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:

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

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

where \( \epsilon \equiv E - E_c \). Define dimensionless variables:

\[
    \eta = \frac{\epsilon}{kT}, \quad \eta_c = \frac{E_c}{kT}, \quad \mu = \frac{E_F}{kT}
\]

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

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

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

\[
    F_n(x) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{z^n \, dz}{1 + \exp(z - x)}
\]
“effective density of states”:

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

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

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

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

**Anisotropic bands**

density of states mass:

$v = \text{degeneracy factor} - \# \text{ of equivalent CB valleys}

= 6 \text{ in Si}

= 1 \text{ in GaAs}

**Maxwell-Boltzmann approximation**

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

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

This expression can be interpreted as if there are $N_c$ states all located at band edge.
Holes: use the distribution for empty states:

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

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

\[
p = N_VF_{1/2}(\eta_V - \mu) \quad \eta_V = \frac{E_V}{kT}
\]

\[
N_V = \frac{1}{4} \left(\frac{2m^*_h kT}{\pi \hbar^2}\right)^{3/2}
\]

Maxwell-Boltzmann approx:

Intrinsic case (pure semiconductor, no doping)

charge neutrality: \( n = p = n_i \)

\[
N_c F_{1/2} \left(\frac{E_F - E_c}{kT}\right) = N_VF_{1/2} \left(\frac{E_V - E_F}{kT}\right)
\]

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

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

\[
E_F = \frac{E_c + E_V}{2} + kT \ln \frac{N_V}{N_c}
\]
\( \rightarrow E_F \) 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 \( \sim 400 \text{K} \).

The intrinsic carrier densities are independent of \( E_F \).

\[
\begin{align*}
n_i &= N_cN_v e^{-E_G/2kT} \\
&= \sqrt{\frac{N_cN_v e^{-E_G/2kT}}{N_cN_v}}
\end{align*}
\]

Measurement of \( n_i \) vs. \( T \) can be used to determine \( E_G \).
Extrinsic case (doped semiconductors)

“shallow impurities”

$E_D$ or $E_A$ close to band edges. Easily “ionized” at RT

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**GaAs dopants**

<table>
<thead>
<tr>
<th>Element</th>
<th>$E_d$ (meV)</th>
<th>$E_a$ (meV)</th>
</tr>
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<tbody>
<tr>
<td>S</td>
<td>6</td>
<td>36</td>
</tr>
<tr>
<td>Se</td>
<td>6</td>
<td>49</td>
</tr>
<tr>
<td>Te</td>
<td>6</td>
<td>26</td>
</tr>
<tr>
<td>Si</td>
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<td>40</td>
</tr>
<tr>
<td>Ge</td>
<td>6</td>
<td>40</td>
</tr>
<tr>
<td>Sn</td>
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<td>171</td>
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<tr>
<td>C</td>
<td>6</td>
<td>26</td>
</tr>
<tr>
<td>Zn</td>
<td>6</td>
<td>31</td>
</tr>
<tr>
<td>Be</td>
<td>28</td>
<td></td>
</tr>
</tbody>
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**Si dopants**

<table>
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<th>Element</th>
<th>$E_d$ (meV)</th>
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<td>P</td>
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<tr>
<td>As</td>
<td>49</td>
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<tr>
<td>Sb</td>
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<td>B</td>
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<tr>
<td>Al</td>
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<tr>
<td>Ga</td>
<td>73</td>
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<tr>
<td>In</td>
<td>160</td>
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</table>
Notice that these ionization energies are very similar. This suggests a simple hydrogenic model:

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

For GaAs, \( m^*_e = 0.67m_0 \), \( \varepsilon = 13.1\varepsilon_0 \), so \( E_d = 5 \text{ meV} \).

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
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,

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

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

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

For a simple monovalent donor
For acceptors, the analogous expression is:

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

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

\[
N_{di} = n - p \approx n,
\]
(assuming n-type: \(n >> p\))

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

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

(1)

Eliminate \(\mu\) by using \(n = N_c e^{\mu - \eta_c}\).

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

so

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

which is a quadratic equation for \(n\). The solution is:

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

- 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”

\[
n \approx \frac{N_c}{4} e^{-\left(\eta_c - \eta_d\right)} \left(\frac{N_d}{N_c}\right)^{1/2} e^{-\left(\eta_c - \eta_d\right)/2}
\]

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

\[
\frac{E_c}{E_F} - \ldots - \ldots - \ldots - \ldots - \ldots - \frac{E_d}{E_F}
\]

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

\[
n \approx \frac{N_c}{4} e^{-\left(\eta_c - \eta_d\right)} \left[ 1 + \frac{N_d}{N_c} e^{-\left(\eta_c - \eta_d\right)} \right]
\]

\[
n \approx N_d
\]

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?

\[
-E_G/2kT \geq \ln \left( \frac{N_d}{N_cN_v} \right)
\]

\[
E_G/2kT \leq \frac{1}{2} \ln \left( \frac{N_cN_v}{N_d^2} \right)
\]

or finally:
\[ kT \geq \frac{E_g}{\ln(N_c N_v / N_d^2)} \]

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

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log n
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\[ n \sim e \quad \frac{-E_g}{2kT} \]

\[ n \sim N_d \quad \text{"exhaustion"} \]

\[ n \sim e \quad \frac{-(E_c - E_d)}{2kT} \]

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1/T