PHYS 551 Lecture #24

Title: Doped Semiconductors

Last time we saw that, at finite T, there were electrons in the conduction band and holes in the valence band. Since charge neutrality was implicit, the # of holes in the valence band equalled the the # of electrons in the conduction band ($p_{\rm VB} = n_{\rm CB}$). We also derived the relationships:

$$n = \int_{Eg}^{\infty} \mathcal{D}_{CB}(\epsilon) f(\epsilon) d\epsilon = 2\left(\frac{m_e^* k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-(Eg - E_F(T))/k_B T}$$

AND

$$p = \int_{-\infty}^{0} \mathcal{D}_{VB}(\epsilon)(1 - f(\epsilon)) d\epsilon = 2\left(\frac{m_h^* k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-E_F(T)/k_B T}$$

Since $n = p$ $\quad E_F(T) = Eg/2 - \frac{3}{4} k_B T\ \ell n\ (m_e^*/m_h^*)$.

Rather than always worrying about the $\int d\epsilon$, it is convenient to define a new quantity, N_{CB} the "effective" density of states in the conduction band. This quantity assumes that the weighted occupancy, $f(\epsilon)$ and DOS(ϵ) can be all put conceptually at the CB edge such that:

$$\begin{aligned} n &= \#\text{ of } e\text{'s in CB } \equiv N_{CB} f(E_G) \\ &= 2\left(\frac{m_e^* k_B T}{2\pi\hbar^2}\right)^{3/2} e^{-(E_G - E_F(T))/k_B T)} = N_{CB} e^{-(Eg - E_F(T)/k_B T)} \\ \text{or } N_{CB} &= 2\left(\frac{m_e^* k_B}{2\pi\hbar^2}\right)^{3/2} T^{3/2} \end{aligned}$$

For a typical semiconductor at 300K, $N_{CB} \approx 10^{25}$ states/m^3 vs. $\sim 10^{28}$ atoms/m^3.
Similarly: $N_{VB} = 2\left(\frac{m_h^* k_B}{2\pi\hbar^2}\right)^{3/2} T^{3/2}$.

In the presence of an $\vec{E}$-field, both the holes and electrons can be accelerated up to their characteristic relaxation times, τ_h or τ_e.

So $\quad \vec{F} = m_e^* \vec{a} = -e\vec{E} \implies \vec{v}_e = \frac{e}{m_e^*} \vec{E} \tau_e$

Notice that $\vec{v}_e \propto \vec{E}$ but that $\vec{v}/\vec{E}$ is constant of field.

Since

$$\vec{j}_e = \sigma_e \vec{E} = -\left(\frac{n}{V}\right) e\vec{v} \implies \sigma_e = -\left(\frac{n}{V}\right) e\vec{v}/\vec{E}$$

If we define a new quantity $\boxed{\mu_e \equiv \text{ mobility } = \frac{e}{m_e^*}\tau_e}$

$$n_e \equiv \frac{n}{\text{Volume}}$$

$$\sigma_e = n_e\ e\ \mu_e \ \text{ and } \ \sigma_h = p_h\ e\ \mu_h$$

Thus the total conductivity is

$$\sigma = (n_e\mu_e + p_h\mu_h)e \ \text{ and } \mu \text{ has units of } \frac{\text{cm}^2}{\text{V s}}$$

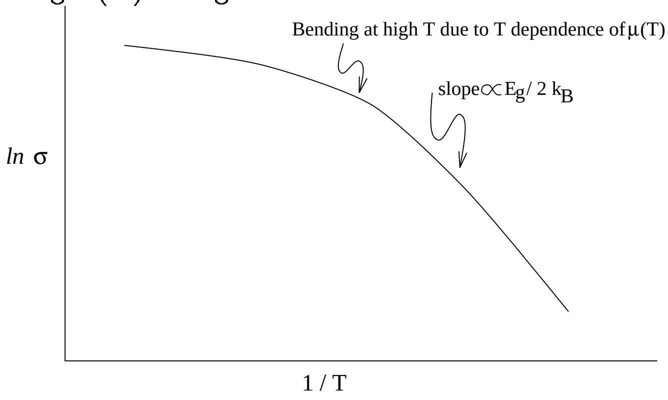
If T is small or if $m_e^* \approx m_h^*$, then $E_F(T) \approx Eg/2$

Then

$$n_e \propto e^{Eg/2k_BT} \quad \text{and} \quad p_h \propto e^{Eg/2k_BT} \ \text{ and } n_e = p_e$$

$$\sigma \approx n_e e(\mu_e + \mu_h) \ \implies \ \ell n\ \sigma = -Eg/2k_BT + \text{ const.}$$

Thus on measuring $\sigma(T)$ this gives

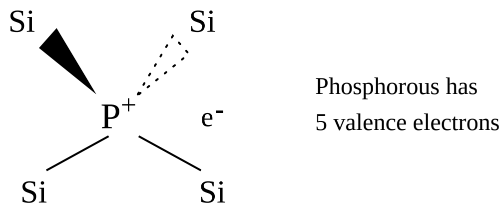


This is just another example of a "bulk" measurement which gives information about a microscopic quantity. Note: μ (mobilities) $\sim 100 - 1000$ cm^2/V s in semiconductors.

Doping of Homogeneous semi-conductors:

Assume that the microstructure of a single crystal can be altered by the random substitution of an impurity which has a slightly different number of valence electrons than the Group IV atoms.

Example:

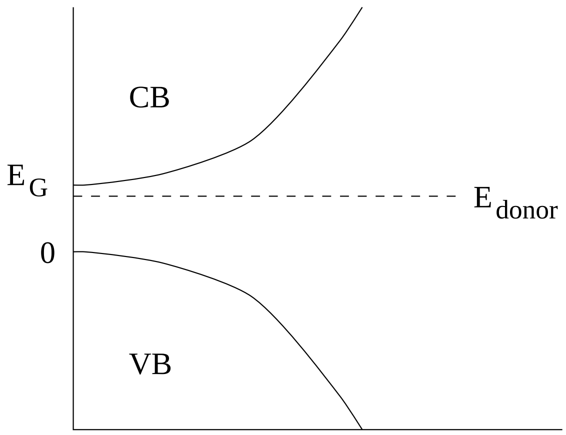


Since only 4 can reside in the valence band, the 5^{th} might be expected to be in the conduction band. If this were the case, then there would be a net $+1$ at the phosphorous site. Clearly, some energy is required to remove the electron from the proximity of the P atom. Thus one should expect the P^+ - e^- to form a bound state exactly analogous to a hydrogen atom. If the electron orbit is sufficiently large ($> 5-10$Å), the electron must travel in the environment of the semiconductor. Thus the electron sees a net charge as a result of the dielectric constant ϵ for the lattice. The eigenstate of the H-atom must be suitably modified

$$E_H = \frac{e\, m_e}{2\epsilon_0^2 \hbar^2} = 13.6 \text{ eV} \ , \quad E_d = \frac{e\, m_e^*}{2\epsilon^2 \hbar^2} = \frac{m_e^*}{m_e}\frac{1}{\epsilon^2}\, 13.6 \text{ eV}$$

$$d \equiv \text{ donor}$$

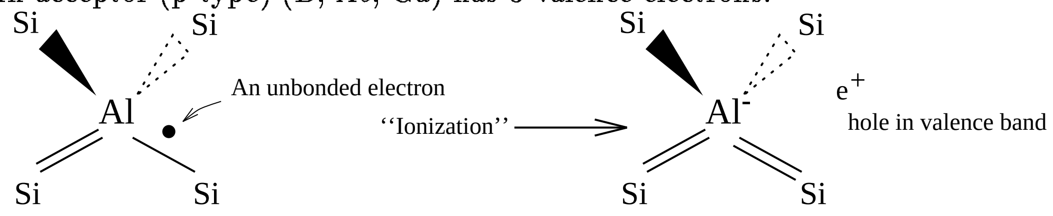
Typical values of $\frac{\epsilon}{\epsilon_0} \approx 10$ and $\frac{m_e^*}{m_e} \approx 0.1$ give a binding energy $E_d \approx 10$ meV (recall that $300^\circ K \sim 1/40$ eV). Clearly, the electron is weakly bound in a localized state. To ionize this state, the electron would have to be excited into the conduction band. Hence this state must lie $\sim$10 meV below the conduction band edge.



Notice that the electron orbit has a radius $= \frac{\epsilon\hbar^2}{m^* e^2}$ which gives a value of $\sim$ 50Å(i.e., the approximation is good).

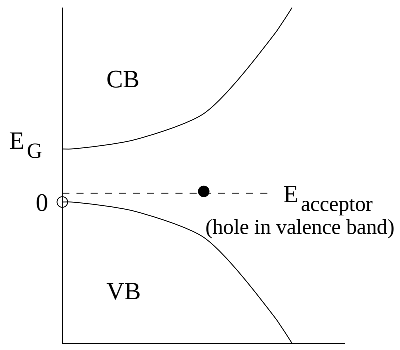
At room temperature (25 meV), there is sufficient thermal energy that states in the conduction band have occupancies close to that of the donor state. However, since the doping density is small (parts per thousand compared to parts per million) the immense abundance of CB states biases the statistics so that virtually all donor atoms will be "ionized". Since electrons are given to the CB, this is a donor (n-type).

An acceptor (p-type) (B, $A\ell$, Ga) has 3 valence electrons.



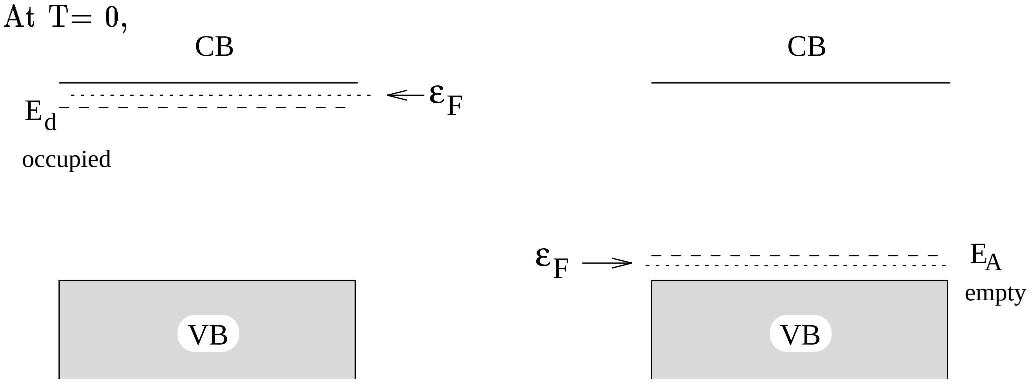
In this case the bound state will lie

$\sim$ 10 meV about the valence band edge.



Question: What happens to $\epsilon_F(T)$?

At T= 0,



At T>0, charge neutrality is still present. However there are four quantities to determine:

$$n, N_d^+, p, N_A^- \text{ where } \begin{aligned} N_d^+ &= \# \text{ of ionized donors} \\ N_A^- &= \# \text{ of ionized acceptors} \end{aligned}$$

and $\quad p + N_d^+ = n + N_A^-$

Now $\quad n = N_C e^{-(Eg - E_F(T))/k_B T}$ and $p = N_V e^{E_F(T)/k_B T}$ $E = 0$ at the VB band edge!

For the ionized donors,

$$
\begin{aligned}
N_d^+ &= N_d(1 - f(\epsilon)) = N_d\left(1 - \frac{1}{e^{((E_d - E_f)/k_BT)} + 1}\right) \\
N_A^- &= N_a(f(\epsilon)) = N_A\left(\frac{1}{e^{((E_A - E_F)/k_BT)} + 1}\right)
\end{aligned}
$$

Substituting into $p + N_d^+ = n + N_A^-$ gives a trancendental equation which must be solved numerically for E_F.

If we assume that only one type of impurity is present, donors for example, then $N_a \rightarrow 0$. $E_F(T)$ will now be near CB edge so $p \approx 0$
Thus $n = N_d^+$ and

$$
\begin{aligned}
N_c e^{-(E_g - E_f(T))/k_BT} &= N_d\left(1 - \underbrace{\frac{1}{e^{(E_d - E_F)/k_BT} + 1}}_{\text{small}}\right) = N_d^+ \\
&\approx N_d
\end{aligned}
$$

So

$$
\frac{N_d^+}{N_c} \approx e^{(E_g - E_f(T))/k_BT} \approx \frac{N_d}{N_c}
$$

$$
-(E_g - E_F(T)) \approx k_BT\ \ell n\ (N_d/N_c)
$$

Typically

$N_D = 5 \times 10^{22}/\mathrm{m}^3$ $\quad$ $N_c = 2.5 \times 10^{25}/\mathrm{m}^3$
$E_G - E_F(T) \approx 0.16$ eV $\quad$ All donors are ionized
$n = N_d \approx 5 \times 10^{22}/\mathrm{m}^3$, $\quad$ and $p \approx 0$

The conduction band is completely dominated by *IMPURITIES*