CHAPTER 4 – THE SEMICONDUCTOR IN EQUILIBRIUM
Chapter 4 – The Semiconductor in Equilibrium

• Chapter 3: considering a general crystal and applying to it the concepts of quantum mechanics in order to determine a few of the characteristics of electrons in a single-crystal lattice.

• Chapter 4: apply these concepts specifically to a semiconductor material.

• Chapter 4: use the density of quantum states in the conduction band and the density of quantum states in the valence band along with the Fermi-Dirac probability function to determine the concentration of electrons and holes in the conduction and valence bands.
Equilibrium, or thermal equilibrium, implies that no external forces such as voltages, electric fields, magnetic fields, or temperature gradients are acting on the semiconductor.

All properties of the semiconductor will be independent of time in this case.

An intrinsic semiconductor = a pure crystal with no impurity atoms or defects.

The electrical properties of an intrinsic semiconductor can be altered in desirable ways by adding controlled amounts of specific impurity atoms, called dopant atoms, to the crystal, thus creating an extrinsic semiconductor.

Adding dopant atoms changes the distribution of electrons among the available energy states, so the Fermi energy becomes a function of the type and concentration of impurity atoms.
Chapter 4 – The Semiconductor in Equilibrium

Fig. 1: Thermal Excitation caused jumping of an electron to CB. There is a corresponding hole created in VB where the electron was located.
Charge Carriers in Semiconductors

- Current is the rate at which charge flows.
- In a semiconductor, **two types of charge carriers, the electron and the hole**, can contribute to a current.
- Since the **current** in a semiconductor is determined largely by the number of **electrons in the conduction band** and the number of **holes in the valence band**, an important characteristic is the **density of these charge carriers**.
Equilibrium Distribution of Electrons and Holes

- The distribution (with respect to energy) of electrons in the conduction band is given by the density of allowed quantum states times the probability that a state is occupied by an electron.

\[ n(E) = g_c(E) f_F(E) \]  \hspace{1cm} \text{eq. (4.1)}

- where \( f_F(E) \) is the Fermi-Dirac probability function and \( g_c(E) \) is the density of quantum states in the conduction band.

- The total electron concentration per unit volume in the conduction band is then found by integrating Equation (4.1) over the entire conduction-band energy.
Equilibrium Distribution of Electrons and Holes

- The distribution (with respect to energy) of holes in the valence band is the density of allowed quantum states in the valence band multiplied by the probability that a state is not occupied by an electron.

\[
p(E) = g_v(E)[1 - f_F(E)] \quad \text{eq. (4.2)}
\]

- The total hole concentration per unit volume is found by integrating this function over the entire valence-band energy.
An ideal intrinsic semiconductor is a pure semiconductor with no impurity atoms and no lattice defects in the crystal (e.g. pure Silicon).

For an intrinsic semiconductor at $T = 0K$, all energy states in the valence band are filled with electrons and all energy states in the conduction band are empty of electrons.

The Fermi energy must, therefore, be somewhere between $E_c$ and $E_v$ (The Fermi energy does not need to correspond to an allowed energy.)
The $n_0$ and $p_0$ Equations

- The equation for the thermal-equilibrium concentration of electrons may be found by integrating Equation (4.1) over the conduction band energy, as:

$$n_0 = \int g_c(E) f_F(E) dE$$

\text{eq. (4.3)}

- Applying the Boltzmann approximation to the Fermi energy calculation, the thermal-equilibrium density of electrons in the conduction band is:

$$n_0 = \int_{E_c}^{\infty} \frac{4\pi(2m_n^*)^{3/2}}{h^3} \sqrt{(E - E_c)} \exp\left[-\frac{(E - E_F)}{kT}\right] dE$$

\text{eq. (4.4)}
The $n_o$ and $p_o$ Equations

- Solving the integral, substitute $N_c$ as the effective density of states function in the conduction band.

$$N_c = 2\left(\frac{\pi m^* kT}{h^2}\right)^{3/2}$$  \hspace{1cm} \text{eq. (4.5)}

- If $m^* = m_o$, then the value of the effective density of states function at $T = 300$ K is $N_c = 2.5 \times 10^{19}$ cm$^{-3}$, which is the value of $N_c$ for most semiconductors.

- If the effective mass of the electron is larger or smaller than $m_o$, then the value of the effective density of states function changes accordingly, but is still of the same order of magnitude.

- The thermal-equilibrium electron concentration in the conduction band is:

$$n_o = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]$$  \hspace{1cm} \text{eq. (4.6)}
The $n_o$ and $p_o$ Equations

- The thermal-equilibrium concentration of holes in the valence band is found by integrating Equation (4.2) over the valence band energy as:

\[
p_0 = \int g_v(E)[1 - f_F(E)]dE \quad \text{eq. (4.7)}
\]

\[
1 - f_F(E) = \frac{1}{1 + \exp \left( \frac{E_F - E}{kT} \right)} \quad \text{eq. (4.8)}
\]

- Defining the effective density of states function in the valence band:

\[
N_v = 2\left( \frac{2\pi m_p^* kT}{h^2} \right)^{3/2} \quad \text{eq. (4.9)}
\]

- The thermal-equilibrium concentration of holes in the valence band is then:

\[
p_0 = N_v \exp \left[ -\frac{(E_F - E_v)}{kT} \right] \quad \text{eq. (4.10)}
\]
The $n_0$ and $p_0$ Equations

- The effective density of states functions, $N_c$ and $N_v$, are constant for a given semiconductor material at a fixed temperature.

- The values of the density of states function and of the effective masses for Silicon, Gallium Arsenide, and Germanium are:

| Table 4.1 Effective Density of States Function and Effective Mass Values |
|-----------------------------|-----------------------------|-----------------|-----------------|
|                            | $N_c$(cm$^{-3}$) | $N_v$(cm$^{-3}$) | $m_n^*/m_o$ | $m_p^*/m_o$ |
| Silicon                    | 2.8*10$^{19}$     | 1.04*10$^{19}$   | 1.08         | 0.56          |
| Gallium Arsenide           | 4.7*10$^{17}$     | 7.0*10$^{18}$    | 0.067        | 0.48          |
| Germanium                  | 1.04*10$^{19}$    | 6.0*10$^{18}$    | 0.55         | 0.37          |

- The thermal equilibrium concentrations of electrons in the conduction band and of holes in the valence band are directly related to the effective density of states constants and to the Fermi energy level.
The Intrinsic Carrier Concentration

- For an intrinsic semiconductor, the concentration of electrons in the conduction band \( (n) \) is equal to the concentration of holes in the valence band \( (p) \).

- These parameters are usually referred to as the intrinsic electron concentration \( (n_i) \) and intrinsic hole concentration \( (p_i) \).

- The Fermi energy level for the intrinsic semiconductor is called the intrinsic Fermi energy, or \( E_f = E_{f^*} \).
The Intrinsic Carrier Concentration

- For an intrinsic semiconductor:

\[ n_0 = n_i = N_c \exp\left[-\frac{(E_c - E_{Fi})}{kT}\right] \]  
\text{eq. (4.11)}

\[ p_0 = p_i = n_i = N_v \exp\left[-\frac{(E_{Fi} - E_v)}{kT}\right] \]  
\text{eq. (4.12)}

\[ n_i^2 = N_c N_v \exp\left[-\frac{(E_c - E_{Fi})}{kT}\right] \cdot \exp\left[-\frac{(E_{Fi} - E_v)}{kT}\right] \]  
\text{eq. (4.13)}

\[ n_i^2 = N_c N_v \exp\left[-\frac{(E_c - E_v)}{kT}\right] = N_c N_v \exp\left[-\frac{(E_g)}{kT}\right] \]  
\text{eq. (4.14)}
The Intrinsic Carrier Concentration

- For a given semiconductor material at a constant temperature, the value of $n_i$ is a constant, and independent of the Fermi energy.

Table 4.2 Commonly Accepted Values of $n_i$ at T=300K

<table>
<thead>
<tr>
<th>Material</th>
<th>$n_i$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>$1.5 \times 10^{10}$</td>
</tr>
<tr>
<td>Gallium Arsenide</td>
<td>$1.8 \times 10^{6}$</td>
</tr>
<tr>
<td>Germanium</td>
<td>$2.4 \times 10^{13}$</td>
</tr>
</tbody>
</table>

Fig. 2: Intrinsic carrier concentration $n_i$ with respect to change in $T$. 
Application of Intrinsic Semiconductors

- High Electron Mobility Transistor
- High resistivity substrate for RF circuits
- Amorphous-Si Solar Cells

Fig. 3: Structure of a Solar Cell.
The $n_0p_0$ Product

- Using the general expressions for $n_0$ and $p_0$:

$$n_0p_0 = N_cN_v \exp\left[-\frac{(E_c - E_F)}{kT}\right] \exp\left[-\frac{(E_F - E_v)}{kT}\right]$$  

\text{eq. (4.15)}

- which is simplified as:

$$n_0p_0 = N_cN_v \exp\left[-\frac{(E_g)}{kT}\right]$$  

\text{eq. (4.16)}

- Thus, for a semiconductor in thermal equilibrium, the \textbf{Mass Action Law} states:

$$n_0p_0 = n_i^2$$  

\text{eq. (4.17)}
Exercise

1. Assume the Fermi energy is 0.25eV below the conduction band. The value of \( N_c \) for Silicon at \( T = 300 \text{ K} \) is \( N_c = 2.8 \times 10^{19} \text{ cm}^{-3} \). Calculate the probability that a state in the conduction band is occupied by an electron and calculate the thermal equilibrium electron concentration in silicon at \( T = 300 \text{ K} \).

2. Assume that the Fermi energy is 0.27eV above the valence band energy. The value of \( N_v \) for Silicon at \( T = 300 \text{K} \) is \( N_v = 1.04 \times 10^{19} \text{ cm}^{-3} \). Calculate the thermal equilibrium hole concentration in silicon at \( T = 400 \text{ K} \).
Solution

1. The probability that an energy state at \( E = E_c \) is occupied by an electron is given by:

\[
f_F(E_c) = \frac{1}{1 + \exp\left(\frac{E_c - E_F}{kT}\right)} \approx \exp\left[-\left(\frac{E_c - E_F}{kT}\right)\right]
\]

\[
f_F(E_c) = \exp\left[-\left(\frac{0.25}{0.0259}\right)\right] = 6.43 \times 10^{-5}
\]

- The electron concentration is given by:

\[
n_0 = N_c \exp\left[-\left(\frac{E_c - E_F}{kT}\right)\right] = (2.8 \times 10^{19}) \exp\left(\frac{-0.25}{0.0259}\right)
\]

\[
n_0 = 1.8 \times 10^{15} \text{ cm}^{-3}
\]
Solution

2. The parameter values at $T = 400$ K are found as:

\[ N_v = (1.04 \times 10^{19})\left(\frac{400}{300}\right)^{3/2} = 1.60 \times 10^{19} \text{ cm}^{-3} \]

\[ kT = (0.0259)\left(\frac{400}{300}\right) = 0.03453eV \]

The hole concentration is given by:

\[ p_0 = N_v \exp\left[-\frac{(E_F - E_v)}{kT}\right] = (1.60 \times 10^{19})\exp\left(-\frac{0.27}{0.03453}\right) \]

\[ p_0 = 6.43 \times 10^{15} \text{ cm}^{-3} \]
Exercise

3. Calculate the intrinsic carrier concentration in Gallium Arsenide at $T = 300$ K and at $T = 450$ K. The values of $N_c$ and $N_v$ at $300$ K for Gallium Arsenide are $4.7 \times 10^{17}$ cm$^{-3}$ and $7.0 \times 10^{18}$ cm$^{-3}$, respectively. Both $N_c$ and $N_v$ vary as $T^{3/2}$. Assume the band gap energy of Gallium Arsenide is $1.42$ eV and does not vary with temperature over this range. The value of $kT$ at $450$ K is:

$$kT = (0.0259)(\frac{450}{300}) = 0.03885\text{eV}$$
Solution

3. For T = 300K:

\[ n_i^2 = (4.7 \times 10^{17})(7.0 \times 10^{18})\exp\left(\frac{-1.42}{0.0259}\right) = 5.09 \times 10^{12} \text{ cm}^{-6} \]

\[ n_i = 2.26 \times 10^6 \text{ cm}^{-3} \]

For T = 450K:

\[ n_i^2 = (4.7 \times 10^{17})(7.0 \times 10^{18})\left(\frac{450}{300}\right)^3\exp\left(\frac{-1.42}{0.03885}\right) = 1.48 \times 10^{21} \text{ cm}^{-6} \]

\[ n_i = 3.85 \times 10^{10} \text{ cm}^{-3} \]

- **Note:** The intrinsic carrier concentration increased by over 4 orders of magnitude as the temperature increased by 150°C.
Dopant Atoms and Energy Levels

- The real power of semiconductors is realized by adding small, controlled amounts of a specific dopant, or impurity atoms.

- Adding a group V element, such as Phosphorus, as a substitution impurity in single-crystalline Silicon lattice, four of the valence electrons will contribute to the covalent bonding with the Silicon atoms, leaving the fifth more loosely bound to the Phosphorus atom.

- The fifth valence electron is called a donor electron.
Dopant Atoms and Energy Levels

- If a small amount of energy, such as thermal energy, is added to the donor electron, it can be elevated into the conduction band, leaving behind a positively charged donor ion.

- The electron in the conduction band can now move through the crystal generating a current, while the positively charged ion is fixed in the crystal.

- This type of impurity atom donates an electron to the conduction band so is called a donor impurity atom.

- The donor impurity atoms add electrons to the conduction band without creating holes in the valence band thus resulting an n-type semiconductor (n for the negatively charged electron).
Dopant Atoms and Energy Levels

Fig. 4: Silicon lattice doped with a donor impurity (P).

Fig. 5: Donor Electron Energy Level
Dopant Atoms and Energy Levels

- Adding a group III element, such as Boron, as a substitution impurity to Silicon. The group III element’s valence electrons are all taken up in the covalent bonding.

- The hole can move through the crystal generating a current, while the negatively charged Boron atom is fixed in the crystal. The group III atom accepts an electron from the valence band and so is referred to as an accepter impurity atom.

- The acceptor atom can generate holes in the valence band without generating electrons in the conduction band. This type of semiconductor material is referred to as a p-type material (*p for the positively charged hole*).
Dopant Atoms and Energy Levels

Fig. 6: Acceptor Impurity, Boron Impurity Atom in a Silicon Lattice

Fig. 7: Acceptor Electron Energy Level
The Extrinsic Semiconductor

- An extrinsic semiconductor is a semiconductor in which controlled amounts of specific dopant or impurity atoms have been added so that thermal-equilibrium electron and hole concentrations are different from the intrinsic carrier concentration.

- Only one carrier type dominates in an extrinsic semiconductor.

- The thermal equilibrium electron and hole concentrations can be found as:

  \[ n_0 = n_i \exp\left(\frac{E_F - E_{Fi}}{kT}\right) \quad p_0 = p_i \exp\left[-\frac{E_F - E_{Fi}}{kT}\right] \] (eq. 4.18, 4.19)
The Extrinsic Semiconductor

- Also, the **Mass Action Law** (eq. 4.17) applies as:

  \[ n_0 p_0 = n_i^2 \]  

  *eq. (4.17)*

- If the impurity concentration increases, the distance between the impurity atoms decreases and a point will be reached when donor electrons, for example, will begin to interact with each other.
- When this occurs, the single discrete donor energy will split into a band of energies.
- As the donor concentration further increases, the band of donor states widens and may overlap the bottom of the conduction band.
- This overlap occurs when the donor concentration becomes comparable with the effective density of states. When the concentration of electrons in the conduction band exceeds
Degenerate and Nondegenerate Semiconductors

- If the number of impurity atoms is small, they would be spread far enough apart so that there is no interaction between donor electrons, for example, in an n-type material.

- Such impurities introduce discrete, non-interacting donor energy states in the n-type semiconductor and discrete, non-interacting acceptor states in the p-type semiconductor.

- These types of semiconductors are referred to as non-degenerate semiconductors.

- If the impurity concentration increases, the distance between the impurity atoms decreases and at some point, donor or acceptor states will begin to interact with each other. When this occurs, the single discrete donor or acceptor energy will split into a band of energies.
Degenerate and Nondegenerate Semiconductors

- When the concentration of electrons in the conduction band exceeds the density of states $N_c$, the Fermi energy lies in the conduction band.
- This type of semiconductor is called a degenerate n-type semiconductor.
- As the acceptor doping concentration increases in a p-type semiconductor, the discrete acceptor energy states will split into a band of energy and may overlap the top of the valence band.
- The Fermi energy will lie in the valence band when the concentration of holes exceeds the density of states $N_v$.
- This type semiconductor is called a degenerate p-type semiconductor.
Degenerate and Nondegenerate Semiconductors

\[ N_d > N_c \quad \text{and} \quad N_a > N_v \]

Fig. 8: (a) Degenerate n-type semiconductor and (b) Degenerate p-type semiconductor
Effect of Temperature on Ionization of Dopants

Fig. 9: Electron Concentration vs. Temperature in Extrinsic Semiconductor

Low Temperature | Moderate Temperature | High Temperature
Charge Neutrality

- This charge-neutrality condition is used determine the thermal-equilibrium electron and hole concentrations as a function of the impurity doping concentration.
- A compensated semiconductor is one that contains both donor and acceptor impurity atoms in the same region.
- A compensated semiconductor can be formed, for example, by diffusing acceptor impurities into an n-type material, or by diffusing donor impurities into a p-type material.
- An n-type compensated semiconductor occurs when $N_d > N_a$, and a p-type compensated semiconductor occurs when $N_a > N_d$.
- If $N_a = N_d$, we have a completely compensated semiconductor that has the characteristics of an intrinsic material.
Charge Neutrality

- The charge neutrality condition is expressed by equating the density of charges to the density of positive charges.

\[
n_0 + N_a^- = p_0 + N_d^+ \quad \text{eq. (4.20, 4.21)}
\]

- where \( n_0 \) and \( p_0 \) are the thermal-equilibrium concentrations of electrons and holes in the conduction band and valence band, respectively.

- The parameter \( n_d \) is the concentration of electrons in the donor energy states, so \( N_d^+ = N_d - n_d \) is the concentration of positively charged donor states. Similarly, \( p_a \) is the concentration of holes in the acceptor states, so \( N_a^- = N_a - p_a \) is the concentration of negatively charged acceptor states.
Charge Neutrality

- If we assume complete ionization, \( n_d \) and \( p_a \) are both zero,
  \[ n_0 + N_a = p_0 + N_d \]

- Using \( p_o = n_i^2/n_o \),
  \[ n_o + N_a = \frac{n_i^2}{n_o} + N_d \]  \( \text{eq. (4.22)} \)

- The electron concentration \( n_o \) can be determined using the quadratic formula:
  \[ n_0^2 - (N_d - N_a)n_0 - n_i^2 = 0 \]  \( \text{eq. (4.23)} \)
  \[ n_0 = \frac{(N_d - N_a)}{2} + \sqrt{\left(\frac{N_d - N_a}{2}\right)^2 + n_i^2} \]  \( \text{eq. (4.24)} \)
  \[ n_0 = \frac{(N_d - N_a)}{2} + \sqrt{\left(\frac{N_a - N_d}{2}\right)^2 + n_i^2} \]  \( \text{eq. (4.25)} \)

- is used to calculate the electron concentration in an n-type semiconductor, or when \( N_d > N_a \).
Exercise

4. Consider an n-type Silicon semiconductor at \( T = 300\,\text{K} \) in which \( N_d = 10^{16}\,\text{cm}^{-1} \) and \( N_a = 0 \). The intrinsic carrier concentration is assumed to be \( n_i = 1.5 \times 10^{10}\,\text{cm}^{-3} \). Determine the thermal equilibrium electron and hole concentrations for the given doping concentration.
Solution

4. Using the formula:

\[
n_0 = \frac{(N_d - N_a)}{2} + \sqrt{\left(\frac{N_d - N_a}{2}\right)^2 + n_i^2}
\]

\[
n_0 = \frac{(10^{16} - 0)}{2} + \sqrt{\left(\frac{10^{16} - 0}{2}\right)^2 + (1.5 \times 10^{10})^2} = 10^{16} \text{ cm}^{-3}
\]

Using Mass Action Law,

\[
n_0 p_0 = n_i^2
\]

\[
p_0 = \frac{n_i^2}{n_0} = \frac{(1.5 \times 10^{10})^2}{(1 \times 10^{16})} = 2.25 \times 10^4 \text{ cm}^{-3}
\]
Position of Fermi Energy Level

- It is possible to determine the position of the Fermi energy level as a function of the doping concentrations and as a function of temperature.

\[
n_0 = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]
\]

\[
(E_c - E_F) = kT \ln\left(\frac{N_c}{n_0}\right)
\]

- For an n-type semiconductor in which \( N_d \gg n_i \), then \( n_o \approx N_d \)

\[
(E_c - E_F) = kT \ln\left(\frac{N_c}{N_d}\right)
\]

- As the donor concentration increases, the Fermi level moves closer to the conduction band.
Position of Fermi Energy Level

- Also using the formula:

\[ n_0 = n_i \exp\left(\frac{E_F - E_{Fi}}{kT}\right) \]  
\[ (E_F - E_{Fi}) = kT \ln\left(\frac{n_0}{n_i}\right) \]

- Similar formulas apply for a p-type semiconductor:

\[ (E_F - E_v) = kT \ln\left(\frac{N_v}{N_a}\right) \]  
\[ (E_F - E_v) = kT \ln\left(\frac{N_v}{P_0}\right) \]  
\[ (E_{Fi} - E_F) = kT \ln\left(\frac{P_0}{n_i}\right) \]

- As the acceptor concentration increases, the Fermi level moves closer to the valence band.
Position of Fermi Energy Level

\[ n_0 = N_c \exp\left[-\frac{(E_c - E_F)}{kT}\right] \]

\[ (E_c - E_F) = kT \ln\left(\frac{N_c}{n_0}\right) \]

\[ n_0 = n_i \exp\left[-\frac{(E_F - E_{Fi})}{kT}\right] \]

\[ (E_F - E_{Fi}) = kT \ln\left(\frac{n_0}{n_i}\right) \]
Summary

- Position of Fermi level for
  - an (a) n-type and (b) p-type semiconductor.

- Variation of $E_F$ with doping concentration

$$E_F = E_c - kT \ln\left( \frac{N_c}{N_d} \right)$$

$$E_F = E_v + kT \ln\left( \frac{N_v}{N_a} \right)$$

Fig. 10: Position of Intrinsic Fermi level $E_{Fi}$ and variation of $E_F$ with doping concentration.
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