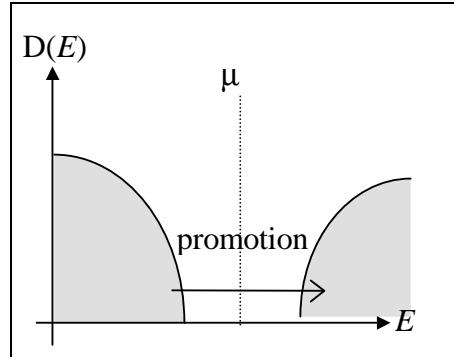


Semiconductors

Basic introduction

Materials with a filled valence band and a bandgap of less than 3eV (practical semiconductors usually have band-gaps of about 1eV) can have populations of electrons and holes from thermal excitations. In this case, carriers in both the upper and lower bands can contribute to current flow. This is an *intrinsic semiconductor*. The most important elemental semiconductors are in Group IV (Si, Ge). Also of great importance are the III-V compounds (GaAs, InP, GaP)



and some II-VI (ZnSe). Many other compounds, particularly oxides, show semiconducting behaviour. If we *dope* materials with impurities, we can produce an *extrinsic semiconductor*. In a *p-type* semiconductor, the impurities have energy levels that are in the band gap just above the filled band (*acceptor states*). Electrons can be excited into these states, leaving an unfilled band that can now conduct. In an *n-type* semiconductor, the impurities have energy levels that are in the band gap just below the empty band (*donor states*). Electrons can be excited out of these states into the upper band, and this can now conduct.

Consider an electron near the top of the lower (valence) band. The steady state drift velocity is given by $v_D = -\tau F / m^*$ where m^* is the effective mass of the unfilled state. This will be negative (since it is at the top of the band), $-m_h$, say, and so $v_D = \tau F / m_h$. If the force in question is an electric field, $F = -eE$, the current density, j , (defined as charge motion per unit volume) is

$$j = -ev_D / V = -e^2 \tau E / V m_h$$

where V is the volume. Now, the current density provided by a band that is complete except for this electron is the opposite of this. In fact the nearly filled band acts as though it were a positively charged particle of mass m_h . We thus consider the nearly-filled band as a *hole* and the promotion of an electron from the valence band to the conduction band as the creation of an electron-hole pair. The transport equations are

$$m_h \left(\frac{dv_{Dh}}{dt} + \frac{v_{Dh}}{\tau} \right) = eE \quad \text{for the hole and} \quad m_e \left(\frac{dv_{De}}{dt} + \frac{v_{De}}{\tau} \right) = -eE \quad \text{for the electron.}$$

m_e and m_h are the effective masses of the electron and hole respectively. The total current is the sum of the electron and hole currents

$$j = j_e + j_h = en_h v_{Dh} - en_e v_{De} = \sigma E$$

where n_e , n_h are the densities of electrons and holes respectively. We can also define *mobilities* as $\mu_h = e\tau/m_h$, $\mu_e = e\tau/m_e$. Note also that if $n_e \ll n_h$, the Hall coefficient is given by $R_H = 1/n_h e$ and is therefore positive.

Intrinsic semiconductors: detailed treatment.

Intrinsic semiconductors have a finite population of thermally-excited electrons in the conduction band. This means that the Fermi level (i.e. the chemical potential of the electrons μ) is somewhere in the gap. Note the distinction between the chemical potential and the Fermi energy, which is the highest energy level filled when temperature is ignored; i.e. the chemical potential at absolute zero). If the energy of the conduction band is E_C , we can write the number of electrons in the conduction band ($n_e V$ where n_e is the density of electrons and V the volume) as

$$n_e V = \int_{E_C}^{\infty} D(E) f_{FD}(E) dE \quad (1)$$

where $f_{FD}(E)$ is the Fermi-Dirac distribution function. If the chemical potential is significantly below the conduction band (several $k_B T$), then we can approximate the function as

$$f_{FD}(E) = \left(\exp[(E - \mu) / k_B T] + 1 \right)^{-1} \approx \exp[-(E - \mu) / k_B T] \quad (2)$$

Also, the shape of the bottom of the conduction band. Hence the energy relation for electrons at the bottom of the conduction band can be written as

$$E = E_C + \hbar^2 k^2 / 2m_e \quad (3)$$

The densities of states are as for the free-electron case except that the energy zero is either the bottom of the conduction band rather than the zero of potential. Thus the density of states for the conduction band is

$$D(E) = D(E - E_C) = \frac{m_e V}{\pi^2 \hbar^3} \sqrt{2m_e (E - E_C)} \quad (4)$$

Hence for the conduction band,

$$n_e V = \int_{E_C}^{\infty} D(E - E_C) \exp[-(E - \mu) / k_B T] dE \quad (5)$$

and, putting in the formula for the density of states, we get

$$n_e = \int_{E_C}^{\infty} \frac{(2m_e)^{3/2}}{2\pi^2 \hbar^3} (E - E_C)^{1/2} \exp[-(E - \mu) / k_B T] dE \quad (6)$$

We can solve this by some creative substitution; Let $y^2 = (E - E_C) / k_B T$. Then

$$\begin{aligned} n_e &= \frac{(2m_e k_B T)^{3/2}}{\pi^2 \hbar^3} \exp[-(E_C - \mu) / k_B T] \int_0^{\infty} y^2 \exp(-y^2) dy \\ &= \frac{1}{4} \left(\frac{2m_e k_B T}{\pi \hbar^2} \right)^{3/2} \exp[-(E_C - \mu) / k_B T] \end{aligned} \quad (7)$$

getting the integral from standard tables. $\int_0^{\infty} y^2 \exp(-y^2) dy = \pi^{1/2} / 4$

A similar argument gives the number of holes in the valence band. We now want the density of states for the holes, and we also require $(1 - f_{FD}(E))$ rather than $f_{FD}(E)$ since we want the probability of the absence of an electron. Therefore,

$$n_h V = \int_0^{R_V} D(E) (1 - f_{FD}(E)) dE \quad (8)$$

where the limits are taken over the valence band. If the chemical potential is several $k_B T$ above the valence band, $(1 - f_{FD}(E)) \approx \exp[(E - \mu) / k_B T]$. If the top of the valence band is approximately parabolic, (i.e. the energy of an electron at the top of the

valence band is given by $E = E_V - \hbar^2 k^2 / 2m_h$) then, referring the energy zero to the top of the valence band, we have

$$D(E) = D(E_V - E) = \frac{m_h V}{\pi^2 \hbar^3} \sqrt{2m_h (E_V - E)} \quad (9)$$

and therefore, substituting all this in,

$$n_h V = \int_0^{E_V} \frac{(2m_h)^{3/2}}{2\pi^2 \hbar^3} (E_V - E)^{1/2} \exp[(E - \mu)/k_B T] dE \quad (10)$$

and setting $y^2 = (E_V - E) / k_B T$ we get

$$n_h = \frac{1}{4} \left(\frac{2m_h k_B T}{\pi \hbar^2} \right)^{3/2} \exp[(E_V - \mu) / k_B T] \quad (11)$$

We can proceed further since we know that this thermal creation must produce pairs of electrons and holes, hence $n_e = n_h$. Hence, equating the two expressions, we can find out the value of the chemical potential of the electrons $\mu(T)$. This is given by

$$\mu(T) = (E_C + E_V)/2 + (3/4)k_B T \ln(m_h/m_e) \quad (12)$$

and lies near the middle of the gap (usually the second term is small) as shown in the diagram at the beginning of this section.

We can also obtain the product of the carrier concentrations. This is given by

$$n_e n_h = \frac{1}{2} \left(\frac{k_B T}{\pi \hbar^2} \right)^3 (m_e m_h)^{3/2} \exp(-E_g / k_B T) \quad (13)$$

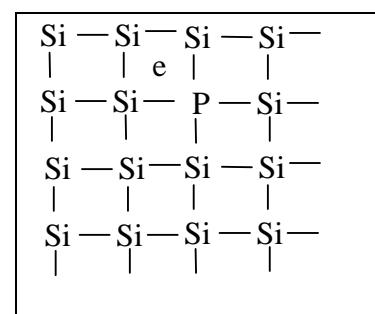
where $E_g = E_C - E_V$ is the band gap. Note that this result is independent of the chemical potential and is, in fact, an expression of the law of mass action. You can treat the problem as though it were a chemical reaction and electrons and holes were chemical species. If $n_e = n_h$ (as in the case of electron-hole pairs produced by thermal excitation), then the equation gives the intrinsic carrier density. For silicon, at room temperature, this gives $2 \times 10^{16} \text{ m}^{-3}$. This is much less than for a typical metal (10^{28} m^{-3}).

This also implies that the thermal conductivity in an intrinsic semiconductor shows an approximate Arrhenius behaviour (the mobilities do vary with temperature but the effect is small compared to the effect of the carrier concentrations).

Extrinsic semiconductors

Another way of obtaining electrons in the conduction band (or holes in the valence band) is to dope the pure semiconductor with impurities.

For example, if we dope silicon with small quantities of a group V element like phosphorus, the phosphorus displaces the silicon from its site. The effect is to add an extra electron - and an extra positive charge (see the diagram of a segment of the Si lattice on the right. It is shown as you would see it looking down the a axis of the structure - all the connections are correct but not all the atoms are in the same plane). The extra electron is weakly bound to the phosphorus and at room temperatures it is easily excited into the conduction band. This impurity has *donated* an electron from a *donor state*. The



density of electrons in the conduction band is thus equal to the density of donors (plus any thermally excited electrons). If the density of donors is much greater than the intrinsic density, $N_D \gg n_i$ then clearly $n_e = N_D$. However, the result for n_e derived for the intrinsic case still remains true. Let us rewrite this (equation 7) as an equation for the chemical potential and set $n_e = N_D$

$$\mu = E_C - k_B T \ln \left(\frac{1}{4N_D} \left\{ \frac{2m_e k_B T}{\pi \hbar^2} \right\}^{3/2} \right) \quad (11)$$

For typical donor levels (N_D about 10^{22} m^{-3} or one dopant atom in 10^6) this gives the chemical potential as several $k_B T$ (0.1-0.2eV at 1000K) below the conduction band (i.e. far above the midpoint). Also, by the standard mass-action effect, we know we will have a negligible concentration of holes (since $n_e n_h = n_i^2$). Thus the conductivity is dominated by negative charge carriers; the system is called an *n-type semiconductor*.

If on the other hand, we dope silicon with a group III element like boron, we get the opposite effect. Boron also displaces silicon from its site, but now it is one electron short of forming the four tetrahedral bonds of the structure. In effect, we have added a hole. Also, we have, in effect, added a negative static charge; the valence state of boron is three, one less than silicon. At zero temperature, this hole is bound to the boron atom, but at room temperature it enters the valence band (or equivalently, an electron from the valence band is promoted into the localised state just above the valence band created by the presence of the boron atom). Boron is an *acceptor impurity*; the state is called an *acceptor state*. Again, for normal doping levels, the number of holes is determined by the number of acceptors, N_A . Thus $n_h = N_A$. Again, we can use the results for the intrinsic case to write an expression for the chemical potential in terms of the hole density

$$\mu = E_V + k_B T \ln \left(\frac{1}{4N_A} \left\{ \frac{2m_h k_B T}{\pi \hbar^2} \right\}^{3/2} \right) \quad (12)$$

and we find that this time, the chemical potential is a few $k_B T$ above the valence band. Again, by mass-action the number of electrons in the conduction band is reduced to negligible amounts and the conductivity is controlled by the positively-charged holes. The material is called a *p-type semiconductor*.

