Module 2

➤ Introduction to Solids, Crystals and Electronic Materials

➤ Formation of Energy Bands

➤ Energy Band Model, Effective Mass

➤ Direct and indirect bandgap

➤ Elemental and compound semi-conductors

➤ Intrinsic and Extrinsic semi-conductors

➤ The density of states

➤ Carrier statistics

➤ Fermi Level

➤ Equilibrium carrier concentration, Quasi Equilibrium and Quasi-Fermi Level
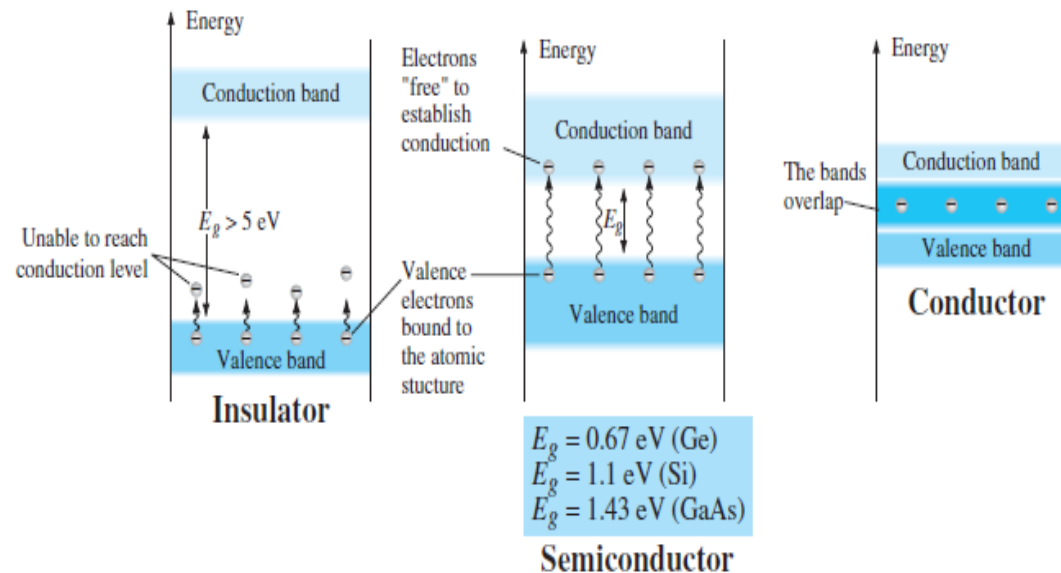
Solid-State Electronic Materials

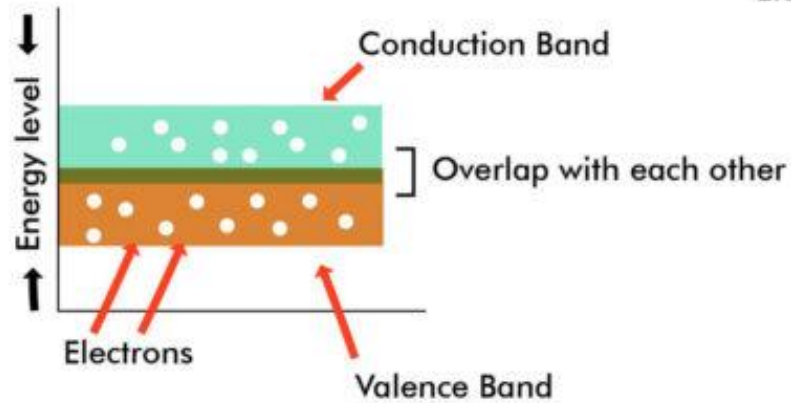- Electronic materials fall into three categories (w.r.t resistivity):
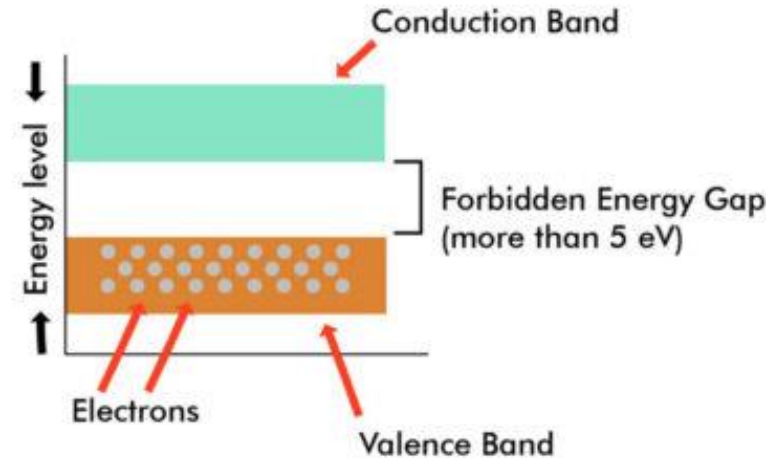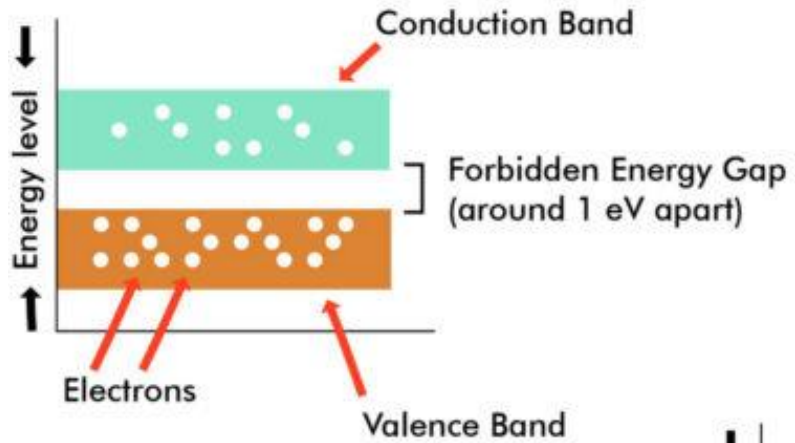
Insulators $\qquad \rho > 10^5\ \Omega\text{-cm}$ (diamond $\rho = 10^{16}$)

Semiconductors $\qquad 10^{-3} < \rho < 10^5\ \Omega\text{-cm}$

Conductors $\qquad \rho < 10^{-3}\ \Omega\text{-cm}$ (copper $\rho = 10^{-6}$)

Insulators/Conductors

•Materials that have large bandgap energies (in the range of 3 to 6 electron-volts (eV)) are **insulators**, because at room temperature, essentially no free electron exists in the material

•Materials that contain very large number of free electrons at room temperature are **conductors**

Energy

Conduction band

$E_g > 5$ eV

Unable to reach
conduction level

Valence band

Insulator

Electrons
"free" to
establish
conduction

Energy

Conduction band

E_g

Valence
electrons
bound to
the atomic
stucture

Valence band

$E_g = 0.67$ eV (Ge)
$E_g = 1.1$ eV (Si)
$E_g = 1.43$ eV (GaAs)

Semiconductor

Energy

The bands
overlap

Conduction band

Valence band

Conductor

Energy Band Model

ENERGY BANDS IN SOLIDS

Semiconductors

• → In a semiconductor, the bandgap energy is in the order of 1 eV. The net flow of free electrons causes a current

• → In a semiconductor, two types of charged particles contribute to the current:
   • negatively charged electrons
   • positively charged holes

Semiconductors are a special class of elements having a conductivity between that of a good conductor and that of an insulator

SEMICONDUCTOR MATERIALS: Ge, Si, AND GaAs

Atomic Structure

An atom is composed of :

• Nucleus (which contains positively charged protons and neutral neutrons)

• Electrons (which are négative charged and that orbit the nucleus)

Helium Atom

⊕ **Proton**

◯ **Neutron**
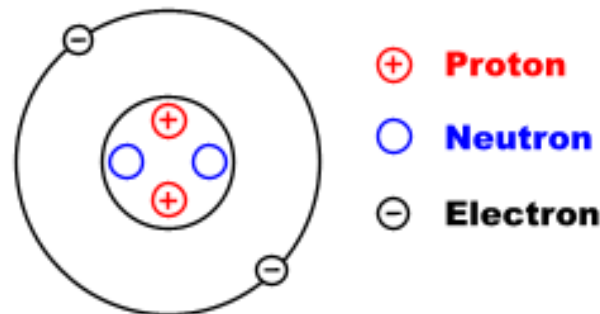
⊖ **Electron**

Valence Electrons

- Electrons are distributed in various shells at different distances from nucleus

- Electron energy increases as shell radius increases.

- Electrons in the outer most Shell are called as valence electrons

- Elements in the period table are grouped according to the number of valence electrons.

Solid-State Electronic Materials

- Elemental semiconductors are formed from a single type of atom of column IV, typically Silicon.

- Compound semiconductors are formed from combinations of elements of column III and V or columns II and VI.

- Germanium was used in many early devices

- Silicon quickly replaced germanium due to its higher bandgap energy, lower cost, and ability to be easily oxidized to form silicon-dioxide insulating layers.

Solid-State Electronic Materials (cont)

Bandgap is an energy range in a <u>solid</u> where no <u>electron</u> states can exist. It refers to the energy difference between the top of the <u>valence band</u> and the bottom of the <u>conduction band</u> in insulators and semiconductors
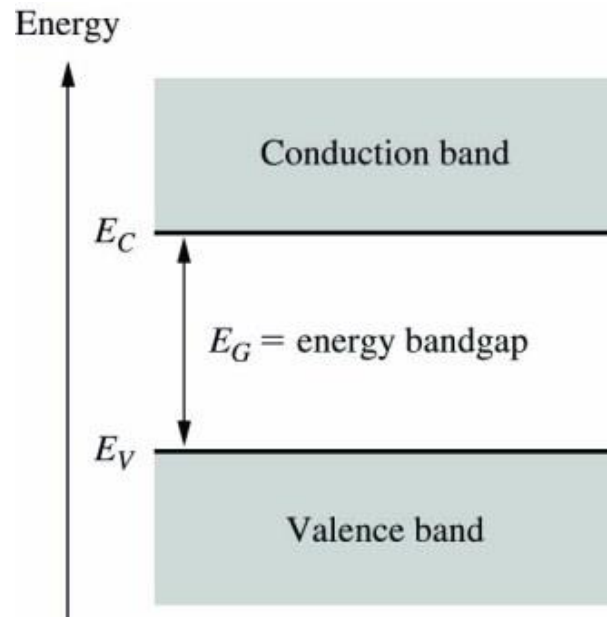
Semiconductor Materials (cont.)

Semiconductor	Bandgap Energy E_G (eV)
Carbon (diamond)	5.47
Silicon	1.12
Germanium	0.66
Tin	0.082
Gallium arsenide	1.42
Gallium nitride	3.49
Indium phosphide	1.35
Boron nitride	7.50
Silicon carbide	3.26
Cadmium selenide	1.70

IIIA	IVA	VA	VIA
5 10.811 **B** Boron	6 12.01115 **C** Carbon	7 14.0067 **N** Nitrogen	8 15.9994 **O** Oxygen
13 26.9815 **Al** Aluminum	14 28.086 **Si** Silicon	15 30.9738 **P** Phosphorus	16 32.064 **S** Sulfur
31 69.72 **Ga** Gallium	32 72.59 **Ge** Germanium	33 74.922 **As** Arsenic	34 78.96 **Se** Selenium
49 114.82 **In** Indium	50 118.69 **Sn** Tin	51 121.75 **Sb** Antimony	52 127.60 **Te** Tellurium
81 204.37 **Tl** Thallium	82 207.19 **Pb** Lead	83 208.980 **Bi** Bismuth	84 (210) **Po** Polonium

IIB — 30 65.37 **Zn** Zinc ; 48 112.40 **Cd** Cadmium ; 80 200.59 **Hg** Mercury
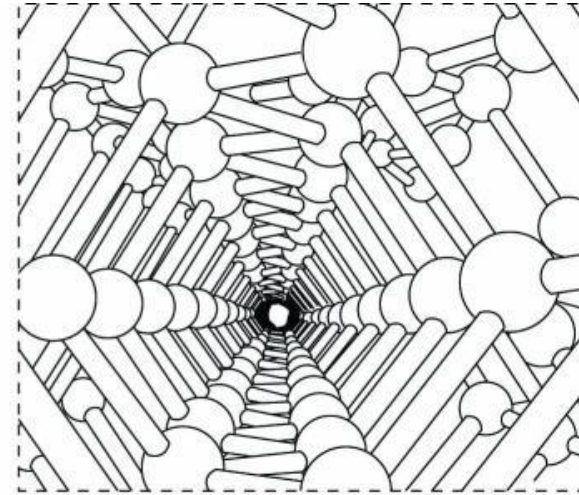
Covalent Bond Model

- Silicon has four electrons in the outer shell.
- Single crystal material is formed by the covalent bonding of each silicon atom with its four nearest neighbors.
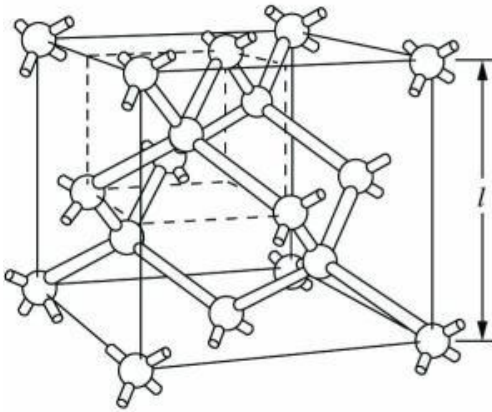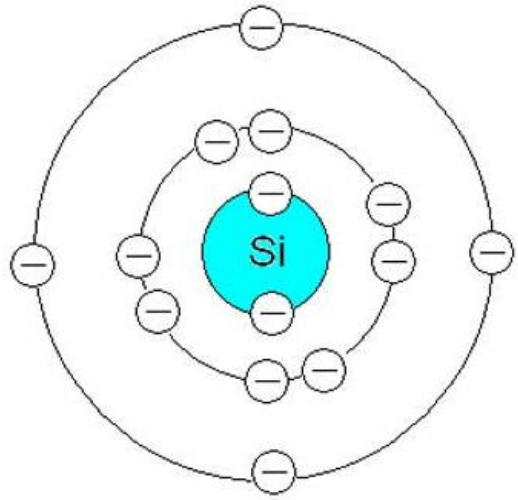

Silicon diamond lattice unit cell.
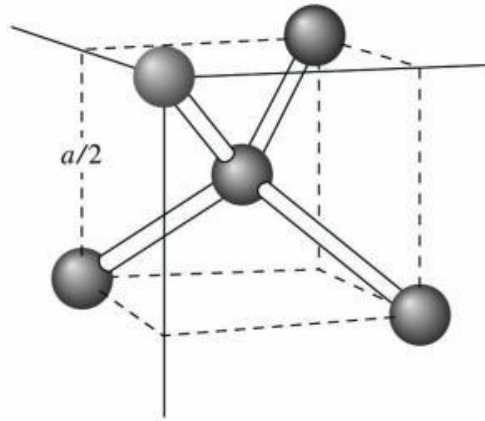
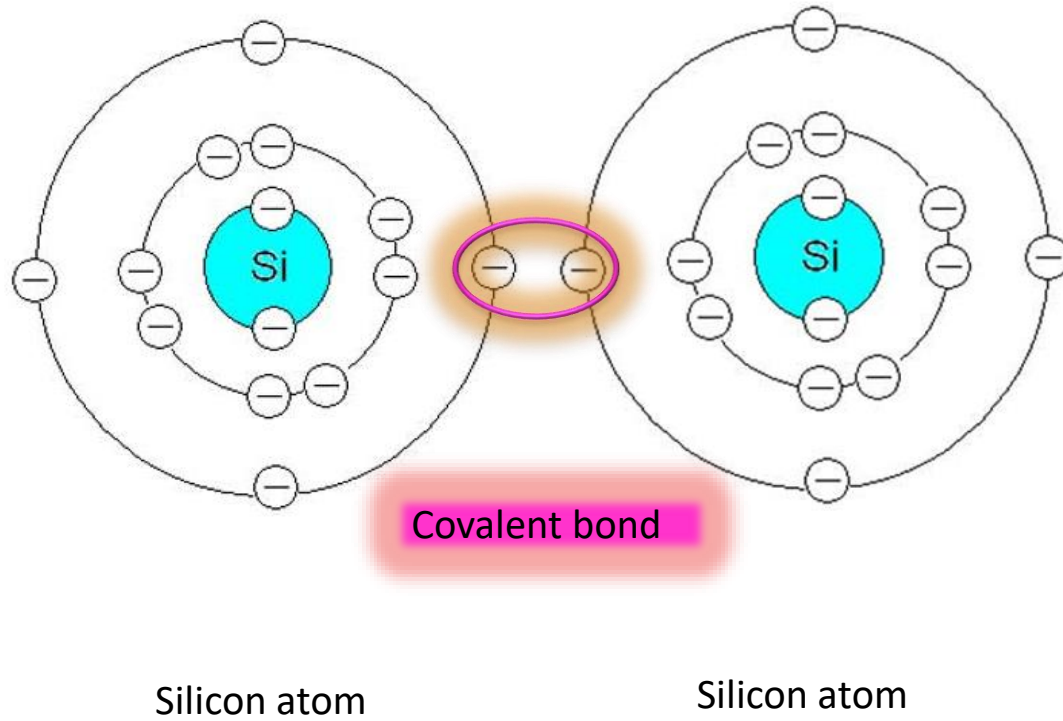Corner of diamond lattice showing four nearest neighbor bonding.

View of crystal lattice along a crystallographic axis.
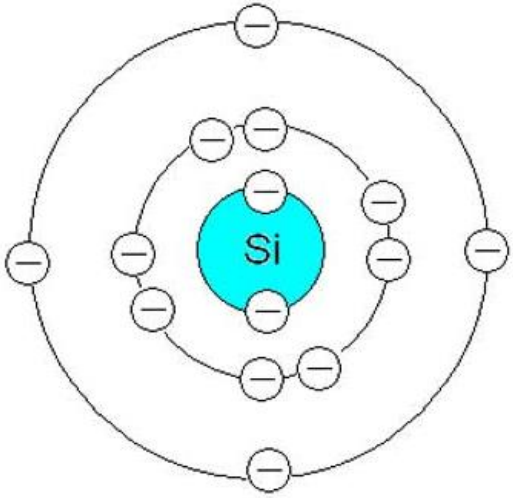
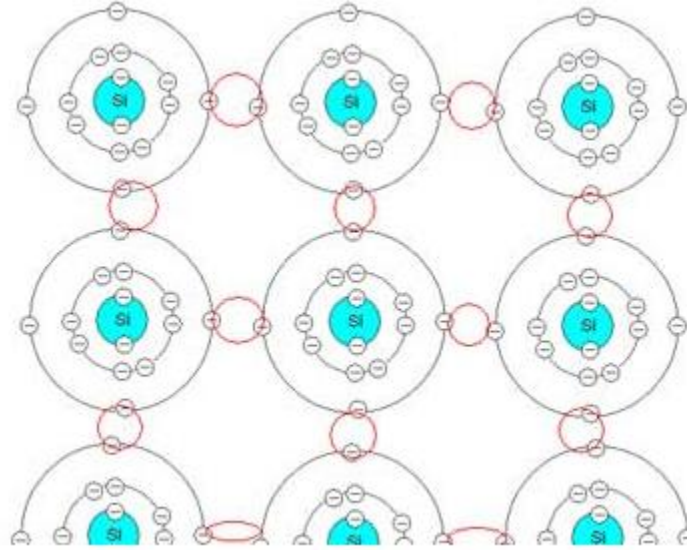# Silicon Covalent Bond Model (cont.)

Silicon atom

Silicon Covalent Bond Model (cont.)

Covalent bond

Silicon atom   Silicon atom

Silicon Covalent Bond Model (cont.)

Silicon atom

Covalent bonds in silicon
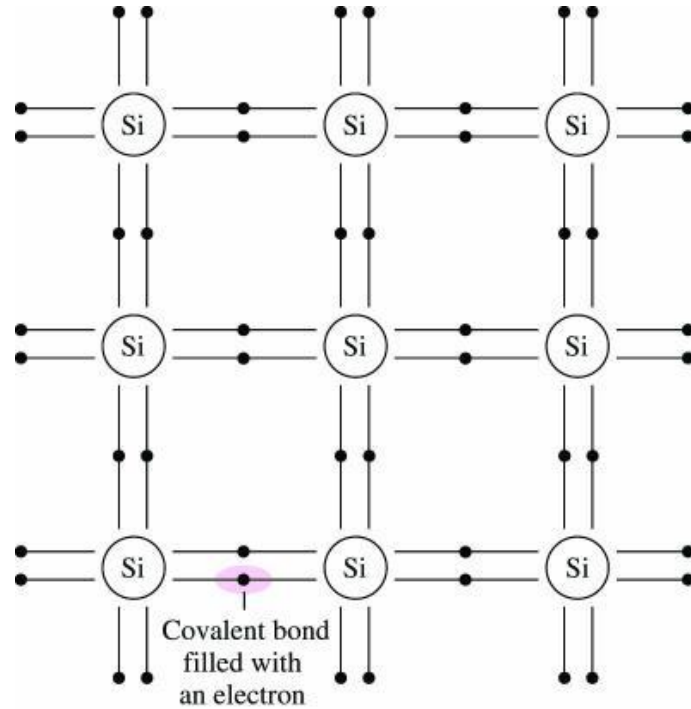
Silicon Covalent Bond Model (cont.)

Covalent bond filled with an electron
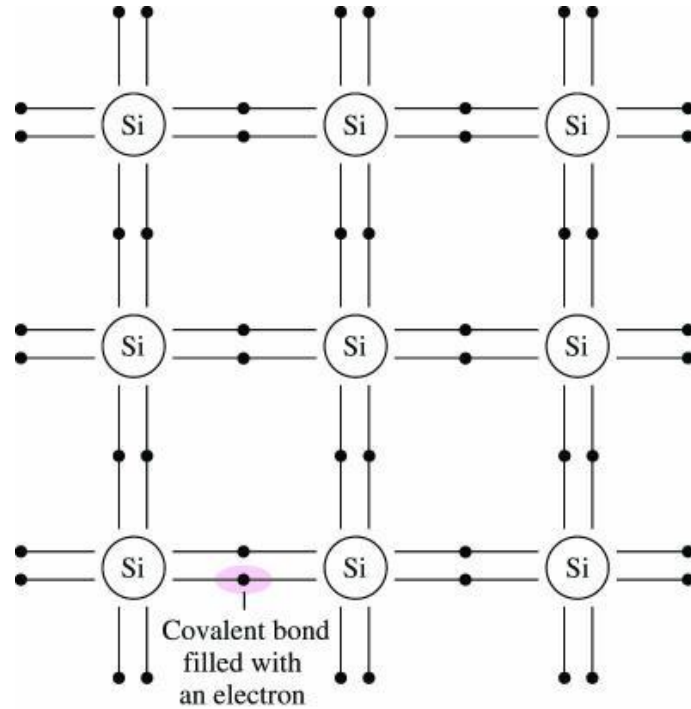
- What happens as the temperature increases?

- **Near absolute zero, all bonds are complete**
- Each Si atom contributes one electron to each of the four bond pairs
- The outer shell is full, no free electrons, silicon crystal is an insulator

Silicon Covalent Bond Model (cont.)

Covalent bond filled with an electron

Hole $(+q)$

Free electron $(-q)$

- Near absolute zero, all bonds are complete
- Each Si atom contributes one electron to each of the four bond pairs
- The outer shell is full, no free electrons, silicon crystal is an insulator
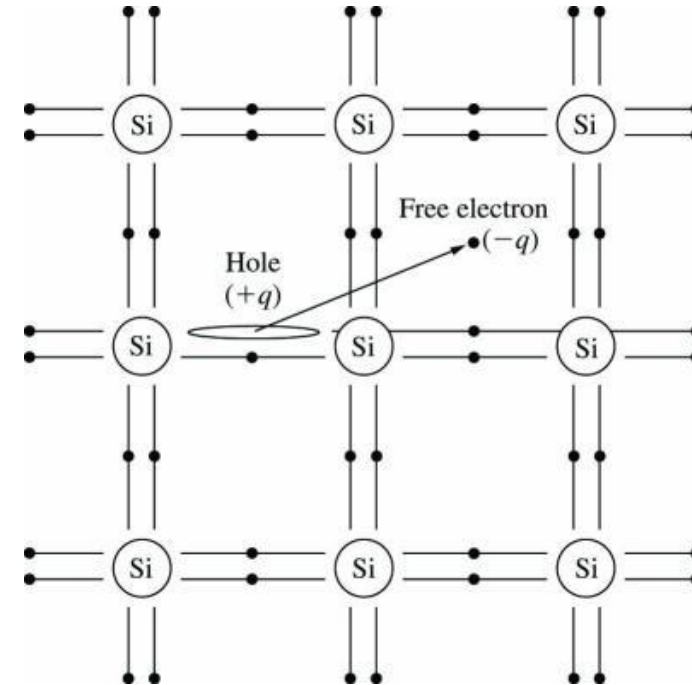
- Increasing temperature adds energy to the system and breaks bonds in the lattice, generating electron-hole pairs.
- The pairs move within the matter forming semiconductor
- Some of the electrons can fall into the holes – recombination.

Silicon and Germanium
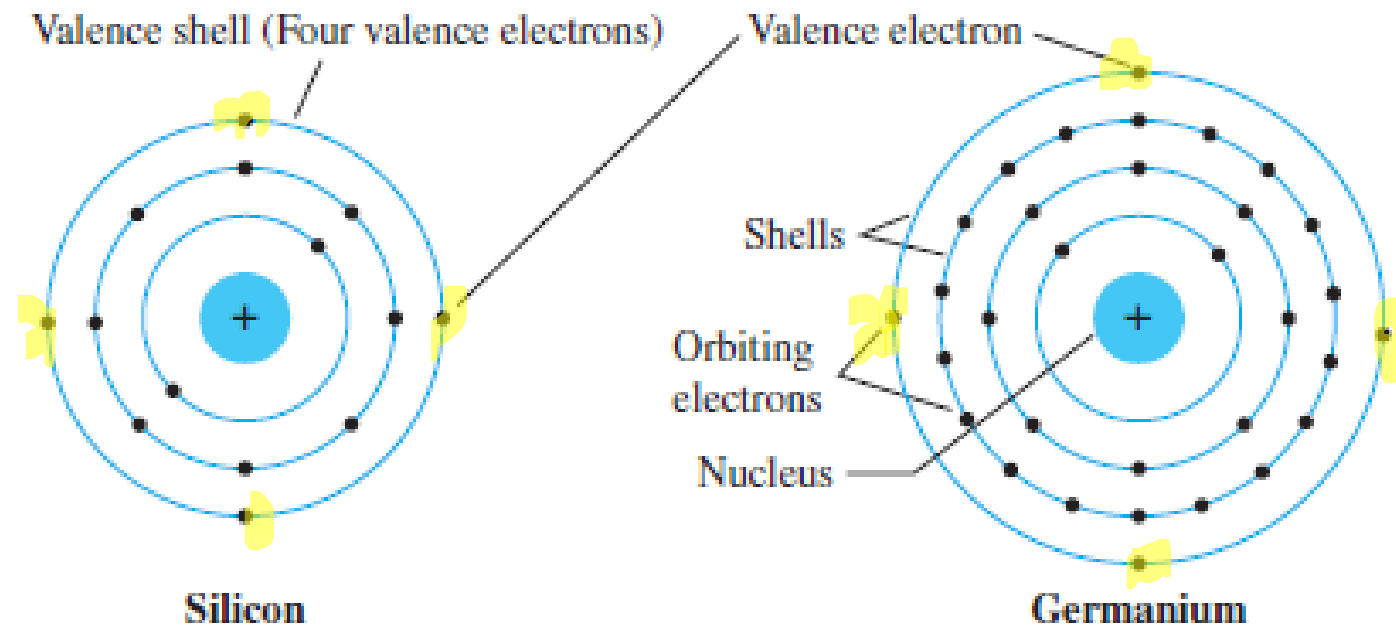
Bonding with the Valence Electrons
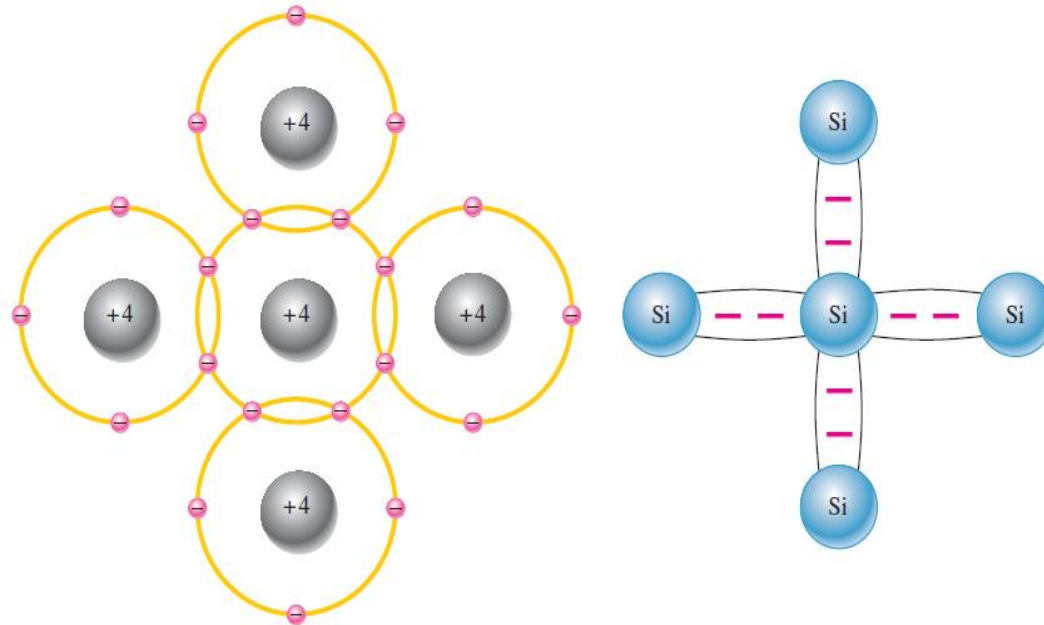
Silicon Crystal

- $\longrightarrow$ At 0°K, each electron is in its lowest possible energy state, and each covalent bounding position is filled.

- $\longrightarrow$ If a small electric field is applied, the electrons will not move $\longrightarrow$ silicon is an **insulator**

Silicon Atom Diagram at 0°K
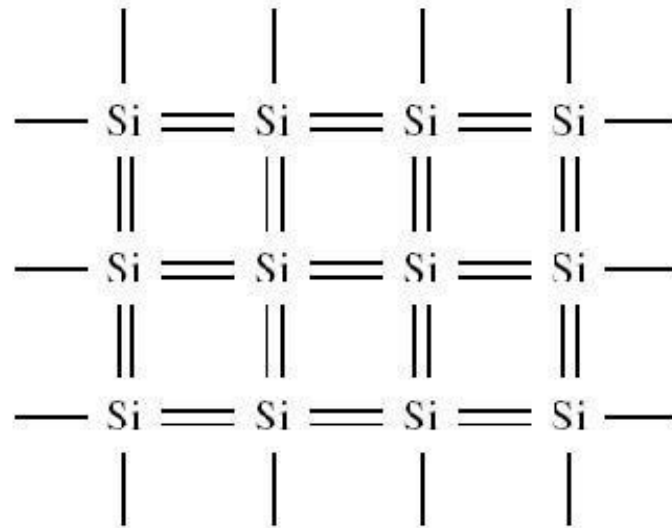
Two-dimensional representation of the silicon crystal at $T = 0\,°K$

Intrinsic Silicon

- →If the temperature increases, the valence electrons will gain some thermal energy, and breaks free from the covalent bond → It leaves a positively charged hole

- → In order to break from the covalent bond, a valence electron must gain a minimun energy **Eg**: **Bandgap energy**

Silicon Atom Diagram at Ambient Temperature
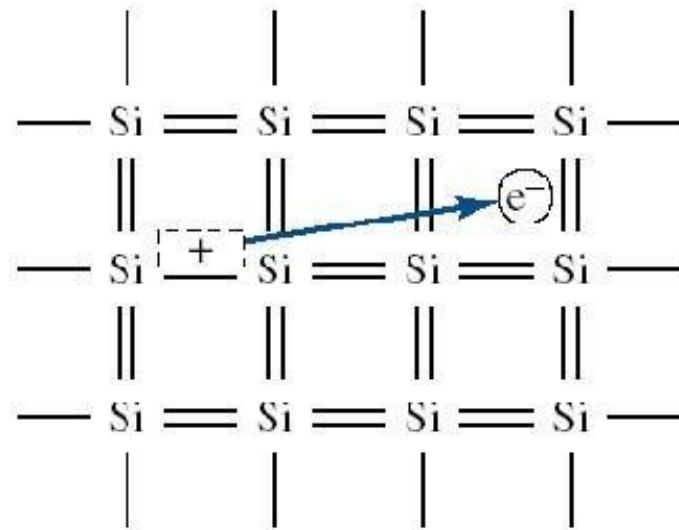
The breaking of
a covalent bond for $T > 0\,^\circ K$

Semiconductor Constants

- The concentration of electrons and holes directly influence the magnitde of the current

- In an intrinsic semiconductor (a single crystal semiconductor) the densities of holes and electrons are equal.

Extrinsic Semiconductor / Doping

The characteristics of a semiconductor material can be altered significantly by the addition of <u>specific impurity atoms</u> to the relatively pure semiconductor material

These impurities, although only added at <u>1 part in 10 million</u>, can alter the band structure <u>sufficiently to totally change the electrical properties of the material</u>

A semiconductor material that has been subjected to the doping process is called an extrinsic material

There are two extrinsic materials

- n -type
- p -type

n-type Semiconductor

- Both *n* -type and *p* -type materials are formed by adding a predetermined number of impurity toms to a silicon base

- An *n* -type material is created by introducing impurity elements that have *five* valence electrons (*pentavalent*), such as *antimony* , *arsenic* , and *phosphorus*

- Diffused impurities with five valence electrons are called donor atoms

- The four covalent bonds are still present

- There is, however, an additional fifth electron due to the impurity atom, which is *unassociated* with any particular covalent bond

- This remaining electron, loosely bound to its parent (antimony) atom, is relatively free to move within the newly formed n-type material

- The inserted impurity atom has donated a relatively "free" electron to the structure

Effect of donor impurities on the energy band structure.
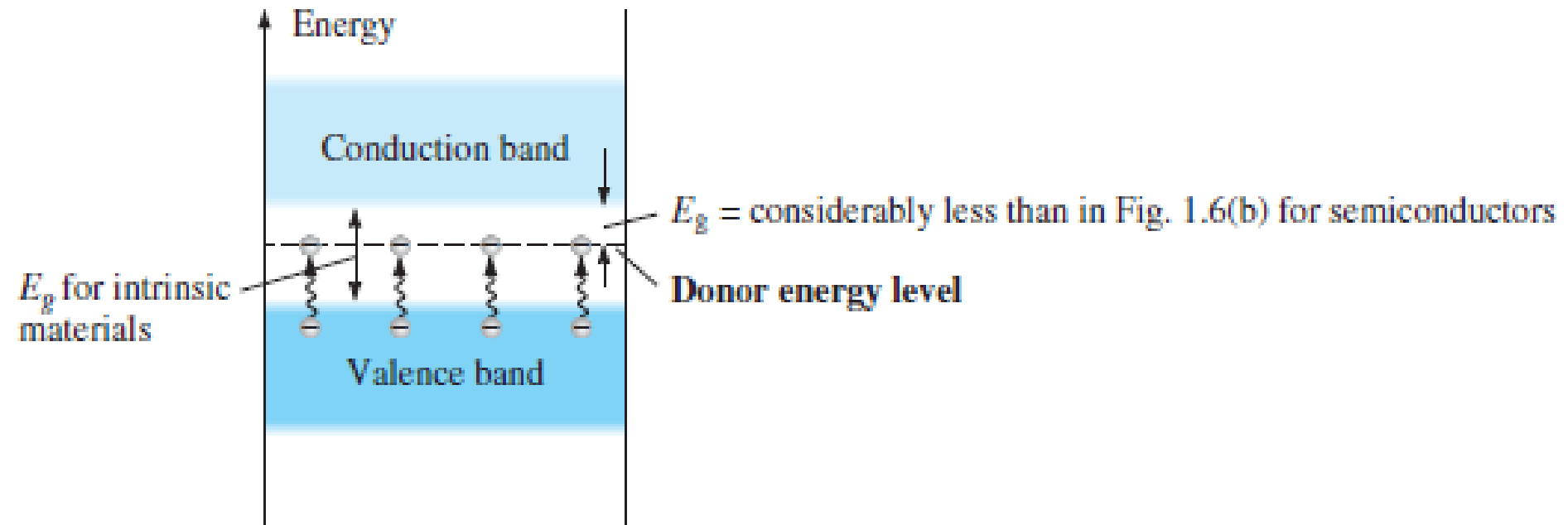
N-Type Semiconductor
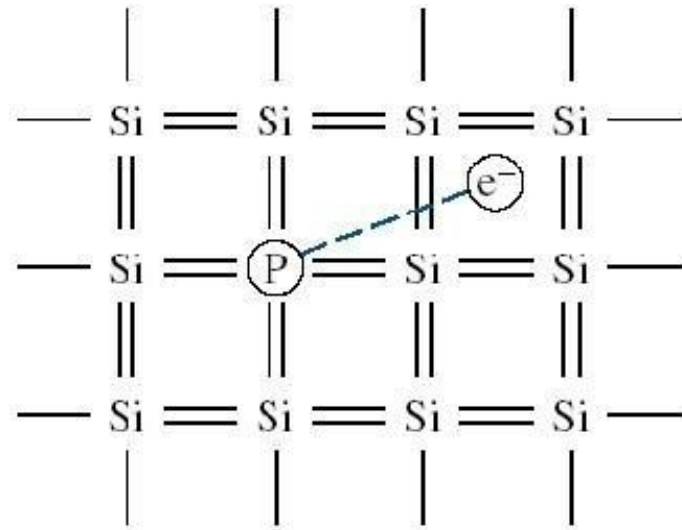
Two-dimensional representation of a silicon lattice doped with a phosphorus atom

p-type Semiconductor

- The p -type material is formed by doping a pure germanium or silicon crystal with impurity atoms having _three valence electrons_.
- The elements most frequently used for this purpose are _boron_, _gallium_, and _indium_
- Diffused impurities with three valence electrons are called acceptor atoms.

- There is now an insufficient number of electrons to complete the covalent bonds of the newly formed lattice

- The resulting vacancy is called a *hole* and is represented by a small circle or a plus sign, indicating the absence of a negative charge

- The resulting vacancy will readily accept a free electron

- The diffused impurities with three valence electrons are called acceptor atoms.

p-type Semiconductor
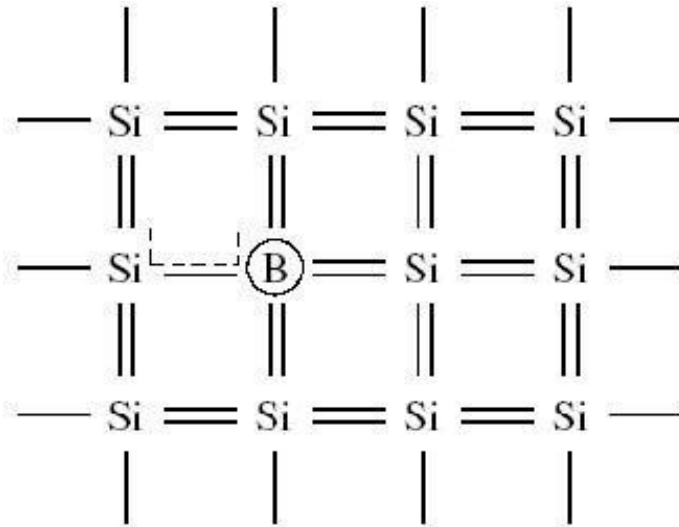
Two-dimensional representation of a silicon lattice doped with a boron atom

Electron versus Hole Flow

The effect of the hole on conduction is shown in Fig.   If a valence electron acquires sufficient kinetic energy to break its covalent bond and fills the void created by a hole, then a vacancy, or hole, will be created in the covalent bond that released the electron. There is, therefore, a transfer of holes to the left and electrons to the right, as shown in Fig. The direction to be used in this text is that of *conventional flow*, which is indicated by the direction of hole flow.
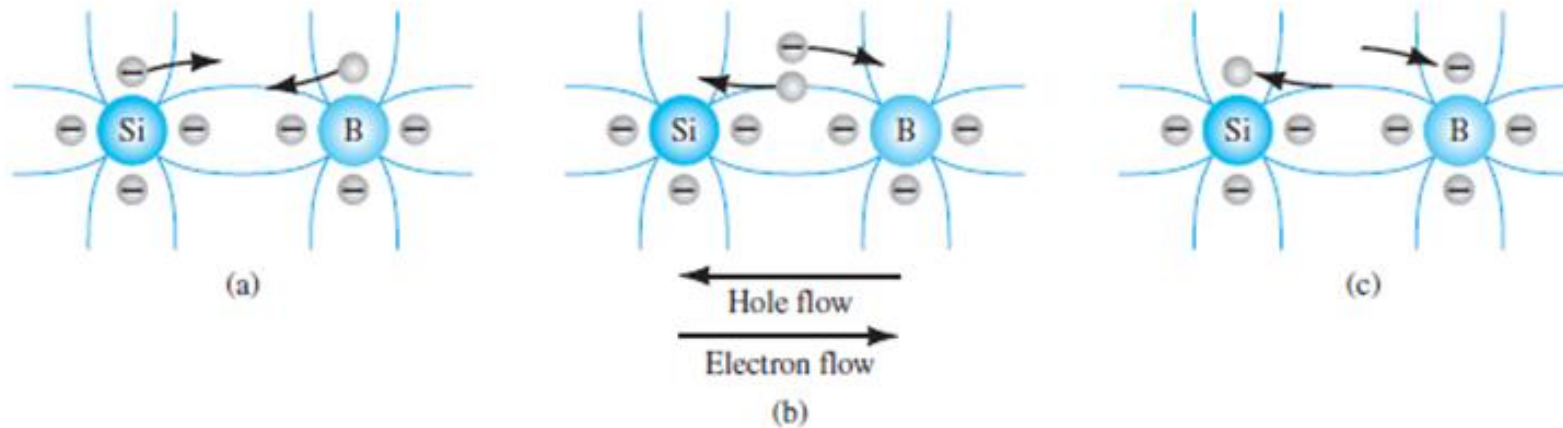
Electron versus hole flow.
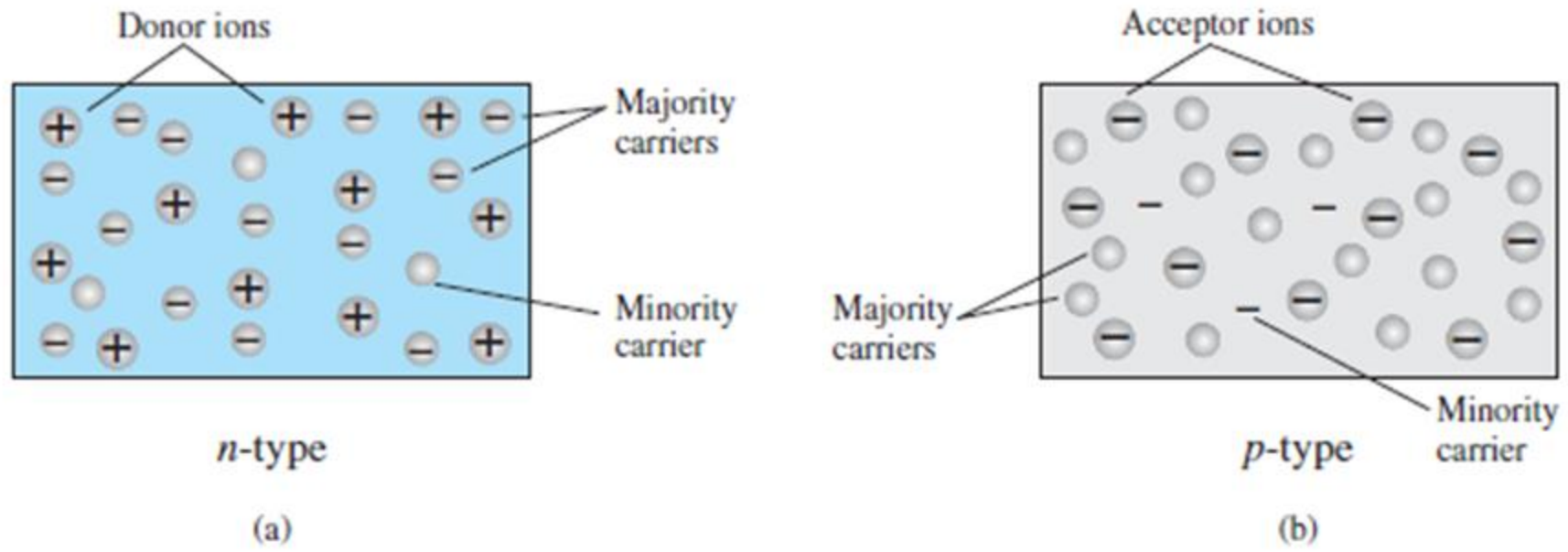
FIG.
(a) n-type material; (b) p-type material.

Direct and Indirect Energy BandGap

In semiconductor physics, the band gap of a semiconductor can be of two basic types:
- Direct band gap
- Indirect band gap

Indirect Bandgap:

- The minimal-energy state in the conduction band and the maximal-energy state in the valence band are each characterized by a certain crystal momentum (k-vector) in the Brillouin zone.
- If the k-vectors are different, the material has an "indirect gap"

Direct Bandgap

- The band gap is called "direct" if the crystal momentum of electrons and holes is the same in both the conduction band and the valence band; an electron can directly emit a photon.
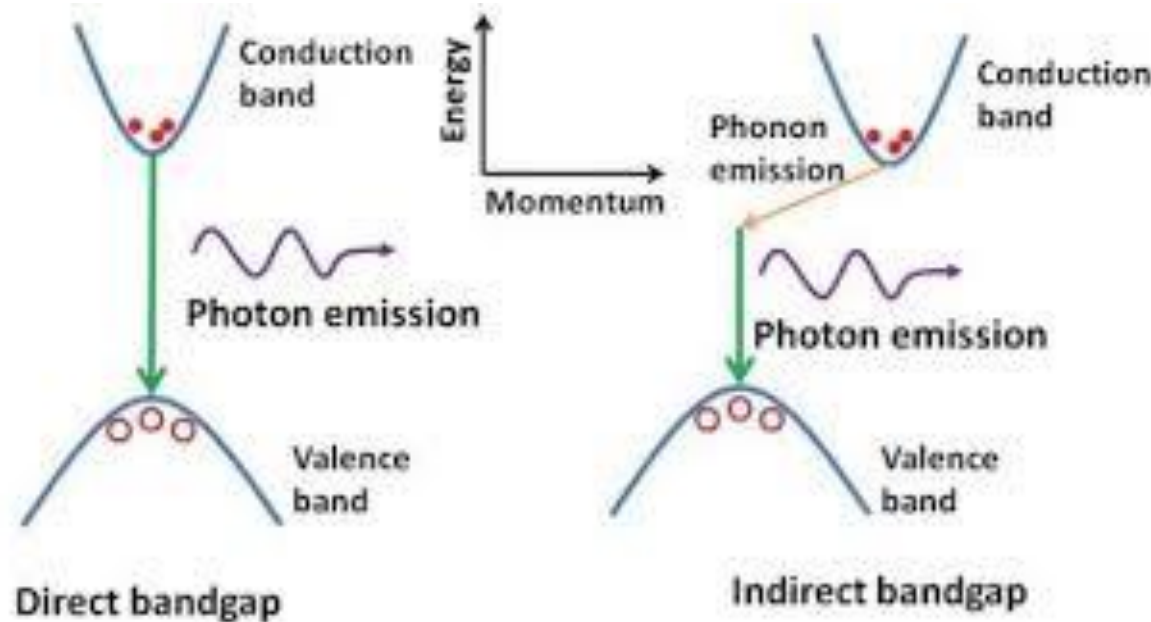
Examples of direct bandgap materials:

Amorphous silicon, InAs and GaAs

Examples of Indirect bandgap materials :

Crystalline Silicon and Ge.

Elemental and Compound Semi Conductors

- The elemental semiconductors are those composed of single species of atoms, such as silicon (Si), germanium (Ge), and tin (Sn) in column IV and selenium (Se) and tellurium (Te) in column VI of the periodic table

- There are, however, numerous compound semiconductors, which are composed of two or more elements

Example: Gallium arsenide (GaAs), for example, is a binary III-V compound, which is a combination of gallium (Ga) from column III and arsenic (As) from column V

They also can be formed by elements from two columns, such as aluminum gallium arsenide ($Al_xGa_{1-x}As$)

S.No	Elemental semiconductors	Compound semiconductors
1.	These are made from single element.	These are made from compound (mixed) element.
2.	These are made from IV group and VI group elements	These are made from III and V [or] II and VI elements.
3.	These are called as indirect band gap semiconductor (electron-hole recombination takes place through traps)	These are called as direct band gap semiconductor (electron-hole recombination takes place directly)
4.	Heat is produced in the recombination recombination	Photons are emitted during
5.	Life time of charge carriers is more due to indirect recombination	Life time of charge carriers is less due to direct recombination.
6.	Current amplification is more	Current amplification is less.
7.	These are used for making diodes, transistor, etc.	These are used for making LED, laser diodes, etc.
8.	Example : Ge, Si	Example : GaAs, GaP, CdS, MgO

INTRINSIC SEMICONDUCTORS

ψ_{hyb} orbitals

Valence electron

Si ion core $(+4e)$

(a)

Electron energy

$E_c + \chi$

Conduction band (CB)
Empty of electrons at 0 K.

E_c

Bandgap = E_g

E_v

Valence band (VB)
Full of electrons at 0 K.

ψ_B

0

(b)

(c)
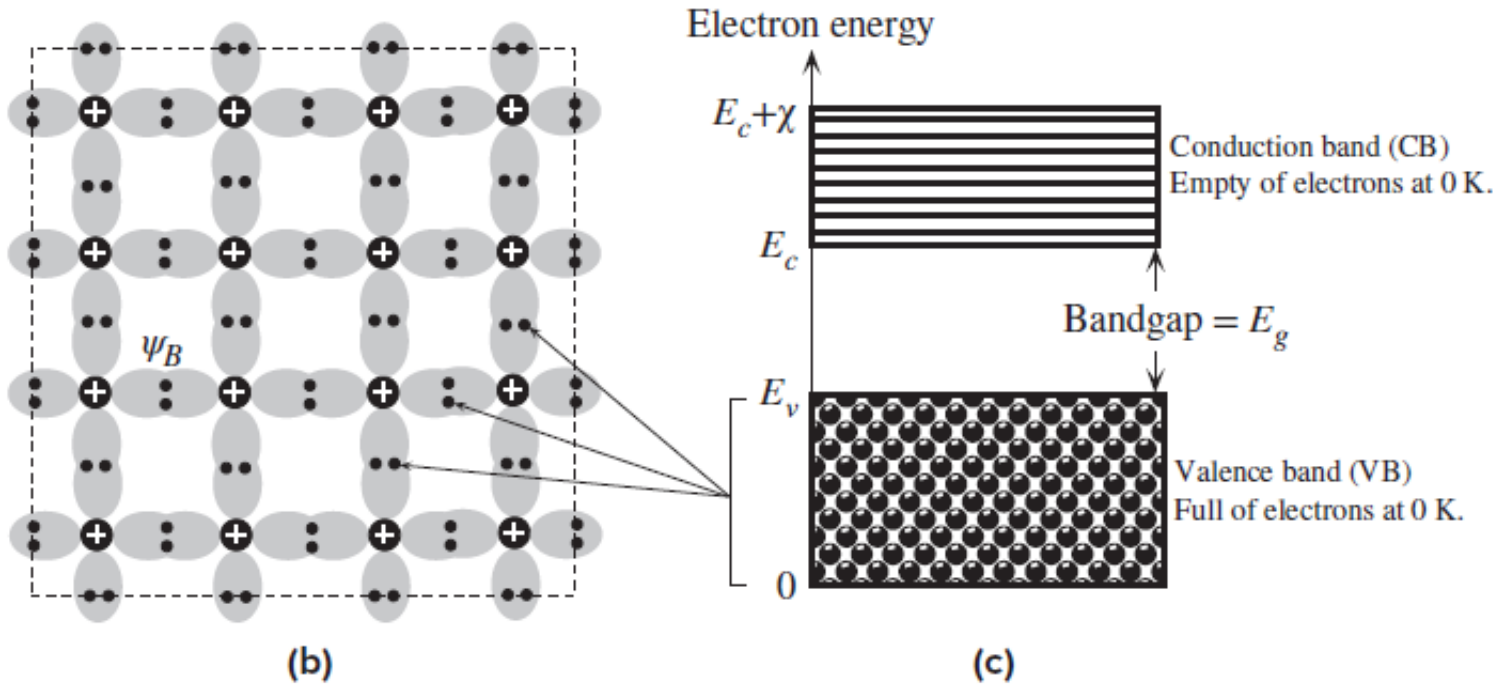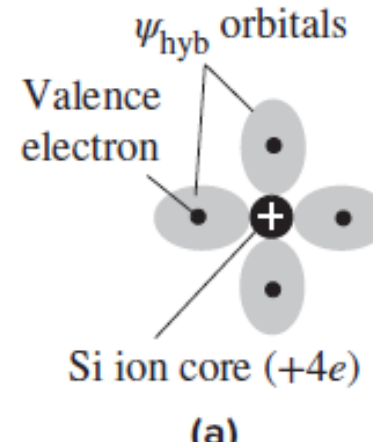
Figure (a) A simplified two-dimensional illustration of a Si atom with four hybrid orbitals ψ_{hyb}. Each orbital has one electron. (b) A simplified two-dimensional view of a region of the Si crystal showing covalent bonds. (c) The energy band diagram at absolute zero of temperature.

- The CB is separated from the VB by an energy gap E_g, called the **bandgap.**
- The energy level E_v marks the top of the VB and E_c marks the bottom of the CB.
- The energy distance from E_c to the vacuum level, the width of the CB, is called the **electron affinity** χ.

ELECTRONS AND HOLES

- The only empty electronic states in the silicon crystal are in the CB
- An electron placed in the CB is free to move around the crystal and also respond to an applied electric field because there are plenty of neighboring empty energy levels.
- An electron in the CB can easily gain energy from the field and move to higher energy levels because these states are empty. Generally we can treat an electron in the CB as if it were free within the crystal
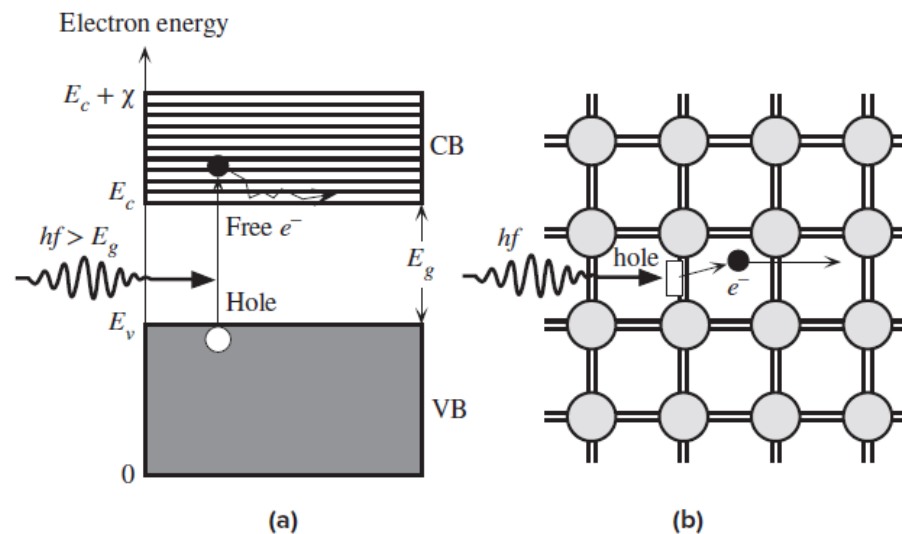
Figure (a) A photon with an energy greater than E_g can excite an electron from the VB to the CB. (b) When a photon breaks a Si–Si bond, a free electron and a hole in the Si–Si bond are created.

- Since the only empty states are in the CB, the excitation of an electron from the VB requires a minimum energy of E_g.
- Figure shows what happens when a photon of energy $hf > E_g$ is incident on an electron in the VB.

- This electron absorbs the incident photon and gains sufficient energy to surmount the energy gap E_g and reach the CB. Consequently, a free electron and <u>a "hole," corresponding to a missing electron</u> in the VB, are created. In some semiconductors such as Si and Ge, the photon absorption process also involves lattice vibrations
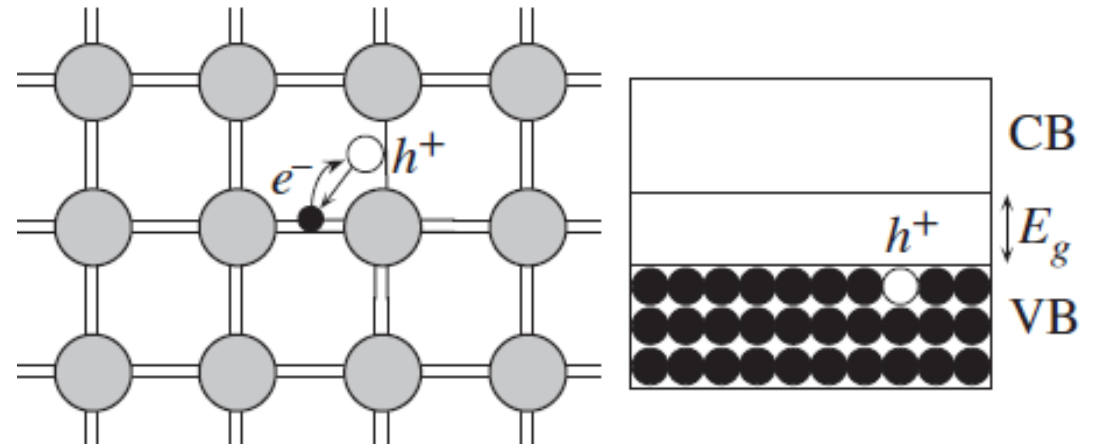
Thermal Generation

- In the absence of radiation, there is an electron–hole generation process going on in the sample as a result of **thermal generation.**

- Due to thermal energy, the atoms in the crystal are constantly vibrating, which corresponds to the bonds between the Si atoms being periodically deformed.
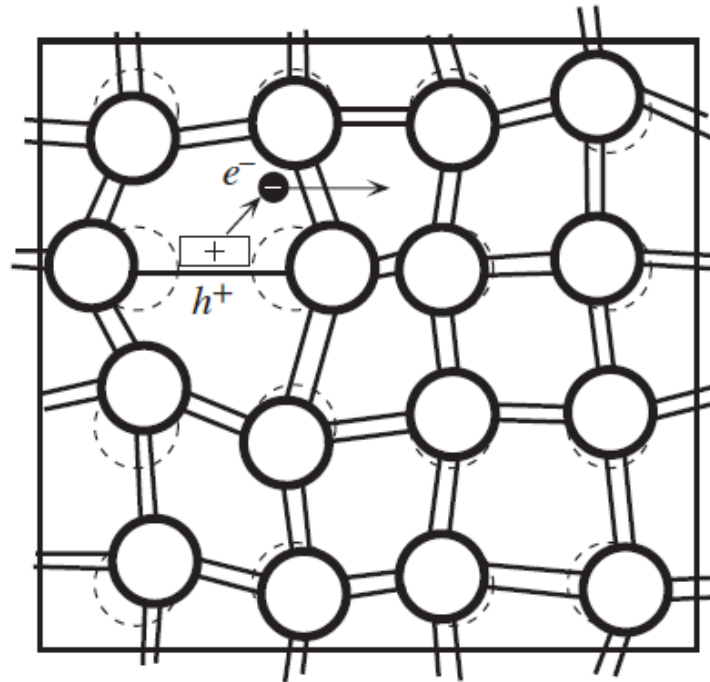
Figure   Thermal vibrations of atoms can break bonds and thereby create electron–hole pairs.
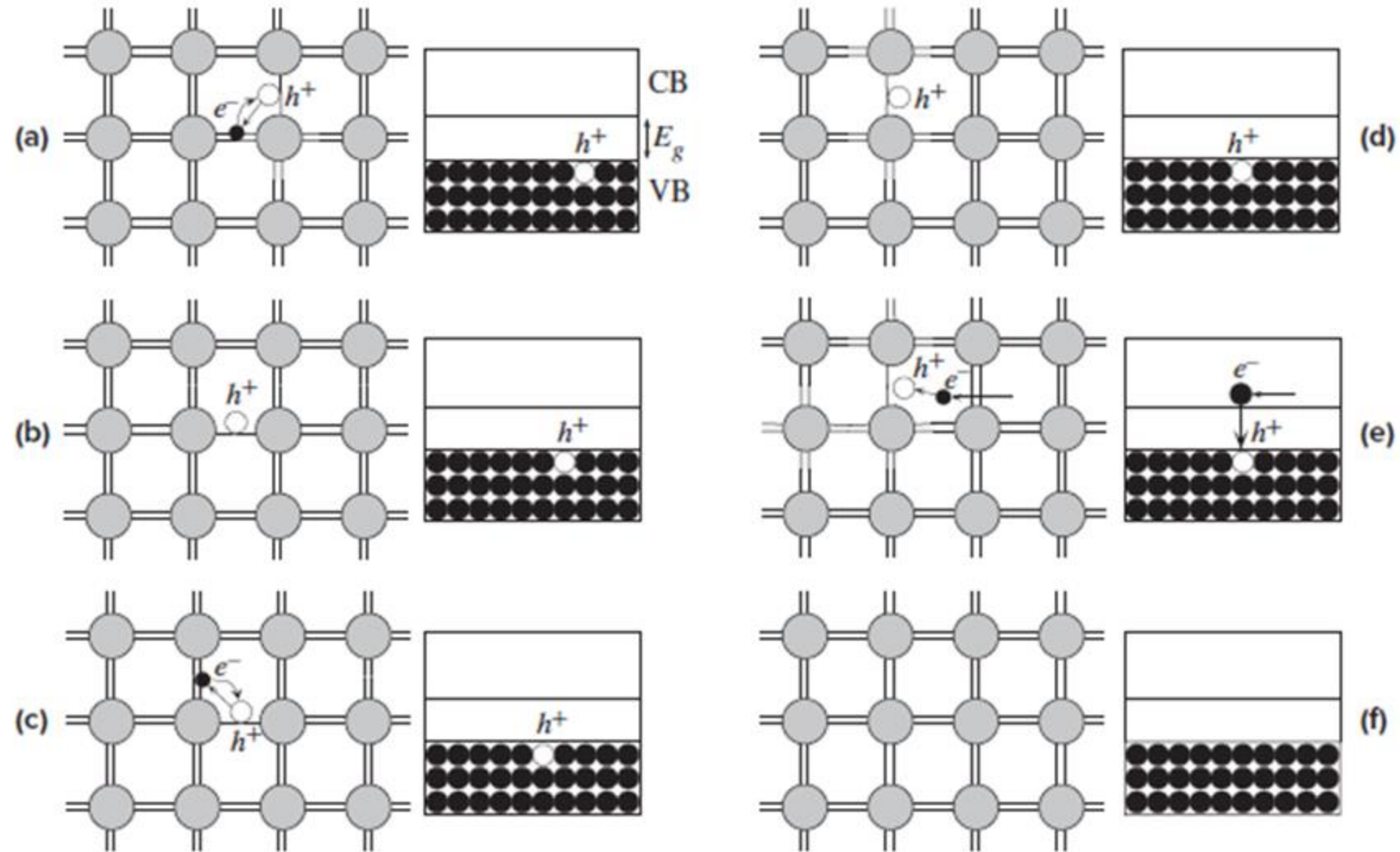
Figure A pictorial illustration of a hole in the valence band wandering around the crystal due to the tunneling of electrons from neighboring bonds.

- When a wandering electron in the CB meets a hole in the VB, the electron has found an empty state of lower energy and therefore occupies the hole

- The electron falls from the CB to the VB to fill the hole, as depicted in Figure e and f. This is called **recombination** and results in the annihilation of an electron in the CB and a hole in the VB. The excess energy of the electron falling from CB to VB in certain semiconductors such as GaAs and InP is emitted as a photon

- In Si and Ge the excess energy is lost as lattice vibrations (heat).

CONDUCTION IN SEMICONDUCTORS

- When an electric field is applied across a semiconductor as shown in Figure , the energy bands bend

- The total electron energy E is $KE + PE$, but now there is an additional electrostatic PE contribution that is not constant in an applied electric field

- A uniform electric field Ex implies a linearly decreasing potential $V(x)$, by virtue of $(dV/dx) = -Ex$

- All the energy levels and hence the energy bands must therefore tilt up in the x direction, in the presence of an applied field.
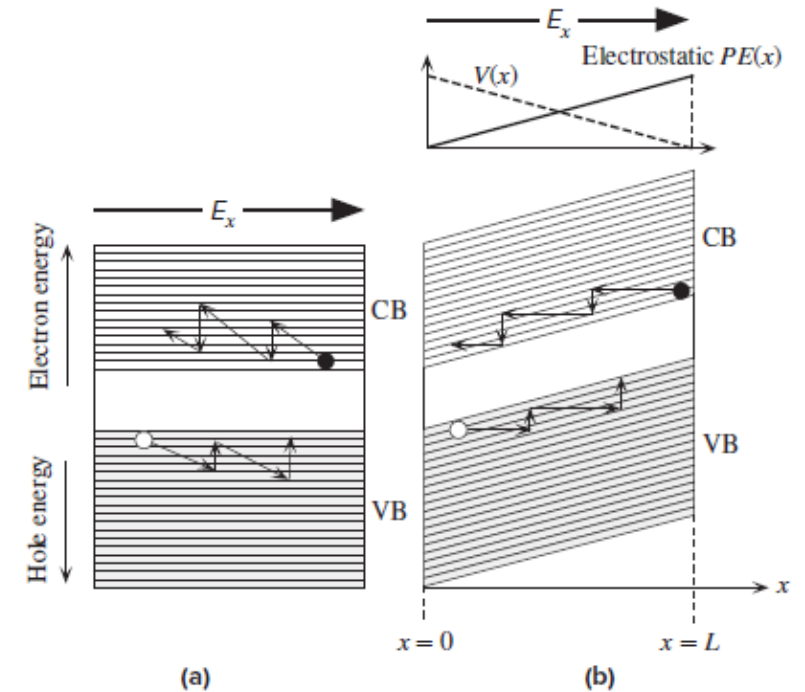
- Under the action of Ex, the electron in the CB moves to the left and immediately starts gaining energy from the field

- When the electron collides with a thermal vibration of a Si atom, it loses some of this energy and thus "falls" down in energy in the CB

- After the collision, the electron starts to accelerate again, until the next collision, and so on

- We recognize this process as the *drift* of the electron in an applied field, as illustrated in Figure

- The drift velocity vde of the electron is μ_eEx where μ_e is the drift mobility of the electron. In a similar fashion, the holes in the VB also *drift* in an applied field, but here the drift is along the field

- Notice that when a hole gains energy, it moves "down" in the VB because the potential energy of the hole is of opposite sign to that of the electron.

Since both electrons and holes contribute to electrical conduction, we may write the current density J, from its definition, as

$$J = env_{de} + epv_{dh}$$

where μe and μh are the electron and hole drift mobilities.
The drift mobility μe of the electrons in a conductor as

$$v_{de} = \mu_e E_x \quad \text{and} \quad v_{dh} = \mu_h E_x$$

where τ_e is the mean free time between scattering events and me is the electronic mass.

$$\mu_e = \frac{e\tau_e}{m_e}$$

Effective Mass of Electrons

The ideas on electron motion in metals can also be applied to the electron motion in the CB of a semiconductor

$$\mu_e = \frac{e\tau_e}{m_e}$$

We must, however, use an effective mass m^*_e for the electron in the crystal rather than the mass m_e in free space.

A "free" electron in a crystal is not entirely free because as it moves it interacts with the potential energy (*PE*) of the ions in the solid and therefore experiences various internal forces

The effective mass m^*_e accounts for these internal forces in such a way that we can relate the acceleration *a* of the electron in the CB to an external force F_{ext} (*e.g.*, $-eE_x$) by

$$F_{ext} = m^*_e \, a$$

just as we do for the electron in

vacuum by $F_{ext} = m_e a$.

We can now speculate on whether the hole can also have a mass

As long as we view mass as resistance to acceleration, that is, inertia, there is no reason why the hole should not have a mass

Accelerating the hole means accelerating electrons tunneling from bond to bond in the opposite direction

Therefore, it is apparent that the hole will have a nonzero finite inertial mass because otherwise the smallest external force will impart an infinite acceleration to it. If we represent the effective mass of the hole in the VB by m^*_h, then the hole drift mobility will be

$$\mu_h = \frac{e\tau_h}{m^*_h}$$

where τ_h is the mean free time between scattering events for holes.

For the current density further, we can write the **conductivity of a semiconductor** as

$$\sigma = en\mu_e + ep\mu_h$$

where n and p are the electron and hole concentrations in the CB and VB, respectively. This is a general equation valid for all semiconductors.

ELECTRON AND HOLE CONCENTRATIONS

The general equation for the conductivity of a semiconductor, depends on n the electron concentration, and p, the hole concentration.

The general equation that determines the free electron and hole concentratio

$$np = N_c N_v \exp\left(-\frac{E_g}{kT}\right)$$

where $E_g = E_c - E_v$ is the bandgap energy

We define $g_{cb}(E)$ as the **density of states** in the CB, that is, the number of states per unit energy per unit volume. The probability of finding an electron in a state with energy E is given by the Fermi–Dirac function $f(E)$

Then $g_{cb}(E)f(E)$ is the actual number of electrons per unit energy per unit volume $n_E(E)$ in the CB. Thus,

$$n_E \, dE = g_{cb}(E)f(E)dE$$

is the number of electrons in the energy range E to $E + dE$. Integrating this from the bottom (E_c) to the top of the CB gives the electron concentration n, number of electrons per unit volume, in the CB. In other words,

$$n = \int_{E_c}^{\text{Top of CB}} n_E(E)dE = \int_{E_c}^{\text{Top of CB}} g_{cb}(E)f(E)dE$$

We will assume that $(E_c - F_F) \gg kT$ (i.e., E_F is at least a few kT below E_c) so that

$$f(E) \approx \exp[-(E - E_F)/kT]$$

We are thus replacing Fermi–Dirac statistics by Boltzmann statistics and thereby inherently assuming that the number of electrons in the CB is far less than the number of states in this band.
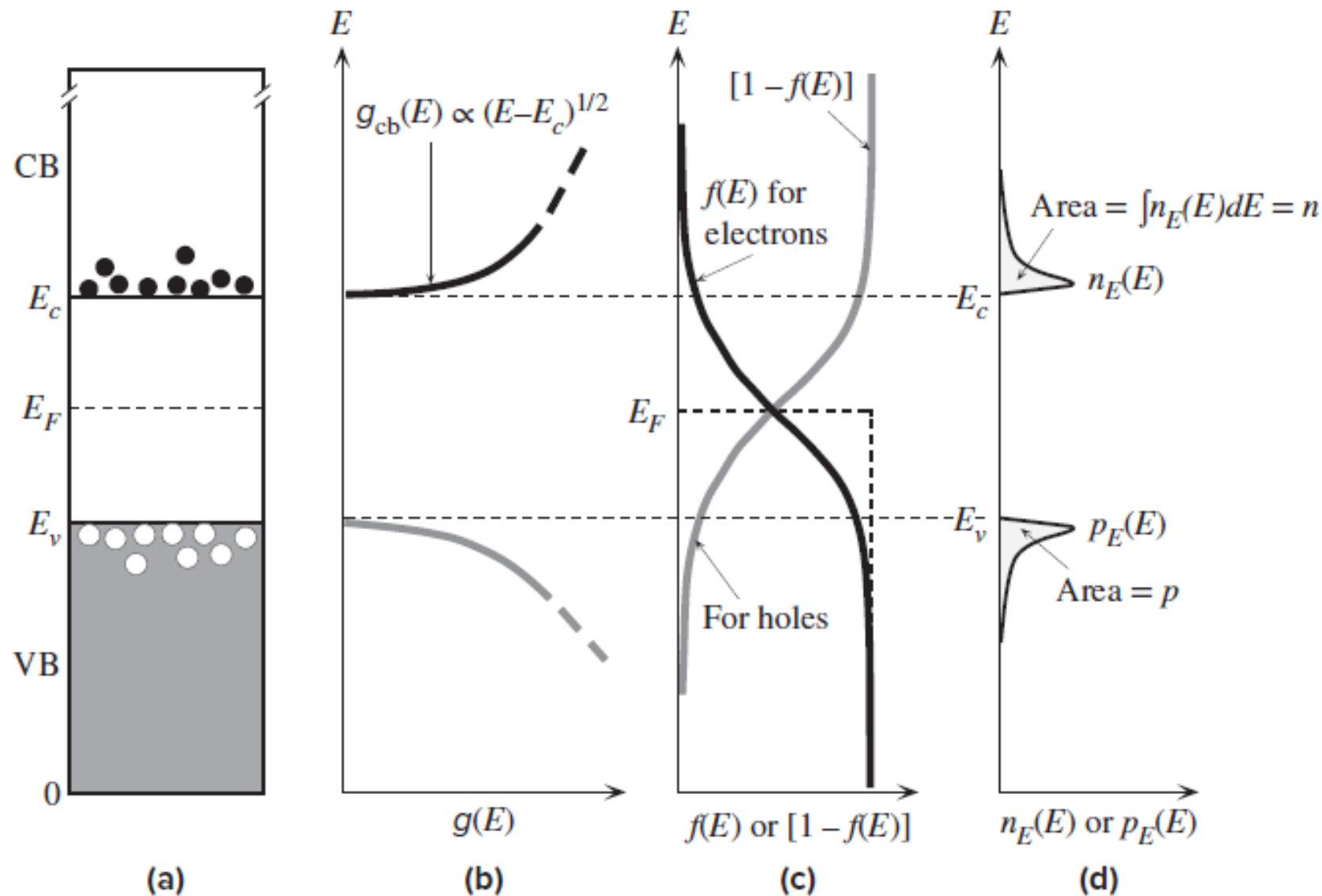
Figure (a) Energy band diagram. (b) Density of states (number of states per unit energy per unit volume). (c) Fermi–Dirac probability function (probability of occupancy of a state). (d) The product of $g(E)$ and $f(E)$ is the energy density of electrons in the CB (number of electrons per unit energy per unit volume). The area under $n_E(E)$ versus E is the electron concentration.

Further, we will take the upper limit to be $E = \infty$ since $f(E)$ decays rapidly with energy so that $g_{cb}(E)f(E) \to 0$ near the top of the band. Furthermore, since $g_{cb}(E)f(E)$ is significant only close to E_c, we can use

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

for an electron in a three-dimensional PE well without having to consider the exact form of $g_{cb}(E)$ across the whole band. Thus

$$n \approx \frac{(\pi 8\sqrt{2})m_e^{*3/2}}{h^3}\int_{E_c}^{\infty}(E - E_c)^{1/2}\exp\left[-\frac{(E - E_F)}{kT}\right]dE$$

which leads to

$$n = N_c \exp\left[-\frac{(E_c - E_F)}{kT}\right]$$

where

$$N_c = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2}$$

Nc is a constant, that is, independent of the Fermi energy, and is called the **effective density of states at the CB edge.**

Notice that *Nc* on the effective mass and has a small temperature dependence

If we take all the states in the conduction band and replace them with an effective concentration *Nc* (**number of states per unit volume**) at E_c and then multiply this simply by the **Boltzmann probability function,** $f(E_c) = \exp[-(E_c - E_F)/kT]$, we obtain the concentration of electrons at E_c, that is, in the conduction band.

Nc is thus an effective density of states at the CB band edge.

We can carry out a similar analysis for the concentration of holes in the VB.

Multiplying the density of states $g_{vb}(E)$ in the VB with the probability of occupancy by a hole $[1 - f(E)]$, that is, the probability that an electron is absent, gives p_E, the hole concentration per unit energy. Integrating this over the VB gives the hole concentration

$$p = \int_0^{E_v} p_E \, dE = \int_0^{E_v} g_{vb}(E)[(1 - f(E)]dE$$

With the assumption that E_F is a few kT above E_v, the integration simplifies to

$$p = N_v \exp\left[-\frac{(E_F - E_v)}{kT}\right]$$ [5.8]

where N_v is the effective density of states at the VB edge and is given by

$$N_v = 2\left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2}$$ [5.9]
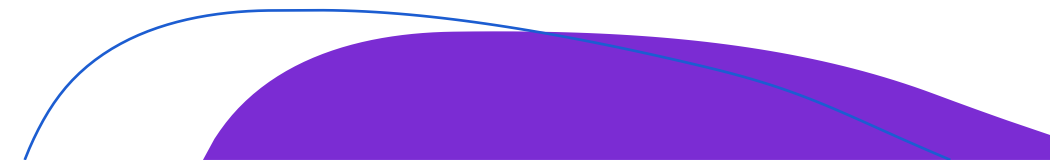
We can now see the virtues of studying the density of states $g(E)$ as a function of energy E and the Fermi–Dirac function $f(E)$. Both were central factors in deriving the expressions for n and p. There are no specific assumptions in our derivations, except for E_F being a few kT away from the band edges

It is interesting to consider the product np,

$$np = N_c \exp\left[-\frac{(E_c - E_F)}{kT}\right]N_v \exp\left[-\frac{(E_F - E_v)}{kT}\right] = N_c N_v \exp\left[-\frac{(E_c - E_v)}{kT}\right]$$

$$np = N_c N_v \exp\left(-\frac{E_g}{kT}\right)$$

where $E_g = E_c - E_v$ is the bandgap energy. First, we note that this is a general expression in which the right-hand side, $N_c N_v \exp(-E_g/kT)$, behaves as if it were a constant for a given material at a given temperature; it depends on the bandgap E_g but not on the position of the Fermi level.

First, we note that this is a general expression in which the right-hand side, behaves as if it were a constant for a given material at a given temperature; it depends on the bandgap E_g but not on the position of the Fermi level.

In the special case of an intrinsic semiconductor, $n = p$, which we can denote as n_i, the **intrinsic concentration,** so that

$$N_c N_v \exp(-E_g/kT) \text{ must be } n_i^2.$$

we therefore have

$$np = n_i^2 = N_c N_v \exp\left(-\frac{E_g}{kT}\right)$$

Mass action law

This is a general equation that is valid as long as we have thermal equilibrium.

- If we somehow increase the electron concentration, then we inevitably reduce the hole concentration

- The constant ni has a special significance because it represents the free electron and hole concentrations in the intrinsic material.

$$n_i = (N_c N_v)^{1/2} \exp\left(-\frac{E_g}{2kT}\right)$$

- An **intrinsic semiconductor** is a pure semiconductor crystal in which the electron and hole concentrations are equal

- By pure we mean virtually no impurities in the crystal. We should also exclude crystal defects that may capture carriers of one sign and thus result in unequal electron and hole concentrations

- Clearly in a pure semico $n_i = (N_c N_v)^{1/2} \exp\left(-\dfrac{E_g}{2kT}\right)$ are generated in pairs by thermal excitation across the bandgap

- It must be emphasized that Equation

$$n_i = (N_c N_v)^{1/2} \exp\left(-\frac{E_g}{2kT}\right)$$

- is generally valid and therefore applies to both intrinsic and nonintrinsic ($n \neq p$) semiconductors.

- When an electron and hole meet in the crystal, they "recombine." The electron falls in energy and occupies the empty electronic state that the hole represents.

- Consequently, the broken bond is "repaired," but we lose two free charge carriers.

- **Recombination** of an electron and hole results in their annihilation

- In a semiconductor we therefore have thermal generation of electron–hole pairs by thermal excitation from the VB to the CB, and we also have recombination of electron–hole pairs that removes them from their conduction and valence bands, respectively

- The rate of recombination R will be proportional to the number of electrons and also to the number of holes. Thus

-
$$R \propto np$$

The rate of generation G will depend on how many electrons are available for excitation at E_v, that is, N_v; how many empty states are available at E_c, that is, N_c; and the probability that the electron will make the transition, that is,

$$\exp(-E_g/kT)$$

so that

$$G \propto N_c N_v \exp\left(-\frac{E_g}{kT}\right)$$

Since in thermal equilibrium we have no continuous increase in n or p, we must have the rate of generation equal to the rate of recombination, that is, $G = R$.

Fermi level in an intrinsic semiconductor   In the case of intrinsic material, the crystal must be electrically neutral.

$$n_i = p_i$$

Therefore, $N_C e^{-(E_C - E_F)/kT} = N_V e^{-(E_F - E_V)/kT}$

Taking the logarithm on both sides,

$$\ln \frac{N_C}{N_V} = \frac{E_C + E_V - 2E_F}{kT}$$

$$E_F = \frac{E_C + E_V}{2} - \frac{kT}{2} \ln \frac{N_C}{N_V}$$

If the effective masses of a free electron and hole are the same,

$$N_C = N_V$$

Then, $$E_F = \frac{E_C + E_V}{2}$$

From the above equation, at the centre of the forbidden energy band, Fermi level is present.
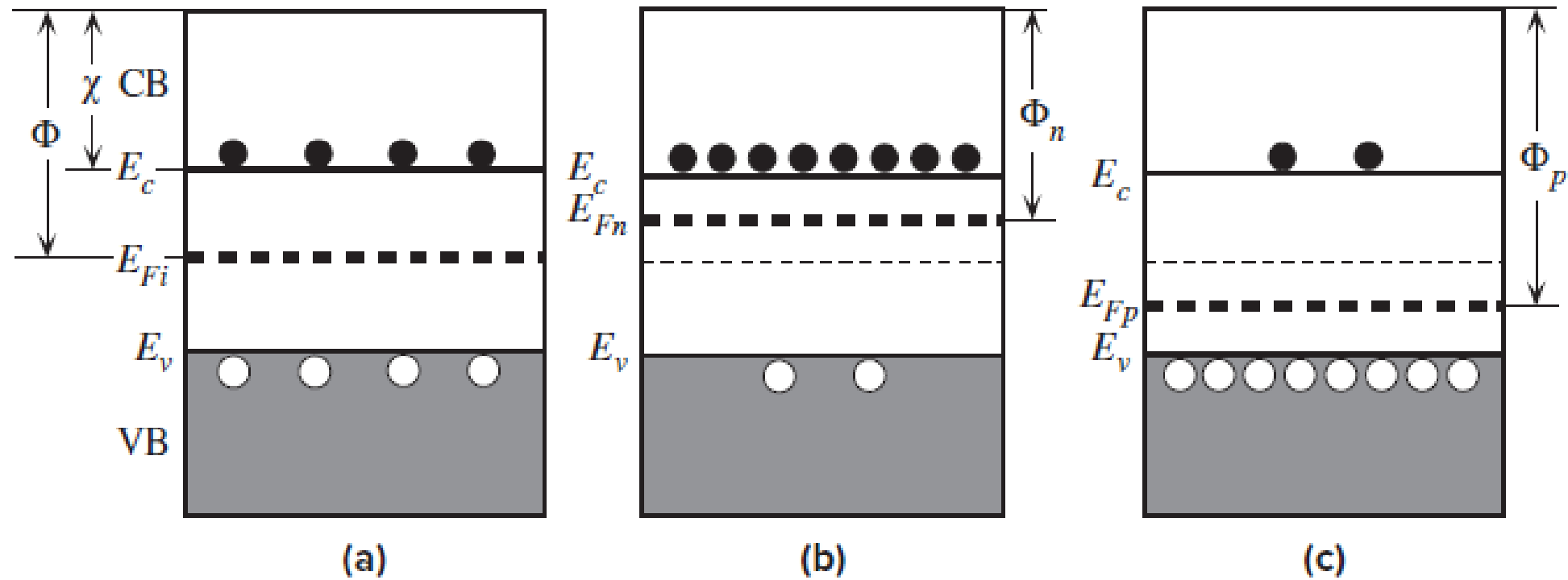
Figure Energy band diagrams for (a) intrinsic, (b) n-type, and (c) p-type semiconductors. In all cases, $np = n_i^2$.

Problem

INTRINSIC CONCENTRATION AND CONDUCTIVITY OF Si Given that the density of states related effective masses of electrons and holes in Si are approximately $1.08m_e$ and $0.60m_e$, respectively, and the electron and hole drift mobilities at room temperature are 1400 and 450 cm^2 V^{-1} s^{-1}, respectively, calculate the intrinsic concentration and intrinsic resistivity of Si.

SOLUTION

We simply calculate the effective density of states N_c and N_v by

$$N_c = 2\left(\frac{2\pi m_e^* kT}{h^2}\right)^{3/2} \qquad \text{and} \qquad N_v = 2\left(\frac{2\pi m_h^* kT}{h^2}\right)^{3/2}$$

Thus

$$N_c = 2\left[\frac{2\pi(1.08 \times 9.1 \times 10^{-31} \text{ kg})(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{(6.63 \times 10^{-34} \text{ J s})^2}\right]^{3/2}$$

$$= 2.81 \times 10^{25} \text{ m}^{-3} \quad \text{or} \quad 2.81 \times 10^{19} \text{ cm}^{-3}$$

and

$$N_v = 2\left[\frac{2\pi(0.60 \times 9.1 \times 10^{-31} \text{ kg})(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{(6.63 \times 10^{-34} \text{ J s})^2}\right]^{3/2}$$

$$= 1.16 \times 10^{25} \text{ m}^{-3} \quad \text{or} \quad 1.16 \times 10^{19} \text{ cm}^{-3}$$

The intrinsic concentration is

$$n_i = (N_c N_v)^{1/2} \exp\left(-\frac{E_g}{2kT}\right)$$

so that

$$n_i = [(2.81 \times 10^{19} \text{ cm}^{-3})(1.16 \times 10^{19} \text{ cm}^{-3})]^{1/2} \exp\left[-\frac{(1.10 \text{ eV})}{2(300 \text{ K})(8.62 \times 10^{-5} \text{ eV K}^{-1})}\right]$$

$$= 1.0 \times 10^{10} \text{ cm}^{-3}$$

The conductivity is

$$\sigma = en\mu_e + ep\mu_h = en_i(\mu_e + \mu_h)$$

that is,

$$\sigma = (1.6 \times 10^{-19} \text{ C})(1.0 \times 10^{10} \text{ cm}^{-3})(1400 + 450 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$$
$$= 3.0 \times 10^{-6} \text{ } \Omega^{-1} \text{ cm}^{-1}$$

The resistivity is

$$\rho = \frac{1}{\sigma} = 3.3 \times 10^5 \text{ } \Omega \text{ cm}$$

EXTRINSIC SEMICONDUCTORS

- By introducing small amounts of impurities into an otherwise pure Si crystal, it is possible to obtain a semiconductor in which the concentration of carriers of one polarity is much in excess of the other type. Such semiconductors are referred to as **extrinsic semiconductors** vis-à-vis the intrinsic case of a pure and perfect crystal.

- For example, by adding **pentavalent impurities**, such as **arsenic**, which have a valency of more than four, we can obtain a semiconductor in which the **electron concentration is much larger than the hole concentration**. In this case we will have an _n-type semiconductor._

- If we add **trivalent impurities**, such as **boron**, which have a valency of less than four, then we find that we have **an excess of holes over electrons**. We now have a _p-type semiconductor._

n-Type Doping
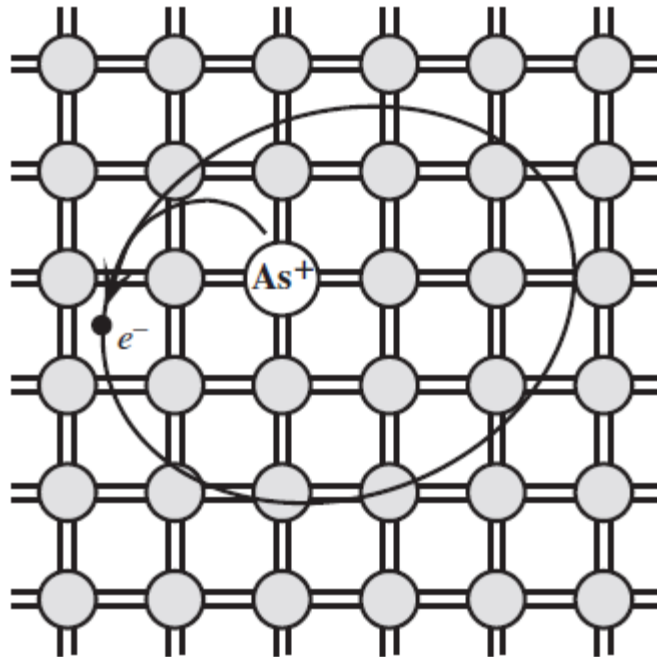

Figure   Arsenic-doped Si crystal.

The four valence electrons of As allow it to bond just like Si, but the fifth electron is left orbiting the As site. The energy required to release the free fifth electron into the CB is very small.

Figure   Energy band diagram for an *n*-type Si doped with 1 ppm As.

There are donor energy levels just below E_c around As$^+$ sites.

p-Type Doping

(a)

(b)

Free
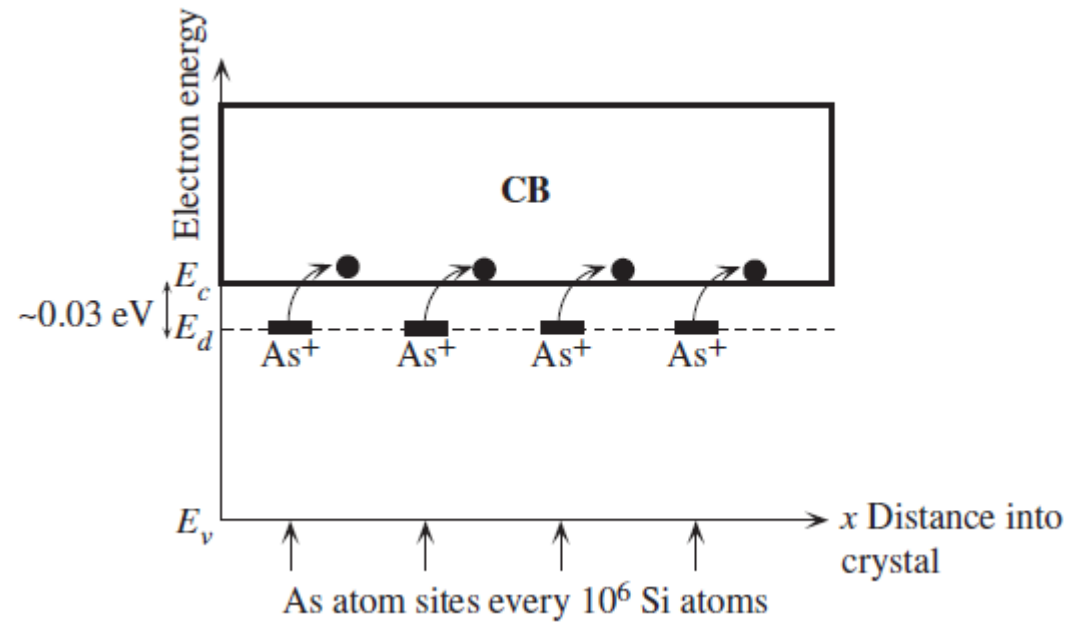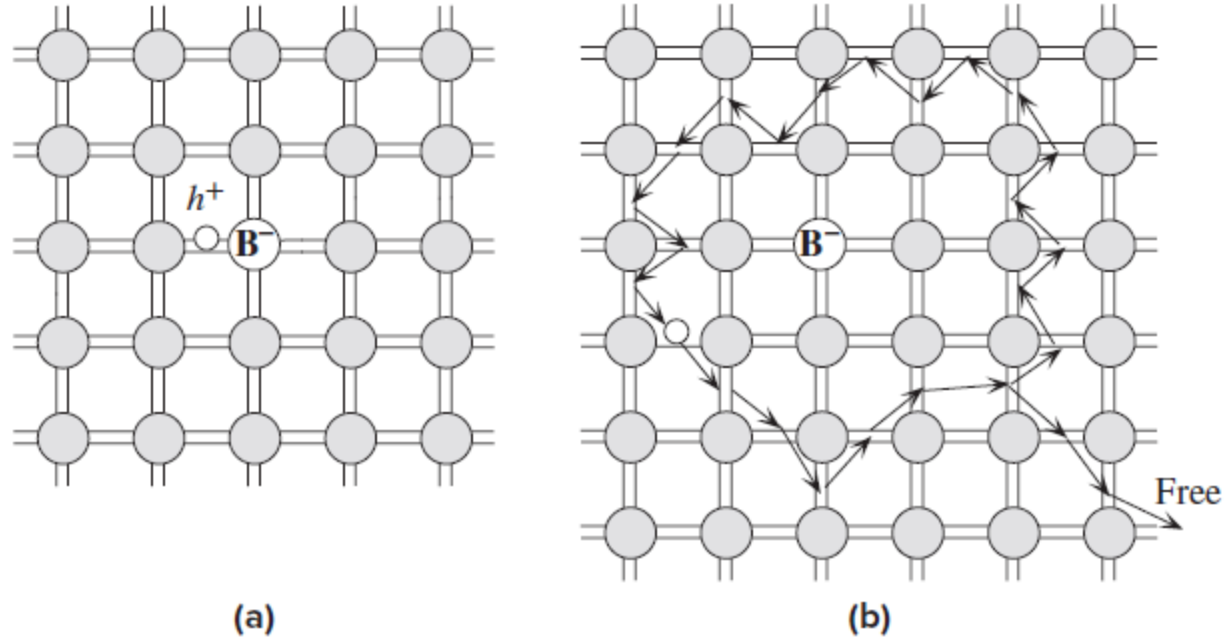
Figure Boron-doped Si crystal.

B has only three valence electrons. When it substitutes for a Si atom, one of its bonds has an electron missing and therefore a hole, as shown in (a). The hole orbits around the B⁻ site by the tunneling of electrons from neighboring bonds, as shown in (b). Eventually, thermally vibrating Si atoms provide enough energy to free the hole from the B⁻ site into the VB, as shown.

Figure Energy band diagram for a *p*-type Si doped with 1 ppm B. There are acceptor energy levels E_a just above E_v around B⁻ sites. These acceptor levels accept electrons from the VB and therefore create holes in the VB.
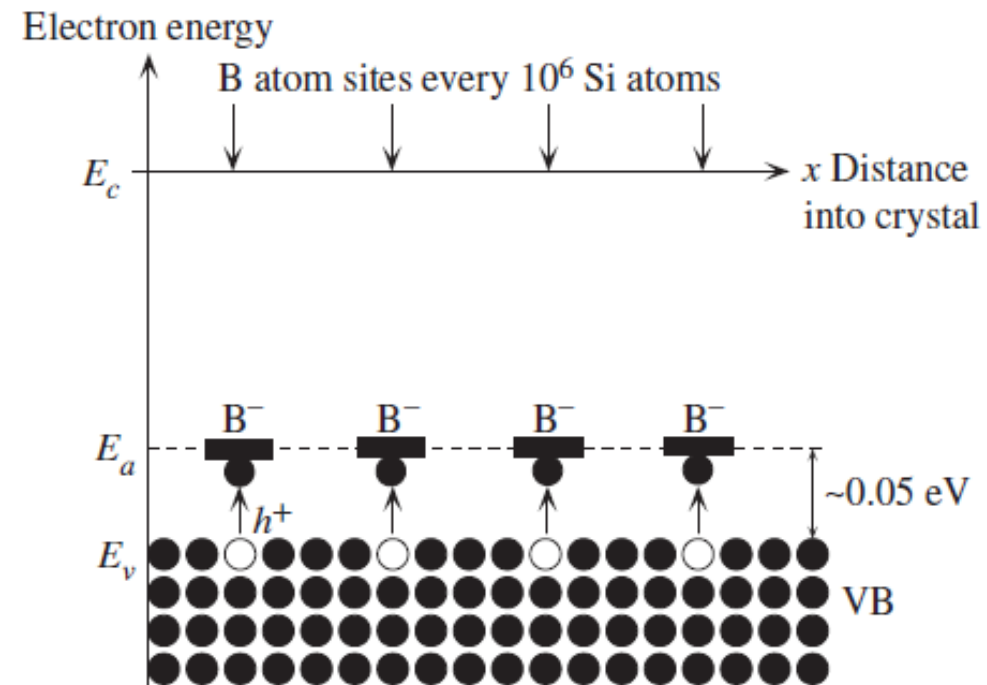
Problem

Find the resistance of a 1 cm^3 pure silicon crystal. What is the resistance when the crystal is doped with arsenic if the doping is 1 in 10^9, that is, 1 part per billion (ppb) (note that this doping corresponds to one foreigner living in China)? Note that the atomic concentration in silicon is 5×10^{22} cm^{-3}, $n_i = 1.0 \times 10^{10}$ cm^{-3}, $\mu_e = 1400$ cm^2 V^{-1} s^{-1}, and $\mu_h = 450$ cm^2 V^{-1} s^{-1}.

Solution

For the intrinsic case, we apply

$$\sigma = en\mu_e + ep\mu_h = en(\mu_e + \mu_h)$$

so

$$\sigma = (1.6 \times 10^{-19} \text{ C})(1.0 \times 10^{10} \text{ cm}^{-3})(1400 + 450 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$$
$$= 2.96 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$$

Since $L = 1$ cm and $A = 1$ cm^2, the resistance is

$$R = \frac{L}{\sigma A} = \frac{1}{\sigma} = 3.47 \times 10^5 \Omega \qquad \text{or} \qquad 347 \text{ k}\Omega$$

When the crystal is doped with 1 in 10^9, then

$$N_d = \frac{N_{Si}}{10^9} = \frac{5 \times 10^{22}}{10^9} = 5 \times 10^{13} \text{ cm}^{-3}$$

At room temperature all the donors are ionized, so

$$n = N_d = 5 \times 10^{13} \text{ cm}^{-3}$$

The hole concentration is

$$p = \frac{n_i^2}{N_d} = \frac{(1.0 \times 10^{10})^2}{(5 \times 10^{13})} = 2.0 \times 10^6 \text{ cm}^{-3} \ll n_i$$

Therefore,

$$\sigma = en\mu_e = (1.6 \times 10^{-19} \text{ C})(5 \times 10^{13} \text{ cm}^{-3})(1400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$$
$$= 1.12 \times 10^{-2} \, \Omega^{-1} \text{ cm}^{-1}$$

Further,

$$R = \frac{L}{\sigma A} = \frac{1}{\sigma} = 89.3 \, \Omega$$

Notice the drastic fall in the resistance when the crystal is doped with only 1 in 10^9 atoms.

Doping the silicon crystal with boron instead of arsenic, but still in amounts of 1 in 10^9, means that $N_a = 5 \times 10^{13}$ cm^{-3}, which results in a conductivity of

$$\sigma = ep\mu_h = (1.6 \times 10^{-19} \text{ C})(5 \times 10^{13} \text{ cm}^{-3})(450 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$$
$$= 3.6 \times 10^{-3} \; \Omega^{-1} \text{ cm}^{-1}$$

Therefore,
$$R = \frac{L}{\sigma A} = \frac{1}{\sigma} = 278 \; \Omega$$

The reason for a higher resistance with p-type doping compared with the same amount of n-type doping is that $\mu_h < \mu_e$.

Problem

THE FERMI LEVEL IN n- AND p-TYPE Si   An n-type Si wafer has been doped uniformly with 10^{16} antimony (Sb) atoms cm^{-3}. Calculate the position of the Fermi energy with respect to the Fermi energy E_{Fi} in intrinsic Si. The above n-type Si sample is further doped with 2×10^{17} boron atoms cm^{-3}. Calculate the position of the Fermi energy with respect to the Fermi energy E_{Fi} in intrinsic Si. (Assume that $T = 300$ K, and $kT = 0.0259$ eV.)

Solution

Sb gives n-type doping with $N_d = 10^{16}$ cm^{-3}, and since $N_d \gg n_i$ ($=1.0 \times 10^{10}$ cm^{-3}), we have

$$n = N_d = 10^{16} \ cm^{-3}$$

For intrinsic Si,

$$n_i = N_c \exp\left[-\frac{(E_c - E_{Fi})}{kT}\right]$$

whereas for doped Si,

$$n = N_c \exp\left[-\frac{(E_c - E_{Fn})}{kT}\right] = N_d$$

where E_{Fi} and E_{Fn} are the Fermi energies in the intrinsic and n-type Si. Dividing the two

expressions,

$$\frac{N_d}{n_i} = \exp\left[\frac{(E_{Fn} - E_{Fi})}{kT}\right]$$

so that

$$E_{Fn} - E_{Fi} = kT \ln\left(\frac{N_d}{n_i}\right) = (0.0259 \text{ eV}) \ln\left(\frac{10^{16}}{1.0 \times 10^{10}}\right) = 0.36 \text{ eV}$$

When the wafer is further doped with boron, the acceptor concentration is

$$N_a = 2 \times 10^{17} \text{ cm}^{-3} > N_d = 10^{16} \text{ cm}^{-3}$$

The semiconductor is compensation doped and compensation converts the semiconductor to p-type Si. Thus

$$p = N_a - N_d = (2 \times 10^{17} - 10^{16}) = 1.9 \times 10^{17} \text{ cm}^{-3}$$

For intrinsic Si,

$$n_i = N_v \exp\left[-\frac{(E_{Fi} - E_v)}{kT}\right]$$

whereas for doped Si,

$$p = N_v \exp\left[-\frac{(E_{Fp} - E_v)}{kT}\right] = N_a - N_d$$

where E_{Fi} and E_{Fp} are the Fermi energies in the intrinsic and p-type Si, respectively. Dividing the two expressions,

$$\frac{p}{n_i} = \exp\left[-\frac{(E_{Fp} - E_{Fi})}{kT}\right]$$

so that

$$E_{Fp} - E_{Fi} = -kT \ln\left(\frac{p}{n_i}\right) = -(0.0259 \text{ eV}) \ln\left(\frac{1.9 \times 10^{17}}{1.0 \times 10^{10}}\right)$$

$$= -0.43 \text{ eV}$$

Equilibrium Carrier Concentration

- Semiconductors contain majority and minority carriers. The more abundant charge carriers are the majority carriers; the less abundant are the minority carriers.

- The equilibrium carrier concentration can be increased through doping.

- **The total number of carriers in the conduction and valence band is called the equilibrium carrier concentration**.

- The product of minority and majority charge carriers is a constant.

- <u>The number of carriers in the conduction and valence band with no externally applied bias is called the equilibrium carrier concentration.</u>

- For majority carriers, the equilibrium carrier concentration is equal to <u>the intrinsic carrier concentration plus the number of free carriers added by doping the semiconductor.</u>

- Under most conditions, the doping of the semiconductor is several orders of magnitude greater than the intrinsic carrier concentration, such that the number of majority carriers is approximately equal to the doping.

- At equilibrium, <u>the product of the majority and minority carrier concentration is a constant, and this is mathematically expressed by the Law of Mass Action</u>.

$$n_0 p_0 = n_i^2$$

where n_i is the intrinsic carrier concentration and n_0 and p_0 are the electron and hole equilibrium carrier concentrations.

Using the Law of Mass Action above, the majority and minority carrier concentrations are given as:

$$\text{n-type: } n_0 = N_D, p_0 = \frac{n_i^2}{N_D}$$

$$\text{p-type: } p_0 = N_A, n_0 = \frac{n_i^2}{N_A}$$
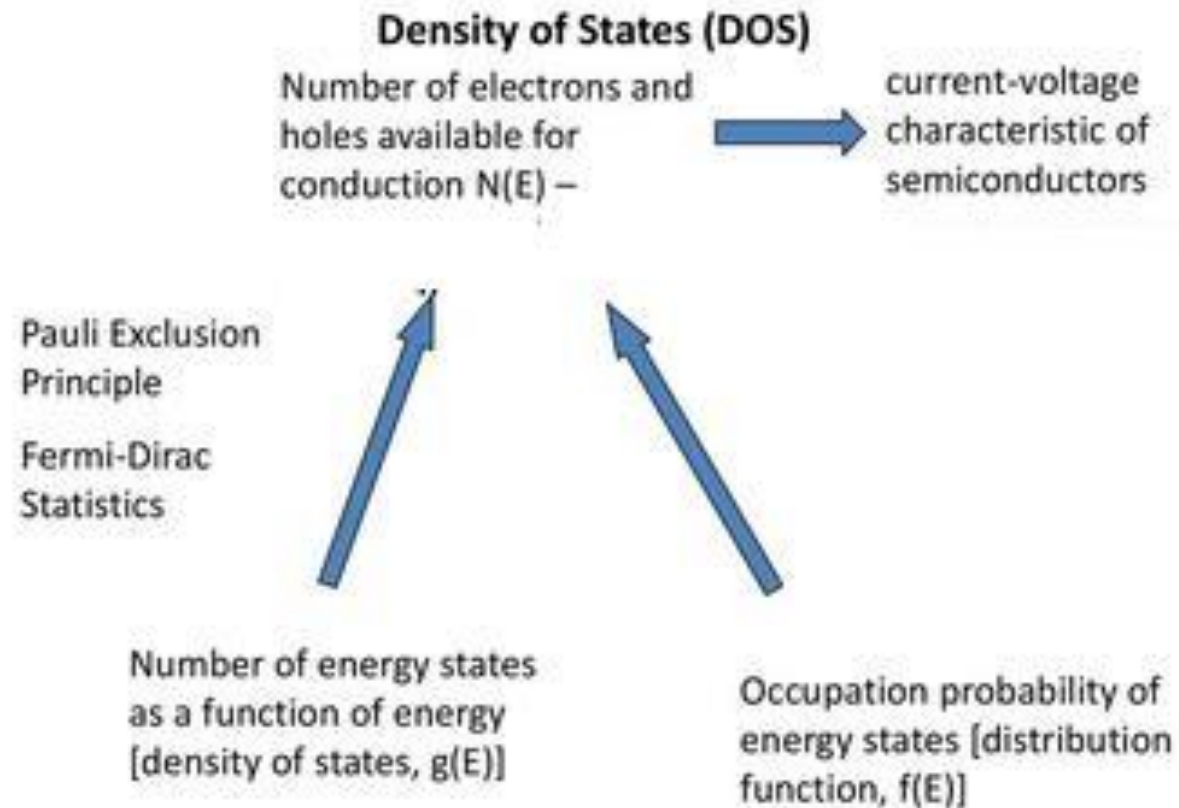
where N_D is the concentration of donor atoms and N_A is the concentration of acceptor atoms.

The above equations show that the _number of minority carriers decreases as the doping level increases_. For example, in _n_-type material, some of the extra electrons added by doping the material will occupy the empty spots (i.e., holes) in the valence band, thus lowering the number of holes.

Charge carrier statistics

$$n = N_c \exp\left[-\frac{(E_c - E_F)}{kT}\right]$$

Carrier Concentration Statistics

Density of States (DOS)

Number of electrons and holes available for conduction N(E) –

current-voltage characteristic of semiconductors

Pauli Exclusion Principle

Fermi-Dirac Statistics

Number of energy states as a function of energy [density of states, g(E)]

Occupation probability of energy states [distribution function, f(E)]

Quasi Equilibrium and Quasi Fermi Level

- When a semiconductor is in thermal equilibrium, the distribution function of the electrons at the energy level of E is presented by a Fermi–Dirac distribution function.

- <u>In this case the Fermi level is defined as the level in which the probability of occupation of electron at that energy is $\frac{1}{2}$.</u>

- In thermal equilibrium, there is no need to distinguish between conduction band quasi-Fermi level and valence band quasi-Fermi level as they are simply equal to the Fermi level.

- When a disturbance from a thermal equilibrium situation occurs, the populations of the electrons in the conduction band and valence band change.

- If the disturbance is not too great or not changing too quickly, the bands each relax to a state of quasi-thermal equilibrium.

- Because the relaxation time for electrons within the conduction band is much lower than across the band gap, we can consider that the electrons are in thermal equilibrium in the conduction band.

- This is also applicable for electrons in the valence band (often understood in terms of <u>holes</u>)

- . We can define a quasi Fermi level and quasi temperature due to thermal equilibrium of electrons in conduction band, and quasi Fermi level and quasi temperature for the valence band similarly.