PHYS 460  LECTURE 15

SEMI CONDUCTORS, CONTINUED

Last lectures, we were discussing semi conductors as small band-gap insulators, and in particular the types of charge carriers which can be excited in these systems, either by light or thermal fluctuations.

We found that there were two types:

**Electrons**

- Occupied states
  - Near bottom of (nearly) empty conduction band
  - \[ E_e = E_{min} + \alpha \left| k - k_{min} \right|^2 \]
  - \[ m_e^* = \frac{\hbar^2}{2\kappa} = \frac{\hbar^2}{2\alpha} \]
  - \[ \vec{U}_e = \frac{1}{\kappa} \nabla_k \vec{E} \]
  - \[ m_e^* \frac{d\vec{u}}{dt} = -e(\vec{E} + \vec{v} \times \vec{B}) - m_e^* \vec{U}_e \]

**Holes**

- Empty states near top of (nearly) full valence band
  - \[ E_h = E_{max} - \alpha \left| k - k_{max} \right|^2 \]
  - \[ m_h^* = \frac{-\hbar^2}{2\kappa} = \frac{\hbar^2}{2\alpha} \]
  - \[ \vec{U}_h = \nabla_{k_{hole}} \vec{E}_h = \frac{1}{\kappa} \nabla \vec{E}_h \]
  - \[ m_h^* \frac{d\vec{u}}{dt} = e(\vec{E} + \vec{v} \times \vec{B}) - m_h^* \vec{U}_h \]

**Note:** Always bear in mind alternate definition of \( m_h^* \) which is \(-\nu_e\).
STATISTICAL MECHANICS OF ELECTRONS/HOLES

SEMICONDUCTORS ARE SPECIAL BECAUSE THEIR BAND GAPS ARE SMALL ENOUGH THAT THERMAL FLUCTUATIONS CAN excite a small number of carriers at accessible temperatures (T ~ 300K). We know how to calculate the carrier density from our previous experience with free electrons (i.e. Sommerfeld theory)

\[ n = \frac{N}{V} = \int_{0}^{\infty} g(\epsilon) f_{FD} (\epsilon - \mu) \, d\epsilon \]

WHERE \( f_{FD} = \frac{1}{e^{\frac{\epsilon - \mu}{kT}} + 1} \) is the Fermi-Dirac distribution.

And \( g(\epsilon) \) = density of states per unit volume

For free electrons, recall that

\[ E(k) = \frac{\hbar^2 k^2}{2m} \quad \Rightarrow \quad k = \sqrt{\frac{2mE}{\hbar^2}} \]

\[ g(\epsilon) dk = \frac{2}{(2\pi)^3} \frac{4\pi k^2 \, dk}{2m} = \frac{1}{(2\pi)^3} \left( \frac{2mE}{\hbar^2} \right)^{\frac{3}{2}} \frac{E}{\hbar^2} \frac{3}{2} \frac{dE}{2} \]

\[ = \frac{(2m)^{\frac{3}{2}}}{2\pi^2 \hbar^3} \epsilon \frac{d\epsilon}{d\epsilon} \]
THROUGH THE SAME REASONING, CONDUCTION ELECTRONS WITH ENERGY

\[ \varepsilon = \varepsilon_c + \frac{h^2 k^2}{2m_e^*} \]

HAVE

\[ g_c (\varepsilon > \varepsilon_c) = \frac{(2m_e^*)^{3/2}}{2\pi^2 \frac{h^3}{4}} (\varepsilon - \varepsilon_c)^{1/2} \]

IF \( \varepsilon_c - \mu \gg k_{BT} \) (GAP IS BIG "ENOUGH")

\[ f_{FD} = \frac{1}{e^{\frac{\varepsilon - \mu}{k_{BT}}} + 1} \]

i.e. FERMI-DIRAC STATISTICS REDUCE TO SIMPLE BOLTZMANN STATISTICS (WHICH WE MIGHT NOTICEM JUSTIFY USE OF DRUDE MODEL)

\[ n(T) \approx \frac{(2m_e^*)^{3/2}}{2\pi^2 \frac{h^3}{4}} \int_{\varepsilon_c}^{\infty} (\varepsilon - \varepsilon_c)^{1/2} e^{-\frac{\varepsilon_c - \mu}{k_{BT}}} d\varepsilon \]

\[ = \frac{(2m_e^*)^{3/2}}{2\pi^2 \frac{h^3}{4}} e^{-\frac{\mu}{k_{BT}}} \int_{\varepsilon_c}^{\infty} (\varepsilon - \varepsilon_c)^{1/2} e^{\frac{\varepsilon - \mu}{k_{BT}}} d\varepsilon \]

SUB \( x = \varepsilon - \varepsilon_c \), \( y = \sqrt{x} \), \( dy = \frac{1}{2}\sqrt{x} dx \)

\[ n(T) = \frac{(2m_e^*)^{3/2}}{2\pi^2 \frac{h^3}{4}} e^{-\frac{\mu}{k_{BT}}} \int_{0}^{\infty} y^2 e^{-\frac{y^2}{2k_{BT}}} dy \]
\[
\frac{(2m_e^*)^{3/2}}{2\pi^2 h^3} e^{\frac{\mu - \varepsilon_c}{k_B T}} \frac{1}{2} \left(\frac{k_B T}{\hbar^2}\right)^{3/2} \frac{1}{2}
\]

\[
\Rightarrow \quad n(T) = \frac{1}{4} \left(\frac{2m_e^* k_B T}{\pi \hbar^2}\right)^{3/2} e^{-\frac{(\varepsilon_c - \mu)}{k_B T}}
\]

We can do a similar calculation for holes at the top of the valence band:

\[
\varepsilon = \varepsilon_v^* - \frac{\hbar^2 k^2}{2 m_v^*}
\]

\[
g_n(\varepsilon < \varepsilon_v^*) = \left(\frac{2m_e^*}{2\pi \hbar^2}\right)^{1/2} \left(\frac{\varepsilon_v^* - \varepsilon}{\hbar^2}\right)^{1/2}
\]

Holes are the absence of electrons:

\[
f_{FP}^h = 1 - f_{FP}^e = 1 - \frac{1}{e^{\frac{(\varepsilon - \mu)}{k_B T}} + 1} = \frac{e^{\frac{(\varepsilon - \mu)}{k_B T}}}{e^{\frac{\varepsilon - \mu}{k_B T}} + 1} = \frac{1}{e^{\frac{(\varepsilon - \mu)}{k_B T}} + 1}
\]
If $\mu - \varepsilon_{v} \gg k_{B}T$ (again, $\mu$ inside gap, gap big enough)

$$f'_{v} \sim e^{\frac{\varepsilon - \mu}{k_{B}T}}$$

$$p(v) = \int_{-\infty}^{\infty} g_{v}(\varepsilon) f'(\varepsilon - \mu) \, d\varepsilon$$

$p$ for "positive" charges

$$= \int_{-\infty}^{\infty} g_{v}(\varepsilon) e^{\frac{\varepsilon - \mu}{k_{B}T}} \, d\varepsilon$$

Math, math, math

$$\Rightarrow p(v) = \frac{1}{4} \left( \frac{2m_{v}^{*}k_{B}T}{\pi \hbar^{2}} \right)^{\frac{3}{2}} e^{-\frac{(\mu - \varepsilon_{v})}{k_{B}T}}$$

The great unknown in both of these equations is the chemical potential $\mu(v)$

However, the product of $n(v)$ and $p(v)$ does not have this issue

$$n(v)p(v) = \frac{1}{2} \left( \frac{k_{B}T}{\pi \hbar^{2}} \right)^{3} (m_{e}^{*}m_{v}^{*})^{\frac{3}{2}} e^{-\frac{(\varepsilon_{c} - \varepsilon_{v})}{k_{B}T}}$$

Note $\varepsilon_{c} - \varepsilon_{v} = \Delta = \text{gap}$

This is known as the semiconductor "law of mass action" (named after same in chem)
When the conduction electrons are always the result of electrons excited from valence band (the only case we have considered so far), we refer to the material as an "intrinsic semiconductor" and

\[ n(T) = p(T) = \frac{1}{\sqrt{2}} \left( \frac{k_B T}{\pi \hbar^2} \right)^{3/2} \left( \frac{m_e^* m_h^*}{m_e^* m_h^*} \right)^{3/4} e^{-\frac{4}{2k_B T}} \]

or taking ratio

\[ \frac{n(T)}{p(T)} = 1 = \left( \frac{m_e^*}{m_h^*} \right)^{3/2} e^{-\frac{(E_c + E_v - 2\mu)}{k_B T}} \]

\[ 0 = \frac{3}{2} \ln \left( \frac{m_e^*}{m_h^*} \right) - \frac{(E_c + E_v - 2\mu)}{k_B T} + 2 \frac{\mu}{k_B T} \]

\[ \therefore \quad \mu(T) = \frac{E_c + E_v}{2} + \frac{3k_B T}{4} \ln \left( \frac{m_h^*}{m_e^*} \right) \]

Note that this confirms the idea that \( \mu \) lies inside the gap. At \( T = 0 \), \( \mu \) is precisely mid-gap, and if \( m_h^* = m_e^* \), it is always mid-gap (for intrinsic semiconductors).
OK, BUT WHY DID I MAKE A POINT OF SAYING THAT THESE FORMULAS (ON THE LAST PAGE) ARE FOR "INTRINSIC" SEMICONDUCTORS? WHEN ARE SEMICONDUCTORS NOT INTRINSIC? **ANSWER:** WHEN THE CARRIERS ARE THE RESULT OF IMPURITIES IN THE CRYSTALS. IN THIS CASE, THE SEMICONDUCTORS (OR CARRIERS) ARE "EXTRINSIC" SEMICONDUCTORS.

**CLASSIC EXAMPLES:** LONG $P$ ATOM INSIDE $Si$ CRYSTAL

$Si$ is a tetravalent atom, and the crystal is stabilized by 4-covalent bonds around each atom → DIAMOND STRUCTURE $P$ has one extra electron, so it's free to hop around.
Or, in band language, a Si crystal with a P impurity is the same as Si with one extra electron (and proton). But the valence band is full → extra electron goes to conduction band.

In this scenario, P is known as an "n-dopant" or electron "donor."

As you might anticipate, you can also manipulate the material in the opposite way. If one instead substitutes one Si atom with an atom of Al (or B), there will be one fewer electrons.

This is the same as adding one holes to the valence band.

For this reason, atoms like Al (in the case of Si) are known as "p-dopants" or electron "acceptor."
But hold on: these impurity atoms also change the number of protons. Doesn't that change things? Well, yes and no.

Consider the case of a P (P-dopant) atom in Si. The n-dopant added 1 electron and 1 proton. The proton creates an excess positive charge in the lattice structure which can bind free electrons. The potential \( V \) between an electron and this excess proton is given by

\[
V = \frac{e^2}{4\pi\varepsilon_0 \varepsilon r}
\]

where \( r \) is the distance between the two particles and \( \varepsilon \) is the relative dielectric constant which accounts for how well the sea of electrons screen the positive charge.

This is just a modified form of the hydrogen atom problem. Recall, for hydrogen, energies were given by

\[
E_n^{\text{hydrogen}} = -\frac{R_y}{n^2}
\]

where

\[
R_y = \frac{m e^2}{8\varepsilon_0^2 \hbar^2} \approx 13.6 \text{ eV}
\]

was the Rydberg constant.
Also, for hydrogen, the orbital radius was given by

\[ r_n = n^2 a_0 \]

where

\[ a_0 = \frac{4\pi e_0 \frac{\hbar^2}{m e^2}}{0.51 \times 10^{-10} \text{ m}} \]

was the Bohr radius.

In the case of P in Si, we can do the exact same calculation (if we were so inclined) with the modifications \( \epsilon_0 \to \epsilon_0 \epsilon_r \) and \( m \to m_e^* \)

\[ E = R_y^{\text{eff}} = R_y \left( \frac{m e^*}{m} \right) \left( \frac{1}{\epsilon_r} \right)^2 \]

and

\[ \Rightarrow a_0^{\text{eff}} = a_0 \left( \frac{m}{m_e^*} \right) \left( \frac{\epsilon_r}{\epsilon_0} \right) \]

Clearly, these values depend on the specific material, but for Si (which is typical)

\[ \frac{m e^*}{m} \sim 0.2 \quad \text{and} \quad \epsilon_r \sim 12 \]

[\( a_0^{\text{eff}} = (0.5\hat{A}) \times 12 = 30\hat{A} \]

\[ R_y^{\text{eff}} = 13.6 \text{ eV} \times 0.2 \times \frac{1}{12} \approx 0.02 \text{ eV} \]
This means that there exists a bound state with energies \( \sim 0.02 \text{ eV} \) below \( \varepsilon_c \), which already partially dislocalized.

At \( T = 0 \text{K} \), this lonely electron is bound and cannot carry current (unless the density of donor atoms is large enough to form a "donor band").

However, the small energy of \( E_{\text{FF}} \) means that electrons can be thermally excited into the conduction band at temperatures \( T \sim 200 \text{K} \). At high temperatures, you get a net excess of electrons. At low temperatures, these electrons "freeze out".

Similar arguments establish the existence of "acceptor bands" (whose name now makes sense) which can steal electrons and form holes at moderate temperatures.