

# Intrinsic carrier concentration in semiconductors

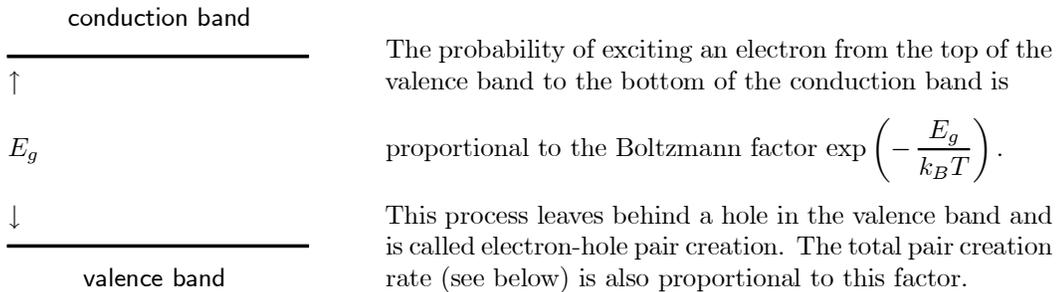
Melissinos, eq.(1.4), gives the formula, valid at thermal equilibrium,

$$n_i = N_s \exp\left(-\frac{E_g}{2k_B T}\right) \tag{1}$$

where,

- $n_i$  is the intrinsic carrier concentration, i.e., the number of electrons in the conduction band (and also the number of holes in the valence band) per unit volume in a semiconductor that is completely free of impurities and defects
- $N_s$  is the number per unit volume of effectively available states; its precise value depends on the material, but it is of order  $10^{19} \text{ cm}^{-3}$  at room temperature and increases with temperature
- $E_g$  is the energy gap (between the bottom of the conduction band and the top of the valence band)
- $k_B$  is Boltzmann's constant,  $k_B = 1.381 \cdot 10^{-23}$  Joules/Kelvin
- $T$  is the absolute temperature in Kelvin; it is assumed that  $k_B T \lesssim E_g/5$ .

The physical basis of eq. (1) can be understood as follows:



At thermal equilibrium, the creation of electron-hole pairs is balanced by their recombination. If  $n$  is the concentration of conduction-band electrons and  $p$  the concentration of valence-band holes, the electron-hole recombination rate is proportional to the product  $np$ , according to the general *law of mass action* of chemical physics. Equating creation to recombination, we conclude that

$$np = K \exp\left(-\frac{E_g}{k_B T}\right) \tag{2}$$

where  $K$  is a proportionality factor. In an *intrinsic semiconductor*, by definition,  $n = p = n_i$ . Then eq. (2) is equivalent to eq. (1) with  $K = N_s^2$ .

To compute  $N_s$ , we must compute the total pair creation rate. We recognize that an electron can make a transition from any state in the valence band to any state in the conduction band and we integrate over all these possible transitions, with a weighting factor to account for the

fact that the most likely transitions are from states near the top of the valence band to states near the bottom of the conduction band. When this is done one finds, to a good approximation,

$$N_s = 2 \left( \frac{m^* k_B T}{2\pi\hbar^2} \right)^{3/2} = \left( \frac{m^*}{m} \right)^{3/2} \left( \frac{T}{300 \text{ K}} \right)^{3/2} \frac{2.5 \cdot 10^{19}}{\text{cm}^3} \quad (3)$$

where  $m^*$  is an effective mass that is of the order of the electron mass  $m$  (for Si,  $m^*/m = 0.543$ ).

$N_s$  increases with temperature because higher states in the conduction band, and deeper states in the valence band, become more accessible as the thermal energy increases. However, around room temperature it is not bad to regard  $N_s$  as a constant, because the dominant  $T$  dependence in eq. (1) comes from the exponential factor. To be accurate, one should also keep the dependence of  $E_g$  on  $T$ , which is usually weak.

We see from eq. (3) that  $N_s$  depends only on fundamental constants and on  $T$ , apart from the fact that the free electron mass  $m$  should be replaced by  $m^*$ . If we ask which combination of  $m^*$ ,  $k_B T$ , and  $\hbar$  has the dimensions of an inverse length, we find that it is  $(m^* k_B T)^{1/2} \hbar^{-1}$ . Since  $N_s$  has dimensions of inverse length cubed, we get eq. (3) from dimensional analysis alone, up to a factor of order 1.

We can also give an intuitive argument to understand  $N_s$ . Consider an electron moving at temperature  $T$  in one dimension. Its momentum fluctuates, but on the average its energy is  $\frac{1}{2} k_B T$ . The uncertainty in momentum is then  $\Delta p = (m^* k_B T)^{1/2}$ . From Heisenberg's principle, the minimum uncertainty in position is such that  $\Delta p \Delta x = \pi \hbar$ . In effect, every electron state occupies an interval of width  $\Delta x$ . The number of states available to an electron of a given spin, per unit length, is

$$\frac{1}{\Delta x} = \frac{\Delta p}{\pi \hbar} = \frac{(m^* k_B T)^{1/2}}{\pi \hbar} \quad (4)$$

For motion in three dimensions, we must similarly consider that each electron state occupies the volume  $(\Delta x)^3$  for a given spin. Taking the cube of eq. (4), and doubling it to account for spin up and spin down, we get the number of effectively available states to a free electron at temperature  $T$  as  $2 (m^* k_B T / \pi^2 \hbar^2)^{3/2}$ , very close to the correct  $N_s$  of eq. (3).

### The rigorous calculation of $n_i$

The probability of finding an electron in a state of energy  $E$ , at temperature  $T$ , is given by the Fermi function

$$f = \frac{1}{\exp\left(\frac{E - E_F}{k_B T}\right) + 1} \quad (5)$$

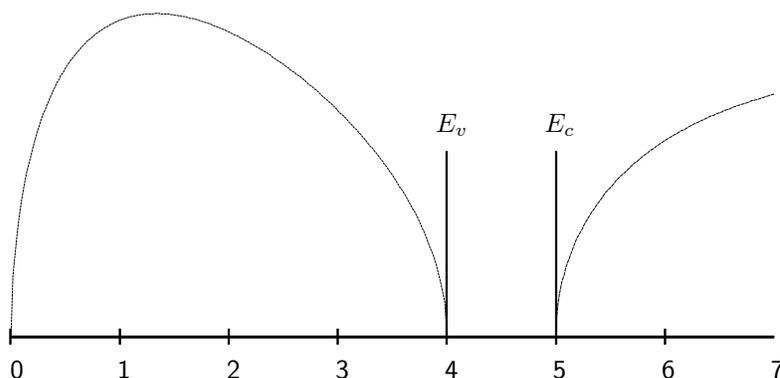
where  $E_F$  is the Fermi energy. For large enough samples, the number of available quantum states in a given energy interval is proportional to the volume of the sample. We denote by  $(dn/dE)dE$  the number of available states per unit volume with energy between  $E$  and  $E + dE$ , and we call  $dn/dE$  the density of states. Then the number per unit volume of electrons in the conduction band is

$$n = \int_{E_c}^{\infty} f \frac{dn}{dE} dE \quad (6)$$

where  $E_c$  is the energy of the bottom of the conduction band.

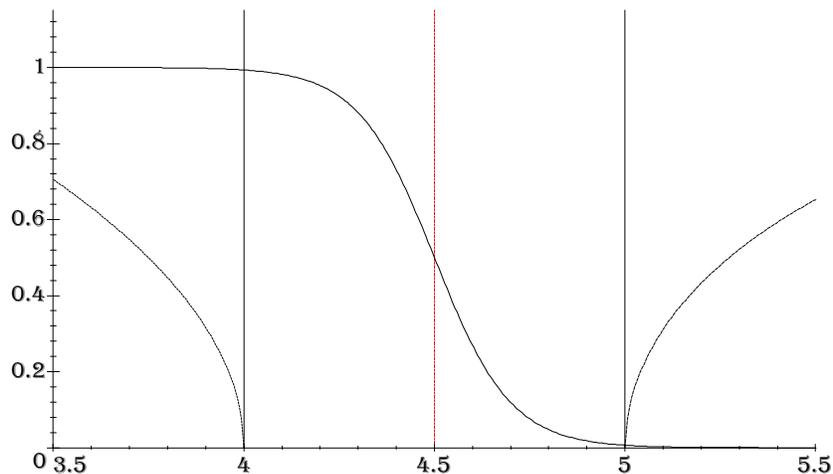
The density of states in a solid is similar to that of free particles near the bottom of a band, but decreases back to zero at the top of a band. Here is a sketch of density of states  $dn/dE$  vs. energy  $E$  (in eV) for a typical semiconductor, showing a valence band (dashed) between 0 and

4, a band gap between 4 and 5, and part of a conduction band (dotted) above 5. At  $T = 0$  the valence band is full and the conduction band is empty.

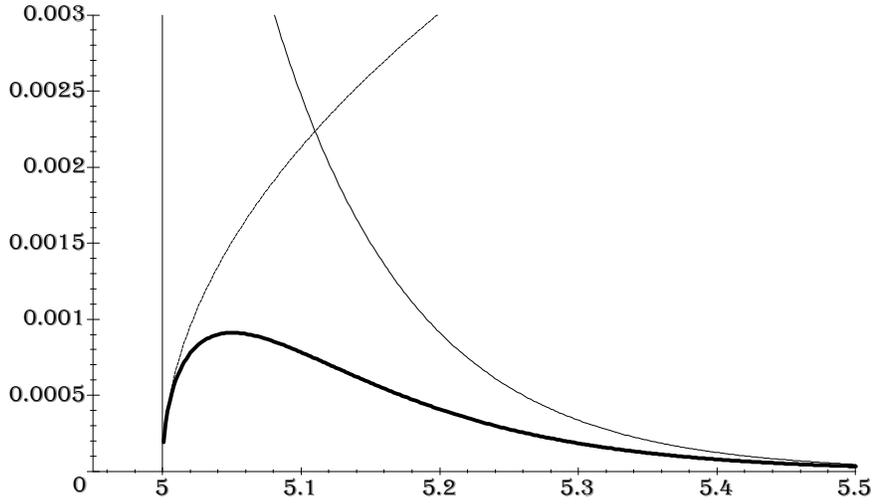


For an intrinsic semiconductor the Fermi level is near the middle of the energy gap. For simplicity, we assume at first that the density of states near the top of the valence band is the mirror image of the density of states near the bottom of the conduction band; then the Fermi level is exactly in the middle of the energy gap.

On the next graph we show an enlargement of the density of states near the gap, along with the Fermi level at  $E_F = 4.5$  eV (dash-dot line), and the Fermi function  $f$  (solid line), for  $k_B T = 0.1$  eV. (This corresponds to the temperature of 1160 K, too high for practical devices, but good for a clear drawing.) The vertical scale applies to  $f$  only.



The next graph shows the density of states near the bottom of the conduction band (dotted), along with  $f$  (thin solid line). These are the factors in the integrand of eq. (6). Also shown is the product of these two factors, which is the density of occupied states (thick line).



To find out how many electrons are thermally excited to the conduction band, i.e. to compute  $n$  in eq. (3), we need to compute the area under the thick line in the graph. This can be done to a good approximation as follows.

The edge of the conduction band,  $E_c$ , is far above the Fermi energy, compared to  $k_B T$  (in the graph,  $E_c = 5$  eV and  $E_c - E_F = 0.5$  eV); hence we can use

$$f \simeq \exp\left(-\frac{E - E_F}{k_B T}\right) \quad (7)$$

Physically, this means that the Fermi factor  $f$  can be approximated by a Boltzmann factor, because there are few electrons in the conduction band.

It will be shown below that the density of states near the bottom of the conduction band is approximately

$$\frac{dn}{dE} = \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} (E - E_c)^{1/2} \quad (8)$$

Clearly it is convenient to use  $E - E_c$  as a variable to deal with states in the conduction band, so we write eq. (7) in the form

$$f \simeq \exp\left(-\frac{E_c - E_F}{k_B T}\right) \exp\left(-\frac{E - E_c}{k_B T}\right)$$

and substituting back in eq. (6) we obtain

$$n = \exp\left(-\frac{E_c - E_F}{k_B T}\right) \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} \int_{E_c}^{\infty} (E - E_c)^{1/2} \exp\left(-\frac{E - E_c}{k_B T}\right) dE$$

The integral gives  $(k_B T)^{3/2} \sqrt{\pi}/2$ . In the intrinsic semiconductor that we consider,  $E_c - E_F = E_g/2$ , where  $E_g = E_c - E_v$  is the energy gap. We obtain then the result

$$n_i = 2 \left(\frac{m^* k_B T}{2\pi \hbar^2}\right)^{3/2} \exp\left(-\frac{E_g}{2k_B T}\right) \quad (9)$$

as anticipated in eqs. (1) and (3).

We must still justify eq. (8). We can start from eq. (1.4) in *Melissinos*, which gives a relation, for free electrons, between the energy  $E$  and the number of states per unit volume having energy less than  $E$ :

$$E = \frac{\hbar^2}{2m} (3\pi^2 \mathbf{n})^{2/3}$$

Inverting this relation between  $\mathbf{n}$  and  $E$  we find

$$3\pi^2 \mathbf{n} = \left( \frac{2mE}{\hbar^2} \right)^{3/2}$$

Differentiating, we obtain the density of states for free electrons:

$$\frac{d\mathbf{n}}{dE} = \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} E^{1/2} \quad (10)$$

States near the bottom of the conduction band represent electrons that are nearly free to move from atom to atom with an effective mass  $m^*$ ; the energy of motion must be reckoned from the bottom of the band. Replacing  $E$  with  $E - E_c$  and  $m$  with  $m^*$  in eq. (10), we obtain eq. (8).

In general, the electrons near the bottom of the conduction band move about with an effective mass  $m_c$  while the holes near the top of the valence move about with a different effective mass  $m_v$ . As a result, the intrinsic Fermi level is not exactly in the middle of the gap, but eq. (9) is still true, provided that we use  $m^* = (m_c m_v)^{1/2}$ . The relevant formulas are given in *Melissinos*, page 11, with

$$N_c = 2 \left( \frac{m_c k_B T}{2\pi \hbar^2} \right)^{3/2}$$

$$N_v = 2 \left( \frac{m_v k_B T}{2\pi \hbar^2} \right)^{3/2}$$

and  $N_s = (N_c N_v)^{1/2}$ .