Chapter IV : Semiconductor at Equilibrium

IV.1. Introduction

This chapter focuses on the fundamental behavior of semiconductors when they are in thermal equilibrium, meaning no external forces (such as applied voltage or light) disturb the distribution of charge carriers. Understanding this equilibrium state is essential for analyzing more complex phenomena like junctions and devices in operation.

We begin by examining how carriers (electrons and holes) are distributed in a semiconductor at equilibrium using the **Fermi-Dirac distribution** and defining the **Fermi level**, a key concept that indicates the probability of occupancy of energy states. We then derive the **equilibrium carrier concentrations** and present the **mass action law**, which relates electron and hole densities. The condition of **electrical neutrality** is also introduced as a governing constraint in real materials.

Next, we explore the **position of the Fermi level** in different types of semiconductor structures and its dependence on doping. Through graphical and analytical illustrations, we demonstrate how the Fermi level reflects the internal charge balance.

Finally, we apply these concepts to a **PN junction at equilibrium**, introducing the important concept of the **built-in potential**, which plays a central role in the operation of semiconductor devices such as diodes.

This chapter lays the theoretical groundwork necessary for understanding carrier dynamics in more complex, non-equilibrium situations addressed in subsequent chapters.

IV.2. Free carrier concentration at equilibrium

To determine the actual number of free electrons and holes in the conduction band (CB) and valence band (VB), knowing only the density of states is not sufficient. It is also necessary to consider the **probability that an energy level E is occupied by an electron**, which is described by the **Fermi-Dirac distribution**.

IV.2.1. Fermi-Dirac distribution and Fermi level

The function $f_n(E)$ represents the probability that an energy level **E** is occupied by an electron at equilibrium. According to **Fermi-Dirac statistics**, it is defined as:

$$f_n(E) = \frac{number\ of\ states\ occupied\ by\ electrons\ (between\ E\ and\ E+dE)}{number\ of\ available\ states\ (between\ E\ and\ E+dE)} = \frac{dn}{dN}$$

$$f_n(E) = \frac{1}{1 + e^{\frac{E-E_F}{KT}}}$$

E_F is the **Fermi level**, K is Boltzmann's constant, and T is the absolute temperature.

The **probability that a level E is occupied by a hole**, fp(E) , is complementary to that of an electron:

$$f_p(E) = 1 - f_n(E) = \frac{1}{1 + e^{\frac{E_F-E}{KT}}}$$

Under certain conditions, the Fermi-Dirac function can be approximated using the **Boltzmann approximation**:

- When : $E - E_F > KT \Longrightarrow\ e^{\frac{E-E_F}{KT}} \gg 1$, we have:

$$f_n(E) \approx \frac{1}{e^{\frac{E-E_F}{KT}}} = e^{-\frac{E-E_F}{KT}}$$

- Conversely, when :

$$E - E_F < -KT (\Leftrightarrow E_F - E \gg KT) \Longrightarrow\ e^{\frac{E_F-E}{KT}} \gg 1 \Longrightarrow f_p(E) \approx \frac{1}{e^{\frac{E_F-E}{KT}}} = e^{-\frac{E_F-E}{KT}}$$

These simplified expressions are known as the **Boltzmann statistics** and are valid when the energy difference is large compared to thermal energy KT.

- **For : $E - E_F = 0 \Longrightarrow f(E = E_F) = 1/2$;**

- **For :** $\boldsymbol{E - E_F > 0 \Longrightarrow f(E > E_F) = \frac{1}{1+e^{+\infty}} = 0;}$
- **For :** $\boldsymbol{E - E_F < 0 \Longrightarrow f(E < E_F) = \frac{1}{1+e^{-\infty}} = 1}$

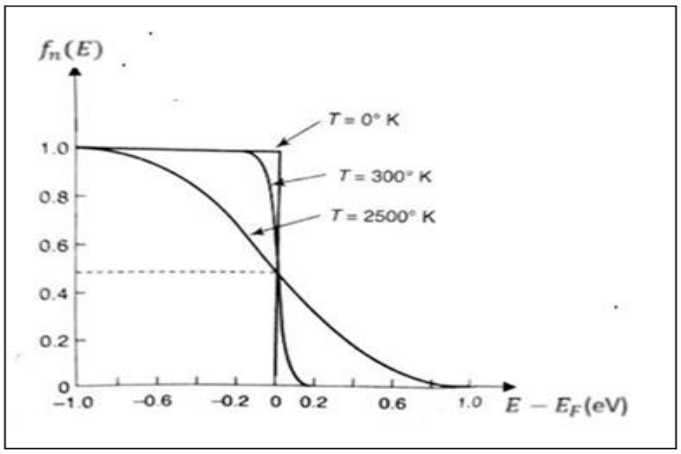

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Figure IV.1. Fermi-Dirac Distribution for several temperatures

In an **intrinsic semiconductor**, the Fermi level is referred to as the **intrinsic Fermi level** E_{FI}, and it lies approximately at the center of the bandgap:

$$E_{Fi}=(E_C+E_V)/2$$

However, in general, the position of the Fermi level depends on the type and concentration of dopants, as well as on temperature.

- In an **n-type semiconductor**, the Fermi level lies **above** the intrinsic level ($E_F > E_{FI}$), reflecting the higher concentration of electrons compared to intrinsic carriers: $n_0 \gg n_i$.
- In a **p-type semiconductor**, the Fermi level is **below** the intrinsic level ($E_F < E_{FI}$), indicating a greater number of holes.

IV.2.2. Equilibrium carrier's concentration and Mass action law

The equilibrium concentration of free electrons, denoted as n_0, is calculated by integrating over all energy levels within the conduction band. This involves the product of the density of available states n_C (E) in the conduction band and the probability f_n (E)that these states are occupied:

$$n_0 = \int dn = \int_{Ec}^{Emax} \frac{dn}{dN}.\frac{dN}{dE}dE = \int_{Ec}^{\infty} \frac{dn}{dN}.\frac{dN}{dE}dE$$

Where :

- The occupation probability is given by the Fermi-Dirac approximation:

$$\frac{dn}{dN} = f_n(E) = e^{-\frac{E-E_F}{KT}}$$

- The density of states in the conduction band is:

$$\frac{dN}{dE} = \frac{1}{2\pi^2}\sqrt{\left(\frac{2m_n}{\hbar^2}\right)^3 (E - E_C)}$$

After integration, we obtain:

$$n_0 = \frac{2}{h^3}\sqrt{(2\pi m_n KT)^3}.e^{-\frac{E_c-E_F}{KT}}$$

By defining the effective density of states in the conduction band N_C (cm^{-3}):

$$N_C = \frac{2}{h^3}\sqrt{(2\pi m_n KT)^3}$$

We can rewrite:

$$n_0 = N_C \mathrm{e}^{-\frac{E_C-EF}{KT}} = N_C f_n(E_C)$$

Similarly, the hole concentration in the valence band is obtained using the density of states $n_V(E)$ and the probability of a state being unoccupied $f_p(E)$:

$$p_0 = \int dp = \int_{Emin}^{Ev} \frac{dp}{dN}.\frac{dN}{dE}dE = \int_{-\infty}^{Ev} \frac{dp}{dN}.\frac{dN}{dE}dE$$

With :

- Hole occupation probability:

$$f_p(E) = \frac{dp}{dN} = e^{-\frac{E_F-E}{KT}}$$

- Density of states in the valence band:

$$\frac{dN}{dE} = \frac{1}{2\pi^2}\sqrt{\left(\frac{2m_p}{\hbar^2}\right)^3 (E_V - E)}$$

After integration, the result becomes:

$$p_0 = N_V \mathrm{e}^{-\frac{E_F-E_V}{KT}} = N_V f_p(E_V)$$

Where N_V (cm^{-3}), the effective density of states in the valence band, is defined as:

$$N_V = \frac{2}{h^3}\sqrt{(2\pi m_p KT)^3}$$

Multiplying the electron and hole concentrations yields a result that is independent of the Fermi level position (and therefore of doping). This relation is known as the **mass action law**:

$$n_0 p_0 = N_c N_v e^{-\frac{(E_c - E_v)}{KT}} = N_c N_v e^{\frac{-E_g}{KT}}$$

In an intrinsic semiconductor, the electron and hole concentrations are equal to the intrinsic carrier concentration ni = p_0 = n_0, which leads to:

$$n_i^2(T) = n_0 p_0 = N_c N_v e^{\frac{-E_g}{KT}}$$

Thus, the intrinsic carrier concentration is:

$$n_i = \sqrt{N_c N_v} e^{\frac{-E_g}{2KT}}$$

- **Intrinsic Fermi level E_{Fi} :**

  The position of the intrinsic Fermi level is derived by equating n_0 and p_0. The resulting expression is:

$$E_{FI} = \frac{E_C + E_V}{2} + \frac{KT}{2}\ln\left(\frac{N_V}{N_C}\right) \approx E_i$$

Where :

$$E_i = \frac{E_C + E_V}{2}$$

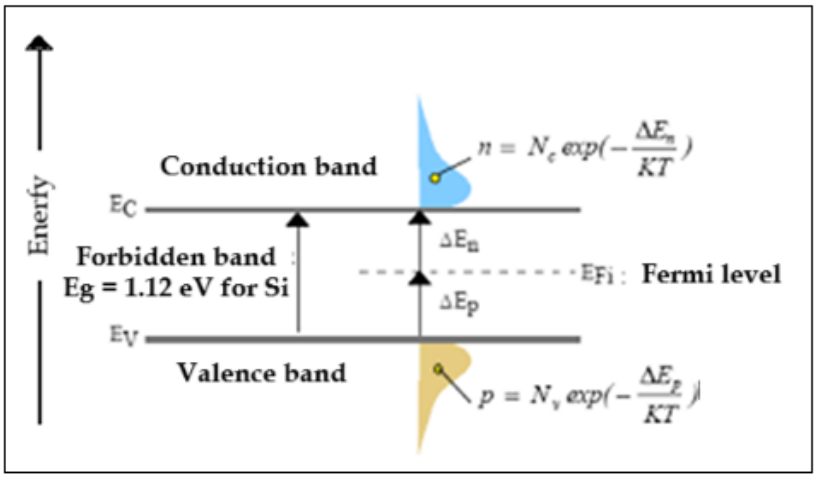

Figure IV.2: illustrates the distribution of electrons and holes in intrinsic silicon along with the position of the intrinsic Fermi level E_{Fi}

IV.2.3. Charge neutrality equation

In a homogeneous semiconductor, the total charge at any point is zero. This means that the sum of free holes and fixed positive charges equals the sum of free electrons and fixed negative charges:

$$\boldsymbol{p_0 + N_D^+ = n_0 + N_A^-}$$

Where :

- N_D^+ is the number of ionized donors, i.e., donors that have released their extra electron.

- N_A^- is the number of ionized acceptors, i.e., acceptors that have captured an additional electron.

Donor atoms are electrically neutral when their extra electron is present. They become positively ionized when they lose that electron, meaning the site is effectively occupied by a hole.

The number of ionized donors and acceptors can be expressed as:

$$N_D^+ = N_D . f_p(E_D) = \frac{N_D}{1+e^{\frac{E_F - E_D}{KT}}}$$

$$N_A^- = N_A . f_n(E_A) = \frac{N_A}{1+e^{\frac{E_A - E_F}{KT}}}$$

However, at room temperature, it is typically assumed that all donors and acceptors are ionized. That is:

$$N_D^+ = N_D \text{ and } N_A^- = N_A$$

Therefore, the charge neutrality condition simplifies to:

$$p + N_D = n + N_A$$

N_A and N_D represent the acceptor and donor concentrations, respectively.

Carrier densities in an n-type semiconductor

In an n-type semiconductor, the majority carrier concentration (electrons) is approximately:

$$n_n = p_n + N_D \approx N_D$$

This leads to

$$n_n \approx N_D = N_c \mathrm{e}^{-\frac{E_C - E_{Fn}}{KT}}$$

Where E_{Fn} : is the Fermi level in the n-type semiconductor.

The minority carrier concentration (holes) is given by :

$$p_n = \frac{n_i^2}{N_D} \quad (\text{since } n_i^2 = n.p)$$

Exercice :

Show that in an n-type semiconductor:

$E_c - E_F < E_F - E_V$.

We know :

$n_n = N_C \mathrm{e}^{-\frac{E_C - EF}{KT}}$ et $p_n = N_V \mathrm{e}^{-\frac{E_F - E_V}{KT}}$

If $n_n \gg p_n, then$:

$N_C . \mathrm{e}^{-\frac{E_C - EF}{KT}} \gg N_V . \mathrm{e}^{-\frac{E_F - E_V}{KT}} \Rightarrow -\frac{E_C - EF}{KT} > -\frac{E_F - E_V}{KT} \Rightarrow E_C - EF < E_F - E_V$

Carrier densities in an p-type semiconductor

In a p-type semiconductor, the majority carrier concentration (holes) is approximately:

$$p_p = n_p + N_A \approx N_A$$

So :

$$p_p \approx N_A = N_v \mathrm{e}^{\frac{E_v - E_{Fp}}{KT}}$$

The minority carrier concentration (electrons) is:

$$n_p = \frac{n_i^2}{N_A}$$

Exercice :

Show that in a p-type semiconductor: $E_c - E_F > E_F - E_V$.

We know:

$$p_p = N_v \mathrm{e}^{-\frac{E_F - E_v}{KT}}, \qquad n_p = N_c \mathrm{e}^{-\frac{E_c - E_F}{KT}}$$

If $p_p \gg n_p$, then:

$$N_V . \mathrm{e}^{-\frac{E_F - E_V}{KT}} \gg N_C . \mathrm{e}^{-\frac{E_C - EF}{KT}} \Rightarrow -\frac{E_F - E_V}{KT} > -\frac{E_C - EF}{KT} \Rightarrow E_c - E_F > E_F - E_V$$

IV.3. Fermi level at equilibrium:

IV.3.1. Fundamental property:

A structure is said to be in **thermodynamic equilibrium** when its temperature is uniform and when no external perturbations—such as light exposure or applied bias voltage—are acting on it. Regardless of whether the material is homogeneous or composed of different regions, **the Fermi level remains constant throughout the structure when it is in thermodynamic equilibrium**.

To verify this principle, consider two regions within the structure, region 1 and region2, for which the following condition holds:

$$E_1 - E_{F1} = E_2 - E_{F2}$$

This condition implies that the electron concentration is the same at energy levels E_1 and E_2

Now, suppose that $E_{F1} < E_{F2}$. From the condition above, this would mean $E_1 < E_2$, which would cause electrons to flow from region 2 (higher energy) to region 1 (lower energy). Such a flow of carriers constitutes a current, which contradicts the assumption of equilibrium.

Therefore, to maintain equilibrium, the Fermi levels must be equal across all regions:

$$E_{F1} = E_{F2} = E_F = constant.$$

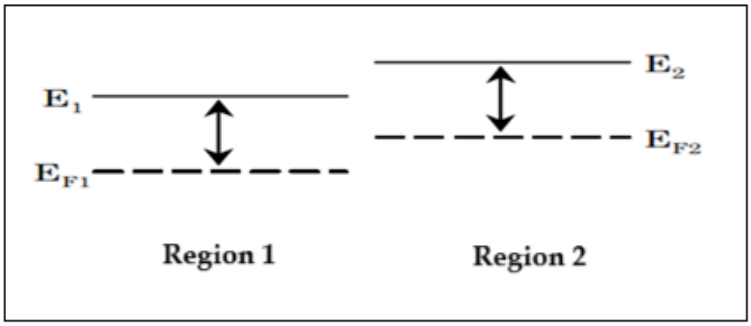

Figure IV.3. Structure composed of two regions where: $\boldsymbol{E_1 - E_{F1} = E_2 - E_{F2}}$

IV.3.2. Illustrations:

The figure below shows an example of a band diagram that represents **a system in thermodynamic equilibrium**, as evidenced by the Fermi level remaining constant along the x-axis. The fact that the bandgap E_G remains unchanged suggests that the material is the same throughout, but the doping concentration is not uniform. The higher concentration of electrons on the left side and of holes on the right results from **Fermi-Dirac statistics ($f_n(E)$ et $f_p(E)$)**.

On the left side, the semiconductor is **n-type** (the Fermi level E_F is closer to the conduction band E_C than to the valence band E_V), whereas on the right side, it is **p-type**.

It can be shown that a **linear variation** o f $E_C - E_F$ E_F corresponds to an **exponential variation in doping**.

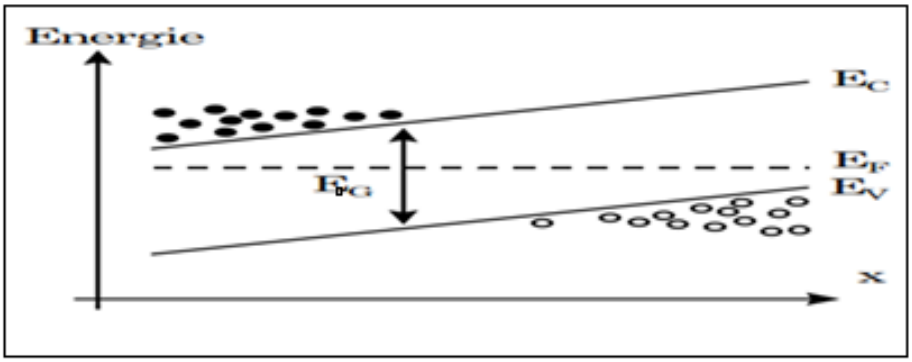

Figure IV.4. Semiconductor in thermodynamic equilibrium.

In the next figure, the **variation of the Fermi level with position x** indicates that the semiconductor is **not in thermodynamic equilibrium**, which results in **a net flow of electrons and holes**.

This situation typically corresponds to a homogeneous semiconductor sample under an externally applied **potential difference** between its two ends.

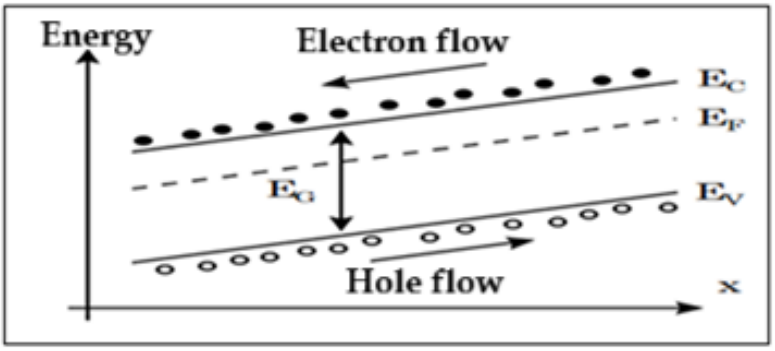

Figure IV.5. Semiconductor under non-equilibrium conditions.

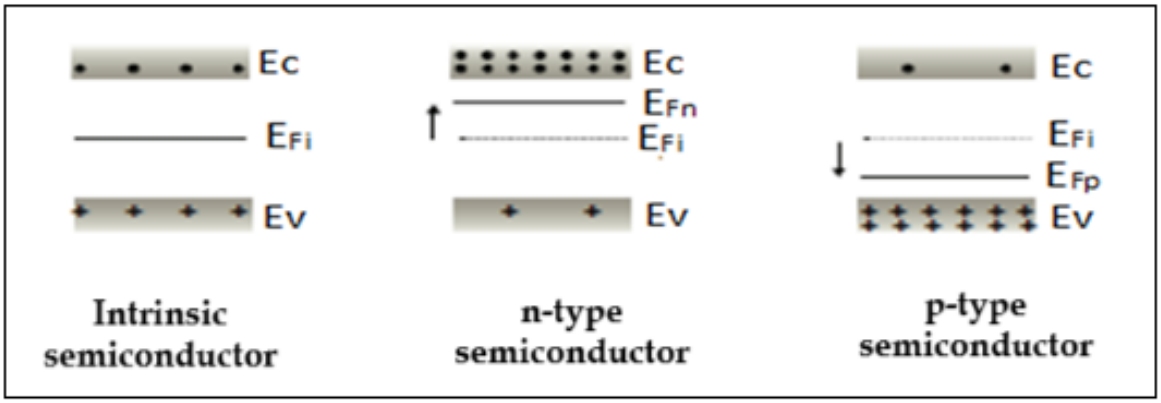

Figure IV.6. Position of the Fermi level in different types of semiconductors.

IV.3.3. Application: Internal Voltage "Built-in Potential) in a PN Junction at Equilibrium

A **PN junction** is formed by bringing into contact a p-type and an n-type region within the same semiconductor crystal. The **difference in donor and acceptor concentrations**, N_D -N_A changes abruptly—from a negative value in the p-region to a positive value in the n-region.

This transition is typically described using two constants in the case of an **abrupt 5junction**.

The PN junction is said to be **in thermal equilibrium** when it is not exposed to any external excitation—electrical, optical, or thermal—and is placed in an environment free of **electric or magnetic fields**.

At equilibrium, **the electron and hole currents are zero throughout the material**, and the **Fermi level is uniform across the entire junction**. The Fermi levels E_{Fp} and E_{Fn}, associated with the p- and n-sides respectively, are aligned.

The **conduction band** on the p-side lies at a higher energy than that on the n-side, and the same applies to the **valence band**.

La loi de variation de cette différence est donnée par deux constantes pour une jonction dite abrupte.

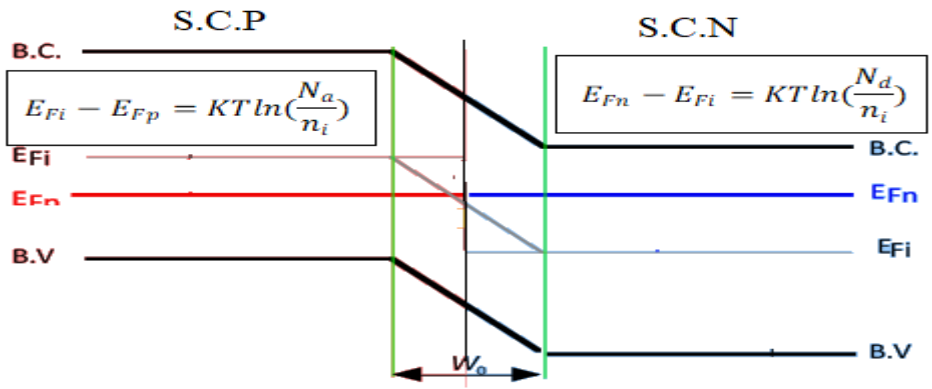

Figure IV. 7. Energy band diagram of a PN junction at equilibrium

The relationship between the Fermi level and the intrinsic level EFiE_{Fi}EFi in each region is given by:

$$(E_{Fi} - E_F)_{région\ p} - (E_F - E_{Fi})_{région\ n} = KTln\left(\frac{N_D}{n_i}\right) + KTln\left(\frac{N_A}{n_i}\right) = qV_{bi}$$

With :

$E_{Fn} = E_{Fp} = E_F$ et : $E_{Fi} = \frac{E_c + E_v}{2}$

and the **built-in potential**:

$$V_{bi} = \frac{KT}{q}\ln(\frac{N_D N_A}{n_i^2})$$

Far from the junction:

- On the **p-side** (as x→ −∞):

$$n(-\infty) = n_p = \frac{n_i^2}{N_A}; \qquad p(-\infty) = p_p = N_A$$

- On the **n-side** (as x→ +∞):

$$n(+\infty) = n_n = N_D; \qquad p(+\infty) = p_n = \frac{n_i^2}{N_D}$$

So the built-in potential remains:

$$V_{bi} = \frac{KT}{q}\ln(\frac{N_D N_A}{n_i^2})$$

Example:

Consider a silicon PN junction with:

- $N_A = 10^{15}/cm^3$ (p-side doping);
- $N_D = 10^{15}/cm^3$ (n-side doping);
- intrinsic carrier concentration: $n_i = 10^{10}\ /cm^3$;
- KT = 26 mV à 300 K (K = $1{,}38\times10^{-23}$ J/K).

Then the built-in potential is:

$$V_{bi} = 0{,}026.\ln\left(\frac{10^{15}\times10^{15}}{10^{20}}\right) = 0{,}6Volts$$