FoP3B Part II Lecture 3: Statistical Physics of Semiconductors

Both **electrons** *in a nearly empty band* and **holes** *in a nearly full band* conduct electricity. Clearly the more electrons and holes there are the better the conductivity. However, **what determines the electron, hole concentrations in a semiconductor?** Here we will restrict our attention to semiconductors in **thermal equilibrium** with their surroundings.

The problem is illustrated schematically in Figure 1a. At 0K temperature the **valence band** is completely full and the **conduction band** completely empty. The semiconductor therefore shows <u>insulating</u> behaviour. As the temperature is raised a few valence electrons gain enough thermal energy to be promoted across the **band gap** into the conduction band. *Since the semiconductor is in equilibrium the promoted conduction band electrons will occupy the lowest energy states*. **The smaller the band gap and the higher the temperature the larger the electron and hole concentrations**.
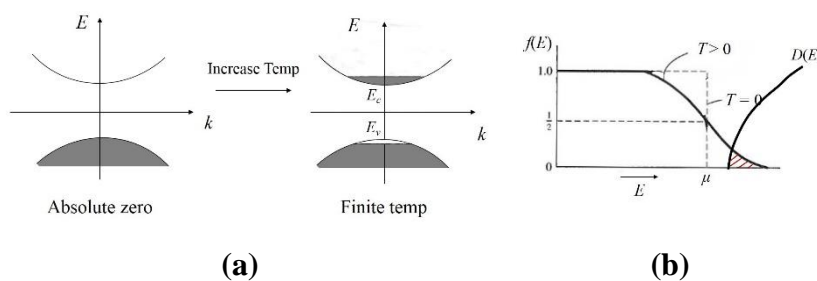

Figure 1: (a) thermal excitation of valence band electrons into the conduction band. (b) The Fermi-Dirac function *f(E)* for absolute zero and non-zero temperatures. Also shown is the density of states curve. The shaded area determines the electron concentration.

Electron concentrations

Since the semiconductor is in equilibrium, the electron concentration can be calculated using statistical physics. **We need to know (i) the number of energy states in the conduction band and (ii) the probability of occupying a given energy state**. The number of states per unit volume between E and $E+dE$ is simply $g(E)dE$, where $g(E)$ is the **density of states**. Let $f(E)$ denote the occupation probability of states with energy E. **Multiplying $g(E)dE$ by $f(E)$ gives the number of electrons between E and $E+dE$**.

Let us now derive expressions for $g(E)$ and $f(E)$. The density of states for a **free electron solid** can be shown to be (see FoP3B Part 1):

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}$$

… (1)

We assume that the density of states for the conduction band in a semiconductor has the same general form as Equation (1). This might seem strange since the semiconductor is <u>not</u> a free electron solid. *Nevertheless this is a reasonable approximation since in most cases there are only few electrons in the conduction band[1], meaning that only states near the bottom of the conduction band are occupied. The fact that the Brillouin zone edges are avoided means that*

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[1] kT at room temperature is 25 meV, while the semiconductor band gap is in the range 1-4 eV. Hence there is a large barrier for thermal excitation and consequently only a few electrons are promoted across the band gap.

we can treat the electrons as being effectively free. However, some modifications to Equation (1) are necessary. In fact **for a conduction band the density of states $g_e(E)$**:

$$g_e(E) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_c}$$

… (2)

Note that the free electron mass m has been replaced by the **effective mass** m_e^* and the energy scale has been modified to take into account that the bottom of the conduction band is at energy E_c (Figure 1a).

Since electrons are **fermions** the occupation probability is given by the **Fermi-Dirac distribution function**:

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - \mu}{kT}\right)}$$

… (3)

Here μ is the **chemical potential**, which at most temperatures is close to the **Fermi energy**. *From Equation (3) μ can be defined as the energy at which the electron occupation probability is ½.* $f(E)$ is shown schematically in Figure 1b. At 0 K it is a step function such that all states below μ are occupied, while all states above μ are unoccupied. At higher temperatures the step becomes increasingly 'smeared', such that the transition from occupied to unoccupied states is no longer abrupt.

To determine the electron concentration 'n' we integrate $g_e(E)f(E)$ over the conduction band:

$$n = \int_{E_c}^{E_{max}} g_e(E)f(E)dE$$

… (4)

where E_{max} is the maximum energy of the conduction band. To solve Equation (4) *analytically* we make **two assumptions**:

(i) **we extend the upper limit of the integral from E_{max} to infinity**. This might seem a bad approximation at first, but note that $f(E)$ decreases exponentially beyond μ. Hence the term $g_e(E)f(E)$ tends to zero for large energy.

(ii) **we assume $(E_c\text{-}\mu) \gg kT$** (i.e. the chemical potential is not too close to the conduction band minimum), **so that from Equation (3), $f(E) \approx \exp[-(E\text{-}\mu)/kT]$**.

Substituting Equations (2), (3) into (4) and making a change of variable $u = (E\text{-}E_c)/kT$ gives:

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e^*kT}{\hbar^2}\right)^{3/2}\exp\left[-\frac{(E_c - \mu)}{kT}\right]\int_0^{\infty}\sqrt{u}\exp(-u)du$$

The integral is equal to $(\sqrt{\pi})/2$, so that:

$$n = N_c \exp\left[-\frac{(E_c - \mu)}{kT}\right] \quad ; \quad N_c = 2\left(\frac{m_e^* kT}{2\pi\hbar^2}\right)^{3/2}$$

$$\dots (5)$$

N_c is the **conduction band effective density of states**. *Equation (5) indicates that the electron concentration increases with temperature T, consistent with what we would expect.* Furthermore, the *electron concentration increases as the separation between the chemical potential μ and conduction band minimum E_c decreases*. This should be clear from Figure 1b, where n is determined by the overlap region of the $g_e(E)$ and $f(E)$ curves (Equation 4).

Hole concentrations

To obtain the hole concentration we multiply the valence band density of states by the probability of states being <u>unoccupied</u>. **The hole concentration between E and $E+dE$ is therefore $g_h(E)[1\text{-}f(E)]dE$, where $g_h(E)$ is the valence band density of states and $[1\text{-}f(E)]$ is the probability of a state being unoccupied**. Using a similar derivation to that of the electron concentration we obtain for the **hole concentration p**:

$$p = N_v \exp\left[-\frac{(\mu - E_v)}{kT}\right] \quad ; \quad N_v = 2\left(\frac{m_h^* kT}{2\pi\hbar^2}\right)^{3/2}$$

$$\dots (6)$$

where N_v is the **valence band effective density of states** and E_v is the valence band maximum. You should attempt deriving Equation (6) yourself. Similar to electrons, the *hole concentration increases with temperature and decreasing separation between chemical potential μ and valence band maximum E_v.*

Law of mass action

Taking the product of n and p gives:

$$np = N_c N_v \exp\left(-\frac{E_g}{kT}\right) \propto T^3 \exp\left(-\frac{E_g}{kT}\right)$$

$$\dots (7)$$

where $E_g = E_c - E_v$ is the band gap. **Equation (7) is the law of mass action**. It states that the product np is a material constant at a given temperature. Furthermore, ***np increases monotonically with decreasing band gap and increasing temperature***. In fact, the temperature dependence is strong, due to the exponential term. <u>*In semiconductors the increase in electrical conductivity with temperature is due to the rapid increase in electron, hole concentrations, which offsets the negative effects of increased scattering at higher temperatures*</u>. *Compare this with metals where the electron, hole concentration is approximately independent of temperature, so that conductivity decreases with temperature due to increased scattering.*

Fermi level position

Thus far nothing has been said about the Fermi energy level or chemical potential μ. Consider an **intrinsic semiconductor**, i.e. a semiconductor with no *impurities* (e.g pure Si, GaAs etc). *For an intrinsic semiconductor all electrons and holes are generated by thermal excitation across the band gap, and consequently n = p.* From Equations (5) and (6) it therefore follows that:

$$\mu = E_{mid-gap} + \frac{3}{4}kTln\left(\frac{m_h^*}{m_e^*}\right)$$

$$\dots (8)$$

where $E_{\text{mid-gap}} = (E_c+E_v)/2$ is the middle of the band gap. Since m_h* is typically of the same order as m_e* the **chemical potential μ for an intrinsic semiconductor is close to the band gap mid-point**. Since $E_F \approx \mu$ this is also approximately the position of the Fermi energy level.