ECE606: Solid State Devices
Lecture 7

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Presentation Outline

• Intrinsic carrier concentration
• Potential, field, and charge
• E-k diagram vs. band-diagram
• Basic concepts of donors and acceptors
• Law of mass-action & intrinsic concentration
• Statistics of donors and acceptor levels
• Intrinsic carrier concentration
• Temperature dependence of carrier concentration
• Multiple doping, co-doping, and heavy-doping
• Conclusions

Reference: Vol. 6, Ch. 3 & 4
Electron Concentration in 3D solids

\[
n = \int_{E_c}^{E_{\text{sup}}} g_c(E) f(E) dE
\]

\[
= \int_{E_c}^{E_{\text{sup}}} 2 \times \frac{m^*_n \sqrt{2m^*_n (E - E_C)}}{2\pi^2 \hbar^3} \frac{1}{1 + e^{\beta(E - E_F)}} dE
\]

\[
= \frac{m^*_n \sqrt{2m^*_n (E - E_C)}}{\pi^2 \hbar^3} \frac{1}{1 + e^{\beta(E - E_F)}} dE
\]

\[
= N_C \frac{2}{\sqrt{\pi}} F_{1/2}(\eta_c) \quad \eta_c \equiv \beta (E_F - E_C)
\]

\[
N_c = 2 \left( \frac{2\pi m_n^* \beta}{\hbar^2} \right)^{\nu/2} F_{1/2}(\eta) = \int_0^\infty \sqrt{\pi} d\xi \frac{1}{1 + e^{\xi^2}}
\]
Boltzmann vs. Fermi-Dirac Statistics

\[ n = N_c \frac{2}{\sqrt{\pi}} F_{1/2}(\eta_c) \rightarrow N_c e^{\eta_c} \quad \text{if} \quad -\eta_c \equiv \beta(E_c - E_F) > 3 \]

Effective Density of States

\[ n = N_c \frac{2}{\sqrt{\pi}} F_{1/2}(\eta_c) \rightarrow N_c e^{-\beta(E_c - E_F)} \quad \text{if} \quad E_c - E_F > 3\beta \]

As if all states are at a single level \( E_c \)
Fermi-Level for Intrinsic Semiconductors

\[ n = N_c e^{-\beta(E_i - E_f)} \]

\[ p = N_v e^{\beta(E_i - E_f)} \]

\[ n \times p = N_c N_v e^{-\beta(E_i - E_f)} \]
\[ = N_c N_v e^{-\beta E_g} \]

Product is independent of the Fermi level!
Very useful balance equation! Will use it often

\[ n = p = n_i \]
\[ n_i^2 = N_c N_v e^{-\beta E_g} \]
\[ n_i = \sqrt{N_c N_v e^{-\beta E_g / 2}} \]
\[ E_F \equiv E_i \]

\[ n = p \Rightarrow N_c e^{-\beta(E_i - E_f)} = N_v e^{\beta(E_i - E_f)} \]
\[ E_i = \frac{E_G}{2} + \frac{1}{2\beta} \ln \frac{N_v}{N_c} \]
• We discussed how electrons are distributed in electronic states defined by the solution of Schrodinger equation.

• Since electrons are distributed according to their energy, irrespective of their momentum states, the previously developed concepts of constant energy surfaces, density of states etc. turn out to be very useful.

=> will not discuss Schrodinger Eq. anymore

=> everything is captured in bandedges and effective masses

• We still do not know where $E_f$ is for general semiconductors ... If we did, we could calculate electron concentration.

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Reference: Vol. 6, Ch. 3 & 4
Potential Energy

\[ P.E. = E_c - E_{ref} = -qV \]
Potential, Field and Charge

\[ P.E. = E_c - E_{ref} = -qV(x) \]

\[ V = 0 \]

In most practical cases start from charge and derive potentials! => Useful to learn “graphical” integration
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Critical items here;
Intrinsic semiconductor has VERY few active electrons
n_i is of the order of 10^{10}/cm^3. In 10^{22}/cm^3 atoms!
Do not include the coulomb interactions of individual free electrons
Often good enough to forget about the
Distribution of carriers in energy
=> Replace by delta functions at band edge
As if all states are at a single level $E_c$

$$n = N_c \frac{2}{\sqrt{\pi}} F_{\eta_c/2} \rightarrow N_c e^{-\beta(E_c-E_F)} \text{ if } \beta(E_c-E_F) > 3$$

Often good enough to forget about the
Distribution of carriers in energy

$=>$ Replace by delta functions at band edge

All quantum mechanics is now hidden in a single point per band!
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Reference: Vol. 6, Ch. 3 & 4
Insulator, Semiconductor, Metal

- **Metal:**
  - Conducts electrons even at very low temperatures
  - Fermi Level crosses multiple bands even at very low temperatures

- **Semiconductor**
  - Very weakly conducting
  - Si: \( E_g = 1.1 \text{eV} \) \( n_i \approx 10^{10}/\text{cm}^3 \) in \( 10^{23}/\text{cm}^3 \) 0.1 in a trillion
  - GaAs: \( E_g = 1.42 \text{eV} \) \( n_i \approx 10^{8}/\text{cm}^3 \) in \( 10^{23}/\text{cm}^3 \)
  - Ge: \( E_g = 0.8 \text{eV} \) \( n_i \approx 10^{13}/\text{cm}^3 \) in \( 10^{23}/\text{cm}^3 \) 0.1 in a billion

- **Insulator**
  - “Not” conducting
  - SiO2, \( E_g = 9 \text{eV} \), \( n_i \approx 10^{-68}/\text{cm}^3 \)
  - The whole earth has about \( 10^{50} \) atoms! If you made the whole world out of glass there would be not one electron conductive at room temperature!

\[
n_i = \sqrt{N_c N_v e^{-\beta E_g / 2}}
\]

\[E_F = E_i\]
Even with donors, material is charge neutral.
Assumption of Large Radius ...

\[ r_{1,p} = \frac{4\pi\varepsilon_0 K_{s,host} \hbar^2}{m^*_0 q^2} \]

\[ = \frac{4\pi\varepsilon_0 \hbar^2}{m^*_0 q^2} \frac{m_0 K_{s,host}}{m^*_0} \]

\[ = r_{1,H} \frac{K_{s,host}}{m^*_0 / m_0} \]

\[ r_{1,p} = 0.53 \times 12.9 \times \frac{12.9}{0.53} = 12.9 \text{ Å} \]

a~0.5nm=5Å => hundreds of Si atoms

Donor Atoms in Real and Energy Space

\[ E_1 = -\frac{m^*_0 q^4}{2(4\pi\varepsilon_0 K_{s,host} \hbar)^2} \]

\[ = -\frac{m_0 q^4}{2(4\pi\varepsilon_0 \hbar)^2} \frac{m^*_0}{m_0} \frac{1}{K_{s,host}^2} \]

\[ = -13.6 \times \frac{m^*_0}{m_0} \frac{1}{K_{s,host}^2} \]

\[ \sim 10\text{s meV} \]

\[ E_T = E_1 \]
The number of donor atoms is much smaller compared to host atoms. Therefore, the electrons from one donor atom can go to the other donor atoms only via the conduction/valence bands of the host crystal.

Just like a Hydrogen atom, it is possible to have multiple localized level for a given atom (see the blue levels).

Good donors live close to the conduction band, so that they can offer electrons easily. However, if they are below the midgap, the donor levels are marked with (D) to differentiate them from acceptor atoms (which live close to the valence band).

Even with acceptor, material is charge neutral.
Characteristics of Acceptor Atoms

Donor-type  acceptor-type

Amphoteric Dopants
Intrinsic carrier concentration is so small that semiconductor must be doped to make it useful.

A doping atom behaves like a H-atom, except that the dielectric constant and effective masses are given by those of the host atom.
A bulk material must be charge neutral over all ... 

$$\int [p - n + N_D^+ - N_A^-] dV = 0$$

Further if the material is spatially homogenous

$$p - n + N_D^+ - N_A^- = 0$$

$$N_v e^{-E_v - E_F}/k_B T - N_c e^{-E_c - E_F}/k_B T + \frac{N_D}{1 + 2e^{E_F - E_D}/k_B T} - \frac{N_A}{1 + 4e^{E_F - E_A}/k_B T} = 0$$

Let us see how the formula come about ...
Characteristics of Donor Atoms

(Localized vs. Delocalized States)

2N states/per-band (with spin)

2N-2 states/per-band (with spin)
Statistics of Donor Levels

\[ P_i = \frac{e^{-(E_i - N_i E_F)/k_B T}}{\sum_i e^{-(E_i - N_i E_F)/k_B T}} = \frac{e^{-(E_i - N_i E_F)/k_B T}}{Z} \]

<table>
<thead>
<tr>
<th>u/d</th>
<th>(E_i)</th>
<th>(N_i)</th>
<th>(P_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/0</td>
<td>0</td>
<td>0</td>
<td>1/Z</td>
</tr>
<tr>
<td>0/1</td>
<td>1</td>
<td>1</td>
<td>(e^{(E_i - E_F)/k_B T}/Z)</td>
</tr>
<tr>
<td>1/0</td>
<td>1</td>
<td>1</td>
<td>(e^{(E_i - E_F)/k_B T}/Z)</td>
</tr>
</tbody>
</table>

Prob. that the donor is empty (charged)

\[
 f_{00} = \frac{P_{00}}{P_{00} + P_{10} + P_{01}} = \frac{1/Z}{1/Z + 2e^{-(E_i - E_F)/k_B T}/Z} = \frac{1}{1 + 2e^{-(E_i - E_F)/k_B T}}
\]

Prob. that the donor is filled with at least one electron (neutral)

\[
 1 - f_{00} = 1 - \frac{1}{1 + 2e^{(E_i - E_F)/k_B T}} = \frac{1}{1 + 2e^{(E_i - E_F)/k_B T}}
\]

Note the extra factor ....
**Localized vs. Band Electrons**

- Two electrons (even with opposite spin) can not be at the same position and same energy because of electrostatic repulsion.
- Band electrons (with opposite spin) need not be at the same position, so they can share occupy same energy level.

When we divide space by a factor of 2, the number of states (e.g., 6 here) does not change.

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**Coulomb Exclusion for Band Electrons?**

\[ E = 4 \]
\[ E = 2 \]
\[ E = 0 \]

\[ P_i = \frac{e^{-(E_i - N_i E_F)/k_B T}}{\sum_i e^{-(E_i - N_i E_F)/k_B T}} \]

<table>
<thead>
<tr>
<th>State</th>
<th>( E_i )</th>
<th>( N_i )</th>
<th>( P_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1/Z</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( e^{-(E_i - E_F)/k_B T} )/Z</td>
</tr>
</tbody>
</table>

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Klimeck – ECE606 Fall 2012 - notes adopted from Alam

Purdue
Statistics of Acceptor Levels in Si and Ge

1. Each atom contributes 2 states (up & down spin) to a band, therefore a band has 2N states.

2. Every time a host atom is replaced by an impurity atom, 2 states are disappear per a band and appear as localized states (sort of).

3. Therefore an acceptor atom close to hh and lh bands removes four states from those bands.

4. Because of Coulomb interaction only 1 hole can seat in these 4 states: the states are 0000, 0001, 0010, 0100, 1000.

State [1] …. Hole present … N-1 charges

State [0] … Hole filled …. N charges
1) [0000] is the charged state as it has N electrons, but N-1 protons.
2) Single hole configuration [0001] is uncharged, as we have N-1 electrons, and N-1 protons … same is true for [0010], [0100], [1000] states.
3) Going from [0000] to [0001] states, the number of electrons goes down by 1 (N=1).
4) Going from [0000] to [0001] states energy goes down by \(-E_{A}\), because one electron is no longer occupying the high energy level at \(E_{A}\).

\[
P_{0000} = \frac{1}{Z} \sum_{i} e^{-\left(0 - 0_{i} e_{F} / k_{B}T \right) / k_{B}T}
\]

\[
P_{0001} = P_{0010} = P_{0100} = P_{1000} = \frac{e^{-\left(-E_{A} - 1_{i} e_{F} / k_{B}T \right) / k_{B}T}}{\sum_{i} e^{-\left( -N_{i} e_{F} / k_{B}T \right) / k_{B}T}} = \frac{e^{\left(-E_{A} - E_{F} / k_{B}T \right)}}{Z}
\]

\[
f_{0000} = \frac{P_{0000}}{P_{0000} + P_{1000} + P_{0100} + P_{0010} + P_{0001}} = \frac{1}{1 + 4e^{\left( -E_{A} - E_{F} / k_{B}T \right)}}
\]
Filled and empty Donor/Acceptor Levels

2N-2 states

\[ N_D^{\text{empty}} = N_D^+ = N_D f_{00} = N_D \frac{1}{1 + 2 e^{(E_F - E_D)/k_B T}} \]

4N-4 States

In HH/LH bands

(Two holes can not seat together)

\[ N_A^{\text{filled}} = N_A^+ = N_A [f_{0000}] = N_A \frac{1}{1 + 4 e^{(E_F - E_D)/k_B T}} \]

Distributions are physical …

\[ f_D = \frac{N_D}{1 + e^{(E_F - E_D)/k_B T}} \]

Degeneracy factor …

\[ f_D = \frac{N_D}{1 + e^{(E_F - E_D)/k_B T} e^{(E_F - E_D)/k_B T}} = \frac{N_D}{1 + e^{(E_F - E_D)/k_B T}} \]

Effective donor level
A bulk material must be charge neutral over all …
\[ \int [p - n + N_D^+ + N_A^-] dV = 0 \]

Further if the material is spatially homogenous

\[ p - n + N_D^+ + N_A^- = 0 \]

\[ N_D e^{-(E_F - E_D)/k_B T} - N_A e^{-(E_F - E_A)/k_B T} + \frac{N_D}{1 + 2e^{(E_A - E_F)/k_B T}} - \frac{N_A}{1 + 4e^{(E_A - E_F)/k_B T}} = 0 \]

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A bulk material must be charge neutral over all ...

\[ \int [p - n + N_D^+ + N_A^-] dV = 0 \]

Further if the doping is spatially homogenous

\[ p - n + N_D^+ + N_A^- = 0 \]

FD integral vs. FD function?

\[ N_e e^{-\beta(E_F - E_v) - \mu_B \phi T} - N_e e^{-\beta(E_F - E_v) + \mu_B \phi T} + \frac{N_D}{1 + 2e^{\beta(E_F - E_v) - \mu_B \phi T}} - \frac{N_A}{1 + 4e^{\beta(E_F - E_v) - \mu_B \phi T}} = 0 \]

(approx.)

Once you know \( E_F \), you can calculate \( n, p, N_D^+, N_A^- \).

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Intrinsic Concentration

\[ p - n + N_D^+ + N_A^- = 0 \]

\[ N_e e^{-\beta(E_F - E_v) - \mu_B \phi T} - N_e e^{-\beta(E_F - E_v) + \mu_B \phi T} + \frac{N_D}{1 + 2e^{\beta(E_F - E_v) - \mu_B \phi T}} - \frac{N_A}{1 + 4e^{\beta(E_F - E_v) - \mu_B \phi T}} = 0 \]

\[ n - p = 0 \Rightarrow N_e e^{-\beta(E_F - E_v)} = N_e e^{\beta(E_F - E_v)} \]

\[ E_F \equiv E_i = \frac{E_G}{2} + \frac{1}{2\beta} \ln \frac{N_v}{N_C} \]
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Carrier Density with Donors

In spatially homogenous field-free region ...

\[ p - n + N_D^+ + N_A^- = 0 \]

\[ N_D e^{-(E_E - E_F)/kT} + N_A e^{-(E_E - E_F)/kT} + \frac{N_D}{1 + 2e^{(E_F - 4E_D)/kT}} + \frac{N_A}{1 + 4e^{(E_F - 4E_A)/kT}} = 0 \]

Assume N-type doping ...

(Will plot in next slide)
Electron concentration with Donors

\[ n = N_C e^{-\beta (E_C - E_F)} \Rightarrow \frac{n}{N_C} e^{\beta E_C} = e^{\beta E_F} \]

\[ N_D^+ = \frac{N_D}{1 + 2e^{\beta (E_F - E_D)}} = \frac{N_D}{1 + 2\left[ \frac{n}{N_C} e^{\beta (E_C - E_D)} \right]} = \frac{N_D}{1 + \frac{n}{N_\xi}} \]

Electron concentration with Donors

\[ p - n + N_D^+ = 0 \]

\[ N_C e^{-(E_F - E_C)/k_B T} - N_C e^{-(E_C - E_F)/k_B T} + \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} = 0 \]

\[ p \times n = n_i^2 \]

\[ \frac{n_i^2}{n} - n + \frac{N_D}{1 + \frac{n}{N_\xi}} = 0 \]

No approximation so far ....
High Donor density/Freeze out T

\[ \frac{n^2}{n} - n + \frac{N_D}{1 + \frac{n}{N_\xi}} = 0 \]

\[ N_D \gg n_i \]

\[ \Rightarrow -n + \frac{N_D}{1 + \frac{n}{N_\xi}} \approx 0 \]

\[ \Rightarrow n^2 + N_\xi n - N_\xi N_D = 0 \]

\[ N_\xi = \frac{N_C}{2} e^{-\beta (E_c - E_D)} \]

\[ n = \frac{N_\xi}{2} \left[ \left( 1 + \frac{4N_D}{N_\xi} \right)^{\frac{1}{2}} - 1 \right] \]

Extrinsic T

\[ N_\xi = \frac{N_C}{2} e^{-\frac{(E_c - E_D)}{kT}} \gg N_D \]

\[ n = \frac{N_\xi}{2} \left[ \left( 1 + \frac{4N_D}{N_\xi} \right)^{\frac{1}{2}} - 1 \right] \]

\[ \approx \frac{N_\xi}{2} \left[ \left( 1 + \frac{1}{2} \frac{4N_D}{N_\xi} \right)^{\frac{1}{2}} - 1 \right] \]

\[ \approx N_D \]

Electron concentration equals donor density
hole concentration by \( n x p = n_i^2 \)

Extrinsic

Intrinsic
Intrinsic T

\[ N_D^+ = \frac{N_D}{1 + 2e^{(E_F - E_D)/k_B T}} \approx N_D \quad \text{for } E_F < E_D \]

\[ \frac{n_i^2}{n} - n + \frac{N_D}{n} = 0 \]

\[ \frac{n_i^2}{n} - n + N_D \approx 0 \]

\[ \Rightarrow -n_i^2 + n^2 - N_D n = 0 \]

\[ n = \frac{N_D}{2} + \left[ \frac{N_D^2}{4} + n_i^2 \right]^{1/2} \]

Extrinsic/Intrinsic T

For \( N_D \gg n_i \)

\[ n = \frac{N_D}{2} + \left[ \frac{N_D^2}{4} + n_i^2 \right]^{1/2} \approx N_D \]

For \( n_i \gg N_D \)

\[ n = \frac{N_D}{2} + \left[ \frac{N_D^2}{4} + n_i^2 \right]^{1/2} \approx n_i \]

What will happen if you use silicon circuits at very high temperatures?

Bandgap determines the intrinsic carrier density.
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Multiple Donor Levels

Multiple levels of same donor …

\[ p - n + \frac{N_D}{1 + 2e^{\frac{E_F - E_D}{k_B T}}} + \frac{N_D}{1 + 2e^{\frac{E_F - E_D}{k_B T}}} - \frac{N_A}{1 + 4e^{\frac{E_F - E_D}{k_B T}}} = 0 \]

Codoping…

\[ p - n + \frac{N_{D1}}{1 + 2e^{\frac{E_F - E_{D1}}{k_B T}}} + \frac{N_{D2}}{1 + 2e^{\frac{E_F - E_{D2}}{k_B T}}} - \frac{N_A}{1 + 4e^{\frac{E_F - E_D}{k_B T}}} = 0 \]

Heavy Doping Effects: Bandtail States
Heavy Doping Effects: Hopping Conduction

Bandgap narrowing

\[ p \times n = N_c N_v e^{-\beta E_g} \]
e.g. Base of HBTs

Band transport vs. hopping-transport
e.g. a-silicon, OLED

Arrangement of Atoms

Poly-crystalline
Thin Film
Transistors

Amorphous
Oxides

Crystalline
Poly-crystalline material

Isotropic bandgap and increase in scattering

Band-structure and Periodicity

Periodicity is sufficient, but not necessary for bandgap. Many amorphous material show full isotropic bandgap
1. Charge neutrality condition and law of mass-action allows calculation of Fermi-level and all carrier concentration.

2. For semiconductors with field, charge neutrality will not hold and we will need to use Poisson equation.

3. Heaving doping effects play an important role in carrier transport.