Lecture 16

Density of charge carriers in semiconductors

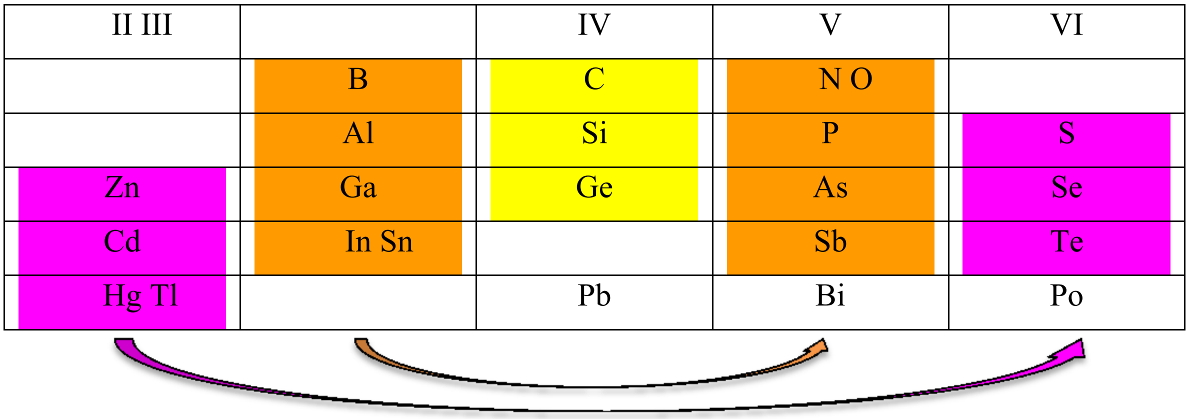
Today:

1. Examining the consequences of Fermi distribution in semiconductors.
   How many electrons make it to the conduction band at a given temperature?
2. Modeling bands as parabolas at the band edge.
3. Density of levels for the parabolic approximation for ***E*** vs. ***k***.
4. Holes as charge carriers.
5. D.O.S. function in semiconductors (SC).
6. Number of carriers in thermal equilibrium.
7. Non-degenerate semiconductors.
8. Law of mass action.
9. Density of charge carriers in intrinsic semiconductors.

Questions you should be able to answer by the end of today's lecture:

1. What is the physical insight at the basis of the parabolic band edge approximation?
2. What is the meaning of holes?
3. What role does the chemical potential play in determining the properties of a SC? How does the position of the chemical potential relative to the band edge affects the type, and density of charge carriers?
4. What are degenerate and non-degenerate semiconductors?
5. What is the physical significance of the exponential-like behavior of the Fermi-function in non-degenerate semiconductors?
6. What is the Law of Mass Action?
7. How many charge carriers does a SC have at temperature ***T***?
8. Where is the Fermi level within the bandgap in intrinsic SC?

Identifying semi-conducting elements and compounds in the periodic table



II III		IV	V	VI
	B	C	N O	
	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In Sn		Sb	Te
Hg Tl		Pb	Bi	Po

Graph removed due to copyright restrictions. Shows Energy bandgap vs. lattice constant in III-V materials. Unknown source.

A number of ways to classify SC:

1. Elemental vs. compound
2. Direct vs indirect gaps
3. Intrinsic vs. extrinsic

Plugging in the numbers into the Fermi function: $\frac{E_c - \mu}{k_B T} = \frac{0.55eV}{0.025eV} = 22$

$$f(E) = \frac{1}{e^{(E-\mu)/k_B T} + 1} \approx 10^{-10}$$

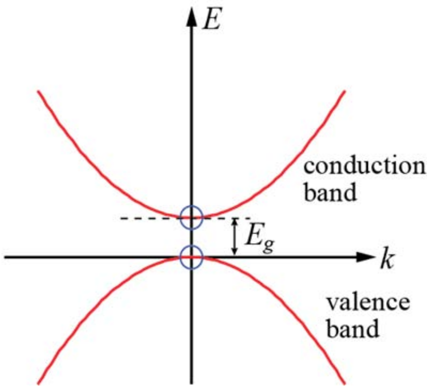
Thus fermi's function tells us that very few electrons make it to the conduction band in order to figure out how many states are actually populated we need to multiply the Fermi function $f(E)$ with the density of states $g(E)$ to give us the density of occupied states.

The Fermi function tells us that for $\frac{E_c - \mu}{kT} \gg 1$ the number of electrons promoted to the conduction band will be small and will occupy the lowest energy levels in that band.

Figure removed due to copyright restrictions. Fig. 3: Kittel, Charles. *Introductionto Solid Sate Physics*. 8th ed. Wiley, 2004, p. 147.

Review: Band Structure – "parabolic shape"

The simplest band structure for a semiconductor is given by the following diagram:



1. Allowed and forbidden bands. Identification of the gap energy.
2. Curvature of bands – effective mass.
3. DOS.
4. Slope of the bands – group velocity.

Near the band edges (extrema) the shape of the bands can be approximated as:

$$E_c\left(\vec{k}\right) = E_g + \frac{\hbar^2 k^2}{2m_c^*}$$

$$E_v\left(\vec{k}\right) = -\frac{\hbar^2 k^2}{2m_v^*}$$

Where $\boldsymbol{E_g}$ is the band gap and the effective masses are $m_{c,v}^*$ (given by the curvature of the conduction and valence band).

Holes as charge carriers

An empty state in a band filled with electrons is called a hole. This vacant state behaves in many ways as if it were a charge carrier of positive sign +e and equal mass to that of the missing electron.

Then the distribution function for holes is simply: $1 - f\left(E\right) = 1 - \frac{1}{e^{(E-\mu)/k_B T} + 1} = \frac{1}{e^{(\mu-E)/k_B T} + 1}$

Density of States (D.O.S.) in Semiconductors.

Akin to metals, we will use an approximation to the D.O.S function, which is based on our 3D free electron gas. However, here we need to take into account the fact that we are considering charge carriers within the bands, i.e. for electrons we only look at the conduction band and for holes we only look at the valence band.

D.O.S for electrons in the conduction band: $g_c\left(E\right) = \sqrt{2\left(E - E_c\right)}\,\frac{m_c^{3/2}}{\pi^2 \hbar^3}$

D.O.S. for holes in the valence band: $g_v\left(E\right) = \sqrt{2\left(E_v - E\right)}\,\frac{m_v^{3/2}}{\pi^2 \hbar^3}$

Density of carriers in Semiconductors at thermal equilibrium

The number of charge carriers per unit volume at a given temperature is the most important property of any semiconductor. The values of these are highly dependent on the number of impurities. We will first consider the relations which hold regardless of whether the material is doped or not.

$$n_c\left(T\right) = \int_{\varepsilon_c}^{\infty} g_c\left(E\right) f\left(E\right) dE = \int_{\varepsilon_c}^{\infty} g_c\left(E\right) \frac{1}{e^{(E-\mu)/k_B T} + 1} dE$$

$$p_v\left(T\right) = \int_{-\infty}^{\varepsilon_v} g_v\left(E\right)\left(1 - f\left(E\right)\right) dE = \int_{-\infty}^{\varepsilon_v} g_v\left(E\right)\left(\frac{1}{e^{(\mu-E)/k_B T} + 1}\right) dE$$

In the equations above n_c is the number of electrons in the conduction band and p_v is the number of holes in the valence band.

The impurities affect the values of n_c and p_v through their effect on the chemical potential.

Figure removed due to copyright restrictions. Fig. 2.16: Pierret, Robert F. *Semiconductor Fundamentals*. 2nd ed. Prentice Hall, 1988.

Degenerate and non-degenerate semiconductors

In non-degenerate SC the chemical potential satisfies:

$$E_c - \mu >> k_B T$$
$$\mu - E_v >> k_B T$$

When the electron energy is far from the Fermi energy, we can approximate Fermi-Dirac distribution function with an exponential – a Maxwell-Boltzmann distribution. We can simply treat the electrons as a classical gas.

$$\frac{1}{e^{(E-\mu)/k_B T}+1} \approx e^{-(E-\mu)/k_B T}, \ \mathrm{E{>}E_c}$$
$$\frac{1}{e^{(\mu-E)/k_B T}+1} \approx e^{-(\mu-E)/k_B T}, \ \mathrm{E{<}E_v}$$

Figure removed due to copyright restrictions. Fig. 18: Kittel, Charles. *Introduction to Solid Sate Physics*. 8th ed. Wiley, 2004, p. 219.

Then the expressions we have derived for the carrier densities can be approximated by:

$$n_c(T) = \int_{E_c}^{\infty} g_c(E) f(E) dE \approx \left(\underbrace{\int_{E_c}^{\infty} g_c(E) e^{-(E-E_c)/k_B T} dE}_{N_c(T)} \right) e^{-(E_c-\mu)/k_B T} = N_c(T) e^{-(E_c-\mu)/k_B T}$$

$$p_v(T) = \int_{E_c}^{\infty} g_v(E)\left(1-f(E)\right) dE \approx \left(\underbrace{\int_{-\infty}^{E_v} g_v(E) e^{-(E_v-E)/k_B T} dE}_{P_v(T)} \right) e^{-(\mu-E_v)/k_B T} = P_v(T) e^{-(\mu-E_v)/k_B T}$$

Because of the rapidly decaying function in the integrand **only energies that are within k_BT of the band edge will contribute significantly**, therefore we can assume a quadratic density of states, which yields the following form of $N_c(T)$ and $P_v(T)$:

$$N_c(T) = \int_{E_c}^{\infty} g_c(E) e^{-(E-E_c)/k_BT} \, dE = \frac{1}{4}\left(\frac{2m_c^* k_B T}{\pi\hbar^2}\right)^{3/2}$$

$$P_v(T) = \int_{-\infty}^{E_v} g_v(E) e^{-(E_v-E)/k_BT} \, dE = \frac{1}{4}\left(\frac{2m_v^* k_B T}{\pi\hbar^2}\right)^{3/2}$$

While we cannot calculate the carrier density without specific knowledge of the chemical potential, the product of the hole and electron carrier densities does not depend on the chemical potential:

$$\boxed{n_c p_v = N_c P_v e^{(E_v-E_c)/k_BT} = N_c P_v e^{-E_g/k_BT}}$$

This equation is called the ***law of mass action***. **It states that at a given temperature it is sufficient to know the density of one carrier type to calculate the concentration of the other.**

Up till now the results were valid regardless of whether the SC is intrinsic or extrinsic, the only assumption made was that the material was non-degenerate. One of the results of the law of mass action is that the product $n_c p_v$ is constant. **This means that by adding a large number of carriers of one type we cause the carrier concentration of the other type to decline.** Leading to an overall decline in the total number of charge carriers.

Intrinsic Semiconductors

Figure removed due to copyright restrictions. Fig. 2.20: Pierret, Robert F. Semiconductor Fundamentals. 2nd ed. Prentice Hall, 1988.

If the crystal is pure such that there is a negligible contribution of the impurities to the charge density – it is called an intrinsic SC.

$$n_c(T) = p_v(T) \equiv n_i(T)$$

$$n_i = \sqrt{n_c p_v} = \sqrt{N_c P_v} e^{-E_g/2k_BT}$$

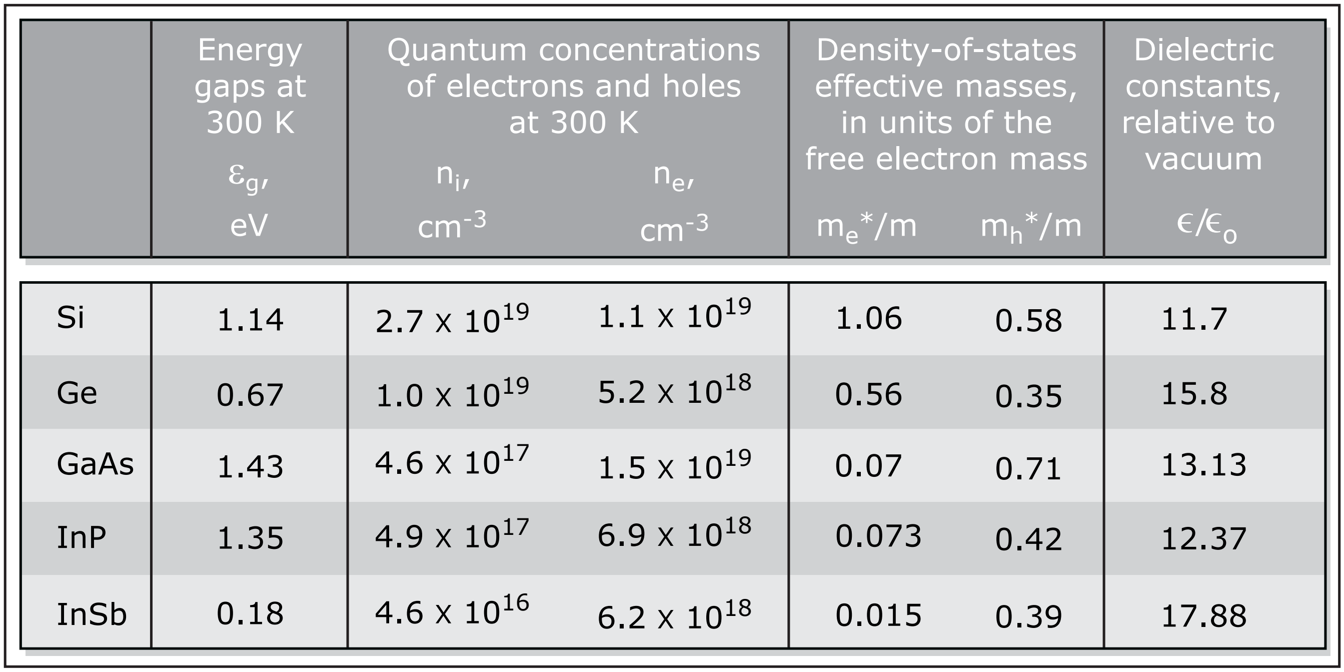
$$n_c(T) = N_c(T) e^{-(\varepsilon_c-\mu)/k_BT}$$

$$p_v(T) = P_v(T) e^{-(\mu-\varepsilon_v)/k_BT}$$

As we saw above, while the density of electrons in the conduction band and holes in the valence band depends on the chemical potential the product of vacancies and electrons depends only on the magnitude of the bandgap. Such that:

$$np = N_e P_v e^{-\frac{E_g}{k_BT}}$$

It is important to remember that this expression is valid for both intrinsic and extrinsic semiconductors that satisfy the non-degeneracy condition.



	Energy gaps at 300 K	Quantum concentrations of electrons and holes at 300 K		Density-of-states effective masses, in units of the free electron mass		Dielectric constants, relative to vacuum
	ε_g, eV	n_i, cm^{-3}	n_e, cm^{-3}	m_e^*/m	m_h^*/m	ϵ/ϵ_o
Si	1.14	2.7×10^{19}	1.1×10^{19}	1.06	0.58	11.7
Ge	0.67	1.0×10^{19}	5.2×10^{18}	0.56	0.35	15.8
GaAs	1.43	4.6×10^{17}	1.5×10^{19}	0.07	0.71	13.13
InP	1.35	4.9×10^{17}	6.9×10^{18}	0.073	0.42	12.37
InSb	0.18	4.6×10^{16}	6.2×10^{18}	0.015	0.39	17.88

Image by MIT OpenCourseWare.

The position of the chemical potential is obtained from the expressions for the charge carrier density. In intrinsic SC the number of electrons in the conduction band equals the number of holes in the valence band, thus:

$$n_i = p_i, \Rightarrow n_i^2 = N_c P_v e^{-\frac{E_g}{k_B T}}$$

$$n_i(T) = n_c(T) = N_c(T) e^{-(\varepsilon_c-\mu)/k_BT} = P_v(T) e^{-(\mu-\varepsilon_v)/k_BT} = p_v(T) = n_i(T) = \sqrt{P_v(T) N_c(T)}\, e^{-\frac{Eg}{2k_BT}}$$

This in turn enables us to solve for the chemical potential:

$$P_v(T) e^{-(\mu-E_v)/k_BT} = \sqrt{P_v(T) N_c(T)}\, e^{-\frac{Eg}{2k_BT}} \Rightarrow e^{\left(\mu-E_v-\frac{E_g}{2}\right)\Big/k_BT} = \sqrt{\frac{P_v(T)}{N_c(T)}} = \left(\frac{m_v^*}{m_c^*}\right)^{\frac{3}{4}}$$

$$\boxed{\mu = E_v + \frac{1}{2} E_g + \frac{3}{4} k_B T \ln\left(\frac{m_v^*}{m_c^*}\right)}$$

And taking into account: $\left(\frac{m_v^*}{m_c^*}\right) \approx 1$

We find that the position of the chemical potential is close to center of the bandgap in an intrinsic SC. Note that the only assumption we used was that of non-degeneracy.

3.024 Electronic, Optical and Magnetic Properties of Materials
Spring 2013