Lecture notes

Extrinsic semiconductors:

Carrier concentration, Fermi energy, impurity density and energy gap

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These notes are based on a series of lectures given to graduate physics students at YCM, University of Mysore, as part of the PHYS404 specialisation course in solid state physics.

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A note on references: Footnotes are marked by superscript numbers ^{x}, equations by parentheses (x) and references to the appendix by square brackets [x].

Contents

Semiconductors are extremely useful as electronic devices but, perhaps, even more interesting from a physics perspective. However, most intrinsic semiconductors do not conduct well enough for practical use, which is one of the reasons why we add impurities to them. This process of adding impurities to a semiconductor, called **doping**, also gives us better control over the properties we would want the semiconductor to exhibit. Our study in these notes will cover the fundamental notions behind such semiconductors.

We will not be discussing the exact process of doping here or any basic statistical ideas (these were parts of previous lectures). Our study will begin with the Fermi energy associated with semiconductors.

1 Fermi energy

1.1 Effects of temperature

Before we calculate the Fermi level (which, for now, it is sufficient to understand is an energy level associated with semiconductors) let us take a moment to discuss how semiconductor behaviour changes with temperature. We look at four cases: extreme low and high, and moderate low and high temperatures.

At higher temperatures valence electrons overwhelmingly move to the conduction band, outnumbering those contributed by donor impurities. The number of electrons in the conduction band will equal the number in intrinsic conductors: $n_C \approx n_i$.

At more standard temperatures some electrons from the valence band will move to the conduction band: $n_C \approx N_D$. Electrons from donor impurities will be ionised to the as well.

At lower temperatures valence electrons rarely move to the conduction band, and most of the conduction arises due to donors: $n_C \approx N_D^+$.

At near absolute zero electrons of the semiconductor occupy energy states below the Fermi level and there is almost no conduction: $n_C \approx 0$.

1.2 The Fermi energy level

The **electric neutrality condition** balances the number of ionised donors, N_D^+, ionised acceptors, N_A^-, conduction band electrons, n_C, and valence band holes, p_V. The aim is to ensure charge neutrality since charge imbalance would make the semiconductor unstable. The terms n_C and p_V are called the **effective densities of state**.

The equation we arrive at, involving the Fermi energy, is

$$p_V e^{(E_V-E_F)/k_BT} + n_C e^{(E_F-E_C)/k_BT} + \frac{N_D}{1+2e^{(E_F-E_D)/k_BT}} - \frac{N_A}{+2e^{(E_A-E_F)/k_BT}} = 0$$

where the population term $e^{\Delta E/k_BT}$ arises from Boltzmann's approximation.

In case of n-type semiconductors $E_{F_n} > E_{F_i}$ and, for p-type semiconductors, $E_{F_p} < E_{F_i}$, with the donor atoms generally having an energy $E_C < E_D < E_{F_i}$ and acceptors having $E_{F_i} > E_A > E_V$, where

$$E_{F_i} = E_v + \frac{E_g}{2} + \frac{3}{4}\,k_BTln\left(\frac{m_p^*}{m_n^*}\right)$$

Assuming all donor atoms are ionised we have,

$$n_0 = n_C e^{(E_F - E_C)/k_BT}$$

and

$$p_0 = p_V e^{(E_V - E_F)/k_BT}$$

from the first two terms of the above equation which can be put into the electrical neutrality condition

$$p_0 + N_D^+ = n_0 + N_A^- \qquad \Longrightarrow \qquad n_0 - (N_D^+ - N_A^-) - p_0 = 0$$

to get

$$n_C e^{(E_F - E_C)/k_BT} - (N_D - N_A) - p_V e^{(E_V - E_F)/k_BT} = 0$$

The values of the effective state densities is given by

$$n_C = 2\left[\frac{2\pi m_n^* k_B T}{h^2}\right]^{3/2} \qquad \text{and} \qquad p_v = 2\left[\frac{2\pi m_p^* k_B T}{h^2}\right]^{3/2}$$

Say $e^{E_F/k_BT} = \alpha$, $e^{E_C/k_BT} = \beta_C$ and $e^{E_V/k_BT} = \beta_V$. We then have

$$\frac{n_C\alpha}{\beta_C} - (N_D - N_A) - \frac{p_V\beta_V}{\alpha} = 0$$

$$\alpha^2 - (N_D - N_A)\left(\frac{\beta_C}{n_C}\right)\alpha - \frac{p_V\beta_V\beta_C}{n_c} = 0$$

in which can solve for α using the quadratic formula and discard the negative root and consider the ln of both sides to arrive at

$$\ln\alpha = \frac{E_F}{k_BT} = \ln\left\{\frac{(N_D - N_A)\beta_C}{2n_C} + \sqrt{\left[\frac{(N_D - N_A)\beta_C}{2n_C}\right]^2 + \frac{p_V\beta_V\beta_C}{n_C}}\right\}$$

which is of the form $\ln\alpha = \ln[a + \sqrt{a^2 + x^2}]$ and has the solution $\ln\alpha = \ln x + \sinh^{-1}(a/x)$. The above equation can be solved [A1] in this manner (and using $n_i^2 = n_0 p_0$ where necessary) to arrive at

$$E_F = k_BT\left[\sinh^{-1}\left(\frac{N_D - N_A}{2n_i}\right)\right] + \left[\left(\frac{E_C + E_V}{2k_BT}\right) + \left(\frac{3}{4}\right)k_BT\ln\left(\frac{m_p^*}{m_n^*}\right)\right] \tag{1}$$

where the two terms within square brackets arise from the terms $\ln x$ and $\sinh^{-1}(a/x)$. Notice that the term $(E_C + E_V)/2$ is the Fermi energy of the intrinsic semiconductor. The Fermi energy E_F of the extrinsic semiconductor is therefore given by

$$E_F = E_{F_i} + k_BT\sinh^{-1}\left(\frac{N_D - N_A}{2n_i}\right) \tag{2}$$

The observed inequality relations between E_F (for n- and p-types), and E_C, E_V and E_{F_i} explained earlier make sense now thanks to this equation.

1.3 Effect of low temperatures on E_F

It is clear from (2) that temperature and impurity density both affect the Fermi energy level of an extrinsic semiconductor considerably. The effects at low temperatures, tending to absolute zero, is particularly interesting.

Consider a purely n-type semiconductor at $T \to 0$ so that our electrical neutrality condition becomes

$$n_0^- - (N_D - n_D)^+ = 0$$

We have also seen before that

$$n_0 = n_C e^{(E_F - E_C)/k_B T}$$

and, we know from Fermi statistics that

$$n_D = \frac{N_D}{\frac{1}{2} e^{(E_D - E_F)/k_B T} + 1}$$

Combining the above two equations into the neutrality condition we get

$$n_0 - \left(N_D - \frac{N_D}{\frac{1}{2} e^{(E_D - E_F)/k_B T} + 1} \right) = 0$$

$$\frac{n_0 e^{(E_D - E_F)/k_B T}}{2} + n_0 - \frac{N_D e^{(E_D - E_F)/k_B T}}{2} - N_D + N_D = 0$$

$$n_C e^{(E_F - E_C)/k_B T} e^{(E_D - E_F)/k_B T} + 2 n_C e^{(E_F - E_C)/k_B T} - N_D e^{(E_D - E_F)/k_B T} = 0$$

$$n_C e^{(E_D - E_C)/k_B T} + 2 n_C e^{(E_F - E_C)/k_B T} - N_D e^{(E_D - E_F)/k_B T} = 0$$

Dividing by $e^{(E_D - E_F)/k_B T}$ we end up with

$$n_C e^{(E_F - E_C)/k_B T} + 2 n_C e^{(2E_F - E_C - E_D)/k_B T} - N_D = 0$$

Now if we let $e^{E_F/k_B T} = \alpha$, $e^{-E_C/k_B T} = \beta_C$ and $e^{-E_D/k_B T} = \beta_D$, we can write

$$0 = 2 n_C \alpha^2 \beta_C \beta_D + n_C \alpha \beta_C - N_D$$

$$0 = \alpha^2 + \left(\frac{1}{2\beta_D} \right) \alpha + \frac{N_D}{2 n_C \beta_C \beta_D}$$

$$\Rightarrow \alpha = \frac{-1}{4\beta_D} + \sqrt{\frac{1}{16\beta_D^2} - \frac{N_D}{2 n_C \beta_C \beta_D}}$$

$$\therefore \ln \alpha = \frac{E_F}{k_B T} = \ln \left\{ \frac{-1}{4\beta_D} + \sqrt{\frac{1}{16\beta_D^2} - \frac{N_D}{2 n_C \beta_C \beta_D}} \right\}$$

We have ignored the negative term once again just as before. The right-hand side of this equation, once again, looks like $\ln[a + \sqrt{a^2 + x^2}]$ and has a solution of the form $\ln x + \sinh^{-1}(a/x)$. All of this is exactly as we saw in §1.2 and we can solve this equation in a manner similar to [A1] to arrive at our final result:

$$E_F = \left[\frac{E_C + E_D}{2} \right] + \left[\left(\frac{k_B T}{2} \right) ln \left(\frac{N_D}{n_C} \right) \right] - k_B T \sinh^{-1} \left[\left(\frac{n_C}{8 N_D} \right)^{1/2} e^{-\Delta E_i / 2 k_B T} \right] \quad (3)$$

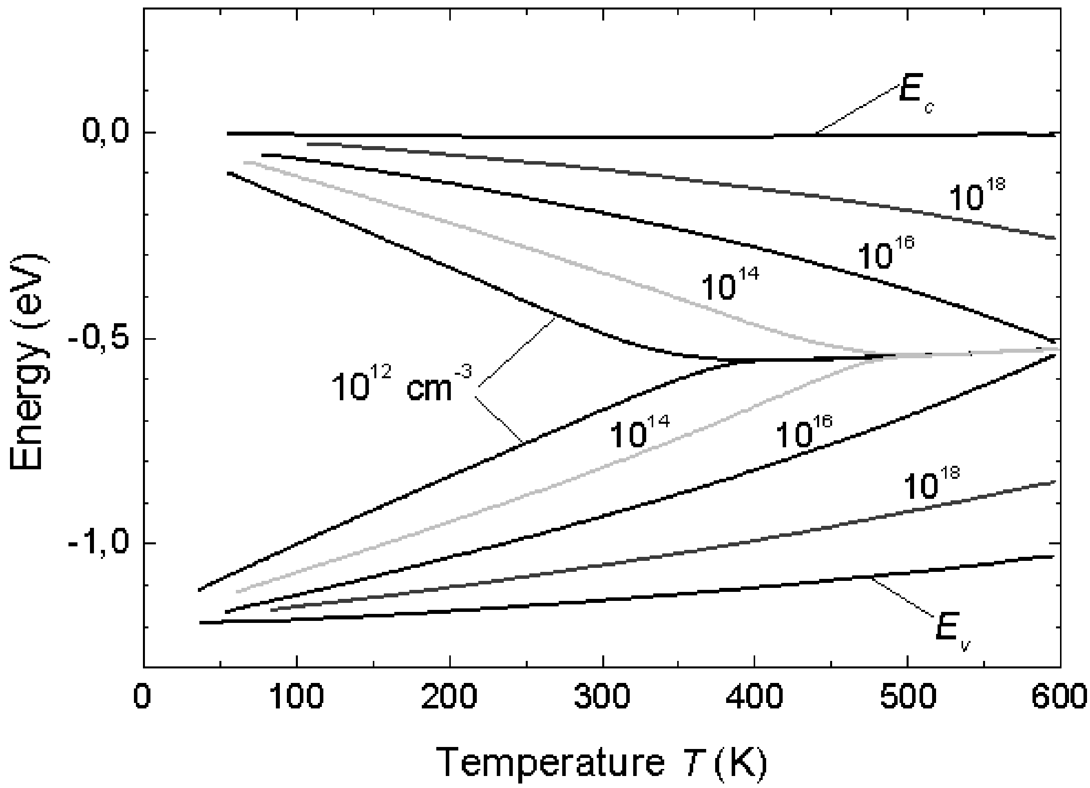

Figure 1: Variation of Fermi energy of extrinsic semiconductors with temperature. The upper bands $\geq E_{F_i}$ correspond to n-type impurity semiconductors E_{F_n} and the lower bands $\leq E_{F_i}$ correspond to p-type impurity semiconductors E_{F_p}. The lines, as they go away from E_{F_i}, correspond to increasing impurity density, shown here from a minimum of 10^{12} atoms per cm^3 up to 10^{18} atoms per cm^3. Credit: `http://www.ioffe.ru/SVA/NSM/Semicond/Si/bandstr.html`.

2 Electrical conductivity and carrier mobility

2.1 Conductivity of extrinsic semiconductors

The net current density of a semiconductor in an electric field $\mathbf{E}$ is

$$\mathbf{J} = \mathbf{E}[n_0\mu_n + p_0\mu_p]e$$

where n_0 and p_0 are the number densities of the carriers and μ are their mobilities. This is the general equation. In case of intrinsic semiconductors, since $n_0 = p_0 = n_i$ (say) we end up with $\mathbf{J} = \mathbf{E}n_i[1+b]\mu_p e$, where $b = \mu_n/\mu_p$.

From Ohm's law, since $\mathbf{J} \propto \mathbf{E}$ we can write some constant σ_i, called the **conductivity** of the intrinsic semiconductor, as

$$\sigma_i = n_i e\mu_p[1+b]$$

based on the above equations. For extrinsic semiconductors, likewise, we then have conductivity σ defined by

$$\sigma = [n_0\mu_n + p_0\mu_p]e = \mu_p[n_0 b + p_0]e$$

Suppose we have N_D donors and N_A acceptors we know that, at any given time,

$$n_0 = \left(\frac{N_D - N_A}{2}\right) + \sqrt{\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2}$$

$$p_0 = \left(\frac{N_A - N_D}{2}\right) + \sqrt{\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2}$$

for n-type semiconductors.

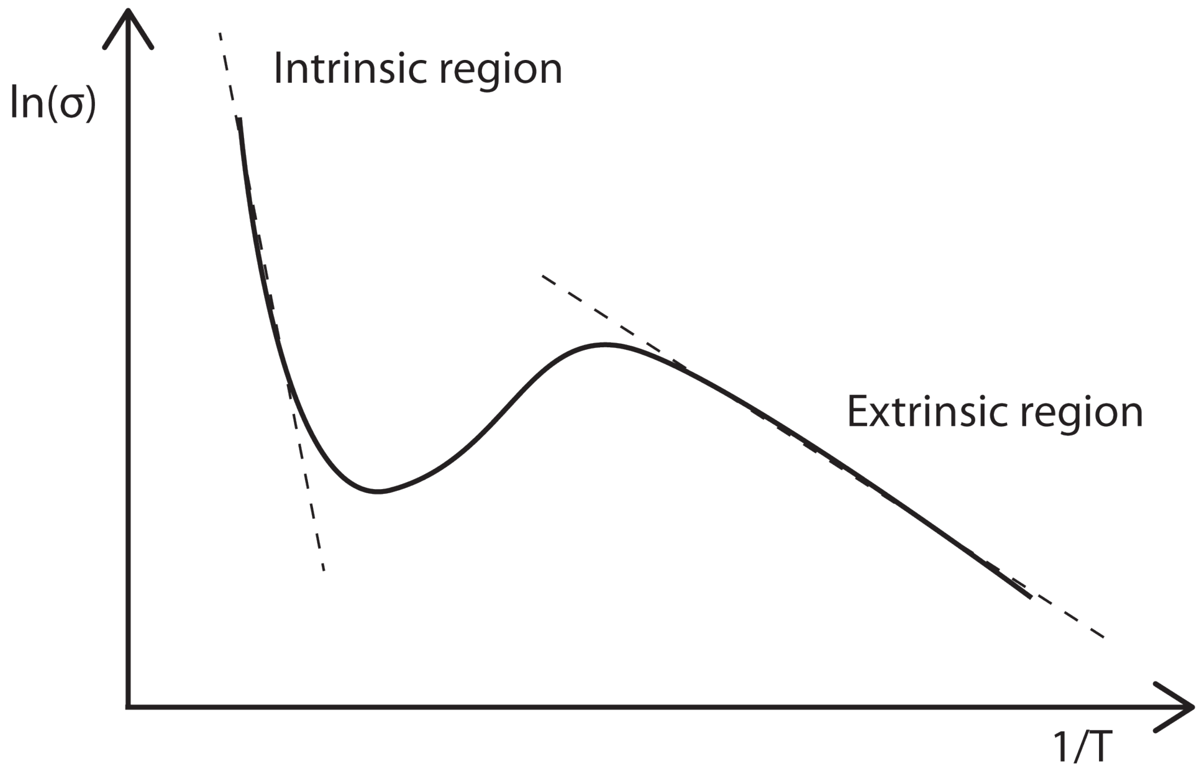

Figure 2: Variation of conductivity σ with temperature T. Note how at higher temperatures extrinsic semiconductors show intrinsic behaviour. Credit: `https://www2.warwick.ac.uk/fac/sci/physics/current/postgraduate/regs/mpags/ex5/techniques/electronic/hall-effect/temperature/`.

The above three equations lead to the following expression for conductivity:

$$\sigma = e\mu_p\left[(1+b)\left(\frac{N_D - N_A}{2}\right) + (1+b)\sqrt{\left(\frac{N_D - N_A}{2}\right)^2 + n_i^2}\right]$$

However, knowing that

$$n_i = 2\left(\frac{2\pi k_B T}{h^2}\right)^{3/2}\left(m_p^* m_n^*\right)^{3/4} e^{-E_g/2k_BT}$$

we can write down the conductivity as

$$\sigma = (\text{constant})e^{E_g/2k_BT}$$

where the constant terms includes $e[\mu_n + \mu_p]$ for extrinsic semiconductors.

Note that at lower temperatures we have few ionised donors and acceptors to start with and we notice a straight-line region. Beyond this low-temperature region we notice an increase in n_i, N_D and N_A in what is called the **transition region**. Finally, in the intrinsic region at higher temperatures, we observe another straight-line region but with a steeper slope.

The transition region is so called because temperatures there begin to ionise donors almost fully but cannot ionise lattice electrons. At higher temperatures this is, in fact, possible, making the semiconductor behave more intrinsically.

2.2 Carrier mobility

In the absence of an electric field, the net mobility of a charge carrier is rarely determinable. However, since a net velocity arises under the influence of an applied electric field, the mean free path and time of carriers may be calculated so long as $\mathbf{E} \neq 0$.

For a single charge carrier, say a hole, we can write

$$\mathbf{v}_p(t) = \mathbf{v}_p(0) + \left(\frac{e\mathbf{E}}{m_P^*}\right)t$$

where $\mathbf{v}_p(0)$ is at clock start; also, we have used $\mathbf{v} = e\mathbf{E}t/m_p^*$ based on $\mathbf{F} = e\mathbf{E}$ and $\mathbf{F} = \mathrm{d}\mathbf{p}_p/\mathrm{d}t = m_p^*\mathbf{v}/t$ to arrive at the third term.

Since the net value $\langle\mathbf{v}_p(0)\rangle = 0$ for all holes in our semiconductor, we are left with the average velocity

$$\langle\mathbf{v}_p(t)\rangle = \left(\frac{e\mathbf{E}}{m_P^*}\right)\tau_p$$

where τ_p is the mean free time period between collisions. The above equation can be written in terms of a new term called the **mobility** represented by μ as

$$\mathbf{v}_{d,\,p} = \mu_p\mathbf{E} \tag{4}$$

where $\mathbf{v}_{d,\,p}$ is the drift velocity of holes and $\mu_p = e\tau_p/m_p^*$ as is evident from our previous equations. A similar equation may be built for electrons. The drift velocities vary linearly with $\mathbf{E}$ in opposite directions. Also, since $m_n^* < m_p^*$ it is clear that $\mu_n > \mu_p$ in general.

Lastly, note that mobility is affected by both temperature and impurity density since both of these affect the collisions and, in turn, the mean free period associated with charge carriers. Experimentally, $\mu_n = 1350\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_p = 480\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for Silicon, and $\mu_n = 3900\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_p = 1900\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for Germanium.

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Appendices

A Some useful results

1. Solving the $\ln x + \sinh^{-1}(a/x)$ form from §1.2:

$$\begin{aligned}
\ln x &= \ln\sqrt{\frac{p_V\beta_V\beta_C}{n_C}} \\
&= \ln\sqrt{\left(\frac{m_p^*}{m_n^*}\right)^{3/2}\beta_V\beta_C} \\
&= \frac{3}{4}\ln\left(\frac{m_n^*}{m_p^*}\right) + \ln e^{(E_C+E_V)/2k_BT} \\
&= \frac{3}{4}\ln\left(\frac{m_n^*}{m_p^*}\right) + \left(\frac{E_C+E_V}{2k_BT}\right) \qquad \text{(a)}
\end{aligned}$$

$$\begin{aligned}
\frac{a}{x} &= \frac{(N_D-N_A)\beta_C}{2n_C}\Bigg/\sqrt{\frac{p_V\beta_V\beta_C}{n_C}} \\
&= \frac{(N_D-N_A)\beta_C\sqrt{n_C}}{2n_C\sqrt{p_V\beta_V\beta_C}} \\
&= \frac{N_D-N_A}{2\sqrt{n_Cp_V}\,e^{-(E_C-E_V)/2k_BT}} \qquad \text{(b)}
\end{aligned}$$

where

$$\begin{aligned}
n_i^2 &= n_0p_0 \\
\Rightarrow n_i &= \sqrt{n_Cp_V\,e^{-(E_C-E_V)/k_BT}} \\
&= \sqrt{n_Cp_V}\,e^{-(E_C-E_V)/2K_BT} \\
\therefore \frac{a}{x} &= \frac{N_D-N_A}{2n_i} \qquad \text{from eq. (b)} \qquad \text{(c)}
\end{aligned}$$

Equations (a) and (c) can be used to arrive at (1).

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