

Chapter 1

PHYSICAL PROPERTIES OF SEMICONDUCTORS

1.0 Introduction

Valence electrons in metals are loosely bound to their parent atoms so that even a very small electric field is sufficient to free them and enable conduction. Therefore, the *valence band* and the *conduction band* in energy diagram of metals overlap. On the other hand, bonds between atoms in insulators are strong. A comparatively large amount of energy (typically more than 3 eV) is needed to free an electron. In terms of energy-band picture, the valence band and the conduction band are separated by a rather large *energy gap (forbidden gap)*. All energy states in the valence band of an insulator are occupied by electrons and all states in the conduction band are completely empty.

Covalent bonds between atoms in semiconductors are moderately strong. At absolute zero temperature ($T=0$ K), all electrons are bound to their parent atoms. There are no free electrons left that would enable electric current to flow. In the energy

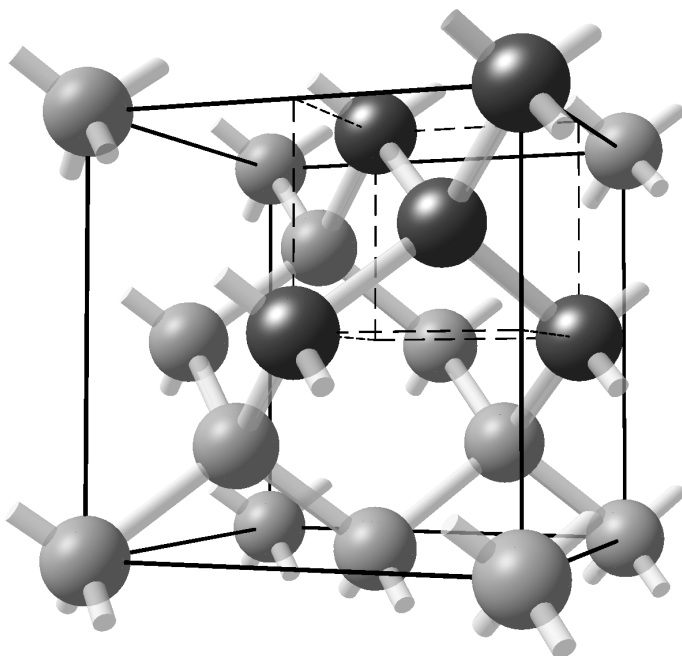


Figure 1.1a. Unit face-centered crystal cell of silicon (after [Blakemore74, Kittel76]).

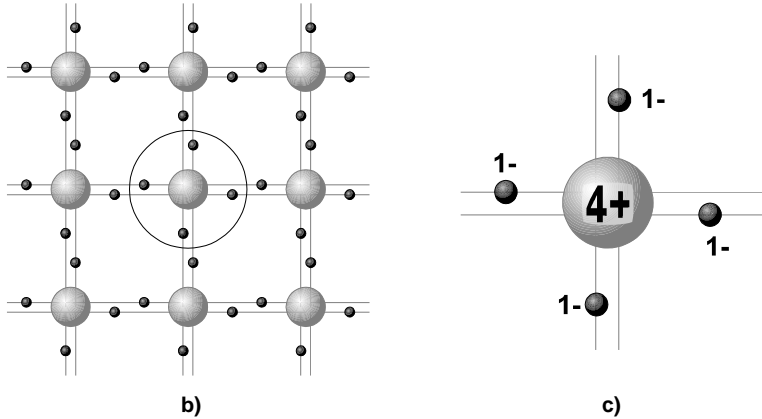


Figure 1.1. **b)** Simplified two-dimensional presentation of the silicon crystal. **c)** Silicon atom with four valence electrons.

diagram, all states in the valence band are occupied and the conduction band is completely empty. Figure 1.1a shows a unit crystal cell of the most important semiconductor - silicon. Each atom of silicon is bound with four neighboring atoms (in the figure, an atom with the four neighbors has been depicted darker) and shares four valence electrons with them, forming a covalent bond. Figure 1.1b gives a two-dimensional presentation of the silicon crystal lattice with four valence electrons attached to each silicon atom (Figure 1.1c). Germanium has the same crystal structure, while the crystal structure of some other semiconductors, such as gallium arsenide or indium phosphide, is very similar.

Above absolute zero temperature, lattice vibrations can cause some covalent bonds to break. A broken bond will result in a free electron, thus enabling electric current to flow. The missing electron in a broken bond is represented by a *hole*, a positive charge carrier. Valence electrons from neighboring bonds can jump into the place of a missing electron, contributing to electric conductivity of the semiconductor. This process of free electron formation is called *electron-hole pair generation*. Figure 1.2 illustrates electron-hole pair generation (label 1). As the temperature rises, the energy of lattice vibrations increases, producing a larger amount of thermally generated electron-hole pairs, thus increasing electrical conductivity of the semiconductor.

Moving through the crystal (label 2 in Figure 1.2), the free electron will after some time jump into another broken bond somewhere in the crystal, canceling the hole existing there at that precise moment. This process is called *electron-hole recombination* (label 3 in Figure 1.2).

The introduction of the hole as a positive charge carrier simplifies the analysis; instead of observing the movement of a very large amount of electrons in the valence

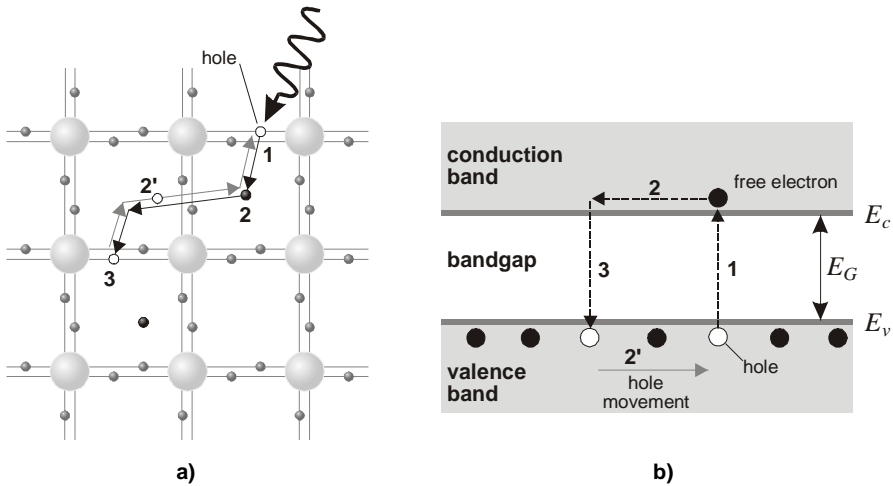


Figure 1.2. Generation and recombination of an electron-hole pair: **a)** presented in the twodimensional crystal lattice; **b)** in energy diagram.

band, our view is focused on a relatively small number of holes that move in the opposite direction[†].

The generation of a free electron is represented in the energy diagram by an electron jumping from the valence into the conduction band (Figure 1.2b). The electron at the bottom of the conduction band has only potential energy. Under the influence of the electric field it will gain some kinetic energy, which will enable electric current to flow. The increase of the kinetic energy is represented by the electron moving upward from the bottom of the conduction band. On the other hand, the increase of the kinetic energy of the hole is represented by the hole moving downward in the valence band.

In pure semiconductors, free carriers are generated exclusively by the process of electron-hole pair generation described above. Therefore, the concentration of electrons in the equilibrium equals the concentration of holes. Such semiconductor is called an *intrinsic* semiconductor.

By adding some impurities to a semiconductor its electrical properties can be changed. Impurities that cause the increase of electron concentration are called *donors*. A semiconductor in which concentration of electrons is higher than the concentration of holes is said to be an (*extrinsic*) *n*-type semiconductor. The concentration of electrons in silicon and germanium (which are tetra-valent elements, i.e. have four valent electrons) can be increased by doping with penta-valent elements, such as phosphorus and arsenic. These elements have five valence electrons, but only four are necessary to form a covalent bond with the host semiconductor. The extra electron will be loosely bound to

[†] The movement of a hole can be compared to the movement of an air bubble in a liquid: although it is the the liquid that actually moves, it is easier to observe the movement of a bubble in the opposite direction [Grove67].

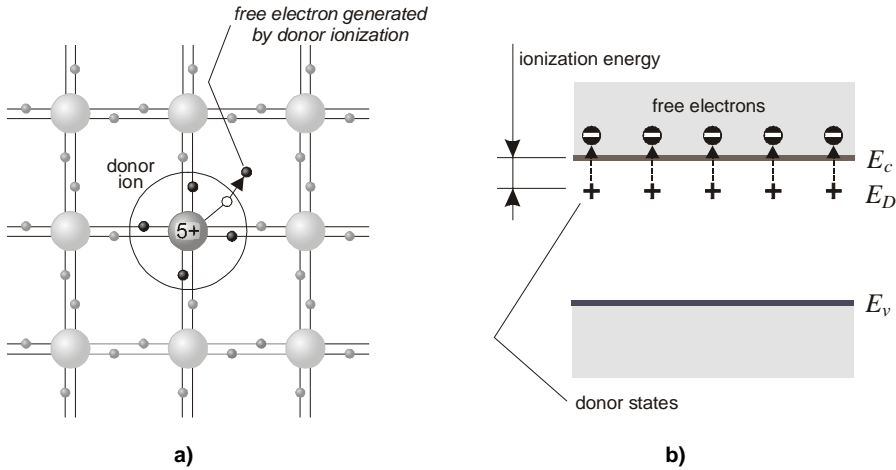


Figure 1.3. An n -type semiconductor: **a)** simplified two-dimensional presentation of the crystal lattice; **b)** energy diagram.

its parent atom and a very small amount of energy (referred to as *ionization energy*) will be sufficient to tear it off (Figure 1.3a). Naturally, when the fifth electron leaves, the donor atom becomes a positive (donor) ion. At room temperature, this ion is "frozen" in the semiconductor crystal, and does not contribute to the current flow. The presence of a donor impurity is represented by discrete states within the energy gap, very close to the conduction band (Figure 1.3b).

A p -type semiconductor, in which hole concentration is higher than electron concentration, is obtained by adding *acceptor* impurities. In silicon and germanium, acceptors are usually tri-valent elements, such as boron. Since these elements have only three valence electrons, one is missing to complete covalent bonds with host semiconductor atoms. Therefore, such an atom will bind an electron that would otherwise jump from the valence band into the conduction band, thus preventing the formation of an electron-hole pair (Figure 1.4a). By catching an electron, the acceptor impurity will become a negatively charged ion. Acceptor impurities thus introduce energy states within the energy gap, very close to the valence band (Figure 1.4b). Since ionization energies of typical donor and acceptor impurities are rather small (10 to 50 meV), at room temperature ($T=300$ K) almost all impurities are ionized.

Compound semiconductors consist of a tri-valent and a penta-valent element (*III-V compounds*, such as gallium arsenide GaAs, gallium phosphide GaP) or a di-valent and a hexa-valent element (*II-VI compounds*, such as zinc sulfide ZnS). The chemical bond is formed by the component with higher valence lending some electron(s) to the component with lower valence (Figure 1.5a). Donor impurities in compound semiconductors are elements with valence higher than that of the component they substitute, and acceptor impurities are elements with valence lower than that of the component they substitute. Figure 1.5b shows a donor atom of hexa-valent sulfur that

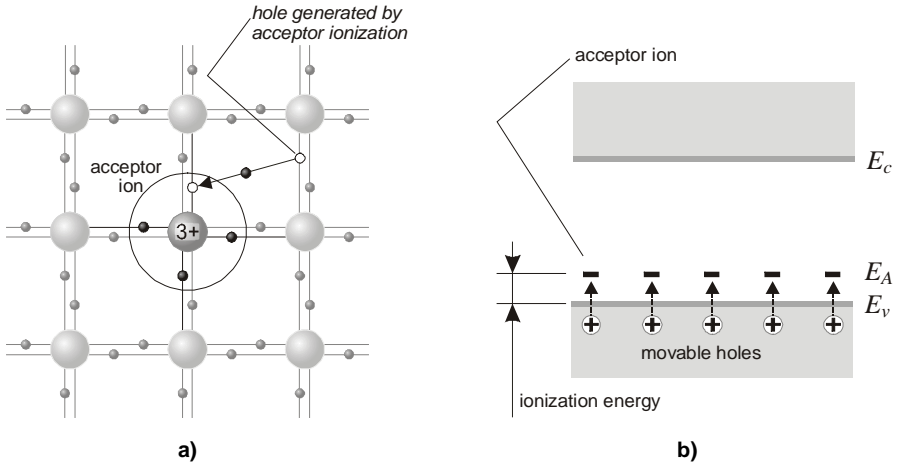


Figure 1.4. A *p*-type semiconductor: **a)** simplified two-dimensional presentation of the crystal lattice; **b)** energy diagram.

substituted penta-valent phosphorus in a gallium arsenide crystal. Sulfur's sixth valence electron is not necessary for the chemical bond with the surrounding gallium atoms; it is loosely bound to its parent sulfur atom and can easily become a free electron. It is interesting to notice that a tetra-valent element, such as silicon and germanium, in III-V compound can be both, a donor impurity (if it substitutes a tri-valent component) or an acceptor impurity (if it substitutes a penta-valent component).

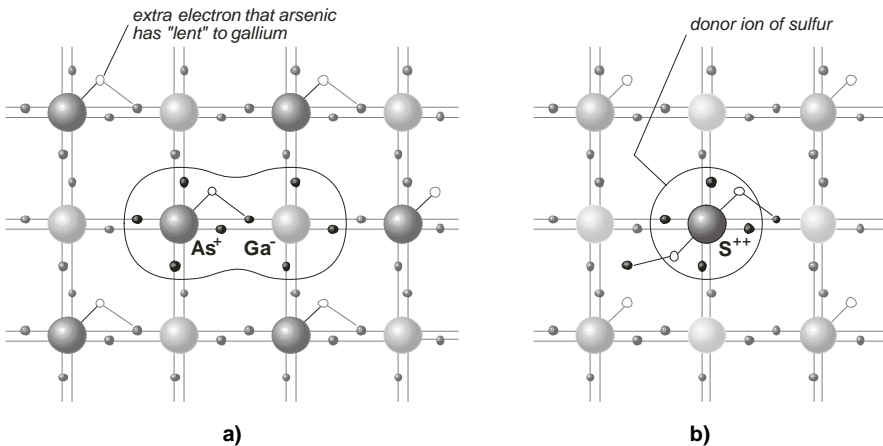


Figure 1.5. Simplified two-dimensional presentation of the crystal lattice of gallium arsenide: **a)** intrinsic semiconductor; **b)** *n*-type semiconductor.

1.1 Bandgap Width

Bandgap widths (or, *bandgaps*) of semiconductors most widely used (silicon, germanium and gallium arsenide) are given in Table 1.1. The bandgaps of these semiconductors can be related to temperature by [Thurmond75]

$$E_G(T) = E_G(0) - \frac{\alpha \cdot T^2}{T + \beta}, \quad (1.1)$$

where α and β are coefficients given in Table 1.1. Figure 1.6 is a plot of function (1.1). It is obvious that the bandgaps of silicon, germanium and gallium arsenide will decrease

Table 1.1. Bandgaps of silicon, germanium and gallium arsenide [Thurmond75].

semiconductor	$\frac{E_G(0 \text{ K})}{\text{eV}}$	$\frac{E_G(300 \text{ K})}{\text{eV}}$	$\frac{\alpha}{\text{eV K}^{-1}}$	$\frac{\beta}{\text{K}}$
Si	1.170	1.12	4.73×10^{-4}	636
Ge	0.7437	0.66	4.774×10^{-4}	235
GaAs	1.519	1.42	5.405×10^{-4}	204

if the temperature is raised. Bandgaps of some other semiconductors, on the other hand (e.g. lead sulfide PbS) will increase with temperature [Sze81].

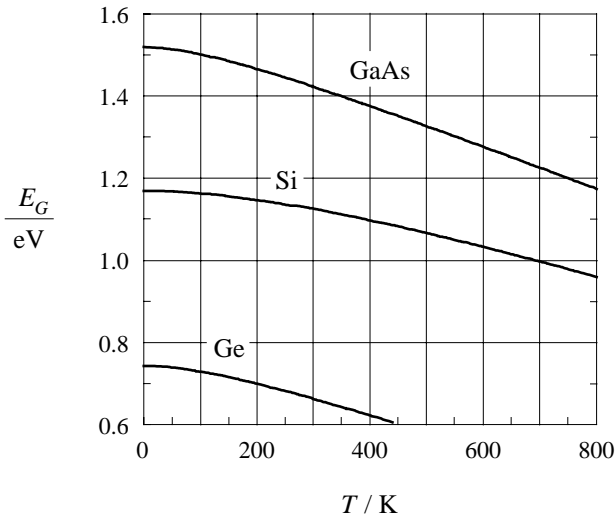


Figure 1.6. Temperature variation of bandgaps in silicon, germanium and gallium arsenide [Thurmond75].

For silicon, however, the formula most frequently used for bandgap variation is [Gaensslen79, Selberherr89]

$$\frac{E_G(T)}{\text{eV}} = \begin{cases} 1.17 - 1.059 \cdot 10^{-5} \cdot \left(\frac{T}{K}\right) - 6.05 \cdot 10^{-7} \cdot \left(\frac{T}{K}\right)^2, & T \leq 170 \text{ K} \\ 1.1785 - 9.025 \cdot 10^{-5} \cdot \left(\frac{T}{K}\right) - 3.05 \cdot 10^{-7} \cdot \left(\frac{T}{K}\right)^2, & T > 170 \text{ K} \end{cases} \quad (1.2)$$

Entering temperature in kelvins, one obtains bandgap in electron-volts.

Problem 1.1

Calculate the bandgap of silicon for temperatures ranging from 0 K to 500 K. Derive the linear approximation of the bandgap narrowing with temperature around room temperature, $T = 300 \text{ K}$, and find the interval in which the error of the approximation is less than 1 %.

Solution:

The values in Table 1.2 were calculated by means of formula (1.2) and Figure 1.7 plotted. A tangent to the curve was drawn at room temperature and a straight line

$$E'_G(T) = E_{G0} + a \cdot T, \quad (1.3)$$

was obtained, where a is the slope and E_{G0} is the intersection of tangent with energy axis. By differentiating function (1.2) and by entering the values for $T = 300 \text{ K}$, one obtains the linear approximation for the bandgap around room temperature

$$\frac{E'_G(T)}{\text{eV}} = 1.206 - 2.733 \cdot 10^{-4} \cdot \left(\frac{T}{K}\right). \quad (1.3a)$$

In Table 1.2, values of $E_G(T)$ and relative errors of the linear approximation are also listed. From these results and from Figure 1.7 it is clear that the linear approximation offers satisfactory accuracy in the temperature range from 150 K to 450 K. Since we are almost exclusively concerned with room temperatures, we will use this simpler approximation (1.3) in all calculations.

If function (1.1) is used instead of (1.2), by differentiating the slope

$$a = -\frac{\alpha \cdot T}{(T + \beta)^2} \cdot (T + 2 \cdot \beta). \quad (1.4)$$

is obtained. In this case the bandgap extrapolated to $T = 0 \text{ K}$ is

Table 1.2. Temperature variation of the bandgap in silicon.

$\frac{T}{K}$	$\frac{E_G}{\text{eV}}$	$\frac{E'_G}{\text{eV}}$	$\frac{E'_G - E_G}{E_G}$
0	1.170	1.206	3.073 %
50	1.169	1.192	1.991 %
100	1.165	1.179	1.169 %
150	1.158	1.165	0.603 %
200	1.148	1.151	0.266 %
250	1.137	1.138	0.067 %
300	1.124	1.124	0 %
350	1.110	1.110	0.069 %
400	1.094	1.097	0.279 %
450	1.076	1.083	0.638 %
500	1.057	1.069	1.154 %

$$E_{G0} = E_G(T) + \frac{\alpha \cdot T^2}{(T + \beta)^2} \cdot (T + 2 \cdot \beta) . \tag{1.5}$$

Entering values from Table 1.1 for $T = 300$ K, results are obtained as shown in Table 1.3.

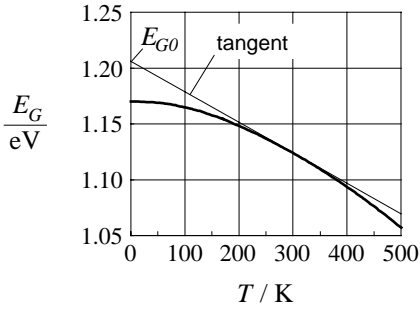


Figure 1.7. Linear approximation of silicon bandgap variation with temperature.

Table 1.3. Coefficients of linear approximations of bandgaps in silicon, germanium and gallium arsenide.

semiconductor	$\frac{E_{G0}}{\text{eV}}$	$\frac{a}{\text{eV K}^{-1}}$
Si	1.196	-2.546×10^{-4}
Ge	0.776	-3.853×10^{-4}
GaAs	1.556	-4.519×10^{-4}

1.2 Fermi-Dirac and Maxwell-Boltzmann Distributions

Distributions of electrons in the conduction band and holes in the valence band are described by the *Fermi-Dirac* distribution

$$dn(E) = \rho_c(E) \cdot f_n(E) \cdot dE, \quad (1.6)$$

$$dp(E) = \rho_v(E) \cdot f_p(E) \cdot dE. \quad (1.7)$$

$\rho_c(E)$ and $\rho_v(E)$ are *density of states* functions in the conduction band and the valence band. $f_n(E)$ and $f_p(E)$ are *Fermi-Dirac distribution* functions of electrons in the conduction band and holes in the valence band, respectively.

Density of states functions

$$\rho_c(E) = \frac{8\sqrt{2} \cdot \pi \cdot (m_c^*)^{3/2}}{h^3} \cdot \sqrt{E - E_c}, \quad (1.8)$$

$$\rho_v(E) = \frac{8\sqrt{2} \cdot \pi \cdot (m_v^*)^{3/2}}{h^3} \cdot \sqrt{E_v - E}, \quad (1.9)$$

express the number of available quantum states in the conduction band and in the valence band per unit volume per unit energy interval. m_c^* and m_v^* are density-of-state effective masses of electrons and holes, E_c and E_v are energies of the bottom of the conduction band and the top of the valence band, respectively, and h is *Planck's constant*.

Fermi-Dirac function

$$f_n(E) = \frac{1}{1 + \exp\left(\frac{E - E_{Fn}}{k \cdot T}\right)} \quad (1.10)$$

shows the probability that an available state with energy E is occupied by an electron, while

$$f_p(E) = \frac{1}{1 + \exp\left(\frac{E_{Fp} - E}{k \cdot T}\right)} \quad (1.11)$$

shows the probability that a state with energy E is not occupied by an electron, i.e. that is occupied by a hole. In non-equilibrium *Fermi energy* E_{Fn} for electrons in (1.10) differs from Fermi energy E_{Fp} for holes in (1.11). However, since we are primarily concerned with the cases of equilibrium or quasi-equilibrium, we will assume that these energies are equal, i.e. $E_{Fn} = E_{Fp} = E_F$. In that case

$$f_p(E) = 1 - f_n(E), \quad (1.12)$$

i.e. Fermi-Dirac distribution function of electrons is complementary to Fermi-Dirac distribution function of holes. In other words: the sum of the probability that a quantum

state is occupied by an electron and the probability that the state is unoccupied (occupied by a hole) must equal one.

In above equations T is the absolute temperature and k is the *Boltzmann's constant*. Usually, it is more convenient to express $k \cdot T$ product in electron-volts (eV). Therefore, a simple numeric formula will be used

$$k \cdot T = \frac{\left(\frac{T}{\text{K}}\right)}{11605} \text{ eV} . \tag{1.13}$$

By entering the absolute temperature (in kelvins) into (1.13), one obtains $k \cdot T$ in electron-volts. At room temperature ($T = 300 \text{ K}$) $k \cdot T = 25.8 \text{ meV}$.

Problem 1.2

Starting from the distribution functions, derive the expressions for equilibrium concentrations of electrons and holes in an intrinsic semiconductor.

Solution:

Figure 1.8 shows energy diagram, density of states functions, Fermi functions for electrons and holes, and the resulting distribution function of electrons in the conduction band and that of holes in the valence band. As shown in the figure, concentrations of electrons and holes correspond to the areas under their respective distribution functions. Hence, in order to express the concentration of electrons, we have to integrate the distribution function (1.6) from the bottom of the conduction band ($E = E_c$) to its top. Due to an exponentially falling nature of the Fermi function, the distribution function rapidly diminishes with energy. Consequently, the upper limit of the integral can be extended to infinity ($E = \infty$), so that

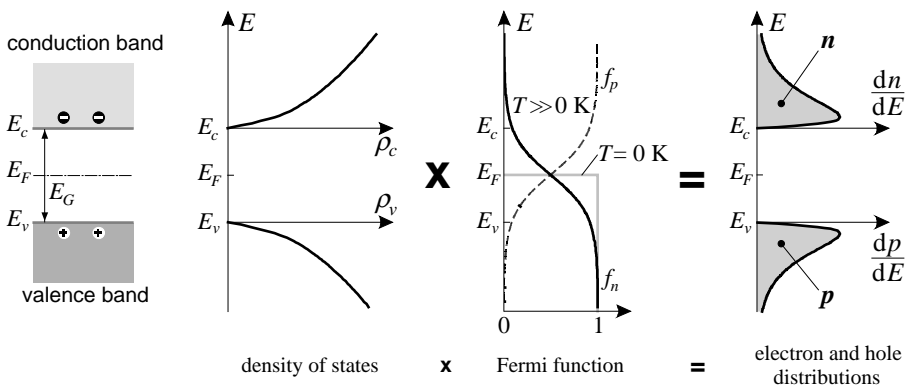


Figure 1.8. Distributions of electrons and holes in an intrinsic semiconductor.

$$\begin{aligned}
 n &= \int_{E_c}^{\infty} \rho_c(E) \cdot f_n(E) \cdot dE = \\
 &= \frac{8\sqrt{2} \cdot \pi \cdot (m_c^*)^{3/2}}{h^3} \cdot \int_{E_c}^{\infty} \sqrt{E - E_c} \cdot \frac{1}{1 + \exp\left(\frac{E - E_F}{k \cdot T}\right)} dE. \quad (1.14)
 \end{aligned}$$

Using substitution

$$\eta = \frac{E - E_c}{k \cdot T}, \quad d\eta = \frac{dE}{k \cdot T}, \quad dE = k \cdot T \cdot d\eta, \quad (1.15)$$

we obtain

$$n = \frac{8\sqrt{2} \cdot \pi \cdot (m_c^*)^{3/2}}{h^3} \cdot (k \cdot T)^{3/2} \cdot \int_0^{\infty} \frac{\sqrt{\eta}}{1 + \exp(\eta - \eta_F)} d\eta, \quad (1.16)$$

which can be written as

$$n = N_c \cdot \frac{2}{\sqrt{\pi}} \cdot F_{1/2}(\eta_F), \quad (1.17)$$

where

$$\eta_F = \frac{E_F - E_c}{k \cdot T} \quad (1.18)$$

is the distance between the Fermi level and the top of the bandgap, in fractions of $k \cdot T$. N_c is the *effective density of states* in the conduction band

$$N_c = 2 \cdot \left(\frac{2 \cdot \pi \cdot k \cdot T \cdot m_c^*}{h^2} \right)^{3/2}. \quad (1.19)$$

$F_{1/2}(\eta_F)$ is the Fermi integral of order 1/2

$$F_{1/2}(\eta_F) = \int_0^{\infty} \frac{\sqrt{t}}{1 + \exp(t - \eta_F)} dt. \quad (1.20)$$

There is no closed form solution to the Fermi integral, but there are analytic approximations of the solution for certain ranges of η_F [Shockley50, Kireev78]

$$F_{1/2}(\eta_F) = \begin{cases} \frac{\sqrt{\pi}}{2} \cdot \exp(\eta_F), & \eta_F \ll -1 \\ \frac{2}{3} \cdot \eta_F^{3/2}, & \eta_F \gg 1 \end{cases}. \quad (1.21)$$

Figure 1.9 shows the plots of the Fermi integral and the above approximations (1.21). In addition to these simplest and most common approximations, some others are available [Blakemore82].

The first approximation can be used in semiconductors when

$$\eta_F = \frac{E_F - E_c}{k \cdot T} \ll -1, \quad (1.22a)$$

or

$$E_F - E_c \ll -k \cdot T. \quad (1.22b)$$

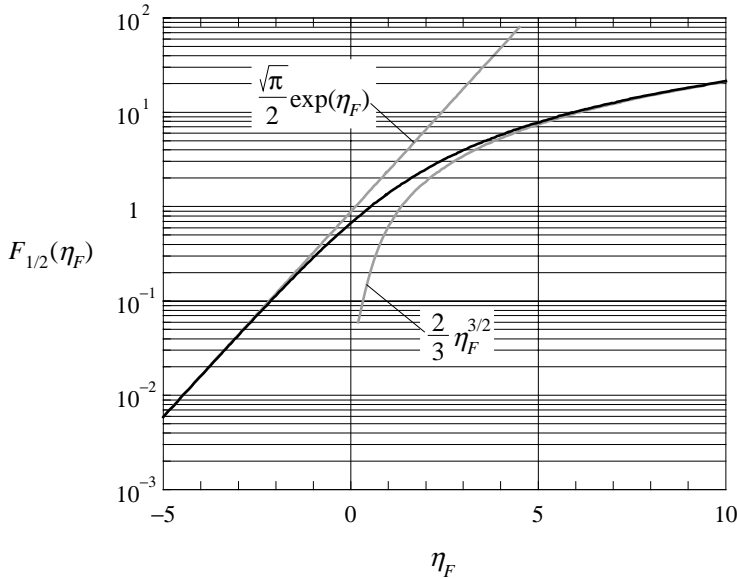


Figure 1.9. The Fermi integral of order 1/2 and its approximations.

In our problem this means that Fermi level must be at least several $k \cdot T$ away from all energy states in which electrons can exist. In other words, the Fermi level must be within bandgap and at least several $k \cdot T$ apart from the bandgap top (conduction band bottom). For the majority of practical calculations, a distance of $3 \cdot k \cdot T$ or more, i.e. $E_c - E_F \geq 3 \cdot k \cdot T$, is sufficient.

This approximation to the solution corresponds to a case of *non-degenerate* semiconductors, in which the distribution of electrons in the conduction band can be quite well described by the *Maxwell-Boltzmann* distribution. Mathematically, the tail in the Fermi-Dirac distribution (1.10), which lies in the conduction band, is approximated by an exponential function

$$f_n(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k \cdot T}\right)} \doteq \exp\left(-\frac{E - E_F}{k \cdot T}\right). \quad (1.23)$$

On the other hand, the second approximation to $F_{1/2}(\eta_F)$ in (1.21) corresponds to *highly degenerate* semiconductors, in which the Fermi level lies deeply inside the conduction band. Electrical properties of such semiconductors are similar to those of metals. We are almost exclusively concerned with non-degenerate semiconductors, thus the Maxwell-Boltzmann statistics will be used exclusively, which is much easier to use.

In an intrinsic semiconductor the condition (1.22) is fulfilled. Accordingly, the concentration of electrons in the conduction band is obtained as

$$n = N_c \cdot \exp\left(\frac{E_F - E_c}{k \cdot T}\right). \quad (1.24)$$

Similarly, the equilibrium concentration of holes in the valence band can be derived by integrating the distribution function of holes (1.7) over all energies in the valence band, from $E = -\infty$ to $E = E_v$ at the top of the valence band

$$\begin{aligned}
 p &= \int_{-\infty}^{E_v} \rho_v(E) \cdot f_p(E) \cdot dE = \\
 &= \frac{8\sqrt{2} \cdot \pi \cdot (m_v^*)^{3/2}}{h^3} \cdot \int_{-\infty}^{E_v} \sqrt{E_v - E} \cdot \frac{1}{1 + \exp\left(\frac{E_F - E}{k \cdot T}\right)} dE. \quad (1.25)
 \end{aligned}$$

Substituting

$$\eta = \frac{E_v - E}{k \cdot T}, \quad d\eta = -\frac{dE}{k \cdot T}, \quad dE = -k \cdot T \cdot d\eta, \quad (1.26)$$

the integral (1.25) changes to

$$p = \frac{8\sqrt{2} \cdot \pi \cdot (m_v^*)^{3/2}}{h^3} \cdot (k \cdot T)^{3/2} \cdot \int_0^{\infty} \frac{\sqrt{\eta}}{1 + \exp(\eta - \eta_F)} d\eta, \quad (1.27)$$

or

$$p = N_v \cdot \frac{2}{\sqrt{\pi}} \cdot F_{1/2}(\eta_F), \quad (1.28)$$

where

$$\eta_F = \frac{E_v - E_F}{k \cdot T} \quad (1.29)$$

is the distance between the Fermi energy and the conduction band bottom, relative to $k \cdot T$. Comparing this to (1.18) we may notice that the reference (positive) direction has changed. N_v is the *effective density of states in the valence band*

$$N_v = 2 \cdot \left(\frac{2 \cdot \pi \cdot k \cdot T \cdot m_v^*}{h^2} \right)^{3/2}. \quad (1.30)$$

Applying the first approximation of the Fermi integral in (1.21), the concentration of holes can be expressed as

$$p = N_v \cdot \exp\left(-\frac{E_F - E_v}{k \cdot T}\right). \quad (1.31)$$

This expression is again valid for non-degenerate semiconductors only, which means that the Fermi energy must be within the energy gap, at least several $k \cdot T$ apart from the valence band top.

It is important to notice that the product of concentrations of electrons (1.24) and holes (1.31) in equilibrium

$$n \cdot p = N_c \cdot N_v \cdot \exp\left(-\frac{E_c - E_v}{k \cdot T}\right) = N_c \cdot N_v \cdot \exp\left(-\frac{E_G}{k \cdot T}\right) \quad (1.32)$$

does not depend on the Fermi level position, but is constant for a semiconductor at a certain temperature. In the above expression E_G is the bandgap width.

In an intrinsic semiconductor carriers are formed by electron-hole pair generation only. Therefore, the concentration of electrons equals the concentration of holes. If density of states functions in the valence and conduction bands are symmetrical to each other, then electron distribution in the conduction band will be a mirror image of the hole distribution in the valence band. The mirror plane of these functions lies at the center of the energy gap (Figure 1.8). We can

deduce that the Fermi energy will be at the center of the bandgap. This means that the assumptions introduced by approximation of the exact Fermi-Dirac statistics with the Maxwell-Boltzmann distribution, are correct. In other words, Fermi energy is within the bandgap, being several $k \cdot T$ apart from the edges of the bandgap. In fact, density of states functions are not symmetrical, but in silicon, germanium and gallium arsenide this non-symmetry can be neglected in most cases (cf. chapter 1.5 *Fermi level*).

It should be emphasized that for the sake of clarity plots in Figure 1.8 have been drawn out of scale; the distributions shown correspond to a very high temperature. To illustrate a real situation, we can analyze silicon at $T = 300$ K. Bandgap at that temperature is $E_G = 1,12$ eV. Probability that a state at the bottom of the conduction band is occupied by electron is given by (1.10)

$$f_n(E_c) = \frac{1}{1 + \exp\left(\frac{E_c - E_F}{k \cdot T}\right)} = \frac{1}{1 + \exp\left(\frac{E_G}{2 \cdot k \cdot T}\right)} = 3,62 \cdot 10^{-10}.$$

For states away from the conduction band bottom the probability will be even smaller. If the figure 1.8 were drawn to scale, Fermi function would coincide with energy axis already at the bottom of the conduction band. Consequently, the distribution of minority carriers would not be observable. Although occupation probabilities are very small, a large density of quantum states results in a considerable concentration of free electrons. For example, intrinsic silicon at room temperature contains about 10^{10} electrons per cubic centimeter that are formed by thermal generation of electron-hole pairs. The same consideration applies to holes. When calculating the above probability, we could notice that the exponential function in the denominator is much larger than one. This proves that Maxwell-Boltzmann statistics offers satisfactory accuracy.

In metals the Fermi energy is usually defined as the topmost energy level occupied by electrons at the absolute zero temperature. Above zero temperature the probability of that level being occupied equals $1/2$. Obviously, this definition is not applicable to semiconductors since Fermi level lies within bandgap, where no electron can exist. The topmost energy that an electron can occupy at absolute zero in a semiconductor lies at the top of the valence band E_v . If we assumed that the Fermi level coincides with the valence band top, than the Fermi functions in Figure 1.8 would be translated downward. Consequently, the concentration of holes would not be equal to that of electrons, which is contrary to our original premises. Accordingly, we can introduce a modified definition of the Fermi level in a semiconductor, which is stated in terms of mathematical theorems:

Let E_F be an energy level. We denote the probability that a level $E_F + \Delta E$ inside the conduction band is occupied by an electron as $f_n(E_F + \Delta E)$ and the probability that a level $E_F - \Delta E$ inside the valence band is occupied by a hole (unoccupied by an electron) as $f_p(E_F - \Delta E)$. If these probabilities in the equilibrium are mutually equal

$$f_n(E_F + \Delta E) = f_p(E_F - \Delta E),$$

then E_F is the Fermi level.

It is obvious from (1.12) that the Fermi energy is the symmetry axis between the Fermi function for electrons and the mirrored Fermi function for holes.

Problem 1.3

Find energies at which the distribution of electrons in the conduction band and the distribution of holes in the valence band have maxima, if distributions are governed by Maxwell-Boltzmann statistics.

Solution:

The maximum in electron distribution in the conduction band is at $E = E_c + k \cdot T/2$, while the maximum in hole distribution in the valence band is at $E = E_v - k \cdot T/2$. It is interesting to notice that the position of maxima does not depend on the position of the Fermi level, as long as Maxwell-Boltzmann statistics is applicable.

Problem 1.4

Estimate relative errors in the calculation of free carriers concentration when the Maxwell-Boltzmann statistics is applied for semiconductors with Fermi energy within the energy gap, if the Fermi level is $3 \cdot k \cdot T$, $2 \cdot k \cdot T$, $k \cdot T$ away from the bandgap edge or if it coincides with the edge. *Hint:* Split the Fermi integral (1.20) into two integrals

$$\int_0^\infty f(x) \cdot dx \doteq \int_0^1 f(x) \cdot dx + \int_1^b f(x) \cdot dx,$$

and calculate each of them using trapezoidal rule with 16 subintervals each. Let the upper limit of the integral be $b = 11 + \eta_F$.

Solution:

The results of calculations are given in Table 1.4. $F_{1/2}^\Sigma$ are the results of a numerical integration by the above-suggested method, $F_{1/2}^{MB}$ are the results of the Maxwell-Boltzmann approximation, and ε_1 is the corresponding error. For a reference, the exact values of the Fermi integral ($F_{1/2}$) and the corresponding errors ε_2 are also given.

Table 1.4. Errors of Maxwell-Boltzmann approximation.

η_F	-3	-2	-1	0
$F_{1/2}^\Sigma$	0.0433	0.115	0.291	0.679
$F_{1/2}^{MB}$	0.0441	0.120	0.326	0.886
ε_1	-1.90 %	-4.66 %	-12.1 %	-30.6 %
$F_{1/2}$	0.0434	0.115	0.291	0.678
ε_2	-1.74 %	-4.67 %	-12.2 %	-30.7 %

1.3 Carrier Concentrations

Concentrations of electrons and holes in equilibrium are determined by concentrations of donor and acceptor impurities. They can be calculated by the use of the *law of mass action* and *law of charge neutrality*.

1.3.1 The pn Product at Equilibrium

According to the law of mass action, the product of concentrations of electrons and holes in equilibrium at a certain temperature is constant (cf. (1.32) on p. 13), irrespective of their individual concentrations, i.e.

$$n_0 \cdot p_0 = n_i^2. \quad (1.33)$$

n_0 i p_0 are concentrations of free electrons and holes in equilibrium, and n_i is *intrinsic* concentration of carriers. The above formula is valid only if Maxwell-Boltzmann statistics for electron and hole distributions is valid, i.e. for non-degenerate semiconductors.

Concentrations of electrons and holes in a pure (*intrinsic*) semiconductor are equal to each other, and equal to intrinsic concentration, since free carriers are formed by electron-hole pair generation only. Intrinsic concentration depends on the temperature of the semiconductor and its bandgap. By equating the formula (1.32) to (1.33), one obtains

$$n_i = \sqrt{N_v \cdot N_c} \cdot \exp\left(-\frac{E_G}{2 \cdot k \cdot T}\right). \quad (1.34)$$

Since

$$\sqrt{N_v \cdot N_c} = 2 \cdot \left(\frac{2 \cdot \pi \cdot k \cdot T}{h^2}\right)^{3/2} \cdot (m_c^* \cdot m_v^*)^{3/4}, \quad (1.35)$$

(1.34) can be written as

$$n_i = C' \cdot \left(\frac{m_c^* \cdot m_v^*}{m_0^2}\right)^{3/4} \cdot T^{3/2} \cdot \exp\left(-\frac{E_G}{2 \cdot k \cdot T}\right). \quad (1.36)$$

m_0 is the mass of free electron, and

$$C' = 2 \cdot \left(\frac{2 \cdot \pi \cdot k \cdot m_0}{h^2}\right)^{3/2} = 4.83 \cdot 10^{15} \text{ cm}^{-3} \text{ K}^{-3/2} \quad (1.37)$$

is a physical constant.

Effective masses of electrons in the conduction band and those of holes in the valence band in silicon, germanium and gallium arsenide increase with temperature [Thurmond75]. In gallium arsenide and germanium this increase is almost negligible in the whole temperature range from 0 K to the melting point. Figure 1.10 shows the increase of effective masses of electrons and holes in silicon. It is obvious that for temperatures around the room temperature (300 K) variations of effective masses are

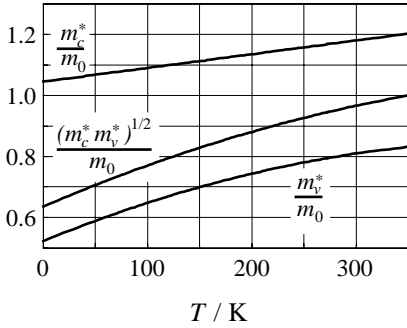


Figure 1.10. Temperature variation of effective masses of carriers in silicon [Barber67, Gaensslen79].

Table 1.5. Effective masses of carriers in silicon, gallium arsenide and germanium at 300 K [Selberherr84].

semiconductor	m_c^* / m_0	m_v^* / m_0
Si	1.18	0.81
GaAs	0.068	0.5
Ge	0.55	0.3

small, so we can use constant values in our calculations. Table 1.5 gives values for effective masses of carriers in silicon, germanium and gallium arsenide at $T = 300$ K. However, if we enter values from Table 1.5 in formula (1.36), calculated values of intrinsic concentration will differ considerably from experimental results.

Table 1.6. Intrinsic carrier concentrations at $T = 300$ K [Morin54, Morin54a, Thurmond75].

semiconductor	n_i / cm^{-3}
Si	$1.38 \cdot 10^{10}$
GaAs	$\sim 9 \cdot 10^8$
Ge	$2.33 \cdot 10^{13}$

Therefore, we will calculate the pre-exponential factor in (1.36) according to experimentally measured intrinsic concentrations, listed in Table 1.6.

Problem 1.5

According to measured values of intrinsic concentrations at $T = 300$ K given in Table 1.6, and using the linear approximation for the bandgap variation with temperature, derive numeric expressions for intrinsic concentrations in silicon, gallium arsenide and germanium.

Solution:

In order to derive numerical expressions for intrinsic concentrations around $T = 300$ K, we start from expression (1.36)

$$n_i = C' \cdot \left(\frac{m_c^* \cdot m_v^*}{m_0^2} \right)^{3/4} \cdot T^{3/2} \cdot \exp\left(-\frac{E_G}{2 \cdot k \cdot T} \right).$$

According to this formula, the variation of intrinsic concentration with temperature change is caused by:

1. variation of effective masses of carriers,
2. pre-exponential term $T^{3/2}$,
3. variation of the bandgap E_G , and
4. $k \cdot T$ term in the denominator of the exponential function argument.

As already discussed, variation of effective masses of carriers for small temperature changes can be neglected. Therefore, we assume them to be constant, and rewrite (1.36) as

$$n_i = C'' \cdot T^{3/2} \cdot \exp\left(-\frac{E_G}{2 \cdot k \cdot T}\right). \quad (1.38)$$

The variation of bandgap for small temperature changes can be described by linear function (cf. Problem 1.1)

$$E_G \doteq E_{G0} + a \cdot T,$$

where E_{G0} is the bandgap extrapolated to zero temperature using the linear approximation of the bandgap variation. Substituting in (1.38) we obtain

$$n_i = C'' \cdot T^{3/2} \cdot \exp\left(-\frac{E_{G0}}{2 \cdot k \cdot T}\right) \cdot \exp\left(-\frac{a}{2 \cdot k}\right), \quad (1.39)$$

or

$$n_i = C \cdot T^{3/2} \cdot \exp\left(-\frac{E_{G0}}{2 \cdot k \cdot T}\right). \quad (1.40)$$

If we calculate values of E_{G0} by using formula (1.1) for germanium and gallium arsenide, or (1.2) for silicon, and enter them in the above expression, we will obtain pre-exponential factors C (cf. Table 1.7[†]). Plots of variations of intrinsic carrier concentrations with temperature in silicon

Table 1.7. Coefficients for intrinsic carrier concentration calculation.

semiconductor	$C'' / (\text{K}^{-3/2} \text{ cm}^{-3})$	E_{G0} / eV	$C / (\text{K}^{-3/2} \text{ cm}^{-3})$
Si	$7.33 \cdot 10^{15}$	1.206	$3.58 \cdot 10^{16}$
GaAs	$1.54 \cdot 10^{15}$	1.558	$2.12 \cdot 10^{16}$
Ge	$1.67 \cdot 10^{15}$	0.779	$1.57 \cdot 10^{16}$

and germanium are shown in Figure 1.11. Since there are no experimental data available for gallium arsenide [Thurmond75], the curve for the latter has been plotted on the right diagram only. Intrinsic concentration closely follows $\exp(1/T)$ functional dependence (scale on the ordinate is logarithmic!). This is even more obvious in the right diagram, in which the reciprocal of the temperature is on the abscissa scale. Intrinsic concentrations of carriers in silicon are two to three orders lower than in germanium at the same temperature (scales on the ordinate differ for

[†] Coefficients shown in Table 1.7 were derived by above procedure for temperatures around room temperature. Therefore, they differ from experimentally obtained coefficients in [Morin54] and [Morin54a]. For example, according to results of measurements on silicon in the temperature range between 450 K and 1100 K, Morin and Maita [Morin54a] proposed a formula

$$n_i^2 = 1.5 \cdot 10^{33} \cdot T^3 \cdot \exp\left(-\frac{1.21 \text{ eV} + \Delta E_G}{k \cdot T}\right) \text{ cm}^{-6}, \quad \Delta E_G = -7.1 \cdot 10^{-10} \cdot \left(\frac{n_i / \text{cm}^{-3}}{T / \text{K}}\right)^{1/2} \text{ eV}.$$

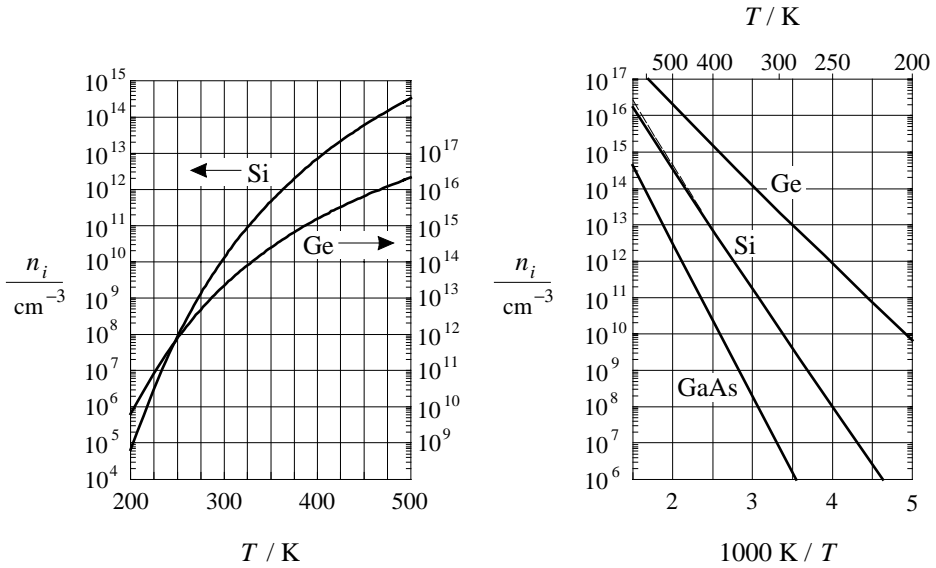


Figure 1.11. Temperature dependence of intrinsic carrier concentrations in silicon, germanium and gallium arsenide.

silicon and germanium). This is a direct consequence of a wider bandgap in silicon; in gallium arsenide the intrinsic carrier concentration is still lower. To illustrate the influence of above effects, we have plotted the exact curve for silicon, taking into account variations of effective masses and bandgap (dashed curve in the right diagram) [Selberherr89]. It is obvious that their influence is noticeable only at temperatures above 400 K.

Problem 1.6

Calculate the concentrations of free carriers in intrinsic silicon at $T = 350$ K and the change of it if the temperature changes:

- a) 0.2 %,
- b) 20 %.

Solution:

By entering values from Table 1.7 into formula (1.40), we can calculate intrinsic carrier concentration in silicon. For $T = 350$ K we obtain

$$n_i = 4.86 \cdot 10^{11} \text{ cm}^{-3}.$$

a)

Despite the exponential dependence, a very small change of temperature causes a small change of intrinsic concentration. To calculate a relative change of intrinsic concentration, we proceed as follows:

By applying logarithmic function on formula (1.40)

$$n_i = C \cdot T^{3/2} \cdot \exp\left(-\frac{E_{G0}}{2 \cdot k \cdot T}\right)$$

the equation

$$\ln(n_i) = \ln(C) + \frac{3}{2} \cdot \ln(T) - \frac{E_{G0}}{2 \cdot k \cdot T}, \quad (1.41)$$

is obtained, which is then differentiated

$$\frac{dn_i}{n_i} = \left(\frac{3}{2} + \frac{E_{G0}}{2 \cdot k \cdot T}\right) \cdot \frac{dT}{T}. \quad (1.42)$$

For small temperature changes, differentials can be replaced by finite differences

$$\frac{\Delta n_i}{n_i} = \left(\frac{3}{2} + \frac{E_{G0}}{2 \cdot k \cdot T}\right) \cdot \frac{\Delta T}{T}.$$

For imposed temperature change ($\Delta T/T = 0.2\% = 0.002$), we obtain

$$\frac{\Delta n_i}{n_i} = 0.0430 = 4.30\%.$$

By comparison of components within parenthesis in (1.42), we can notice how much weaker the influence of the term $T^{3/2}$ is, compared to the exponential function term. The second component in (1.42), which comes from the exponential function in (1.40), at a given temperature is

$$\frac{E_{G0}}{2 \cdot k \cdot T} = 20.0.$$

This is much larger than the first component ($3/2$ regardless of the temperature), which arises from term $T^{3/2}$ in formula (1.40). For example, both components in (1.42) would become equal at $T = 4665$ K. Although this result is not completely proper, since expression (1.40) assumes a linear variation of the bandgap with temperature (moreover, the melting point of silicon is at 1415°C), it illustrates the qualitative relation.

If expression (1.36) was used and differentiated by using a more accurate second-order approximation of the bandgap with variation (cf. formula (1.2))

$$E_G = a + b \cdot T + c \cdot T^2,$$

but neglecting the variations of effective masses of carriers, the formula

$$\frac{dn_i}{n_i} = \left(\frac{3}{2} + \frac{a - c \cdot T^2}{2 \cdot k \cdot T}\right) \cdot \frac{dT}{T}. \quad (1.43)$$

would have been obtained. Constants $a = 1.1785$ eV i $c = -3.05 \cdot 10^{-7}$ eV/K² are coefficients in approximation of the bandgap variation, formula (1.2). Replacing differentials by finite differences and entering given values, we obtain $\Delta n_i/n_i = 0.0433 = 4.33\%$. It is evident that the difference between the two calculations is negligible.

b)

For large temperature changes the above linearization approach cannot be utilized. We have to calculate intrinsic concentrations both at temperature T_1 and at temperature $T_2 = T_1 + \Delta T$. From the ratio of the corresponding concentrations

$$\frac{n_{i2}}{n_{i1}} = \left(\frac{T_2}{T_1}\right)^{3/2} \cdot \exp\left[\frac{E_{G0}}{2} \cdot \left(\frac{1}{k \cdot T_1} - \frac{1}{k \cdot T_2}\right)\right], \quad (1.44)$$

we can obtain its relative change

$$\frac{\Delta n_i}{n_i} = \frac{n_{i2} - n_{i1}}{n_{i1}} = \left(\frac{T_2}{T_1}\right)^{3/2} \cdot \exp\left[\frac{E_{G0}}{2} \cdot \left(\frac{1}{k \cdot T_1} - \frac{1}{k \cdot T_2}\right)\right] - 1. \quad (1.45)$$

For a given temperature change $\Delta T/T = 20\% = 0.2$, the higher temperature is $T_2 = 1.2 \cdot T_1$. Hence, for $T_1 = 350$ K, we obtain $T_2 = 420$ K, and the corresponding change of intrinsic concentration

$$\frac{\Delta n_i}{n_i} = 35.5 = 3550\% .$$

Since intrinsic concentration rises almost exponentially with temperature, a 20 % change of temperature causes a much larger relative change in intrinsic concentration of carriers. Intrinsic concentration has risen to $n_{i2} = 1.79 \cdot 10^{13} \text{ cm}^{-3}$. We will see later that such a strong dependence of intrinsic concentrations on temperature can have a considerable influence on electrical properties of semiconductors.

1.3.2 Charge Neutrality

Under the conditions of electrical neutrality the total of positive charges (free holes and fixed ionized donor atoms) must equal the total of negative charges (free electrons and fixed ionized acceptor atoms) in a semiconductor

$$p + N_D^+ = n + N_A^- . \quad (1.46)$$

N_D^+ and N_A^- are concentrations of ionized donors and acceptors, respectively. If concentrations of impurities are not too high, almost all of them will be ionized at room temperatures. Consequently, it can be assumed that concentrations of ionized impurities equal total concentrations. In highly doped semiconductors, only a fraction of impurities replaces atoms in crystal lattice of the host semiconductor, which results in part of them remaining electrically inactive.

At very low temperatures (typically below 200 K), the energy of crystal lattice vibrations is not sufficient to ionize all impurities. The temperature range where this takes place is referred to as *partial ionization range*. For a known concentration of donors N_D that introduce energy level E_D within the bandgap, the concentration of ionized donors is given as

$$N_D^+ = \frac{N_D}{1 + 2 \cdot \exp\left(\frac{E_F - E_D}{k \cdot T}\right)} . \quad (1.47)$$

Similarly, for a known concentration of acceptors N_A that introduce energy level E_A within the bandgap, the concentration of ionized acceptors is given as

$$N_A^- = \frac{N_A}{1 + 4 \cdot \exp\left(\frac{E_A - E_F}{k \cdot T}\right)} \tag{1.48}$$

The factor in front of the exponential function in the denominator of the expression (1.47) equals 2 since each donor level can accept an electron of either spin. This factor in (1.48) equals 4 because each acceptor impurity level can accept a hole of either spin and the impurity is doubly degenerate as a consequence of the two degenerate valence bands at wave vector $k = 0$ in silicon, germanium and gallium arsenide [Sze81].

At very low temperatures $E_F - E_D \gg k \cdot T$ in (1.47) and $E_A - E_F \gg k \cdot T$ in (1.48), respectively, which results in exponential functions in the denominators of the above formulas being much larger than one, and N_D^+ and N_A^- approaching zero. As the temperature increases, the exponential function diminishes and ionized impurity concentrations approach total concentrations.

Table 1.8. Ionization energies of donor and acceptor impurities in silicon [Sze68].

impurity	type	ionization energy
phosphorus, P	donor	0.045 eV
arsenic, As	donor	0.054 eV
antimony, Sb	donor	0.039 eV
boron, B	acceptor	0.045 eV

In Table 1.8 ionization energies of the most frequently used silicon impurities are given. Ionization energy is the energy necessary to free the fifth valence electron from the donor atom, or to capture the fourth electron onto the acceptor atom. Accordingly, for the case of a donor impurity ionization energy equals the distance of the donor impurity level from the top of the bandgap. For the case of an acceptor impurity it equals the distance of

the acceptor impurity level from the bottom of the bandgap (cf. Figure 1.3b and Figure 1.4b). Usually, each impurity introduces several energy levels into the bandgap. Energy levels given in Table 1.8 are the dominant ones for the corresponding impurities. Other data for silicon, as well as data for germanium and gallium arsenide can be found in [Sze68].

Problem 1.7

Derive expressions for concentrations of free carriers in a semiconductor doped with both, donor and acceptor impurities. Determine the conductivity type and calculate the concentrations of carriers in silicon at $T = 300$ K, if it is doped with:

- a) $N_A = 10^{16} \text{ cm}^{-3} \gg N_D$,
- b) $N_D = 10^{16} \text{ cm}^{-3} \gg N_A$,
- c) $N_D = N_A = 10^{16} \text{ cm}^{-3}$.

Assume that all impurities are ionized.

Solution:

From the expression for pn product (1.33)

$$n \cdot p = n_i^2$$

and from charge neutrality (1.46)

$$n + N_A^- = p + N_D^+,$$

we obtain the concentration of electrons

$$n = \frac{N_D^+ - N_A^- + \sqrt{(N_D^+ - N_A^-)^2 + 4 \cdot n_i^2}}{2}, \quad (1.49)$$

and the concentration of holes

$$p = \frac{N_A^- - N_D^+ + \sqrt{(N_A^- - N_D^+)^2 + 4 \cdot n_i^2}}{2}. \quad (1.50)$$

If all impurities are ionized, we can replace concentrations N_D^+ and N_A^- in (1.49) and (1.50) with actual concentrations N_D and N_A .

a)

For the case when $N_A > N_D$, the semiconductor is p -type, and the concentration of holes is higher than the concentration of electrons. Thus, we say that the holes are *majority carriers*, and the electrons are *minority carriers*. We calculate the concentration of majority holes by means of formula (1.50). Since at $T = 300$ K the given net impurity concentration $N_A - N_D = 10^{16} \text{ cm}^{-3}$ is much higher than the intrinsic concentration in silicon, the first component under the square root of (1.50) dominates, i.e.

$$(N_A - N_D)^2 \gg 4 \cdot n_i^2,$$

so that (1.50) is simplified to

$$p = N_A - N_D.$$

This means that the concentration of majority carriers is determined exclusively by the net concentration of impurities. Hence, in our case $p = 10^{16} \text{ cm}^{-3}$.

The concentration of minority carriers can be calculated by the use of the pn product relation (1.33)

$$n = \frac{n_i^2}{p} = \frac{n_i^2}{N_A - N_D}.$$

By entering the intrinsic carrier concentration in silicon at 300 K ($n_i = 1.38 \cdot 10^{10} \text{ cm}^{-3}$) and the above calculated concentration of majority carriers, we obtain $n = 1.90 \cdot 10^3 \text{ cm}^{-3}$.

b)

A semiconductor in which $N_D > N_A$ is of n -type; the electrons are majority carriers and the holes are minority carriers. If $N_D - N_A \gg n_i$, according to expression (1.49), the concentration of majority carriers is determined by net concentration of impurities

$$n = N_D - N_A,$$

and the concentration of minority holes is

$$p = \frac{n_i^2}{n} = \frac{n_i^2}{N_D - N_A}.$$

For the given values, we obtain $n = 10^{16} \text{ cm}^{-3}$ and $p = 1.90 \cdot 10^3 \text{ cm}^{-3}$.

Theoretically, we could calculate the concentrations of minority carriers in the above cases by means of general formulas (1.49) and (1.50). In actual calculations this should be avoided. The modulus of the first component in the nominator of the above expressions (net concentration of impurities) is often very close to the modulus of the second component (square root), and since (when calculating minority concentrations) they have opposite signs, we would have a subtraction of two numbers very close in value. Since the number of digits in our calculators is limited, this can cause a significant relative error. Moreover, if the intrinsic concentration is negligible with respect to the net concentration of impurities, the square root term can become equal to the net concentration, thus resulting in zero concentration of minority carriers.

From above results we can conclude that the type of semiconductor which is doped with both donor and acceptor impurities is determined by the impurity of higher concentration. Furthermore, if the net concentration of impurities is much higher than the intrinsic concentration, the concentration of majority carriers is determined exclusively by the net concentration of impurities. In that case, the concentration of majority carriers is much higher than the concentration of minority carriers and the semiconductor is said to be *extrinsic*.

It is interesting to notice that the concentration of minority carriers decreases if the concentration of a certain type of impurities increases. This is most easily clarified by an energy diagram of a semiconductor doped with donor impurities only, shown in Figure 1.12a. The electrons released by donor atoms will jump into the conduction band, thus establishing majority carriers. These electrons will occupy the states in the conduction band nearest to its bottom. In order to generate an electron-hole pair under these conditions, the electron from the valence band must skip not only the bandgap, but the occupied states at the bottom of the conduction band as

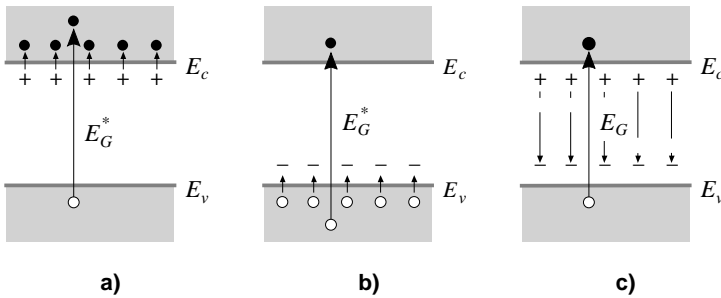


Figure 1.12. Representation of electron-hole pair generation in energy diagram: **a)** semiconductor doped only with donor impurities, **b)** semiconductor doped only with acceptor impurities, **c)** compensated semiconductor.

well. Having distribution functions of electrons in mind, we can see clearly that at a certain temperature the number of electrons that are able to surmount this larger energy difference (labeled in the figure as E_G^*) is smaller. Consequently, less electron-hole pairs will be generated, and hence a smaller number of minority carriers. When the impurity concentration is much higher than the intrinsic concentration, the number of valence electrons that can surmount the increased energy gap is negligible, so that the concentration of electrons is practically equal to the number of electrons released by donor impurities. The same applies for a semiconductor doped with acceptors only (cf. Figure 1.12b).

The decrease of minority carriers concentration can be accounted for by an increased probability of recombination with majority carriers as well. Suppose that a concentration of electron-hole pairs equal to intrinsic concentration was created. Due to a large number of majority carriers generated by impurity ionization each minority carrier will be surrounded by a large number of majority carriers. Statistically, this will increase the probability of recombination, since among a large number of majority carriers, it will be easier to find the one ready to recombine with available minority carriers (cf. chapter 1.7 *Recombination Processes*). The final result is a decrease of the minority concentration.

c)

A semiconductor doped with equal concentrations of donor and acceptor impurities is said to be *compensated*. From the charge neutrality (1.46)

$$n + N_A = p + N_D$$

follows that the concentrations of electrons and holes are equal. Furthermore, according to the *pn* product (1.33)

$$n \cdot p = n_i^2,$$

they are equal to the intrinsic concentration, i.e. $n = p = n_i$. In silicon at 300 K the intrinsic concentration is $n_i = 1.38 \cdot 10^{10} \text{ cm}^{-3}$, and the carrier concentrations asked for are the same.

Such a semiconductor is referred to as *quasi-intrinsic*; carrier concentrations correspond to intrinsic semiconductor, but some electrical properties (e.g. electrical conductivity, carrier lifetimes) are modified due to the presence of impurities.

Energy diagram in Figure 1.12c can provide an explanation as to why carrier concentrations in a completely compensated semiconductor equal the intrinsic concentration despite the impurities added. For the sake of simplicity, we shall assume that all electrons released by donor impurities will occupy acceptor states. In that case the energy difference the valence electrons have to surmount in order to jump into the conduction band is equal to the bandgap again. Consequently, the concentration of electron-hole pairs generated will equal the intrinsic concentration, just as in a pure semiconductor. Although this illustration is not completely correct (the probability of an electron in donor state jumping into a distant acceptor state is much smaller than it jumping in the nearby conduction band), due to the system symmetry, the energy balance has been preserved, and the explanation is acceptable.

Problem 1.8

Calculate the concentration of acceptor impurities and determine the type of semiconductor, if at $T = 300 \text{ K}$ the concentration of electrons is $5 \cdot 10^{11} \text{ cm}^{-3}$, and the concentration of donor impurities is 10^{15} cm^{-3} .

Solution:

At $T = 300 \text{ K}$ the intrinsic concentration in silicon is $n_i = 1.38 \cdot 10^{10} \text{ cm}^{-3}$. Since the concentration of electrons set ($n = 5 \cdot 10^{11} \text{ cm}^{-3}$) is higher than the intrinsic concentration, the electrons are majority carriers, and hence the semiconductor is of *n*-type. Therefore, the concentration of donors has to be higher than that of acceptors ($N_D > N_A$). From the *pn* product relation (1.33) and charge neutrality (1.46) we obtain

$$N_A = \frac{n_i^2}{n} - n + N_D = 9.995 \cdot 10^{14} \text{ cm}^{-3}.$$

Problem 1.9

Calculate concentrations of carriers in silicon doped by acceptors $N_A = 10^{14} \text{ cm}^{-3}$ at:

- 0 °C,
- 27 °C, and
- 175 °C.

Solution:

For the temperatures imposed we can assume that all acceptor impurities are ionized, so that the concentrations of ionized impurities are constant (i.e. independent of temperature), and equal to $N_A = 10^{14} \text{ cm}^{-3}$.

a)

At the temperature $T = 0 \text{ °C} = 273 \text{ K}$, the intrinsic concentration in silicon is

$$n_i = C \cdot T^{3/2} \cdot \exp\left(-\frac{E_{G0}}{2 \cdot E_T}\right) = 1.19 \cdot 10^9 \text{ cm}^{-3}.$$

Since the condition that $N_A \gg n_i$ is fulfilled, the concentration of majority holes is

$$p = N_A = 10^{14} \text{ cm}^{-3},$$

while the concentration of minority electrons is

$$n = \frac{n_i^2}{p} = 1.42 \cdot 10^4 \text{ cm}^{-3}.$$

b)

At the temperature $T = 27 \text{ °C} = 300 \text{ K}$, $n_i = 1.38 \cdot 10^{10} \text{ cm}^{-3}$. The concentration of impurities is still considerably higher than the intrinsic concentration ($N_A \gg n_i$), so that we can calculate concentrations of majority holes and minority electrons as

$$p = N_A = 10^{14} \text{ cm}^{-3},$$

$$n = \frac{n_i^2}{p} = 1.90 \cdot 10^6 \text{ cm}^{-3}.$$

c)

At the temperature $T = 175 \text{ °C} = 448 \text{ K}$ the intrinsic concentration is $n_i = 5.59 \cdot 10^{13} \text{ cm}^{-3}$, which is comparable to the impurity concentration. Since the condition $N_A \gg n_i$ is not fulfilled any more, we must calculate the concentration of majority carriers by the general formula (1.50)

$$p = \frac{N_A + \sqrt{N_A^2 + 4 \cdot n_i^2}}{2} = 1.25 \cdot 10^{14} \text{ cm}^{-3},$$

The concentration of minority carriers is

$$n = \frac{n_i^2}{p} = 2.50 \cdot 10^{13} \text{ cm}^{-3} .$$

The comparison of the above results shows that the increase of intrinsic concentration with temperature is followed by an increase of the concentrations of electrons and holes. Since the increase of carrier concentrations is caused exclusively by the increase of the number of thermally generated electron-hole pairs, concentrations of electrons and holes rise by the same amount! Therefore, the difference between concentrations of majority and minority carriers is constant (except for very low temperatures) and equal to the net concentration of impurities. This can be easily deduced from the charge neutrality condition

$$p - n = N_A - N_D ,$$

because N_A and N_D are independent of temperature.

The increase of thermally generated pairs causes a very steep rise of the concentration of minority carriers, since they are generated exclusively by this mechanism. At temperatures for which the intrinsic concentration is much lower than the net concentration of impurities, the increase of thermally generated carriers is negligible with respect to the concentration of majority carriers generated by impurity ionization. Therefore, the concentration of majority carriers is almost constant and equal to the net concentration of impurities. The semiconductor is extrinsic, and this temperature range is referred to as *extrinsic temperature region* (examples *a*) and *b*)). With a further temperature increase, the number of thermally generated electron-hole pairs becomes comparable to the concentration of majority carriers. Consequently, the concentration of minority carriers approaches the concentration of majority carriers. Although the difference between the concentrations of majority and minority carriers remains constant, at very high temperatures this difference vanishes in the increasing concentration of thermally generated electron-hole pairs. Toward high temperatures, concentrations of carriers get closer to the intrinsic concentration and the semiconductor enters a quasi-intrinsic state (case *c*)).

Figure 1.13a shows a plot of variation of carrier concentrations with temperature for the semiconductor being analyzed. A region of partial ionization is visible at low temperatures where thermal excitation is not strong enough to ionize all impurities. Boundaries between various temperature regions are not clearly defined. Their position depends on the net concentration of impurities and on the semiconductor material; for a higher net concentration of impurities the region of partial ionization and the extrinsic region are wider, and the semiconductor would become quasi-intrinsic at a higher temperature. This is clearly visible by comparison with Figure 1.13b in which a plot for a silicon doped with $N_A = 10^{16} \text{ cm}^{-3}$ is also given. In Figure 1.14 curves from Figure 1.13a have been

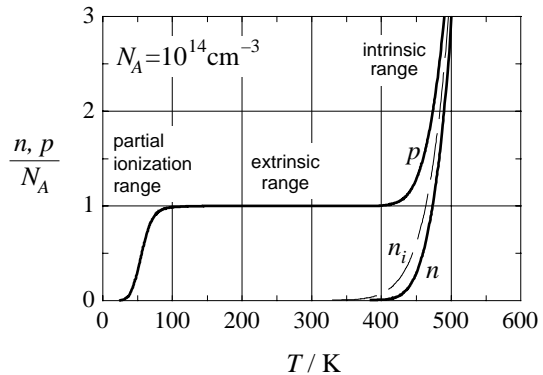


Figure 1.13a. Temperature dependence of carrier concentrations in silicon doped with $N_A = 10^{14} \text{ cm}^{-3}$.

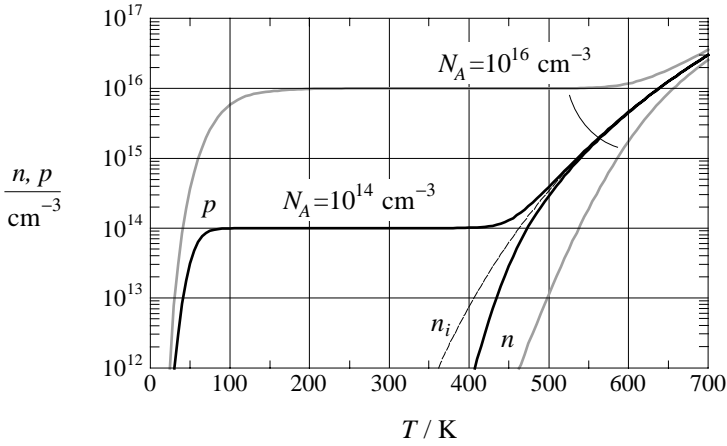


Figure 1.13b. Temperature dependence of carrier concentrations in silicon doped with $N_A=10^{14} \text{ cm}^{-3}$ and $N_A=10^{16} \text{ cm}^{-3}$ (logarithmic scale on the ordinate).

plotted again, but with a reciprocal of temperature on the abscissa and with a logarithmic scale on the ordinate. Since the intrinsic concentration is equal to the geometric mean value of the majority and minority concentrations, i.e. $n_i = (n \cdot p)^{1/2}$, in a logarithmic plots of Figures 1.13b and 1.14, the curve for intrinsic concentration lies exactly halfway between the curves for majority and minority carriers.

For intrinsic (pure) semiconductors and for completely compensated semiconductors (in which the concentration of donors equals that of acceptors), the extrinsic temperature range does not exist at all. To illustrate temperature dependence of entering the quasi-intrinsic range on net concentration, Figure 1.15 has been plotted. On the ordinate there is the *intrinsic temperature* at

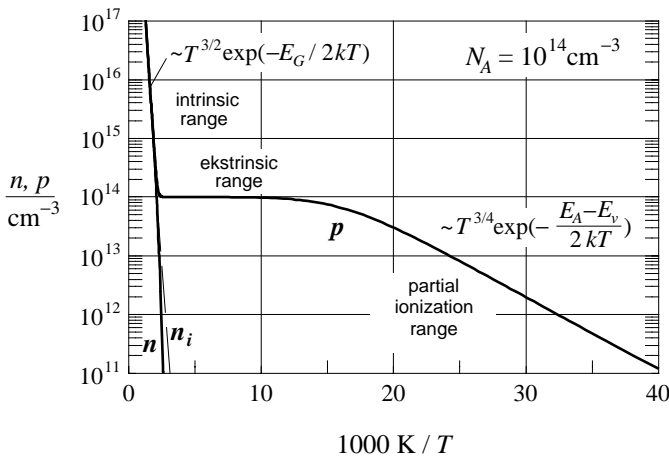


Figure 1.14. Concentrations of carriers as a function of a reciprocal of temperature.

which the intrinsic concentration is exactly equal to the net concentration of impurities. For the sake of comparison, curves for gallium arsenide and germanium are plotted in the same diagram as well. Clearly, a semiconductor with a narrower bandgap (germanium) will for a certain net concentration of impurities, enter quasi-intrinsic region at lower temperatures. This diagram clearly illustrates why electron devices made of a semiconductor with a wider bandgap have a wider temperature range of operation. It should be noted that the concentration of majority carriers in the extrinsic region is not constant. It rises with temperature as much as the concentration of minority carriers does, although this is not evident in Figures 1.13 and 1.14. However, the number of majority carriers created by thermal generation of electron-hole pairs is negligible with respect to the total concentration of majority carriers. For example, in the *b*) part of the problem, the concentration of thermally generated majority holes (equal to the concentration of minority electrons) is $1.41 \cdot 10^4 \text{ cm}^{-3}$, which is much lower than 10^{14} holes per cubic centimeter generated by ionization of acceptors.

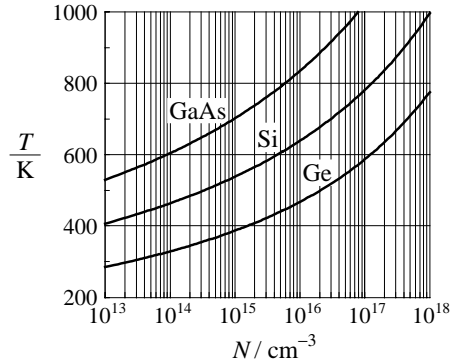


Figure 1.15. Intrinsic temperature as a function of the net concentration of impurities.

Problem 1.10

Silicon is doped by donors in concentration $N_D = 5 \cdot 10^{15} \text{ cm}^{-3}$. Calculate concentrations of electrons and holes at $T = 300 \text{ K}$, and the relative change of concentrations when the temperature rises by 1 K.

Solution:

At $T = 300 \text{ K}$ the net concentration given is much higher than the intrinsic concentration. Therefore, the concentration of majority carriers equals the concentration of donors

$$n = N_D = 5 \cdot 10^{15} \text{ cm}^{-3},$$

while the concentration of minority holes is

$$p = \frac{n_i^2}{n} = 3.81 \cdot 10^4 \text{ cm}^{-3}.$$

Let us calculate the relative increase of minority carrier concentration first. By applying a logarithm on the pn product relation

$$p = \frac{n_i^2}{n},$$

we obtain

$$\ln(p) = 2 \cdot \ln(n_i) - \ln(n).$$

The differentiation yields

$$\frac{dp}{p} = 2 \cdot \frac{dn_i}{n_i} - \frac{dn}{n}. \quad (1.51)$$

In this expression, the relative change of majority carrier concentration dn/n can be neglected, since the concentration of majority carriers is much higher than the increase of concentration of thermally generated electron-hole pairs. By the use of expression (1.42) and by substituting differentials with finite differences, we obtain

$$\frac{\Delta p}{p} = 2 \cdot \frac{\Delta n_i}{n_i} = \left(3 + \frac{E_{G0}}{k \cdot T}\right) \cdot \frac{\Delta T}{T} = 0.166 = 16.6 \% .$$

Accordingly, the concentration of minority holes has increased by

$$\Delta p = \frac{\Delta p}{p} \cdot p = 6.30 \cdot 10^3 \text{ cm}^{-3} .$$

Since the growth of minority carriers concentration is caused exclusively by the increased number of thermally generated electron-hole pairs, the concentration of majority carriers must increase by same amount. Hence,

$$\frac{\Delta n}{n} = \frac{\Delta p}{n} = 1.26 \cdot 10^{-12} = 1.26 \cdot 10^{-10} \% .$$

Although this calculation is not completely correct because we neglected the increase of majority carriers concentration in expression (1.51), the results are satisfactorily accurate. If we derived the expression for the increase of majority carriers concentrations from the general formula

$$n = \frac{N_D + \sqrt{N_D^2 + 4 \cdot n_i^2}}{2} ,$$

we would obtain

$$\frac{\Delta n}{n} = \frac{1}{n} \cdot \frac{1}{4 \cdot \sqrt{N_D^2 + 4 \cdot n_i^2}} \cdot 8 \cdot n_i \cdot \Delta n_i = \frac{2 \cdot p}{\sqrt{N_D^2 + 4 \cdot n_i^2}} \cdot \frac{\Delta n_i}{n_i} = 1.26 \cdot 10^{-12} ,$$

This is the same result as before! Of course, the previous simplified derivation is valid only in the extrinsic temperature range, i.e. as long as the concentration of majority carriers is much higher than that of minority carriers.

By comparing the increment of carrier concentrations we calculated ($\Delta p = \Delta n = 6.30 \cdot 10^3 \text{ cm}^{-3}$) with the intrinsic concentration increment

$$\Delta n_i = \frac{\Delta n_i}{n_i} \cdot n_i = \frac{1}{2} \cdot \left(3 + \frac{E_{G0}}{k \cdot T}\right) \cdot \frac{\Delta T}{T} \cdot n_i = 1.14 \cdot 10^9 \text{ cm}^{-3} ,$$

we can see that the intrinsic concentration (i.e. the concentration of carriers in intrinsic semiconductor) grows with temperature much more quickly than the concentration of carriers; this phenomenon can be easily explained by means of energy diagrams in Figure 1.12. Once inside the quasi-intrinsic temperature range, these increments will tend to become equal.

Problem 1.11* [Blakemore62]

Derive the expression for electron concentration in a n -type semiconductor, doped with both donor and acceptor impurities of concentration N_D and N_A , respectively, at very low temperatures.

Solution:

By including expressions (1.47) and (1.48) for concentrations of ionized donors and acceptor impurities, respectively

$$N_D^+ = \frac{N_D}{1 + 2 \cdot \exp\left(\frac{E_F - E_D}{k \cdot T}\right)},$$

$$N_A^- = \frac{N_A}{1 + 4 \cdot \exp\left(\frac{E_A - E_F}{k \cdot T}\right)},$$

and the expressions for electron and hole concentrations

$$n = N_c \cdot \exp\left(\frac{E_F - E_c}{k \cdot T}\right),$$

$$p = N_v \cdot \exp\left(\frac{E_v - E_F}{k \cdot T}\right),$$

into the electrical neutrality law (1.46)

$$p + N_D^+ = n + N_A^-,$$

we obtain

$$N_v \cdot \exp\left(\frac{E_v - E_F}{k \cdot T}\right) + \frac{N_D}{1 + 2 \cdot \exp\left(\frac{E_F - E_D}{k \cdot T}\right)} = N_c \cdot \exp\left(\frac{E_F - E_c}{k \cdot T}\right) + \frac{N_A}{1 + 4 \cdot \exp\left(\frac{E_A - E_F}{k \cdot T}\right)}. \quad (1.52)$$

Since the semiconductor is of n -type, the Fermi level is above the bandgap center (closer to the conduction band), so that we can neglect the exponential function in the denominator of the last component in (1.52). Actually, this means that almost all acceptor impurities are ionized, regardless of the low temperature. The concentration of holes (the first addend in the above expression) is also negligible. With these assumptions, (1.52) becomes

$$\frac{N_D}{1 + 2 \cdot \exp\left(\frac{E_F - E_D}{k \cdot T}\right)} = N_c \cdot \exp\left(\frac{E_F - E_c}{k \cdot T}\right) + N_A. \quad (1.53)$$

We separate the exponential function into two terms

$$\frac{N_D}{1 + 2 \cdot \exp\left(\frac{E_F - E_c}{k \cdot T}\right) \cdot \exp\left(\frac{E_c - E_D}{k \cdot T}\right)} = N_c \cdot \exp\left(\frac{E_F - E_c}{k \cdot T}\right) + N_A. \quad (1.54)$$

Since the ionization energy $E_D - E_c$ changes very slightly with temperature, it can be assumed constant. Therefore, for the sake of clarity, we introduce the substitutions

$$K = 2 \cdot \exp\left(\frac{E_c - E_D}{k \cdot T}\right),$$

and

$$N'_c = \frac{N_c}{K}.$$

By arranging the above expression, we obtain

$$\left[N_c \cdot \exp\left(\frac{E_F - E_c}{k \cdot T}\right) \right]^2 + (N'_c + N_A) \cdot N_c \cdot \exp\left(\frac{E_F - E_c}{k \cdot T}\right) + N'_c \cdot (N_A - N_D) = 0, \quad (1.55)$$

which is a quadratic equation for electron concentration

$$n^2 + (N'_c + N_A) \cdot n + N'_c \cdot (N_A - N_D) = 0, \quad (1.56)$$

The general solution of this equation is

$$\begin{aligned} n &= -\frac{1}{2} \cdot (N'_c + N_A) + \frac{1}{2} \cdot \sqrt{(N'_c + N_A)^2 + 4 \cdot N'_c \cdot (N_D - N_A)} = \\ &= -\frac{1}{2} \cdot (N'_c + N_A) + \frac{1}{2} \cdot \sqrt{(N'_c)^2 + N_A^2 + 2 \cdot N'_c \cdot (2 \cdot N_D - N_A)}. \end{aligned} \quad (1.57)$$

For very low temperatures $E_c - E_D \gg k \cdot T$, so that

$$K = 2 \cdot \exp\left(\frac{E_c - E_D}{k \cdot T}\right) \gg 1. \quad (1.58)$$

Thereafter, the first addend $(N'_c)^2$ under the square root of the solution (1.57) is much smaller than other terms, and can be neglected. The square root can be approximated by a few first terms of the series expansion

$$\sqrt{1+x} = 1 + \frac{1}{2} \cdot x - \frac{1}{8} \cdot x^2 + \dots, \quad |x| \leq 1,$$

In our case, considering only the first two terms of the expansion results in

$$\begin{aligned} n &= -\frac{1}{2} \cdot (N'_c + N_A) + \frac{1}{2} \cdot N_A \cdot \sqrt{1 + 2 \cdot N'_c \cdot \frac{2 \cdot N_D - N_A}{N_A^2}} \doteq \\ &= -\frac{1}{2} \cdot (N'_c + N_A) + \frac{1}{2} \cdot N_A \cdot \left(1 + N'_c \cdot \frac{2 \cdot N_D - N_A}{N_A^2} \right). \end{aligned} \quad (1.59)$$

By arranging this expression, we obtain the final expression for electron concentration

$$n = \frac{N_D - N_A}{N_A} \cdot N'_c = \frac{N_D - N_A}{N_A} \cdot N_c \cdot \exp\left(-\frac{E_c - E_D}{k \cdot T}\right). \quad (1.60)$$

This expression is valid only if $(N_c) \ll N_A$. If $N_A \ll (N_c) \ll N_D$, quadratic equation (1.56) transforms into

$$n^2 + N'_c \cdot n - N'_c \cdot N_D = 0.$$

The solution of this equation is

$$\begin{aligned} n &= -\frac{1}{2} \cdot N'_c + \frac{1}{2} \cdot \sqrt{(N'_c)^2 + 4 \cdot N'_c \cdot N_D} = \\ &= -\frac{1}{2} \cdot N'_c + \sqrt{N'_c \cdot N_D} \cdot \sqrt{1 + N'_c \cdot \frac{1}{4 \cdot N_D}}. \end{aligned} \quad (1.61)$$

By approximating the square root, we obtain

$$\begin{aligned}
 n &\doteq -\frac{1}{2} \cdot N'_c + \sqrt{N'_c \cdot N_D} + \frac{1}{8} \cdot \sqrt{N'_c \cdot \frac{1}{N_D}} \cdot N'_c = \\
 &\doteq \sqrt{N'_c \cdot N_D} = \sqrt{\frac{N_c \cdot N_D}{2}} \cdot \exp\left(-\frac{E_c - E_D}{2 \cdot k \cdot T}\right). \tag{1.62}
 \end{aligned}$$

As can be seen from equations (1.60) and (1.62), at very low temperatures the concentration of majority carriers rises exponentially with temperature. The effective density of states in pre-exponential terms changes with temperature at a much slower rate, and its influence can therefore be neglected. At higher temperatures the assumption (1.58) is not valid any more, and the concentration of majority electrons (according to (1.57)) asymptotically approaches the net concentration of impurities. When using expressions (1.60) and (1.62), one must take into consideration the assumptions introduced in the course of their derivations, i.e. the conditions that must be fulfilled for these expressions to be valid.

In Table 1.9 the concentrations of electrons at low temperatures in silicon doped with 10^{14} and 10^{16} phosphorus atoms per cubic centimeter are given. The values were obtained by the above

Table 1.9. Concentrations of majority electrons in phosphorus doped silicon at very low temperatures.

T / K	$N_D = 10^{14} \text{ cm}^{-3}$			$N_D = 10^{16} \text{ cm}^{-3}$		
	n / cm^{-3}	n^* / cm^{-3}	n^* / N_D	n / cm^{-3}	n^* / cm^{-3}	n^* / N_D
25	$1.97 \cdot 10^{11}$	$1.65 \cdot 10^{11}$	$1.65 \cdot 10^{-3}$	$1.97 \cdot 10^{12}$	$1.65 \cdot 10^{12}$	$1.65 \cdot 10^{-4}$
50	$4.54 \cdot 10^{13}$	$4.06 \cdot 10^{13}$	0.406	$5.96 \cdot 10^{14}$	$5.14 \cdot 10^{14}$	$5.14 \cdot 10^{-2}$
75	$9.59 \cdot 10^{13}$	$9.48 \cdot 10^{13}$	0.948	$3.75 \cdot 10^{15}$	$3.39 \cdot 10^{15}$	0.339
100	$9.95 \cdot 10^{13}$	$9.94 \cdot 10^{13}$	0.994	$7.30 \cdot 10^{15}$	$6.96 \cdot 10^{15}$	0.696
125	$9.99 \cdot 10^{13}$	$9.98 \cdot 10^{13}$	0.998	$8.97 \cdot 10^{15}$	$8.82 \cdot 10^{15}$	0.882
150	$1.00 \cdot 10^{13}$	$9.99 \cdot 10^{13}$	0.999	$9.56 \cdot 10^{15}$	$9.50 \cdot 10^{15}$	0.950
175	$1.00 \cdot 10^{13}$	$1.00 \cdot 10^{14}$	1.00	$9.78 \cdot 10^{15}$	$9.75 \cdot 10^{15}$	0.975
200	$1.00 \cdot 10^{13}$	$1.00 \cdot 10^{14}$	1.00	$9.87 \cdot 10^{15}$	$9.86 \cdot 10^{15}$	0.986

expressions. The ionization energy of phosphorus from Table 1.8 was used ($E_c - E_D = 0.045 \text{ eV}$). The effective density of quantum states has been calculated by means of expression

$$N_c = C'' \cdot T^{3/2},$$

(cf. chapter 1.5 *The Fermi Level*) in which $C'' = 7.33 \cdot 10^{15} \text{ K}^{-2/3} \text{ cm}^{-3}$ is an empirical constant from Table 1.7. This expression does not take into consideration the variation of effective masses with temperature, and is therefore accurate at room temperatures only. Since we are dealing with very low temperatures, effective masses of carriers differ considerably from those at room temperatures, which causes an error in the calculation of effective density of states. For the sake

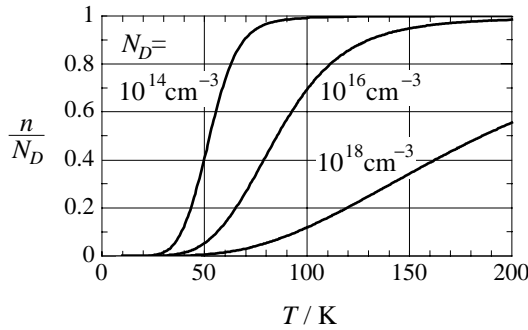


Figure 1.16. Temperature variation of electron concentration at very low temperatures.

of comparison, the concentrations of electrons n^* have been calculated which take into account the temperature variation of effective masses [Selberherr89]. As can be seen from Table 1.9, these concentrations are lower, but the relative difference is not larger than 20 %. The results from Table 1.9 have been plotted in Figure 1.16. It is evident that for higher impurity concentrations the region of partial ionization is wider; at $T = 200$ K for example, for $N_D = 10^{14} \text{ cm}^{-3}$ almost all donors are ionized, whereas for $N_D = 10^{16} \text{ cm}^{-3}$ 98.6 % of donors are ionized. This phenomenon can most easily be explained by means of energies necessary for an electron to skip from donor state into the conduction band (cf. Figure 1.12). In a lightly doped semiconductor, it is sufficient for an electron to gain energy $E_c - E_D$ in order to skip from a donor state into the conduction band. As doping is increased, the bottommost states in the conduction band will be filled with electrons generated by impurity ionization, so that in a semiconductor with a high impurity concentration, some electrons in the donor states must gain much larger energies to jump into the conduction band. An electron can gain such an energy only at higher temperatures.

For larger impurity concentrations the derived formulas would give a still lower percentage of ionized impurities. For example, for $N_D = 10^{18} \text{ cm}^{-3}$ we would obtain that at 300 K only 80 % of donors are ionized (for illustration sake, in Figure 1.16 the curve for this concentration has also been plotted). However, at such a high impurity concentration discrete donor levels split into an energy band, which at a still higher doping level merges with the conduction band, thus causing the ionization energy to be ambiguous (cf. chapter 1.10 *Heavy-Doping Effects*).

Similar results can be obtained for a p -type silicon as well, and were used to plot curves in Figures 1.13 and 1.14 in the region of incomplete ionization.

Problem 1.12

Neglecting the change of pre-exponential term $T^{3/2}$, estimate by how much the temperature has to be increased above 300 K for the intrinsic temperature to be doubled.

Solution: $\Delta T = 9.19 \text{ }^\circ\text{C}$.

Problem 1.13

Calculate the concentration of donors to be added to silicon, so that at $T = 300$ K the concentration of electrons is twice as high as the concentration of holes.

Solution: $N_D = 9.76 \cdot 10^9 \text{ cm}^{-3}$.

Problem 1.14

Determine the type and net concentration of impurities by which silicon has to be doped, so that at $T = 400$ K it contains $2 \cdot 10^{12}$ free electrons per cubic centimeter.

Solution: $N_{A_{net}} = 2.41 \cdot 10^{13} \text{ cm}^{-3}$.

Problem 1.15

Silicon has been doped by 10^{14} acceptor atoms per cubic centimeter. Determine the type and the concentration of impurity to be added, so that at $T = 300$ K:

- a) the concentration of electrons is twice as high as before the second doping process;
- b) the concentration of electrons is five times lower than before the second doping process;
- c) the concentration of electrons is four times lower than the concentration of holes before the second doping process.

Solutions: a) $N_D = 5 \cdot 10^{13} \text{ cm}^{-3}$, b) $N_A = 4 \cdot 10^{14} \text{ cm}^{-3}$, c) $N_D = 1.25 \cdot 10^{14} \text{ cm}^{-3}$.