

**Figure 6.2:** The bonding model for c-Si. (a) No bonds are broken. (b) A bond between two Si atoms is broken resulting in a free electron and hole.

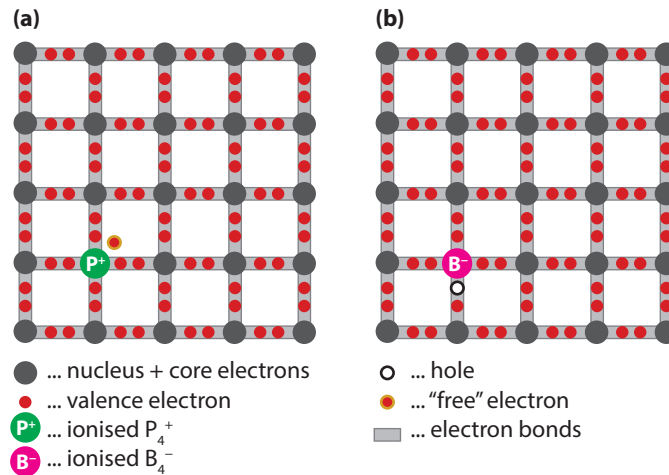
### 6.3 Doping

The concentrations of electrons and holes in c-Si can be manipulated by *doping*. Doping of silicon means that atoms of other elements substitute Si atoms in the crystal lattice. The substitution has to be carried out by atoms with three or five valence electrons, respectively. The most used elements to dope c-Si are boron (B) and phosphorus (P), with atomic numbers of 5 and 15, respectively.

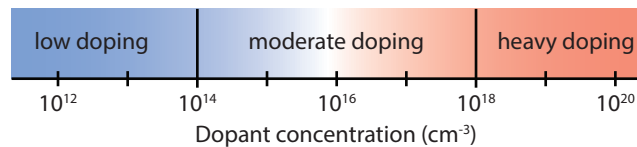
The process of doping action can best be understood with the aid of the bonding model and is illustrated in Fig. 6.3. When introducing a phosphorus atom into the c-Si lattice, four of the five phosphorus atom valence electrons will readily form bonds with the four neighbouring Si atoms. The fifth valence electron cannot take part in forming a bond and becomes rather weakly bound to the phosphorus atom. It is easily liberated from the phosphorus atom by absorbing the thermal energy, which is available in the c-Si lattice at room temperature. Once free, the electron can move throughout the lattice. In this way the phosphorus atom that substitutes a Si atom in the lattice “*donates*” a free (mobile) electron into the c-Si lattice. The impurity atoms that enhance the concentration of electrons are called *donors*. We denote the concentration of donors by  $N_D$ .

An atom with three valence electrons such as boron cannot form all bonds with four neighbouring Si atoms when it substitutes a Si atom in the lattice. However, it can readily “*accept*” an electron from a nearby Si-Si bond. The thermal energy that the c-Si lattice contains at room temperature is sufficient to enable an electron from a nearby Si-Si bond to attach itself to the boron atom and complete the bonding to the four Si neighbours. In this process a hole is created that can move around the lattice. The impurity atoms that enhance the concentration of holes are called *acceptors*. We denote the concentration of acceptors by  $N_A$ .

Note that by substituting Si atoms with only one type of impurity atoms, the concentration of only one type of mobile charge carriers is increased. Charge neutrality of the



**Figure 6.3:** The doping process illustrated using the bonding model. (a) A phosphorus (P) atom substitutes a Si atom in the lattice resulting in the positively-ionised P atom and a free electron, (b) A boron (B) atom substitutes a Si atom resulting in the negatively ionised B atom and a hole.



**Figure 6.4:** The range of doping levels used in c-Si.

material is nevertheless maintained because the sites of the bonded and thus fixed impurity atoms become charged. The donor atoms become positively ionised and the acceptor atoms become negatively ionised.

The possibility to control the electrical conductivity of a semiconductor by doping is one of the most important semiconductor features. The electrical conductivity in semiconductors depends on the concentration of electrons and holes as well as their mobility. The concentration of electrons and holes is influenced by the amount of the doping atoms that are introduced into the atomic structure of the semiconductor. Figure 6.4 shows the range of doping that is used in case of c-Si. We denote a semiconductor as *p*-type or *n*-type when holes or electrons, respectively, dominate its electrical conductivity. In case that one type of charge carriers has a higher concentration than the other type these carriers are called majority carriers (holes in the *p*-type and electrons in the *n*-type), while the other type with lower concentration are then called minority carriers (electrons in the *p*-type and holes in the *n*-type).

## 6.4 Carrier concentrations

### 6.4.1 Intrinsic semiconductors

Any operation of a semiconductor device depends on the concentration of carriers that transport charge inside the semiconductor and hence cause electrical currents. In order to determine and to understand device operation it is important to know the precise concentration of these charge carriers. In this section the concentrations of charge carriers inside a semiconductor are derived assuming the semiconductor is under *thermal equilibrium*. The term equilibrium is used to describe the unperturbed state of a system, to which no external voltage, magnetic field, illumination, mechanical stress, or other perturbing forces are applied. In the equilibrium state the observable parameters of a semiconductor do not change with time.

In order to determine the carrier concentration one has to know the function of density of allowed energy states of electrons and the occupation function of the allowed energy states. The density of energy states function,  $g(E)$ , describes the number of allowed states per unit volume and energy. Usually it is abbreviated with *Density of states* function (DoS). The occupation function is the Fermi-Dirac distribution function,  $f(E)$ , which describes the ratio of states filled with an electron to total allowed states at given energy  $E$ . In an isolated Si atom, electrons are allowed to have only discrete energy values. The periodic atomic structure of single crystal silicon results in the ranges of allowed energy states for electrons that are called *energy bands* and the excluded energy ranges, forbidden gaps or *band gaps*. Electrons that are liberated from the bonds determine the charge transport in a semiconductor. Therefore, we further discuss only those bands of energy levels, which concern the valence electrons. Valence electrons, which are involved in the covalent bonds, have their allowed energies in the *valence band* (VB) and the allowed energies of electrons liberated from the covalent bonds form the *conduction band* (CB). The valence band is separated from the conduction band by a band of forbidden energy levels. The maximum attainable valence-band energy is denoted  $E_V$ , and the minimum attainable conduction-band energy is denoted  $E_C$ . The energy difference between the edges of these two bands is called the band gap energy or band gap,  $E_g$ , and it is an important material parameter.

$$E_g = E_C - E_V. \quad (6.1)$$

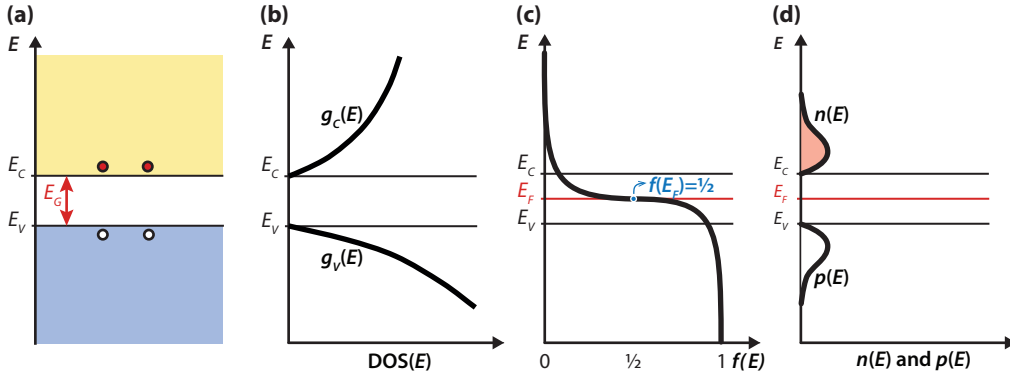
At room temperature (300 K), the band gap of crystalline silicon is 1.12 eV. A plot of the allowed electron energy states as a function of position is called the energy band diagram; an example is shown in Fig. 6.5 (a).

The density of energy states at an energy  $E$  in the conduction band close to  $E_C$  and in the valence band close to  $E_V$  are given by

$$g_C(E) = 4\pi \left( \frac{2m_n^*}{h^2} \right)^{\frac{3}{2}} \sqrt{E - E_C}, \quad (6.2a)$$

$$g_V(E) = 4\pi \left( \frac{2m_p^*}{h^2} \right)^{\frac{3}{2}} \sqrt{E - E_V}, \quad (6.2b)$$

where  $m_n^*$  and  $m_p^*$  is the *effective mass* of electrons and holes, respectively. As the electrons and holes move in the periodic potential of the c-Si crystal, the mass has to be replaced



**Figure 6.5:** (a) The basic energy band diagram with electrons and holes indicated in the conduction and valence bands, respectively. (b) The density of states (DOS) functions  $g_C$  in the conduction band and  $g_V$  in the valence band. (c) The Fermi-Dirac distribution. (d) The electron and hole densities in the conduction and valence bands, respectively, obtained by combining (b) and (c).

by the effective mass, which takes the effect of a periodic force into account. The effective mass is also averaged over different directions to take anisotropy into account. Both  $g_C$  and  $g_V$  have a parabolic shape, which is also illustrated in Fig. 6.5 (b).

The Fermi-Dirac distribution function is given by

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}, \quad (6.3)$$

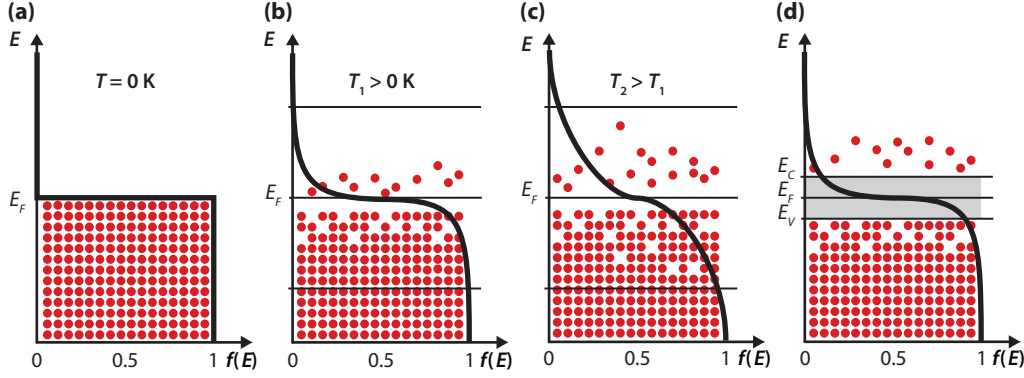
where  $k_B$  is Boltzmann's constant ( $k_B = 1.38 \times 10^{-23}$  J/K) and  $E_F$  is the so-called *Fermi energy*.  $k_B T$  is the *thermal energy*, at 300 K it is 0.0258 eV. The Fermi energy — also called *Fermi level* — is the electrochemical potential of the electrons in a material and in this way it represents the averaged energy of electrons in the material. The Fermi-Dirac distribution function is illustrated in Fig. 6.5 (c). Figure 6.6 illustrates the Fermi-Dirac distribution at different temperatures.

The carriers that contribute to charge transport are electrons in the conduction band and holes in the valence band. The concentration of electrons in the conduction band and the total concentration of holes in the valence band is obtained by multiplying the density of states function with the distribution function and integrating across the whole energy band, as illustrated in Fig. 6.5 (d).

$$n(E) = g_C(E)f(E), \quad (6.4a)$$

$$p(E) = g_V(E)[1 - f(E)]. \quad (6.4b)$$

The total concentration of electrons and holes in the conduction band and valence band,



**Figure 6.6:** The Fermi-Dirac distribution function. (a) For  $T = 0$  K, all allowed states below the Fermi level are occupied by two electrons. (b, c) At  $T > 0$  K not all states below the Fermi level are occupied and there are some states above the Fermi level that are occupied. (d) In an energy gap between bands no electrons are present.

respectively, is then obtained via integration,

$$n = \int_{E_C}^{E_{\text{top}}} n(E) dE, \quad (6.5a)$$

$$p = \int_{E_{\text{bottom}}}^{E_V} p(E) dE. \quad (6.5b)$$

Substituting the density of states and the Fermi-Dirac distribution function into Eq. (6.5) the resulting expressions for  $n$  and  $p$  are obtained after solving the equations. The full derivation can be found for example in Reference [24].

$$n = N_C \exp\left(\frac{E_F - E_C}{k_B T}\right) \quad \text{for} \quad E_C - E_F \geq 3k_B T, \quad (6.6a)$$

$$p = N_V \exp\left(\frac{E_V - E_F}{k_B T}\right) \quad \text{for} \quad E_F - E_V \geq 3k_B T, \quad (6.6b)$$

where  $N_C$  and  $N_V$  are the *effective* densities of the conduction band states and the valence band states, respectively. They are defined as

$$N_C = 2 \left( \frac{2\pi m_n^* k_B T}{h^2} \right)^{\frac{3}{2}} \quad \text{and} \quad N_V = 2 \left( \frac{2\pi m_p^* k_B T}{h^2} \right)^{\frac{3}{2}} \quad (6.7)$$

For crystalline silicon, we have at 300 K

$$N_C = 3.22 \times 10^{19} \text{ cm}^{-3}, \quad (6.8a)$$

$$N_V = 1.83 \times 10^{19} \text{ cm}^{-3}. \quad (6.8b)$$

When the requirement that the Fermi level lies in the band gap more than  $3k_B T$  from either band edge is satisfied the semiconductor is referred to as a *nondegenerate* semiconductor.

If an intrinsic semiconductor is in equilibrium, we have  $n = p = n_i$ . By multiplying the corresponding sides of Eqs. (6.6) we obtain

$$np = n_i^2 = N_C N_V \exp\left(\frac{E_V - E_C}{k_B T}\right) = N_C N_V \exp\left(-\frac{E_g}{k_B T}\right), \quad (6.9)$$

which is independent of the position of the Fermi level and thus valid for doped semiconductors as well. When we denote the position of the Fermi level in the intrinsic material  $E_{Fi}$  we may write

$$n_i = N_C \exp\left(\frac{E_{Fi} - E_C}{k_B T}\right) = N_V \exp\left(\frac{E_V - E_{Fi}}{k_B T}\right). \quad (6.10)$$

From Eq. (6.10) we can easily find the position of  $E_{Fi}$  to be

$$E_{Fi} = \frac{E_C + E_V}{2} + \frac{k_B T}{2} \ln\left(\frac{N_V}{N_C}\right) = E_C - \frac{E_g}{2} + \frac{k_B T}{2} \ln\left(\frac{N_V}{N_C}\right). \quad (6.11)$$

The Fermi level  $E_{Fi}$  lies close to the midgap  $[(E_C + E_V)/2]$ ; a slight shift is caused by the difference in the densities of the valence and conduction band.

### 6.4.2 Doped semiconductors

It has been already mentioned in Section 6.3 that the concentrations of electrons and holes in c-Si can be manipulated by doping. The concentration of electrons and holes is influenced by the amount of the impurity atoms that substitute silicon atoms in the lattice. Under the assumption that the semiconductor is uniformly doped and in equilibrium a simple relationship between the carrier and dopant concentrations can be established. We assume that at room temperature the dopant atoms are ionised. Inside a semiconductor the local charge density is given by

$$\rho = q(p + N_D^+ - n - N_A^-), \quad (6.12)$$

where  $q$  is the elementary charge ( $q \approx 1.602 \times 10^{-19}$  C).  $N_D^+$  and  $N_A^-$  denote the density of the *ionised donor and acceptor* atoms, respectively. As every ionised atom corresponds to a free electron (hole),  $N_D^+$  and  $N_A^-$  tell us the concentration of electrons and holes due to doping, respectively.

Under equilibrium conditions, the local charge of the uniformly doped semiconductor is zero, which means that the semiconductor is charge-neutral everywhere. We thus can write:

$$p + N_D^+ - n - N_A^- = 0. \quad (6.13)$$

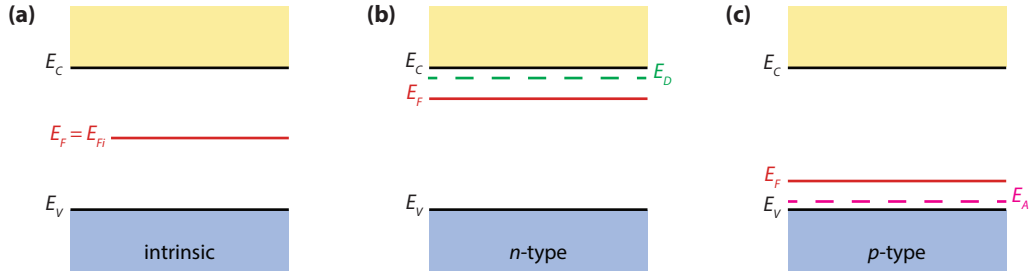
As previously discussed, the thermal energy available at room temperature is sufficient to ionise almost all the dopant atoms. We therefore may assume

$$N_D^+ \approx N_D \quad \text{and} \quad N_A^- \approx N_A, \quad (6.14)$$

and hence

$$p + N_D - n - N_A = 0, \quad (6.15)$$

which is the common form of the *charge neutrality equation*.



**Figure 6.7:** A shift of the position of the Fermi energy in the band diagram and the introduction of the allowed energy level into the bandgap due to the doping.

Let us now consider an  $n$ -type material. At room temperature almost all donor atoms  $N_D$  are ionised and donate an electron into the conduction band. Under the assumption that  $N_A = 0$ , Eq. (6.15) becomes

$$p + N_D - n = 0, \quad (6.16)$$

Further, assuming that

$$N_D \approx N_D^+ \approx n, \quad (6.17)$$

we can expect that the concentration of holes is lower than that of electrons, and becomes very low when  $N_D$  becomes very large. From Eq. (6.9), we can calculate the concentration of holes in the  $n$ -type material more accurately,

$$p = \frac{n_i^2}{n} \approx \frac{n_i^2}{N_D} \ll n. \quad (6.18)$$

In case of a  $p$ -type material almost all acceptor atoms  $N_A$  are ionised at room temperature. Therefore, they accept an electron and leave a hole in the valence band. Under the assumption that  $N_D = 0$ , Eq. (6.15) becomes

$$p - n - N_A = 0. \quad (6.19)$$

Further, when assuming that

$$N_A \approx N_A^- \approx p, \quad (6.20)$$

we can expect that the concentration of electrons is lower than that of holes. From Eq. (6.9), we can calculate the concentration of electrons in the  $p$ -type material more accurately,

$$n = \frac{n_i^2}{p} \approx \frac{n_i^2}{N_A} \ll p. \quad (6.21)$$

Inserting donor and acceptor atoms into the lattice of crystalline silicon introduces allowed energy levels into the forbidden bandgap. For example, the fifth valence electron of the P atom does not take part in forming a bond, is rather weakly bound to the atom and is easily liberated from the P atom. The energy of the liberated electron lies in the CB. The energy levels, which we denote  $E_D$ , of the weakly-bound valence electrons of the donor atoms have to be positioned close to the CB. Note that a dashed line represents the  $E_D$ . This means that an electron, which occupies the  $E_D$  level, is localised in the vicinity of the

donor atom. Similarly, the acceptor atoms introduce allowed energy levels  $E_A$  close to the VB.

Doping also influences the position of the Fermi energy. When we increase the electrons concentration by increasing the donor concentration the Fermi energy will increase, which is represented by bringing the Fermi energy closer to the CB in the band diagram. In the  $p$ -type material the Fermi energy is moved closer to the VB. A change in the Fermi-energy position and the introduction of the allowed energy level into the bandgap due to the doping is illustrated Fig. 6.7.

The position of the Fermi level in an  $n$ -type semiconductor can be calculated with Eqs. (6.6a); in a  $p$ -type semiconductor Eqs. (6.6b) and (6.20) can be used:

$$E_C - E_F = k_B T \ln \left( \frac{N_C}{N_D} \right) \quad \text{for } n\text{-type}, \quad (6.22a)$$

$$E_F - E_V = k_B T \ln \left( \frac{N_V}{N_A} \right) \quad \text{for } p\text{-type}. \quad (6.22b)$$

### Example

*This example demonstrates how much the concentration of electrons and holes can be manipulated by doping. A c-Si wafer is uniformly doped with  $1 \times 10^{17} \text{ cm}^{-3}$  P atoms. P atoms act as donors and therefore at room temperature the concentration of electrons is almost equal to the concentration of donor atoms:*

$$n = N_D^+ \approx N_D = 10^{17} \text{ cm}^{-3}.$$

*The concentration of holes in the  $n$ -type material is calculated from Eq. (6.17),*

$$p = \frac{n_i^2}{n} = \frac{(1.5 \times 10^{10})^2}{10^{17}} = 2.25 \times 10^3 \text{ cm}^{-3}.$$

*We notice that there is a difference of 14 orders of magnitude between  $n$  ( $10^{17} \text{ cm}^{-3}$ ) and  $p$  ( $2.25 \times 10^3 \text{ cm}^{-3}$ ). It is now obvious why electrons in  $n$ -type materials are called the majority carriers and holes the minority carriers. We can calculate the change in the Fermi energy due to the doping. Let us assume that the reference energy level is the bottom of the conduction band,  $E_C = 0 \text{ eV}$ . Using Eq. (6.11) we calculate the Fermi energy in the intrinsic c-Si.*

$$E_{Fi} = E_C - \frac{E_g}{2} + \frac{k_B T}{2} \ln \left( \frac{N_V}{N_C} \right) = -\frac{1.12}{2} + \frac{0.0258}{2} \ln \left( \frac{1.83 \times 10^{19}}{3.22 \times 10^{19}} \right) = -0.57 \text{ eV}.$$

*The Fermi energy in the  $n$ -type doped c-Si wafer is calculated from Eq. (6.6a)*

$$E_F = E_C + k_B T \ln \left( \frac{n}{N_C} \right) = 0.0258 \times \ln \left( \frac{10^{17}}{3.22 \times 10^{19}} \right) = -0.15 \text{ eV}.$$

*We notice that the doping with P atoms has resulted in the shift of the Fermi energy towards the CB. Note that when  $n > N_C$ ,  $E_F > E_C$  and the Fermi energy lies in the CB.*