trapping are of interest in organic semiconductors studied so far. These limitations hamper the use of these materials in technological applications. Semiconducting p-paraphenylene vinylene (PPV) in layer form has been successfully used in conjunction with CdSe as an electroluminescent structure.

10.16 Nonsemiconducting Materials Used in Semiconductor Technology

Silicon dioxide and silicon nitride are widely used as *passivation materials* in the fabrication of semiconducting devices. SiO_2 also constitutes the gate oxide part of metal oxide semiconductor devices. The general characteristics of these materials are presented in Table 10.8.

Table 10.8 Properties of SiO_2 and Si_3N_4 at Room Temperature ($\cong 300$ K)

Properties	Materials	
	SiO_2	Si_3N_4
Physical properties		
Crystalline structure	Amorphous	Amorphous
Specific gravity	2.2	3.1
Electrical properties		
Relative permittivity	3-9	7.5
Dielectric breakdown strength (volt/meter)	10^9	10^9
DC resistivity (ohm-cm)	10^{14} - 10^{16}	$\sim 10^{16}$
Forbidden gap energy (eV)	9	5
Thermal properties		
Melting point $^{\circ}C$	~ 1600	—
Thermal conductivity Watt/cm-K	0.014	—

Another adjunct material used as a substrate in semiconductor devices is sapphire (such as in silicon-on-sapphire (SOS) devices). Essentially sapphire is Al_2O_3 .

Silicon carbide (SiC) has been tried as an integrated circuit material to survive operating temperatures up to $500^{\circ}C$, three times higher than the failure temperature for conventional silicon-based components.

10.17 Applications of Semiconducting Materials

In modern time, semiconducting materials have facilitated the emergence of innumerable electronic devices for a variety of applications. The descriptions of these devices are

abundantly presented in the literature, a few of which are listed as references in this chapter. Essentially, the semiconductor devices can be grouped as follows:

- Junction devices (junction diodes and bipolar transistors)
- Unipolar devices (field effect devices)
- Metal oxide semiconductor devices
- High frequency devices
- Bulk-effect microwave devices
- Optoelectronic devices and semiconductor lasers
- Power rectifiers and thyristor family of devices
- Semiconductor transducers

10.18 Concluding Remarks

Semiconductors are perhaps the most widely studied materials due to their unlimited application potentials in the active device fabrications. The physics of conventional semiconductors have been fairly well comprehended and explained. The exploring trend in finding newer categories of semiconductors is not over. Microminiaturization and high frequency applications of semiconducting devices as well as low power consuming devices are setting the goals in search of better semiconductors in the existing technology and for futuristic trends.

References

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Defining Terms

Effective mass: Mass of charged carriers modified as a result of prevailing interactive field forces on them.

Extrinsic semiconductors: Semiconducting materials with added dopants (impurities).

Intrinsic semiconductors: Pure semiconducting materials with no addition of impurities.

Mobility: Extent of ease of the movement of charge carriers under the influence of applied electric field force, specified as the velocity per unit electric field applied.