Day 13: Wednesday – 50 minutes

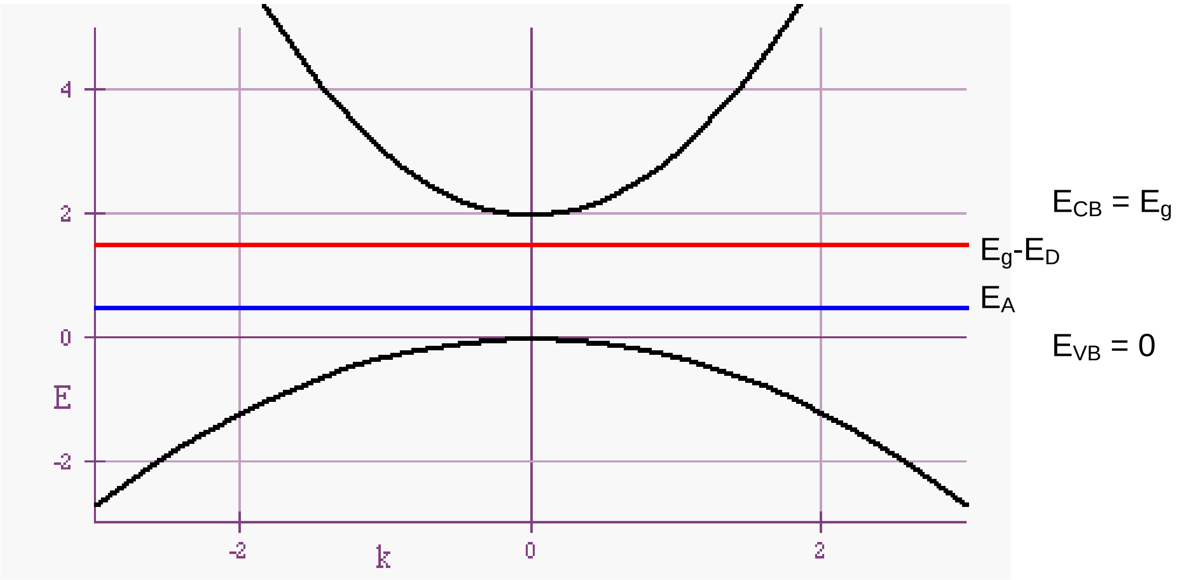
Extrinsic (doped) semiconductors.

The solution to the problem of low intrinsic carrier concentrations is "doping," the intentional introduction of specific elements as impurities in the otherwise pure semiconductor crystal. Consider the example of phosphorous as an impurity in silicon. The electronic configuration of atomic Si is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$. The valence band is derived from the last four electrons, i.e. those in the $3s^2\ 3p^2$ states. Phosphorous, on the other hand, has the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$, almost the same except that there is one more valence electron. When P enters as an impurity in the silicon lattice, four of its valence electrons are used up making chemical bonds to the neighboring Si atoms (P is pretending to be a Si atom), but there is one electron left over. At low temperatures, this extra electron is bound to the P atom where it occupies an impurity level whose energy is very close to the bottom of the conduction band – only about 0.05 eV. (This state is like the impurity states in the energy gap that you saw in the CUPS simulations.) Now, at room temperature, thermal energy $k_B T$ is about 0.025 eV. This is high enough that a significant fraction of the extra electrons on phosphorous atoms (the "donors") can be excited into states at the bottom of the conduction band. It is possible to introduce enough phosphorous atoms that really useful concentrations of electrons, as many as 10^{20} cm^{-3}, can be introduced into the conduction band. As we have seen, the electrons will behave as if they are essentially free, except that they will have an effective mass related to the curvature of the band function $E(k)$ at the bottom of the band. Material in which the electrical conductivity is due primarily to electrons in the conduction band is known as "n-type" for "negative."

What happens if we introduce an impurity that has one less valence electron than silicon? Examples would be boron or aluminum. Such dopants are called "acceptors." Again, at low temperature, the hole occupies an impurity energy level, this time just above the top of the valence band. At room temperature, electrons are thermally excited up into the hole level leaving a hole in the valence band. This is equivalent to saying that the hole is excited from the impurity level to the valence band. If holes are the primary carriers of electric current, the material is known as “p-type” for “positive.”

To calculate the carrier concentrations in an extrinsic (doped) semiconductor, assume that there are N_D donors (per unit volume) and N_A acceptors. The energies of the donor level (electron on the donor atom) will be E_D below the CB and that of the acceptor level (hole on the acceptor atom) will be E_A above the VB.

If there are both donors and acceptors and $N_D > N_A$, we say the semiconductor is n-type, but (partially) compensated. Some electrons from donor states will drop to acceptor levels, thus leaving the donor levels positively charged (with respect to the lattice) and populating acceptor levels with positive charge (with respect to the lattice). Place the zero of energy at the top of the VB; the energy at the bottom of the CB will then be E_{gap}.



Then, the numbers of ionized states are

$$N_D^+ = N_D\left(1 - f\left(E_g - E_D\right)\right) \quad \text{(\# donor states} \times \text{probability of no electron),}$$
$$N_A^- = N_A f\left(E_A\right) \quad \text{(\# acceptor states} \times \text{prob of electron).}$$

Since the acceptor levels are fully occupied (by electrons) at T = 0, the number of un-ionized states donor states is therefore $N_D - N_A$. This means that at T = 0 and close to it, the chemical potential must be $\mu = E_g - E_D$ (level of highest occupied state).

Then the majority carrier (electron) density will be $\boxed{n = N_C e^{-E_D/k_BT}}$ for a heavily *n*-doped extrinsic semiconductor. Compared with intrinsic $n_{\text{int}r} = \sqrt{N_C N_V}\, e^{-E_g/2k_BT}$, this is extremely large because of the relative sizes of the exponential terms.

We also see that the positive (hole) carrier density will be $p = N_V e^{-\left(E_g - E_D\right)/k_BT}$. This is much smaller than n and thus p carriers are called the minority carriers in n-type materials.

Similar arguments apply to the case of a partially compensate p-type semiconductor ($N_A > N_D$). For heavily doped acceptors, $\mu = E_A$, $p = N_V e^{-E_A/k_BT}$, $n = N_C e^{-\left(E_g - E_A\right)/k_BT}$.