A Mini Course for
太陽能電池元件建模與優化設計

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Course Content and Time Schedule

- **Topics 1: 半導體薄膜在熱平衡時的行為 (5/26)**
- **Topics 2: 半導體薄膜材料的電荷傳輸現象(5/26, 6/2)**
- **Topics 3: 非平衡時半導體薄膜材料載子的動態行為 (6/2)**
- **太陽能電池元件物理與一維太陽能電池仿真軟件介紹 (6/9)**
- **以MatLab Script控制光電元件仿真軟件進行材料與元件參數之優化設計 (6/16)**

Topics 1: The Semiconductor in Equilibrium

- Derive the **thermal-equilibrium concentrations of electrons and holes** in a semiconductor as a function of the **Fermi energy**.
- Discuss the process by which the properties of a semiconductor material can be altered **by adding specific impurities** to the semiconductor.
- Determine the thermal-equilibrium concentrations of electrons and holes in a semiconductor as a function of **the concentration of dopant**.
- Determine **the position of the Fermi energy level** as a function of **the concentrations of dopant** added to the semiconductor.

1.1 CHARGE CARRIERS IN SEMICONDUCTORS

1.1.1 Equilibrium Distribution of Electrons and Holes

The distribution (with respect to energy) of electrons in the conduction band is given by the density of allowed quantum states times the probability that a state is occupied by an electron. This statement is written in equation form as

$$n(E) = g_c(E) f_F(E) \tag{4.1}$$

where $f_F(E)$ is the Fermi–Dirac probability function and $g_c(E)$ is the density of quantum states in the conduction band. The total electron concentration per unit volume

ability that a state is *not* occupied by an electron. We may express this as

$$p(E) = g_v(E)[1 - f_F(E)] \tag{4.2}$$

- a plot of the density of states function in the conduction-band $g_c(E)$, the density of states function in the valence-band $g_v(E)$, and the Fermi–Dirac probability function **for T > 0 K** when E_F is approximately halfway between E_c and E_v.
- $f_E(E)$ for *E* > E_F is symmetrical to the function 1 - $f_E(E)$ for *E* < E_F about the energy *E* = E_F.

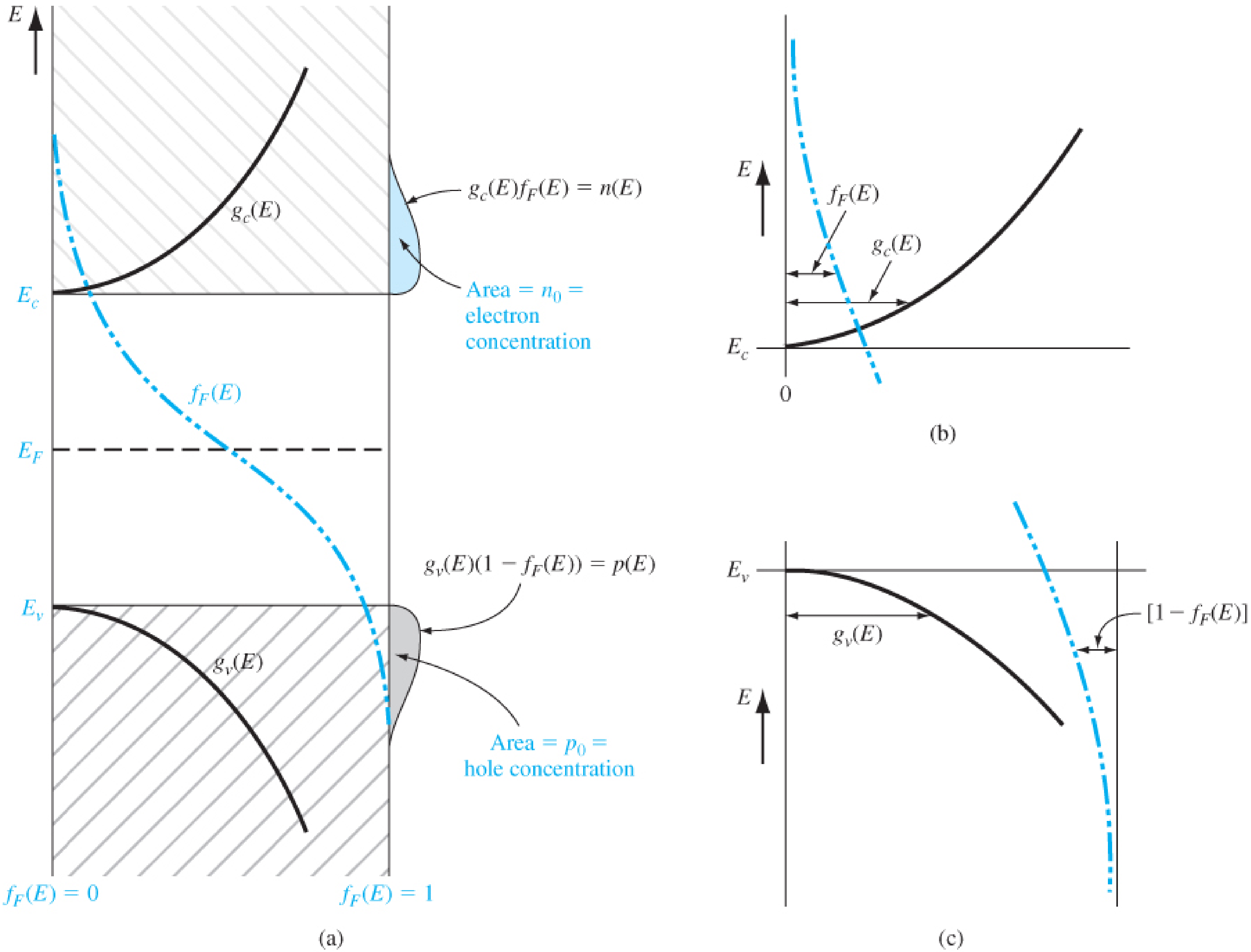


Figure 4.1 | (a) Density of states functions, Fermi–Dirac probability function, and areas representing electron and hole concentrations for the case when E_F is near the midgap energy; (b) expanded view near the conduction-band energy; and (c) expanded view near the valence-band energy.

1.1.2 The n_0 and p_0 Equations

Thermal-Equilibrium Electron Concentration n_0

$$n_0 = \int g_c(E) f_F(E)\, dE \tag{4.3}$$

gap. For electrons in the conduction band, we have $E > E_c$. If $(E_c - E_F) \gg kT$, then $(E - E_F) \gg kT$, so that the Fermi probability function reduces to the Boltzmann approximation,[1] which is

$$f_F(E) = \frac{1}{1 + \exp \dfrac{(E - E_F)}{kT}} \approx \exp\left[\frac{-(E - E_F)}{kT}\right] \tag{4.4}$$

Applying the Boltzmann approximation to Equation (4.3), the thermal-equilibrium density of electrons in the conduction band is found from

$$n_0 = \int_{E_c}^{\infty} \frac{4\pi (2m_n^*)^{3/2}}{h^3} \sqrt{E - E_c} \exp\left[\frac{-(E - E_F)}{kT}\right] dE \tag{4.5}$$

$$\boxed{N_c = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}} \tag{4.10}$$

The parameter m_n^* is the density of states effective mass of the electron. The thermal-equilibrium electron concentration in the conduction band can be written as

$$\boxed{n_0 = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]} \tag{4.11}$$

The parameter N_c is called the *effective density of states function in the conduction*

Thermal-Equilibrium Hole Concentration The thermal-equilibrium concentration of holes in the valence band is found by integrating Equation (4.2) over the valence-band energy, or

$$p_0 = \int g_v(E)[1 - f_F(E)]\, dE \tag{4.12}$$

For energy states in the valence band, $E < E_v$. If $(E_F - E_v) \gg kT$ (the Fermi function is still assumed to be within the bandgap), then we have a slightly different form of the Boltzmann approximation. Equation (4.13a) may be written as

$$1 - f_F(E) = \frac{1}{1 + \exp\left(\frac{E_F - E}{kT}\right)} \approx \exp\left[\frac{-(E_F - E)}{kT}\right] \tag{4.13b}$$

$$\boxed{N_v = 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}} \tag{4.18}$$

which is called the *effective density of states function in the valence band.* The parameter m_p^* is the density of states effective mass of the hole. The thermal-equilibrium concentration of holes in the valence band may now be written as

$$\boxed{p_0 = N_v \exp\left[\frac{-(E_F - E_v)}{kT}\right]} \tag{4.19}$$

The magnitude of N_v is also on the order of 10^{19} cm^{-3} at $T = 300$ K for most

Comment: The parameter values N_c at any temperature can easily be found by using the 300 K values and the temperature dependence.
Note that the value of N_c for **GaAs** is smaller than the typical **10^{19} cm^{-3}** value due to the **small electron effective mass** in gallium arsenide.

Table 4.1 | Effective density of states function and density of states effective mass values

	N_c (cm^{-3})	N_v (cm^{-3})	m_n^*/m_0	m_p^*/m_0
Silicon	2.8×10^{19}	1.04×10^{19}	1.08	0.56
Gallium arsenide	4.7×10^{17}	7.0×10^{18}	0.067	0.48
Germanium	1.04×10^{19}	6.0×10^{18}	0.55	0.37

$$n_0 = n_i = N_c \exp\left[\frac{-(E_c - E_{Fi})}{kT}\right] \tag{4.20}$$

and

$$p_0 = p_i = n_i = N_v \exp\left[\frac{-(E_{Fi} - E_v)}{kT}\right] \tag{4.21}$$

If we take the product of Equations (4.20) and (4.21), we obtain

$$n_i^2 = N_c N_v \exp\left[\frac{-(E_c - E_{Fi})}{kT}\right] \cdot \exp\left[\frac{-(E_{Fi} - E_v)}{kT}\right] \tag{4.22}$$

or

$$\boxed{n_i^2 = N_c N_v \exp\left[\frac{-(E_c - E_v)}{kT}\right] = N_c N_v \exp\left[\frac{-E_g}{kT}\right]} \tag{4.23}$$

where E_g is the bandgap energy. For a given semiconductor material at a constant

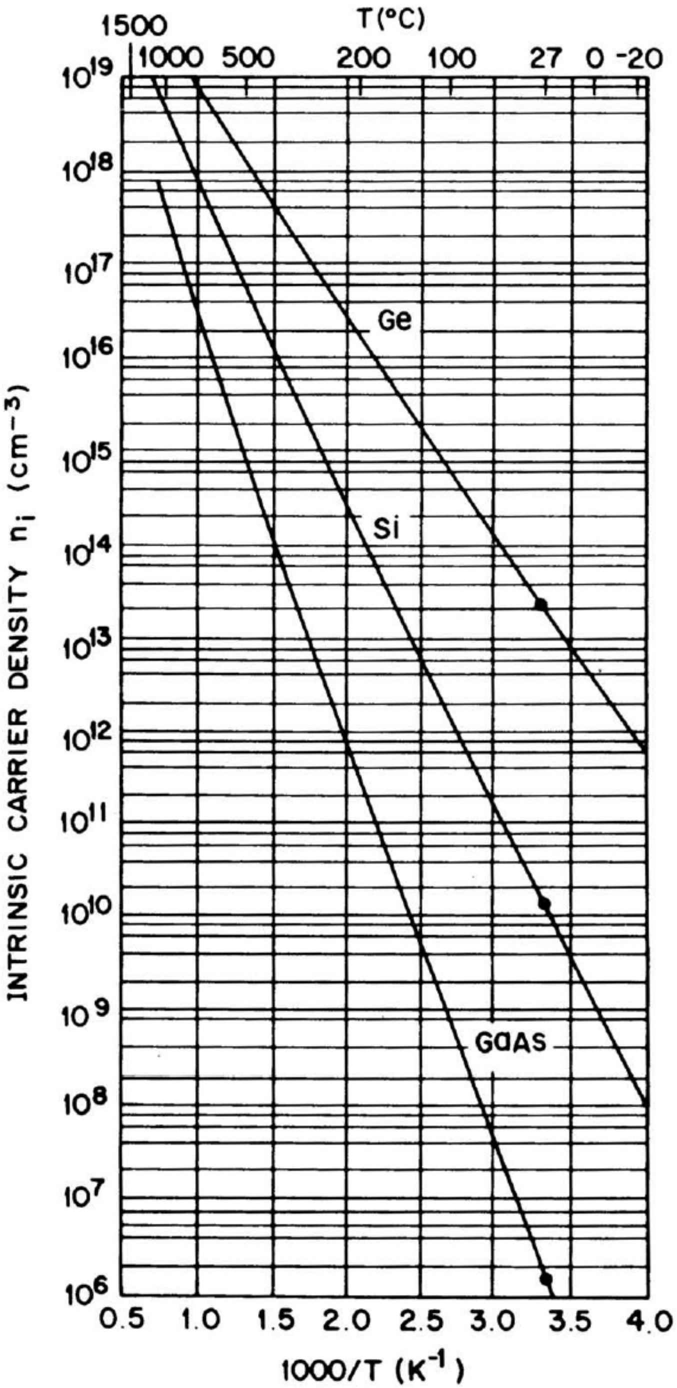


Table 4.2 | Commonly accepted values of n_i at $T = 300$ K

Silicon	$n_i = 1.5 \times 10^{10}$ cm^{-3}
Gallium arsenide	$n_i = 1.8 \times 10^{6}$ cm^{-3}
Germanium	$n_i = 2.4 \times 10^{13}$ cm^{-3}

- **Comment:** The intrinsic carrier concentration n_i can increase by over 4 orders of magnitude as the temperature increased by 150°C.

1.1.4 The Intrinsic Fermi-Level

late the intrinsic Fermi-level position. Since the electron and hole concentrations are equal, setting Equations (4.20) and (4.21) equal to each other, we have

$$N_c \exp\left[\frac{-(E_c - E_{Fi})}{kT}\right] = N_v \exp\left[\frac{-(E_{Fi} - E_v)}{kT}\right] \tag{4.24}$$

If we take the natural log of both sides of this equation and solve for E_{Fi}, we obtain

$$E_{Fi} = \frac{1}{2}(E_c + E_v) + \frac{1}{2}kT\ln\left(\frac{N_v}{N_c}\right) \tag{4.25}$$

From the definitions for N_c and N_v given by Equations (4.10) and (4.18), respectively, Equation (4.25) may be written as

$$\boxed{E_{Fi} = \frac{1}{2}(E_c + E_v) + \frac{3}{4}kT\ln\left(\frac{m_p^*}{m_n^*}\right)} \tag{4.26a}$$

The first term, $\frac{1}{2}(E_c + E_v)$, is the energy exactly midway between E_c and E_v, or the midgap energy. We can define

$$\frac{1}{2}(E_c + E_v) = E_{\text{midgap}}$$

so that

$$\boxed{E_{Fi} - E_{\text{midgap}} = \frac{3}{4}kT\ln\left(\frac{m_p^*}{m_n^*}\right)} \tag{4.26b}$$

The intrinsic Fermi level must shift away from the band with the larger density of states in order to maintain equal numbers of electrons and holes.

1.2 | DOPANT ATOMS AND ENERGY LEVELS

The doped semiconductor, called an **extrinsic** material

- The phosphorus atom without the donor electron is positively charged.

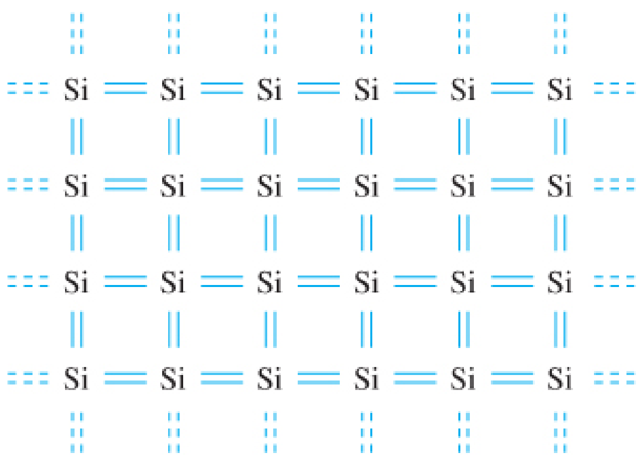


Figure 4.3 | Two-dimensional representation of the intrinsic silicon lattice.

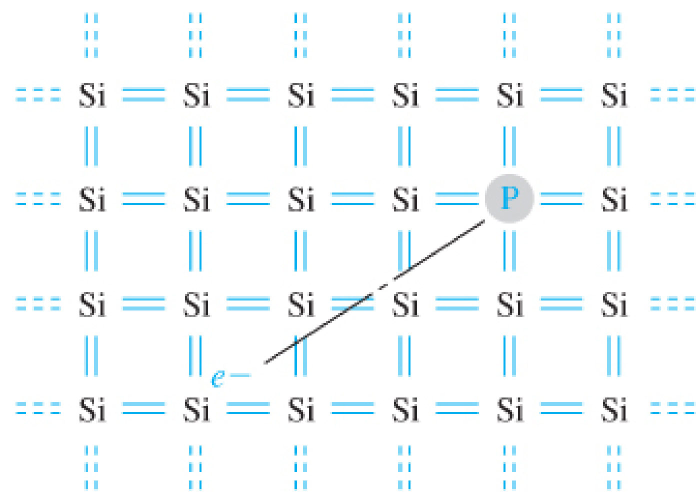
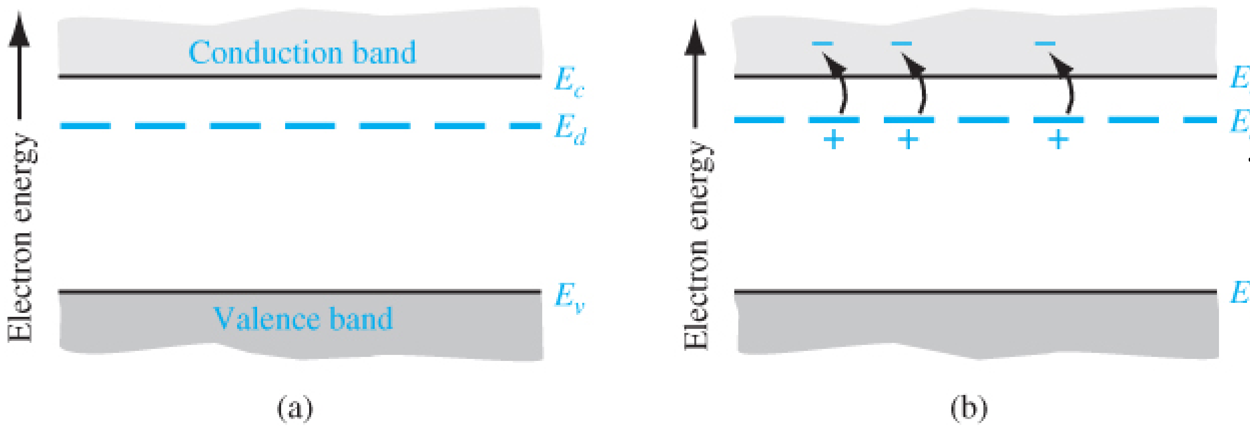
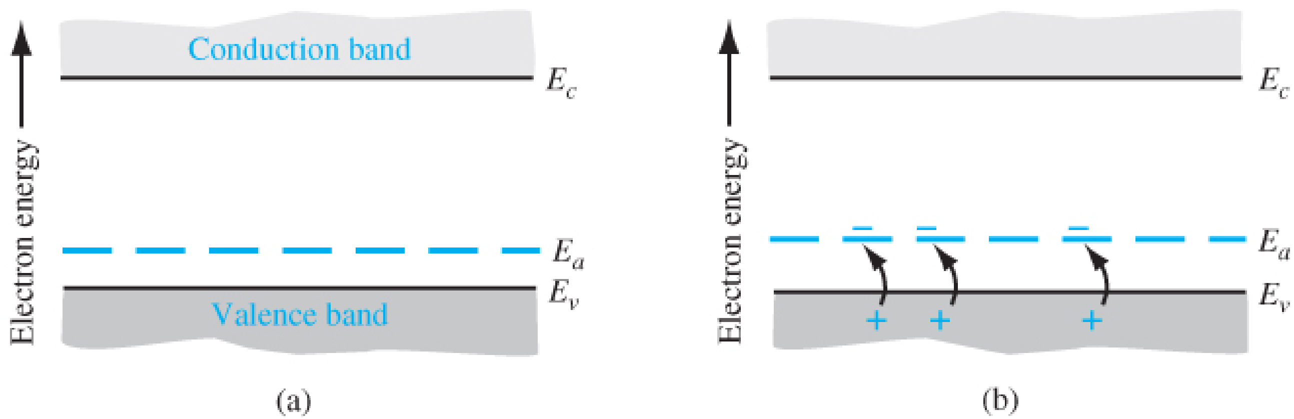


Figure 4.4 | Two-dimensional representation of the silicon lattice doped with a phosphorus atom.



This type of impurity atom donates an electron to the conduction band and so is called a **donor** impurity atom.

Figure 4.5 | The energy-band diagram showing (a) the discrete donor energy state and (b) the effect of a donor state being ionized.



The group III atom accepts an electron from the valence band and so is referred to as an **acceptor** impurity atom.

Figure 4.7 | The energy-band diagram showing (a) the discrete acceptor energy state and (b) the effect of an acceptor state being ionized.

1.2.2 Ionization Energy

ionization energy: the energy required to elevate the donor electron into the conduction band.

$$\frac{e^2}{4\pi\epsilon r_n^2} = \frac{m^* v^2}{r_n} \tag{4.27}$$

where v is the magnitude of the velocity and r_n is the radius of the orbit. If we assume the angular momentum is also quantized, then we can write

$$m^* r_n v = n\hbar \tag{4.28}$$

where n is a positive integer. Solving for v from Equation (4.28), substituting into Equation (4.27), and solving for the radius, we obtain

$$r_n = \frac{n^2 \hbar^2 4\pi\epsilon}{m^* e^2} \tag{4.29}$$

If we consider the lowest energy state in which $n = 1$, and if we consider silicon in which $\epsilon_r = 11.7$ and the conductivity effective mass is $m^*/m_0 = 0.26$, then we have that

$$\frac{r_1}{a_0} = 45 \tag{4.32}$$

or $r_1 = 23.9$ Å. This radius corresponds to approximately four lattice constants of

The donor electron is not tightly bound to the donor atom.

kinetic energy becomes

$$T = \frac{m^* e^4}{2(n\hbar)^2(4\pi\epsilon)^2} \tag{4.35}$$

The potential energy is

$$V = \frac{-e^2}{4\pi\epsilon r_n} = \frac{-m^* e^4}{(n\hbar)^2(4\pi\epsilon)^2} \tag{4.36}$$

The total energy is the sum of the kinetic and potential energies, so that

$$E = T + V = \frac{-m^* e^4}{2(n\hbar)^2(4\pi\epsilon)^2} \tag{4.37}$$

For silicon, the ionization energy is **E = -25.8 meV**, much less than the bandgap energy .

Table 4.3 | Impurity ionization energies in silicon and germanium

	Ionization energy (eV)	
Impurity	**Si**	**Ge**
Donors		
Phosphorus	0.045	0.012
Arsenic	0.05	0.0127
Acceptors		
Boron	0.045	0.0104
Aluminum	0.06	0.0102

1.3 | THE EXTRINSIC SEMICONDUCTOR

An **extrinsic semiconductor** is defined as a semiconductor in which **controlled amounts of specific dopant or impurity atoms have been added** so that the thermal-equilibrium electron and hole concentrations are different from the intrinsic carrier concentration.

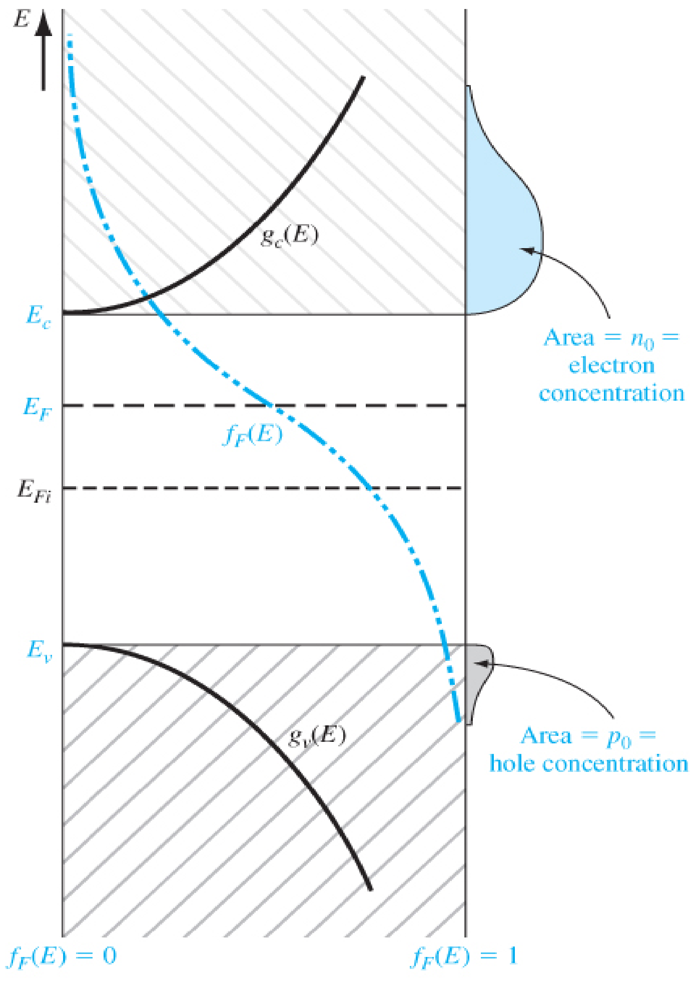


Figure 4.8 | Density of states functions, Fermi–Dirac probability function, and areas representing electron and hole concentrations for the case when E_F is above the intrinsic Fermi energy.

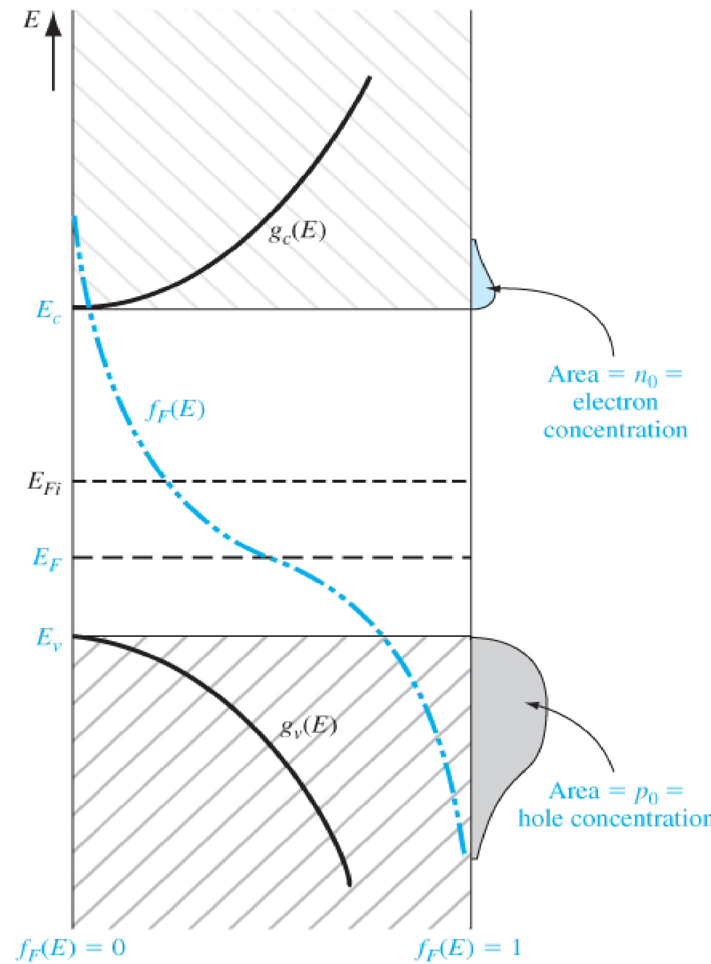


Figure 4.9 | Density of states functions, Fermi–Dirac probability function, and areas representing electron and hole concentrations for the case when E_F is below the intrinsic Fermi energy.

1.3.2 The $n_0 p_0$ Product

$$n_0 p_0 = N_c N_v \exp\left[\frac{-(E_c - E_F)}{kT}\right] \exp\left[\frac{-(E_F - E_v)}{kT}\right] \tag{4.41}$$

which may be written as

$$\boxed{n_0 p_0 = N_c N_v \exp\left[\frac{-E_g}{kT}\right]} \tag{4.42}$$

then have that, for the semiconductor in thermal equilibrium,

$$\boxed{n_0 p_0 = n_i^2} \tag{4.43}$$

1.4 | CHARGE NEUTRALITY

1.4.1 Compensated Semiconductors

A compensated semiconductor is one that contains both donor and acceptor impurity atoms in the same region.

1.4.2 Equilibrium Electron and Hole Concentrations

The charge neutrality condition is expressed by equating the density of negative charges to the density of positive charges.

$$n_0 + N_a^- = p_0 + N_d^+$$

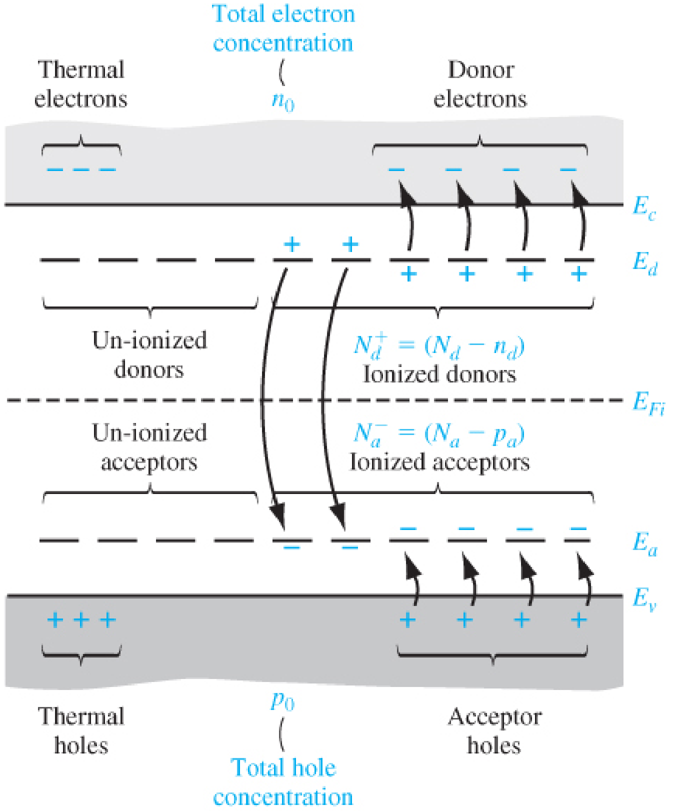


Figure 4.14 | Energy-band diagram of a compensated semiconductor showing ionized and un-ionized donors and acceptors.

Thermal-Equilibrium Electron Concentration If we assume complete ionization, n_d and p_a are both zero, and Equation (4.57) becomes

$$n_0 + N_a = p_0 + n_d \tag{4.58}$$

If we express p_0 as n_i^2/n_0, then Equation (4.58) can be written as

$$n_0 + N_a = \frac{n_i^2}{n_0} + N_d \tag{4.59a}$$

which in turn can be written as

$$n_0^2 - (N_d - N_a)n_0 - n_i^2 = 0 \tag{4.59b}$$

The electron concentration n_0 can be determined using the quadratic formula, or

$$\boxed{n_0 = \frac{(N_d - N_a)}{2} + \sqrt{\left(\frac{N_d - N_a}{2}\right)^2 + n_i^2}} \tag{4.60}$$

Comment

(Nd - Na) > ni, so the thermal-equilibrium majority carrier electron concentration is essentially equal to the difference between the donor and acceptor concentrations.

the majority carrier electron concentration is orders of magnitude larger than the minority carrier hole concentration.

Thermal-Equilibrium Hole Concentration If we reconsider Equation (4.58) and express n_0 as n_i^2/p_0, then we have

$$\frac{n_i^2}{p_0} + N_a = p_0 + N_d \tag{4.61a}$$

$$\boxed{p_0 = \frac{N_a - N_d}{2} + \sqrt{\left(\frac{N_a - N_d}{2}\right)^2 + n_i^2}} \tag{4.62}$$

Comment

If we assume complete ionization and if (Na - Nd) > ni, then the majority carrier hole concentration is, to a very good approximation, just **the difference between the acceptor and donor** concentrations.

1.5 | POSITION OF FERMI ENERGY LEVEL

1.5.1 Mathematical Derivation

$$\boxed{E_c - E_F = kT \ln\left(\frac{N_c}{n_0}\right)} \tag{4.63}$$

$$E_c - E_F = kT \ln\left(\frac{N_c}{N_d}\right) \tag{4.64}$$

$$\boxed{E_F - E_{Fi} = kT \ln\left(\frac{n_0}{n_i}\right)} \tag{4.65}$$

$$\boxed{E_F - E_v = kT \ln\left(\frac{N_v}{p_0}\right)} \tag{4.66}$$

$$\boxed{E_{Fi} - E_F = kT \ln\left(\frac{p_0}{n_i}\right)} \tag{4.68}$$

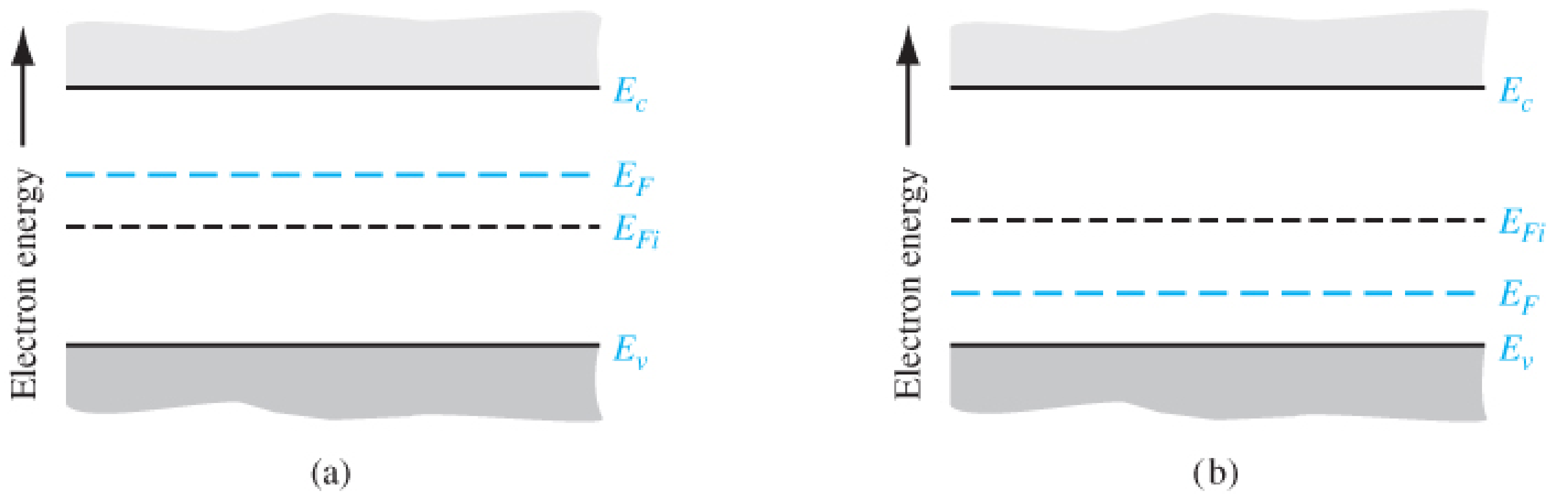


Figure 4.17 | Position of Fermi level for an (a) n-type ($N_d > N_a$) and (b) p-type ($N_a > N_d$) semiconductor.

1.5.2 Variation of E_F with Doping Concentration and Temperature

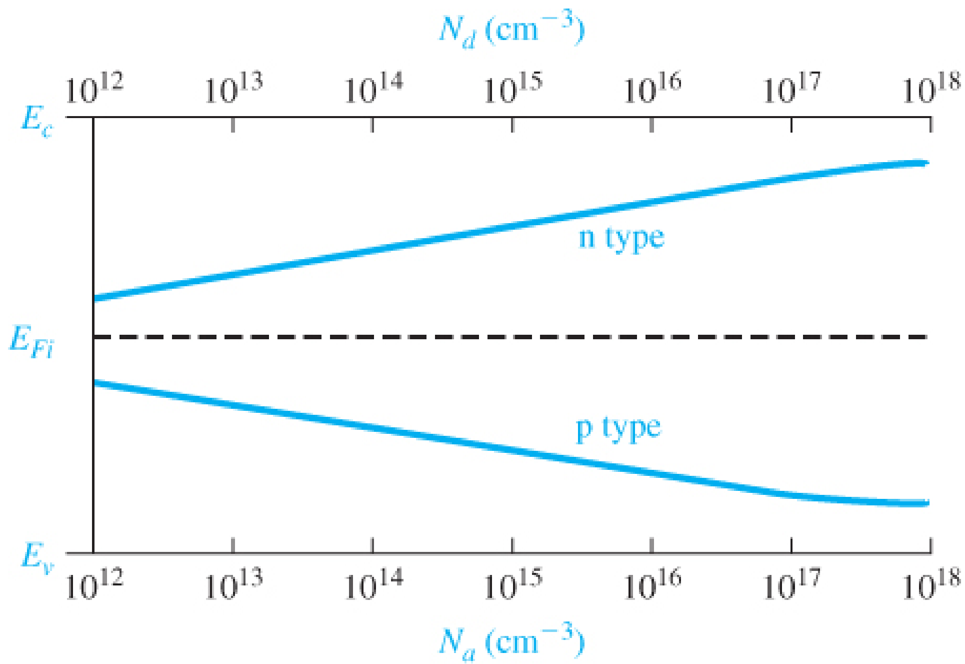


Figure 4.18 | Position of Fermi level as a function of donor concentration (n type) and acceptor concentration (p type).

Comment

If the acceptor (or donor) concentration in silicon is **greater than approximately 3 X 10^{17} cm^{-3}**, then the Boltzmann approximation of the distribution function **becomes less valid** and the equations for the Fermi-level position are no longer quite as accurate.