Chapter II: Key Properties of Semiconductors

II.1. Introduction

This chapter provides a foundational understanding of the physical properties that govern the behavior of semiconductor materials. A solid grasp of these principles is essential for the analysis and design of electronic and optoelectronic devices.

We begin by exploring the **crystal structures** of semiconductors, focusing on the cubic arrangements common to materials such as silicon and germanium (Group IV elements), which crystallize in a **diamond lattice**. Additionally, we examine **compound semiconductors** from Groups III-V (e.g., GaAs) and II-VI (e.g., CdTe), which adopt a **zinc-blende lattice** structure.

Next, we study **energy band formation**, which explains how electrons occupy allowed energy levels and how the **bandgap** separates the valence and conduction bands. A distinction is made between **direct and indirect bandgaps**, which is critical for understanding how semiconductors interact with light.

The chapter then delves into **charge carrier dynamics**, including the conduction of electrons and holes, their **effective masses**, and how this affect mobility. Finally, we introduce the concept of the **density of states**, which describes the number of available electronic states at each energy level in the conduction and valence bands.

Together, these topics form the core theoretical framework for understanding how semiconductors function at the atomic level and how their properties can be engineered for various applications.

II.2. Cubic crystal structures

Crystal structure is obtained by attaching atoms, groups of atoms or molecules. This structure occurs from the intrinsic nature of the constituent particles to produce

symmetric patterns. A small group of a repeating pattern of the atomic structure is known as the unit cell of the structure.

1. Crystal lattices and unit cells

a crystal structure is made of atoms. A crystal lattice is made of points. It can be defined as the geometrical arrangement of the atoms, ions or molecules of the crystalline solid as points in space.

2. Characteristics of crystal lattices

- In a crystal lattice, each atom, molecule or ions (constituent particle) is represented by a single point.
- These points are called lattice site or lattice point.
- Lattice sites or points are together joined by a straight line in a crystal lattice.
- When we connect these straight lines we can get a three-dimensional view of the structure. This 3D arrangement is called Crystal Lattice also known as Bravais Lattices.

Crystal structure = lattice structure + basis.

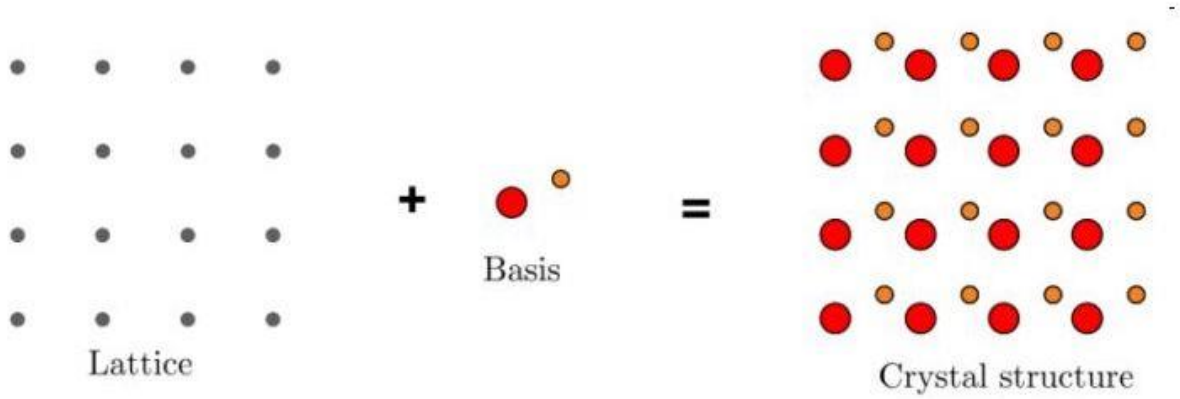


Figure II.1. Two-dimensional representation example of a crystal structure

This representation of two-dimensional can easily be extended to three dimensions to describe a real crystal material.

3. Unit cell

Unit cell is the smallest part (portion) of a crystal lattice. It is the simplest repeating unit in a crystal structure. The entire lattice is generated by the repetition of the unit cell in different directions.

Using this unit cell, the entire space of the crystal can be filled without leaving any gaps.

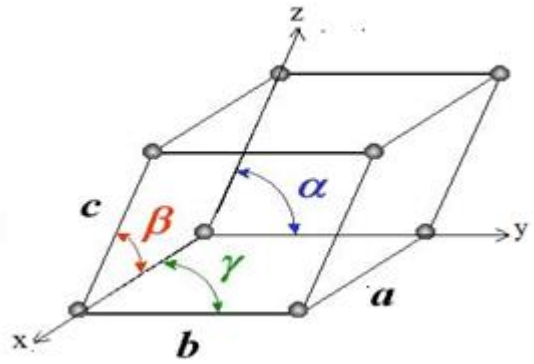


Figure II.2: 3D representation of the unit cell

There are six parameters of a unit cell. These are the 3 edges which are **a, b, c** and the angles between the edges which are **α, β, γ**. The edges of a unit cell may be or may not be perpendicular to each other.

$$\alpha = \{\vec{b}, \vec{c}\}, \quad \beta = \{\vec{a}, \vec{c}\} \text{ et } \gamma = \{\vec{a}, \vec{b}\}$$

This unit cell's volume corresponds to the modulus of the following scalar triple product:

$$V = (\vec{a}, \vec{b}, \vec{c}) = \vec{a} \cdot (\vec{b} \wedge \vec{c}) = \vec{b} \cdot (\vec{c} \wedge \vec{a}) = \vec{c} \cdot (\vec{a} \wedge \vec{b})$$

- A **lattice point** (or node) is the position occupied by an atom within the unit cell.

  Two types of unit cells can be distinguished: **simple** and **complex (multiple)**.
- A **simple unit cell** contains only nodes at the corners of the cell.
- A **complex (or multiple) unit cell** contains, in addition to the corner nodes, one or more nodes located either at the center of the volume, at the centers of all the faces, or at the centers of two opposite faces.

In three dimensions, for the **cubic system**, there are three main structures:

- The **simple cubic structure (SC)** consists of one atom located at each corner of the cube, as in ice.
- The **body-centered cubic (BCC) structure** has one atom at each corner and one node at the center of the cube. This structure is typical of alkali metals such as **sodium** and **potassium**.
- The **face-centered cubic (FCC) structure** consists of one atom at each corner and one node at the center of each face. This structure is found in **noble metals** such as **gold, silver, and platinum**, and in some **noble gases** such as **helium**.

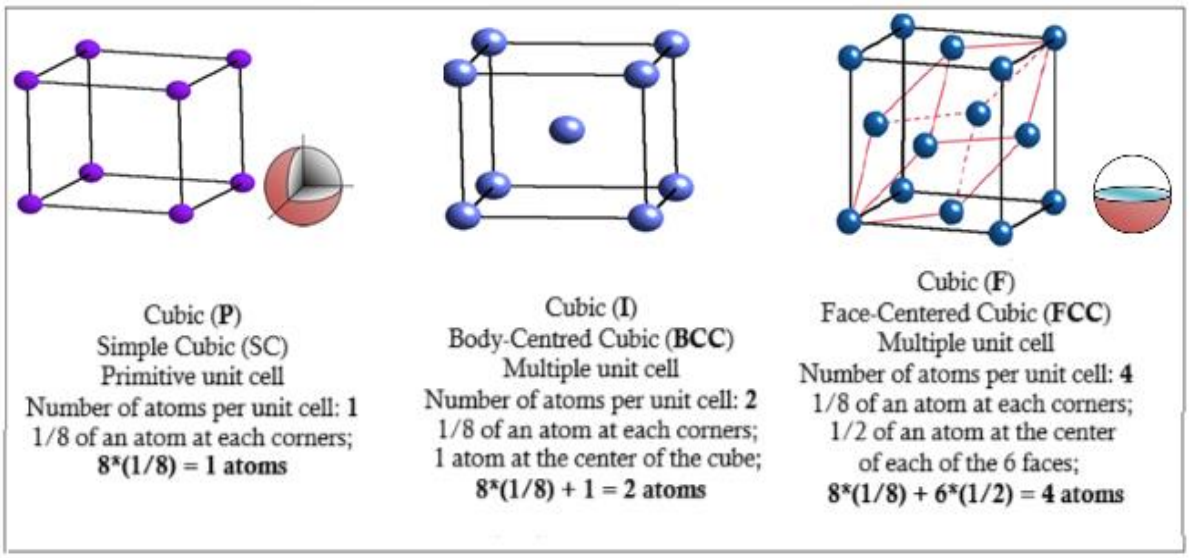


Figure II.3: Simple, Body-Centered, and Face-Centered Cubic Structures with Atom Count

Note: By knowing the crystal structure of a material and its lattice dimensions, we can determine several characteristics of the crystal. For example, we can determine the volume density of atoms.

Example:

Consider a single-crystal material that is a body-centered cubic with a lattice constant a=5A° = 5×10^{-8} cm.

The volume density of atoms is then found as:

$$Density = \frac{2\ atoms}{(5 \times 10^{-8})^3} = 1.6 \times 10^{22} atoms\ per\ cm^3$$

4. Miller Indices of a direction [*h k l*]

According to international conventions, a crystallographic direction (or lattice row) is defined by the vector equation:

$$\vec{V} = h.\vec{a} + k.\vec{b} + l.\vec{c}$$

Steps to determine the Miller indices of a direction vector $\vec{V}$:

1. Reduce the coefficients h, k, and l to a common denominator;
2. Eliminate the denominator and keep the numerators.

Note: If one of the indices is negative, the minus sign is placed over the corresponding index.

Examples

1- $\vec{V} = -\vec{a} + \frac{3}{4}\vec{b} + \frac{1}{2}\vec{c}$

$$\left[-1 \;\; \frac{3}{4} \;\; \frac{1}{2}\right] \rightarrow \left[-\frac{4}{4} \;\; \frac{3}{4} \;\; \frac{2}{4}\right] \rightarrow [-4 \;\; 3 \;\; 2]$$

Thus, the crystallographic direction of this vector is: $[\bar{4} \;\; 3 \;\; 2]$.

2- $\vec{V} = -2\vec{a} + 3\vec{b} - \vec{c} \Longrightarrow [\bar{2} \;\; 3 \;\; \bar{1}]$.

5. Miller Indices of a Plane (h k l)

Consider a crystallographic plane defined by the equation:; $t = hx + ky + lz$

Steps to determine the Miller indices of a plane:

1. Determine the coordinates where the plane intersects the x, y, and z axes;
2. Take the **reciprocals** of these intercepts;
3. Reduce to a common denominator;
4. Eliminate the denominator and keep the numerators.

Example

Given the equation:

$t = 2x + 3y - 4z$

1. $(2, 3, -4)$;
2. Take the reciprocals: $\left(\frac{1}{2} \;\; \frac{1}{3} \;\; -\frac{1}{4}\right)$;

3. Reduce to a common denominator: $\left(\frac{6}{12}\ \frac{4}{12}\ -\frac{3}{12}\right)$;
4. Final result: $(6\ 4\ \bar{3})$.

So the crystallographic plane is: $(6\ 4\ \bar{3})$.

Note

A direction [***h k l***] is **perpendicular** to the plane (h k l).

The direction perpendicular to a crystallographic plane (h, k, l) is denoted by [h, k, l].

The following figure shows some crystallographic planes identified by their Miller indices:

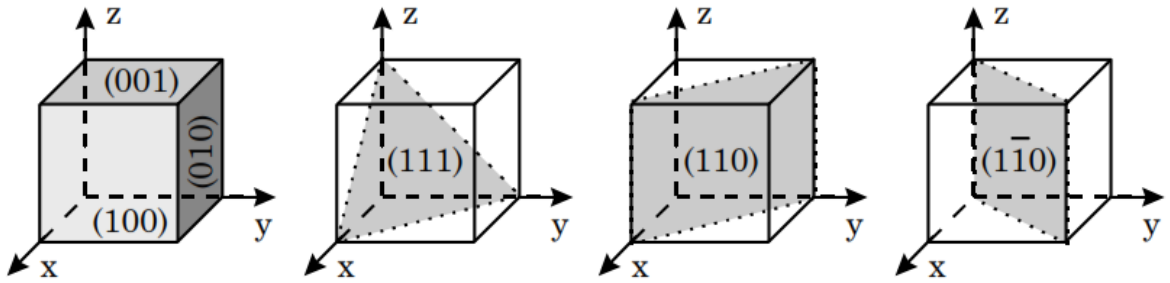


Figure II.4. Crystallographic Planes.

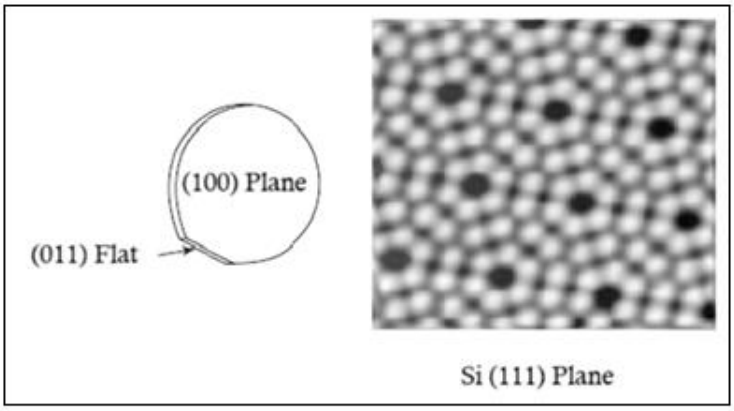


Figure II.5. Silicon wafers are usually cut along the (100) plane with a flat or notch to help orient the wafer during IC fabrication.

6. Elementary and Compound Semiconductors

The **elemental semiconductors** are found in **group IV** of the periodic table. These include **germanium** and, most importantly, **silicon**.

Note:

There are also **compound intrinsic semiconductors**, composed of **at least two different types of atoms**.

- **Binary semiconductors** of the **II–VI group** consist of one element from **group II** and another from **group VI** of the periodic table.
- **III–V semiconductors** are formed by combining one element from **group III** with one from **group V**.
- Similarly, **IV–VI semiconductors** consist of elements from **groups IV and VI**.

The table below provides examples of commonly used inorganic semiconductors, categorized by the constituent elements and their position in the periodic table.

Table II.1: Examples of Common Inorganic Semiconductors

Type of semiconductor		**Group(s)**	**Examples**
Elemental semiconductors		IV	Ge,Si
		VI	Se
Compound semiconductors	Binary	III-V	GaAs,GaN,AlP,InP,GaP,GaSb, InAs, InSb
		II-VI	CdS,HgTe,CdTe,ZnO,ZnTe,ZnS
	Ternary	III-V	$Al_xGa_{1-x}As$ (used in optoelectronic devices such as laser diodes, special transistors)
	quaternary	III-V	GaInAsP(laser diode),$Al_xGa_{1-x}As_yP_{1-y}$

II.2.1. Group IV semiconductors (Ge, Si) – Diamant lattice structure

The electrons of an isolated atom occupy discrete energy levels, with each level able to accommodate a limited number of electrons. This maximum number is given by the formula $2n^2$, where ***n*** is the principal quantum number (i.e., the shell number starting from the nucleus).

Electrons fill the energy levels beginning with those closest to the nucleus, corresponding to the lowest energy states.

In the case of **silicon**, which has an atomic number **Z=14**:

- There are **2 electrons** in the **first shell** (complete),
- **8 electrons** in the **second shell** (also complete),
- and **4 electrons** in the **third shell**, which is **not full**, since it can hold up to **18 electrons**.

Elemental semiconductors are characterized by their **tetravalency**, meaning their outermost electron shell contains **four valence electrons**.

Examples: Silicon (Si), Germanium (Ge).

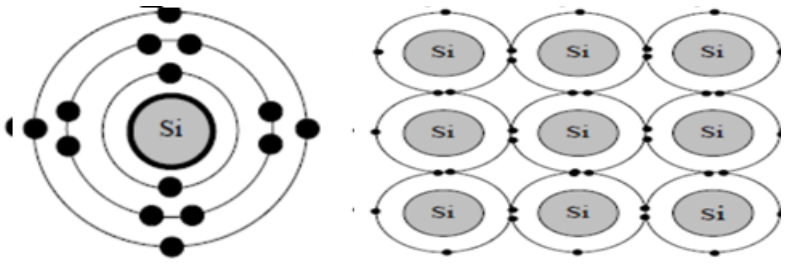


Figure II.6. Energy levels and electron distribution of a silicon atom and crystal (covalent bonding).

Silicon is a **tetravalent** atom: it has **four valence electrons**, which it shares with neighboring silicon atoms to form the **crystalline structure**.

At **absolute zero**, there is no thermal agitation, and **all valence electrons participate in covalent bonds**. As a result, **no free electrons** are available for electrical conduction — the material behaves as an **insulator**.

When the **temperature increases**, thermal agitation allows **some electrons to break free** from their covalent bonds, becoming mobile within the crystal. This phenomenon is known as **covalent bond breaking**, which enables **electrical conduction** in the material.

- **Diamant structure of Silicon and Germanium**

Silicon and germanium both crystallize in the **diamond structure**. In this structure, each atom has **four nearest neighbors**, arranged in a **regular tetrahedron** via **covalent bonds**.

The **diamond lattice** is composed of **two interpenetrating face-centered cubic (FCC) lattices**, offset by **one-quarter of the main body diagonal** of the cube.

- The **nearest-neighbor distance** corresponds to **one-quarter of the cube's main diagonal**.
- Each atom has **four nearest neighbors**.

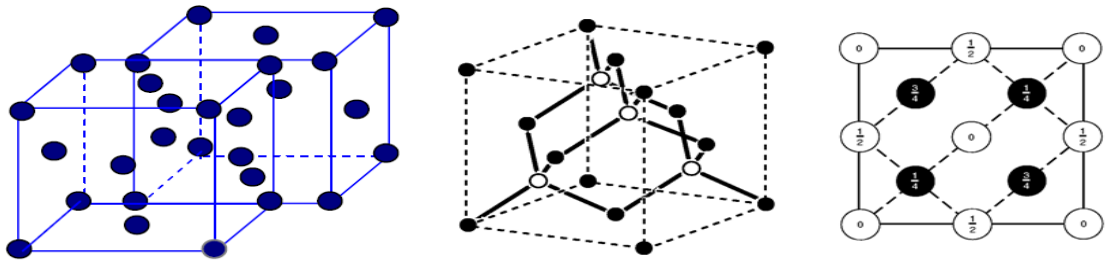
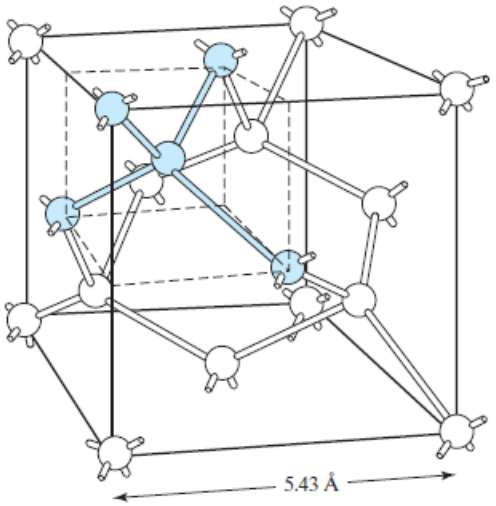


Figure II.7. Diamond structure and atomic positions within the unit cell.

Figure II.8. Silicon structure.



II.2.2. Compound semiconductors (III-V or II-VI) –Zinc blende structure

The **zinc blende lattice** has a structure identical to that of **diamond**, except that the basis consists of **two different types of atoms**.

In this structure, each atom also has **four nearest neighbors** (from the other element), and the bonding is **covalent**.

The table below lists the **crystal structure** and **lattice parameter** of some common semiconductors at **300 K**.

Table II. 2: Crystal structure and lattice parameter of some semiconductors

Semiconductor	Symbol	Structure	Lattice Constant a (Å) at 300K
Germanium	Ge	Diamond	5,65748
Silicon	Si	Diamond	5,43086
Gallium Arsenide	GaAs	Zinc blende	5,6534
Indium Antimonide	InSb	Zinc blende	6,4788
Indium Arsenide	InAs	Zinc blende	6,0585

II.3. Energy Band - Silicon

According to band theory, when many atoms combine, their molecular orbitals merge into nearly continuous energy bands.

The **valence band** (lower half) consists of bonding molecular orbitals and is **filled with electrons**. The **conduction band** (upper half) consists of antibonding molecular orbitals and is **empty**.

- **Origin of Valence Band Electrons:**
  - Electrons in the valence band come from the **incomplete outer shells** of atoms.
  - Example: In a silicon (Si) crystal, the valence band is formed from these outer electrons.
- **Electronic Configuration of Isolated Si Atom:**
  - A single Si atom has **14 electrons** in the following orbitals: 1s, 2s, 2p, 3s, and 3p (all paired).
- **Effect of Atomic Distance on Band Formation:**
  - When Si atoms are **far apart**, outer electrons do **not interact**.
  - When the interatomic distance is **reduced to d_1**:
    - **Electron wave function overlap** occurs across adjacent atoms.
    - **Energy level splitting** happens due to the **Pauli exclusion principle**, forming bands.
- **Band Splitting Details:**
  - **3s band** splits into **2N states**.
  - **3p band** splits into **6N states** (N = number of Si atoms).
  - With further distance reduction:
    - 3s and 3p bands **merge into one band** with **8N states**.
    - This band **splits again** into two bands of **4N states** each:
      - Lower band = **Valence band** (filled at 0 K).
      - Upper band = **Conduction band** (empty at 0 K).

- **Core Electrons in Crystal Si (at lattice spacing d_0):**
  - **Core-level electrons** do **not interact** at this spacing.

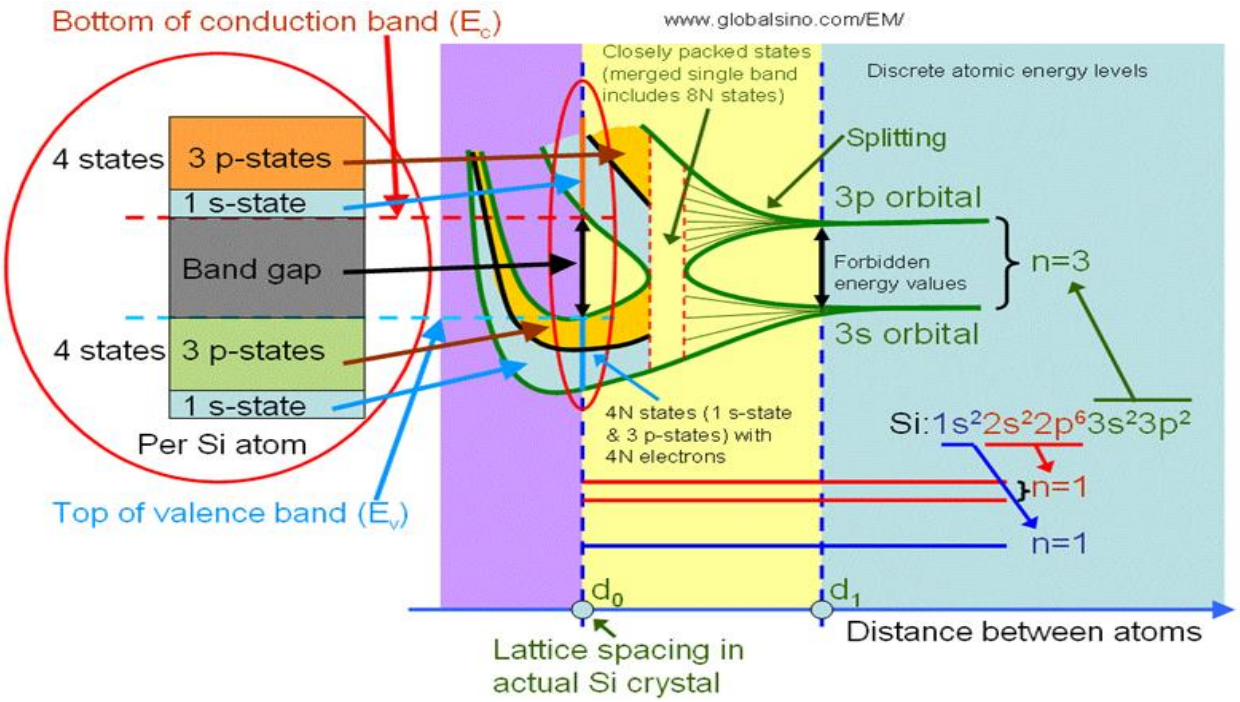


Figure II.9. Detailed illustration of the electronic structure of silicon as a function of the distance between atoms.

The **left red circle** provides a **magnified view** of the area highlighted by the **right red circle**.

II.4. Direct and indirect band Gaps

The curves $E_{C,,V}(\vec{k})$, also known as **dispersion relations**, represent the energy of electrons as a function of the wave vector $\vec{k}$.

- Ec is the bottom of the **conduction band**,
- Ev is the top of the **valence band**, and
- $\vec{k}$ is the **wave vector** associated with an electron's momentum, given by :

$$\vec{p} = m\vec{v} = \hbar\vec{k}$$

Where :

$\hbar$ is the reduced Planck constant.

These dispersion relations reveal **two types of semiconductors**:

- **Direct bandgap semiconductors**: the **minimum of E_C** and the **maximum of E_V** occur at the **same $\vec{k}$ value**.
- **Indirect bandgap semiconductors**: the **minimum of E_C** and the **maximum of E_V** occur at **different $\vec{k}$ value**.

Note:

- **Planck's constant** ($h = 6.626 \times 10^{-34} J.s$) is a fundamental constant in quantum physics that relates the energy of a photon to the frequency of its associated electromagnetic wave.

$$E = h.\nu$$

where:

- **E** is the energy of the photon (in joules),
- $\boldsymbol{\nu}$ is the frequency (in hertz),
- **h** Planck's constant.

Planck's constant:

  - marks the **quantization of energy** — energy is not continuous but comes in discrete packets called *quanta*.
  - is central to the **photoelectric effect**, quantum mechanics, and energy levels in atoms.

- **Reduced Planck constant,** also known as "**h-bar**" ($\hbar = 1.055 \times 10^{-34} J.s$) is derived from Planck's constant by dividing it by 2π:

$$\hbar = \frac{h}{2\pi}$$

Reduced Planck constant:

- Commonly appears in **wave mechanics**, **quantum field theory**, and **angular momentum quantization**.

Essential in expressing de Broglie's relation $\vec{p} = \hbar\vec{k}$ and **Heisenberg's uncertainty principle**:

$$\Delta x . \Delta p \geq \frac{\hbar}{2}$$

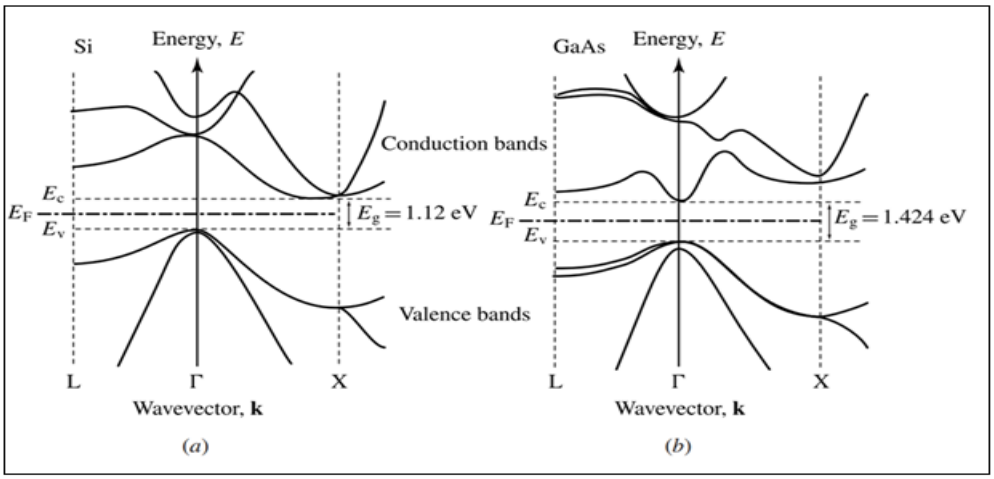


Figure II.10: (a) Indirect bandgap semiconductor, (b) Direct bandgap semiconductor.

II.5. Conductivity by Electrons or Holes. Effective Mass. Density of States

II.5.1. Conductivity by Electrons or Holes

At low temperatures (e.g., 0 K), a semiconductor crystal does not receive any external energy. All valence electrons are engaged in covalent bonds, and their energies lie within the valence band (VB). As a result, there are no free electrons to move through the crystal — the conduction band (CB) remains empty.

As the temperature increases (for example, to 300 K), the crystal absorbs thermal energy. Some electrons gain enough energy to break free from their atomic bonds and become free carriers, able to move throughout the material. These free electrons no longer participate in the crystal's bonding structure.

The energy levels of these free electrons lie within the conduction band (CB). When a covalent bond is broken, the atom that loses an electron becomes a positively charged ion and leaves behind a vacancy known as a **hole**. This positively charged ion can attract an electron from a neighboring atom to fill the vacancy. As it regains a neutral charge, the neighboring atom becomes positively charged. This transfer results in the hole effectively moving in the opposite direction to the electron's motion.

Therefore, both free electrons and holes contribute to the electrical conductivity of the semiconductor.

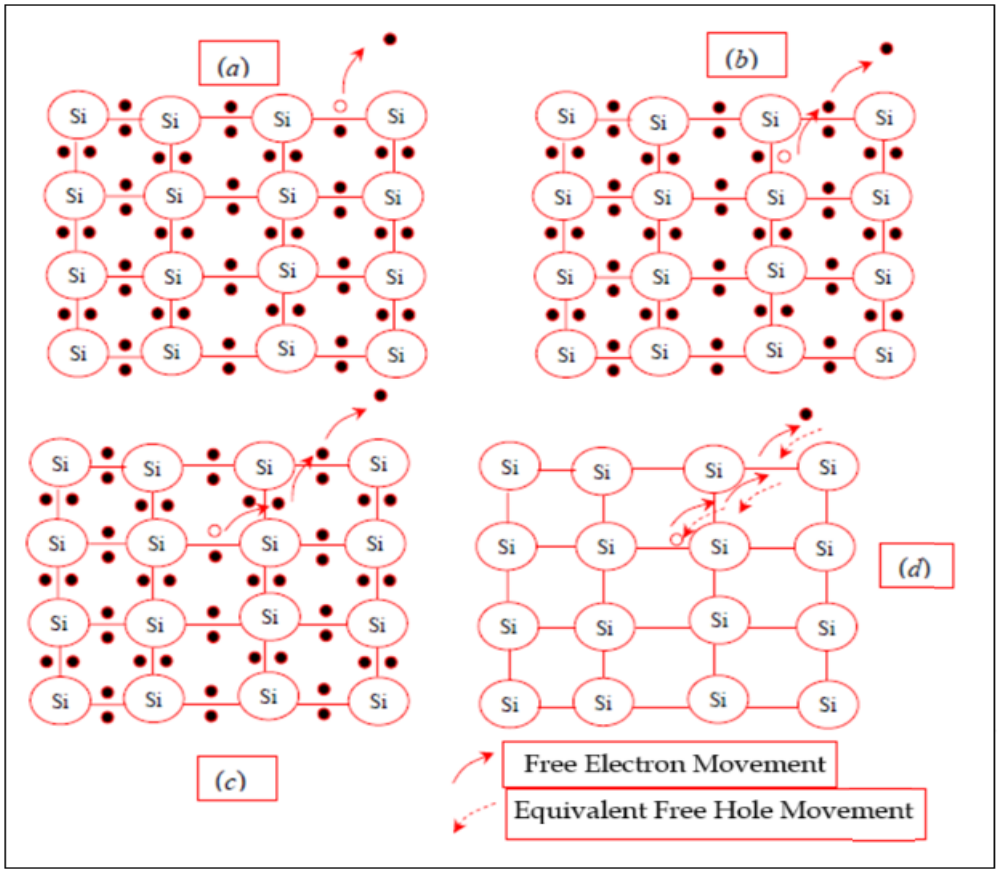


Figure II.11: Free electron and hole movement

When analyzing electrical conduction in semiconductors, both **free electrons** in the conduction band and **holes** in the valence band act as charge carriers. While a free electron is a real particle, a hole is a conceptual representation of the absence of an electron in an otherwise filled band. Despite this difference, the motion of a hole can be described as equivalent to that of a positively charged particle. The following table highlights the main differences and the equivalence between the movement of free electrons and free holes:

Table II.3: Summary of the equivalence between free electron and free hole

	Free Electron	***Free Hole***
Charge	Negative	Positive
Location	Conduction band	Valence band
Behavior in electric field	Moves opposite to the field	Moves in the direction of the field
Effective particle	Real particle	Conceptual(absence of electron)
Direction of motion	Same as its actual motion	Opposite to the motion of electrons filling the hole

II.5.2. Effective mass

In solid-state physics, a **free electron** within a semiconductor is modeled as a free particle, but with an **effective mass** « m_n » that differs from the **rest mass of a free electron in vacuum**, denoted by: « $m_0 = 0{,}91\times10^{-30}$ kg»

Similarly, m_p represents the effective mass of hole.

Near an **extremum** of an energy band (either the **valence band (VB)** or the **conduction band (CB)**), the **dispersion relation** E(k) can be approximated using a Taylor expansion. For example, **near the minimum of the conduction band** (also known as a **"valley"**), the energy can be written as:

$$E(k) = E_C + \frac{\hbar^2 k^2}{2m_n}$$

Which is equivalent to (using the momentum $\vec{p} = \hbar\vec{k}$):

$$E(p) = E_C + \frac{p^2}{2m_n}$$

Where:

- $p = \|\vec{p}\|$ is the magnitude of momentum;
- $k = \left\|\vec{k}\right\|$ is the magnitude of the wave vector.

This is known as the **parabolic approximation** of the conduction band. Since the term $\frac{p^2}{2m_n}$ represents the **kinetic energy** of a free electron, the additional energy (above E_C) is treated as kinetic energy. From this comparison, we deduce that the **effective mass** of electrons in the conduction band valley is:

$$m_n = \left(\frac{d^2E}{dp^2}\right)^{-1}$$

Thus, the effective mass is **inversely proportional to the curvature** of the E(p) curve.

II.5.3. Density of states

The **density of states** refers to the number of **available energy states per unit energy range** that electrons or holes can occupy in a band.

In the **conduction band** (CB), the **electron density of states** is given by:

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

In the **valence band** (VB), the **hole density of states** is given by:

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

Where:

- **E** is the energy level,

- E_C is the conduction band minimum,
- E_V is the valence band maximum,
- $\hbar$ is the reduced Planck constant,
- m_n and m_p are the effective masses of electrons and holes, respectively.

These expressions show that the density of states increases with the square root of the energy difference from the band edge.