Semiconductor Statistical Mechanics (Read Kittel Ch. 8)

Conduction band occupation density:

$$n = \int_{E_c}^{\infty} f(E)g(E)dE$$

f(E) - occupation probability - Fermi-Dirac function:

g(E) - density of states / unit volume.

For an isotropic, parabolic band, generalize free-electron theory:

$$g(E) = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}(E-E_c)^{1/2}$$

$$\therefore \quad n = \frac{1}{2\pi^2}\left(\frac{2m_e^*}{\hbar^2}\right)^{3/2}\int_0^{\infty}\frac{\varepsilon^{1/2}d\varepsilon}{1+\exp[(\varepsilon - E_F + E_c)/kT]}$$

where $\varepsilon \equiv E - E_c$. Define dimensionless variables:

$$\eta = \frac{\varepsilon}{kT} \quad \eta_c = \frac{E_c}{kT} \quad \mu = \frac{E_F}{kT}$$

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e^*kT}{\hbar^2}\right)^{3/2}\int_0^{\infty}\frac{\eta^{1/2}d\eta}{1+\exp(\eta-\mu+\eta_c)}$$

$$\equiv N_c F_{1/2}(\mu - \eta_c)$$

"Fermi-Dirac integrals" (tabulated in Semiconductor Statistics, J.S. Blakemore, Pergamon, 1962)

$$F_n(x) \equiv \frac{2}{\sqrt{\pi}}\int_0^{\infty}\frac{z^n dz}{1+\exp(z-x)}$$

"effective density of states":

Recall the discussion of degenerate / non-degenerate Fermi-gas. N_C is ≅ density for the degenerate case.

Some numbers:

For Si, $m_e^* = 1.18 m_o$ ("density of states" mass); $N_c = 2.8 \times 10^{19} cm^{-3}$ at 300K .

For GaAs, $m^*_e = 0.067 m_o$; $N_c = 4.3 \times 10^{17} cm^{-3}$ at 300K

$= 6.6 \times 10^{14} cm^{-3}$ at 4K

<u>Anisotropic bands</u>

density of states mass:

ν = degeneracy factor - # of equivalent CB valleys
= 6 in Si
= 1 in GaAs

<u>Maxwell-Boltzmann approximation</u>

If E_F is well inside band-gap (non-degenerate case): $E_c - E_F \gg kT$, then the Fermi function → Boltzmann factor

$$F_n(x) \cong \frac{2}{\sqrt{\pi}} \int_0^{\infty} z^n e^{x-z} dz = e^x \qquad \text{for } n = \frac{1}{2}$$

This expression can be interpreted as if there are N_c states all located at band edge.

<u>Holes</u>: use the distribution for empty states:

$$f_p(E) = 1 - f_{FD}(E) = \frac{1}{1 + \exp[(E_F - E)/kT]}$$

$$p = \int_{-\infty}^{E_v} g(E)[1 - f_{FD}(E)]dE$$

$$p = N_V F_{1/2}(\eta_V - \mu) \qquad \eta_V \equiv \frac{E_V}{kT}$$

$$N_V = \frac{1}{4}\left(\frac{2m_h^* kT}{\pi\hbar^2}\right)^{3/2}$$

Maxwell-Boltzmann approx:

<u>Intrinsic case</u> (pure semiconductor, no doping)

charge neutrality: $n = p = n_i$

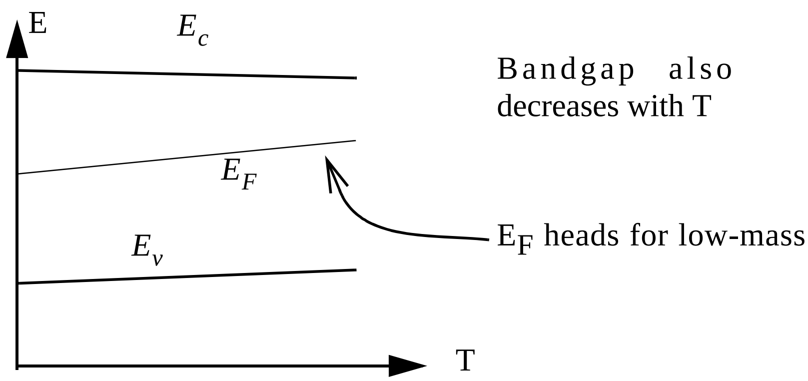
$$N_c F_{1/2}\left(\frac{E_F - E_c}{kT}\right) = N_V F_{1/2}\left(\frac{E_V - E_F}{kT}\right)$$

The intrinsic case is nearly always non-degenerate, so we can write:

Now, take the log of both sides, and solve for E_F:

$$E_F = \frac{E_c + E_V}{2} + \frac{kT}{2}\ln\frac{N_V}{N_c}$$

$\rightarrow$ E_F is near midgap. E_F is exactly at midgap at T=0.



For high enough T, large mass ratio, can get “high temperature degeneracy. Examples: InSb, InAs above ~ 400K.

The intrinsic carrier densities are independent of E_F.

$$= N_c N_V e^{-E_G/kT} \qquad E_G \text{ : energy gap}$$

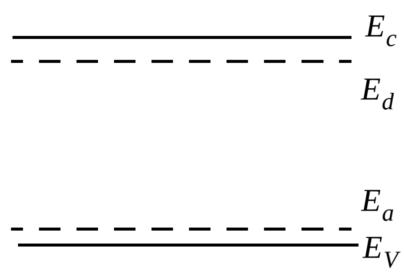
$$n_i = \sqrt{N_c N_V} e^{-E_G/2kT}$$

$$= \frac{1}{4}(m_e^* m_h^*)^{3/4}\left(\frac{2kT}{\pi\hbar^2}\right)^{3/2} e^{-E_G/2kT}$$

Measurement of n_i vs. T can be used to determine E_G.

<u>Extrinsic case</u> (doped semiconductors)

"shallow impurities"
E_D or E_A close to band edges. Easily "ionized" at RT



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

<u>GaAs dopants</u>

	E_d(meV)	E_a(meV)
S	6	
Se	6	
Te	6	
Si	6	36
Ge	6	40
Sn	6	171
C	6	26
Zn		31
Be		28

<u>Si dopants</u>

	E_d(meV)	E_a(meV)
P	44	
As	49	
Sb	39	
B		45
Al		69
Ga		73
In		160

Notice that these ionization energies are very similar. This suggests a simple hydrogenic model:

For Si, $m^*_e = 0.74 m_0$ (mobility mass), $\varepsilon = 11.9\varepsilon_0$. So in this model, E_d = 71 meV.

For GaAs, $m^*_e = 067 m_0$, $\varepsilon = 13.1\varepsilon_o$, so $E_d =$ 5 meV.

In general, we may have both donors & acceptors.

Complete ionization case

Charge neutrality:

$$N_d - N_a = n - p$$

For the non-degenerate case still holds.

$$n = N_d - N_a + \frac{n_i^2}{n}$$

Solve this quadratic equation for *n:*

$$n = \frac{N_d - N_a}{2}\left[1 + \sqrt{1 + 4\frac{n_i^2}{(N_d - N_a)^2}}\right]$$

Similarly:

$$p = \frac{N_d - N_a}{2}\left[\sqrt{1 + 4\frac{n_i^2}{(N_d - N_a)^2}} - 1\right]$$

For $N_d - N_a \gg n_i$:

, and .

Statistical Mechanics for Donors & Acceptors

Incomplete ionization

Remove assumption of complete ionization of the dopants. Find the temperature dependence of n, p, E_F

For simplicity, consider n-type case, donors only $N_a = 0$. Can generalize later.

N_{di} - density of ionized donors

N_{dn} - density of neutral donors

N_d - total density of donors

Assume 1 electronic state per donor atom.

$$N_{dn} = N_d \frac{1}{1 + \exp[(E_d - E_f)/kT]}$$

$$N_{di} = N_d - N_{dn} = \frac{N_d \exp[(E_d - E_F)/kT]}{1 + \exp[(E_d - E_F)/kT]}$$

then,

If the donor states have degeneracies, g_i, g_n (i.e. spin), then this expression is modified to:

$$\frac{N_{di}}{N_{dn}} = \frac{g_i}{g_n} \exp[(E_d - E_F)/kT]$$

$$N_{dn} = \frac{N_d}{1 + \frac{g_i}{g_n} \exp[(E_d - E_F)/kT]}$$

For a simple monovalent donor

For acceptors, the analogous expression is:

$$N_{an} = \frac{N_a}{1 + \frac{g_n}{g_i}\exp[-(E_a - E_F)/kT]}$$

What we want to do is determine the free carrier density: (non degenerate statistics)

$$N_{di} = n - p \cong n, \quad \text{(assuming n-type: } n >> p\text{)}$$

let $\eta_d = E_d/kT$; $\eta_c = E_c/kT$; $\mu = E_F/kT$

$$n = N_d - N_{dn} = N_d - \frac{N_d}{1 + \frac{1}{2}e^{\eta_d - \mu}}$$

Eliminate μ by using $n = N_c e^{\mu - \eta_c}$.

$$e^{\mu - \eta_d} = e^{\mu - \eta_d}\left(\frac{n}{N_c e^{\mu - \eta_c}}\right) = e^{\eta_c - \eta_d}\frac{n}{N_c}$$

so

$$n = \frac{N_d}{1 + 2\frac{n}{N_c}e^{\eta_c - \eta_d}}$$

which is a quadratic equation for *n.* The solution is:

$$n = \frac{N_c}{4}e^{-(\eta_c - \eta_d)}\left[-1 \pm \sqrt{1 + 8\frac{N_d}{N_c}e^{\eta_c - \eta_d}}\right]$$

- root is unphysical

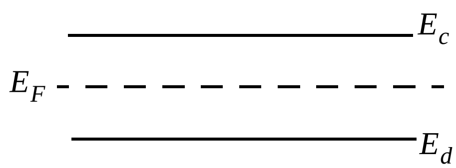
To gain physical insight we examine limiting behaviors of this relation:

Low temperature, $\eta_c - \eta_d \gg 1$ $(kT \ll E_c - E_d)$ "reserve region"

$$n \cong \frac{N_c}{4} e^{-(\eta_c - \eta_d)} \left(8 \frac{N_d}{N_c} e^{\eta_c - \eta_d}\right)^{1/2}$$

$$= \left(\frac{N_c N_d}{2}\right)^{1/2} e^{-(\eta_c - \eta_d)/2}$$

Here, E_F falls in between E_c, E_d. Sort of a mini-gap



For moderate T, such that $8 \frac{N_d}{N_c} e^{\eta_c - \eta_d} < 1$, or $kT > \frac{E_c - E_d}{\ln(N_c / 8N_d)}$, expand the $\sqrt{\quad}$:

$$n \cong \cancel{\frac{N_c}{4}} \cancel{e^{-(\eta_c - \eta_d)}} \left[\cancel{4} \frac{N_d}{\cancel{N_c}} \cancel{e^{\eta_c - \eta_d}}\right]$$

$$n \cong N_d$$

This is called the "exhaustion region" (Here's where we usually want to be - complete ionization.)

For really high T, $n >> p$ is no longer true. How high does T have to be for this?

$$-E_G / 2kT \gtrsim \ln\left(\frac{N_d}{\sqrt{N_c N_v}}\right)$$

$$E_G / 2kT \lesssim \frac{1}{2} \ln\left(\frac{N_c N_v}{N_d^2}\right)$$

or finally:

$$kT \gtrsim \frac{E_g}{\ln(N_c N_v / N_d^2)}$$

When this condition is true, then we basically have intrinsic: