Semiconductors

Law of Mass Action

Near the band edges, electrons behave as if they were free but with a conjugated mass. The conduction band is empty at zero temperature, thus at finite temperature we essentially have electrons with mass m_c^* filling an empty 3D box. The density of states will be proportional to square root of energy measured from band bottom and occupancy is determined by Fermi-Dirac distribution. Therefore the concentration of conduction electrons is given by

$$\begin{aligned} n_c &= \int_{E_c}^{\infty} f(E)D(E)dE \\ &= \int_{E_c}^{\infty} \frac{1}{e^{\beta(E-\mu)}+1} \cdot A_c\sqrt{E-E_c}dE \end{aligned} \tag{1}$$

Similar reasoning leads to concentration of valance holes

$$\begin{aligned} p_v &= \int_{-\infty}^{E_v} (1-f(E))D(E)dE \\ &= \int_{E_c}^{\infty} (1-\frac{1}{e^{\beta(E-\mu)}+1}) \cdot A_v\sqrt{E_d-E}dE \end{aligned} \tag{2}$$

where the proportionality factors for densities of states at the band edges

$$A_{c/v} = \frac{1}{2\pi^2}\left(\frac{2m_{c/v}^*}{\hbar^2}\right)^{3/2} \tag{3}$$

can be derived by solving the particle-in-a-box problem at the band edges (since the dispersion relations are just parabolas with different curvatures). Notice (1) and (2) are *always* true given the usual assumptions in quantum and statistical mechanics. I have not mentioned anything about the source of electrons/holes or where the chemical potential μ lies.

Empirically, semiconductors are poor conductors at low but finite temperatures. This means $E_v \ll \mu \ll E_c$, because otherwise appreciable filling/emptying of conduction/valance band will result in conduction. In this limit, Fermi-Dirac statistics reduce to Boltzmann statistics

$$\begin{aligned} n_c &= \int_{E_c}^{\infty} e^{-\beta(E-\mu)} \cdot A_c\sqrt{E-E_c}dE \\ &= \frac{\sqrt{\pi}}{2\beta^{3/2}}A_c e^{-\beta(E_c-\mu)} = N_c e^{-\beta(E_c-\mu)} \end{aligned} \tag{4}$$

$$p_v = \frac{\sqrt{\pi}}{2\beta^{3/2}}A_v e^{-\beta(\mu-E_v)} = N_v e^{-\beta(\mu-E_v)} \tag{5}$$

and the product

$$n_c p_v = N_c N_v e^{-\beta(E_c - E_v)} \tag{6}$$

is independent of the chemical potential, aka the environment the semiconductor is in! That is, regardless of whether the material is doped or not, or if there's any external potential the *law of mass action* (6) holds.

The nice forms of (4-6) make semiconductors very teachable without lengthy excursions into quantum and stat mech. The collection of constants $N_{c/v} = \frac{\sqrt{\pi}}{2\beta^{3/2}} A_{c/v}$ can be interpreted as the number of available quantum states at the conduction/valance band edges respectively. Thus it feels natural to write down the concentration of conduction electron and valance holes as a product of the number of available states with average occupancy

$$\boxed{\begin{cases} n_c = N_c e^{-\beta(E_c - \mu)} \\ p_v = N_v e^{-\beta(\mu - E_v)} \end{cases}} \tag{7}$$

Intrinsic

When the semiconductor is intrinsic (no doping), there must be the same number of holes as electrons, therefore

$$n_i = p_i = \sqrt{N_c N_v e^{-\beta(E_c - E_v)}} \tag{8}$$

also, by equating the RHS of (7), we obtain the chemical potential

$$\mu = \frac{1}{2}(E_c + E_v) + \frac{1}{2} k_B T \ln \frac{N_v}{N_c} \tag{9}$$

At zero temperature, chemical potential lies at the middle of the band gap.

$$\lim_{T \to 0} \mu = \frac{1}{2}(E_d + E_c) \tag{10}$$

Extrinsic

When the semiconductor is doped, all that changes is the chemical potential

$$\mu = \frac{1}{2}(E_c + E_d) + \frac{1}{2} k_B T \ln \frac{N_d}{N_c} \tag{11}$$

where N_d is the concentration of donor atoms (each with one electron to contribute). With N_a as acceptor concentration

$$\mu = \frac{1}{2}(E_a + E_v) + \frac{1}{2} k_B T \ln \frac{N_v}{N_a} \tag{12}$$