

ED_Block 1

Block 1: General Material Concepts: Structural and electrical properties of semiconductors

1. Crystal Properties and Growth of Semi Conductors
2. Atoms and Electrons
3. Energy bands and Charge Carriers in Semiconductors

Crystal Properties and Growth of Semi Conductors

Semiconductor Materials: Semiconductors are a group of materials having electrical conductivities intermediate between metals and insulators

Electrical conductivity: represents a material's ability to conduct electric current. Electrical conductivity is closely related to resistivity: $\sigma = \frac{1}{\rho}$ where σ (Sigma) is the conductivity (m/Ohm) and ρ (Rho) is the resistivity (Ohm/m).

Ohms Law Equation:

$$I = \frac{V}{R}$$

Electrical Conductivity: (A: Area, l: length)

$$\sigma = \frac{l}{RA}$$

Elemental semiconductors: The column IV semiconductors, silicon and germanium, are called

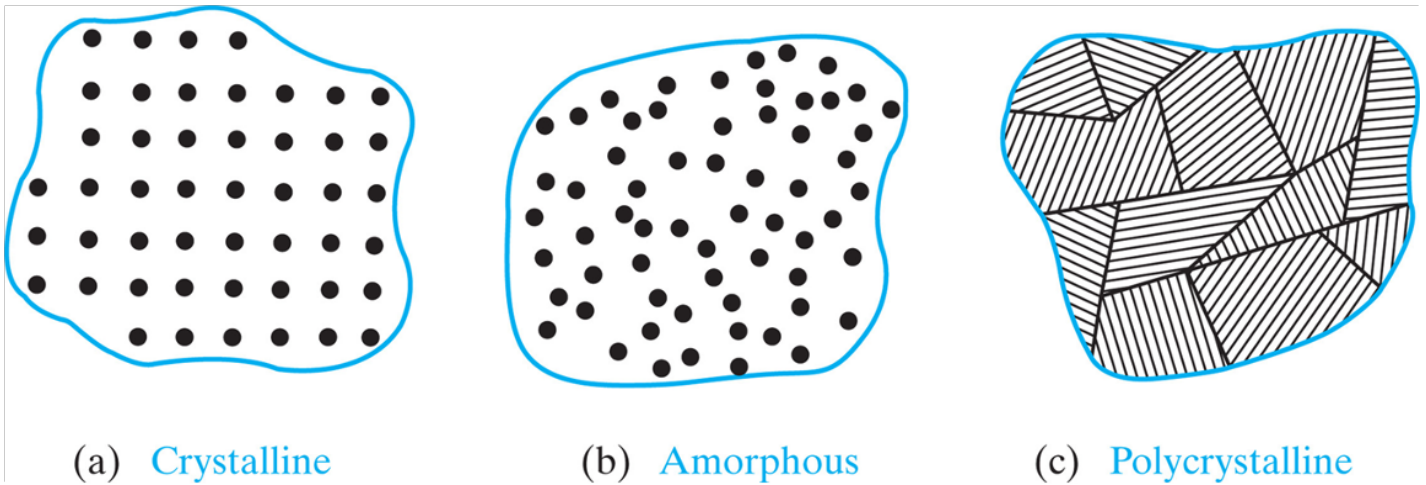
elemental semiconductors because they are composed of single species of atoms.

Compound semiconductors: In addition to the elemental materials, compounds of column

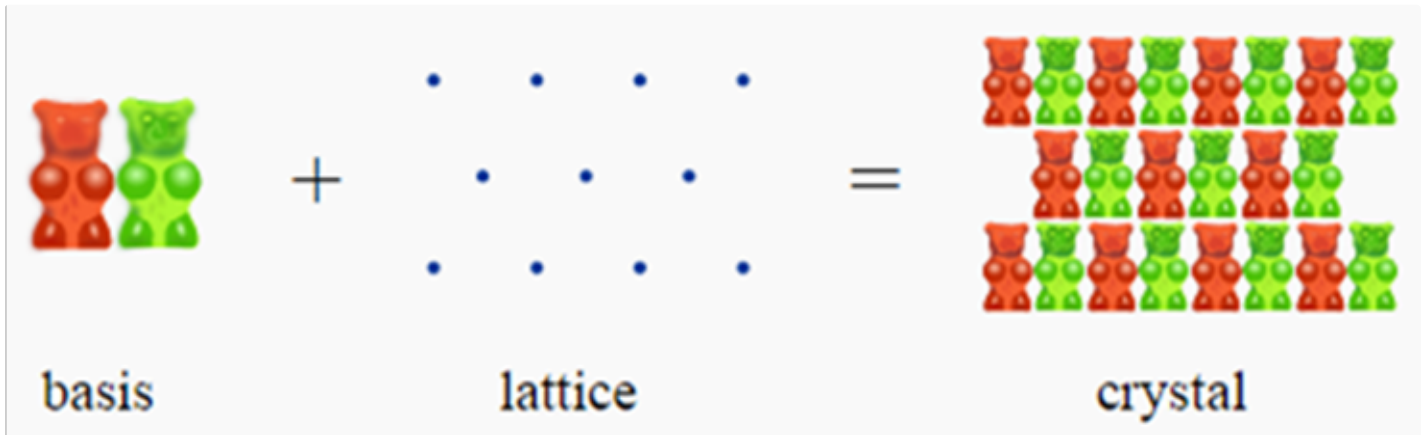
III and column V atoms, as well as certain combinations from II and VI, and from IV, make up the compound semiconductors.

Crystal Lattices:

1. Energy Band Gap: One of the most important characteristics of a semiconductor, which distinguishes it from metals and insulators
2. The atomic arrangements in the materials
3. Crystal lattice (Crystalline, Amorphous, Polycrystalline): is the symmetrical three-dimensional arrangement of atoms inside a crystal.

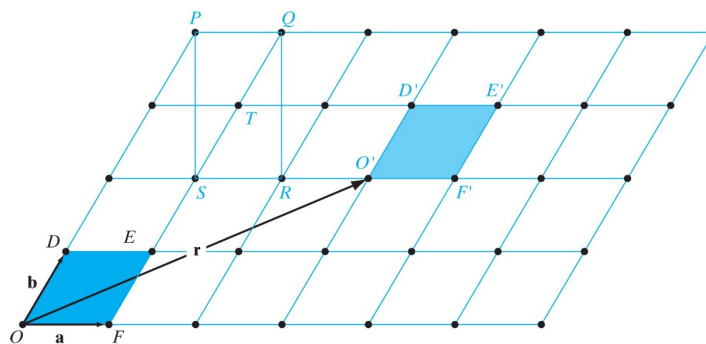


4. Crystalline solid: is distinguished by the fact that the atoms making up the crystal are arranged in a **periodic fashion**. That is, there is some basic arrangement of atoms that is repeated throughout the entire solid.
5. Not all solids are crystals; some have *no periodic structure at all* (amorphous solids), and others are composed of many small regions of single-Crystal material (**polycrystalline solids**).
6. The periodicity in a crystal is defined in terms of a symmetric array of points in space called the **lattice**. We can add atoms at each lattice point in an arrangement called **abasis**, which can be one atom or a group of atoms having the same spatial arrangement, to get a crystal.

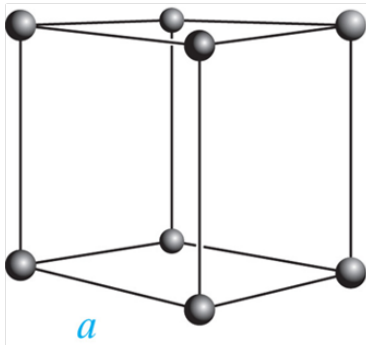


7. Points within the lattice are indistinguishable if the vector between the points is (p, q, s) (where p, q and s are integers)

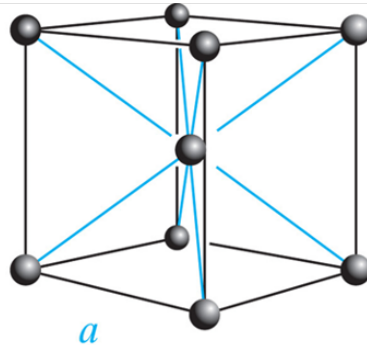
$$\vec{r} = p\vec{a} + q\vec{b} + s\vec{c}$$



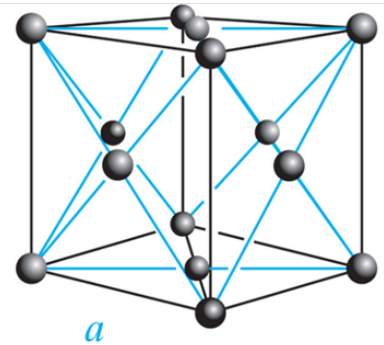
8. Since there are many different ways of placing atoms in a volume, the distances and orientation between atoms can take many forms, leading to different lattice and crystal structures.
9. The simplest 3D lattice is one in which the unit cell is a cubic volume. The **simple cubic** structure (abbreviated **sc**) has an atom located at each corner of the unit cell.
10. The **body-centered cubic (bcc)** lattice has an additional atom at the center of the cube, and the **face-centered cubic (fcc)** unit cell has atoms at the eight corners and centered on the six faces.



Simple cubic



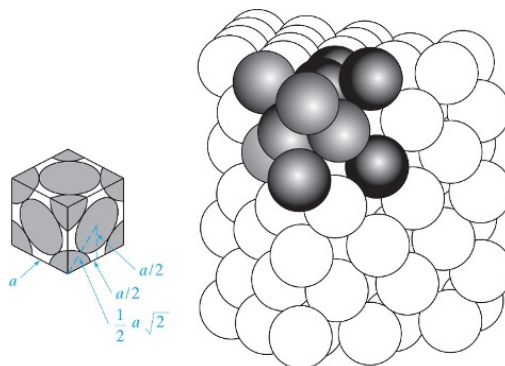
Body-centered cubic



Face-centered cubic

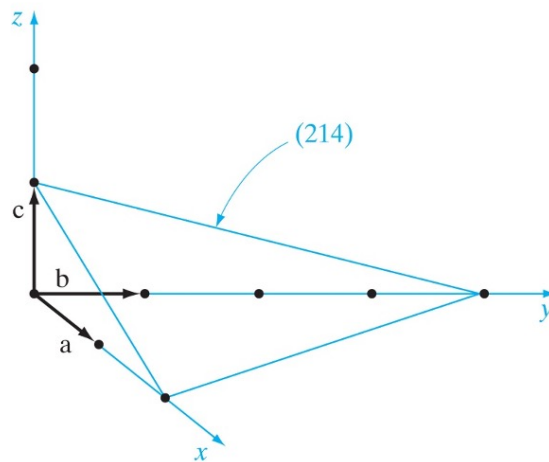
11. As atoms are packed into the lattice in any of the arrangements, the distances between **neighboring atoms** will be determined by a balance between the forces that attract them together and other forces that hold them apart.
12. One can calculate the maximum fraction of the lattice volume that can be filled with atoms by approximating the atoms as hard spheres.

For example, Figure illustrates the packing of spheres in a fcc cell of side a , such that the nearest neighbor touch. The dimension a for a cubic unit cell is called the **lattice constant**. For the fcc lattice the nearest neighbor distance is one-half the diagonal of a face, or $1/2(a\sqrt{2})$. Therefore, for the atom centered on the face to just touch the atoms at each corner of the face, the radius of the sphere must be one-half the nearest neighbor distance, or $1/4(a\sqrt{2})$.



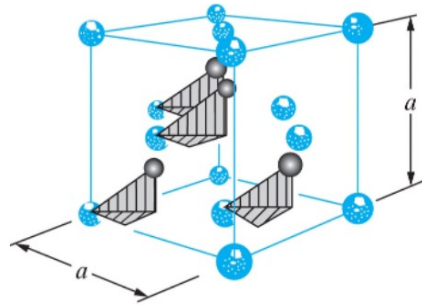
13. In discussing crystals it is very helpful to be able to refer to **planes and directions within** the lattice. The notation system uses a set of three integers to describe the position of a plane or the direction of a vector within the lattice. The three integers describing a particular plane are found in the following way: (The three integers h , k , and l are called the **Miller indices**; these three numbers define a set of parallel planes in the lattice.)

1. Find the intercepts of the plane with the crystal axes and express these intercepts as integral multiples of the basis vectors (the plane can be moved in and out from the origin, retaining its orientation, until such an integral intercept is discovered on each axis).
2. Take the reciprocals of the three integers found in step 1 and reduce these to the smallest set of integers h , k , and l , which have the same relationship to each other as the three reciprocals.
3. Label the plane (hkl).

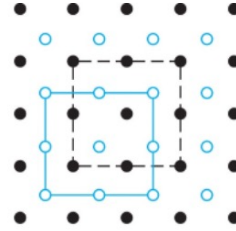


14. From a crystallographic point of view, many planes in a lattice are equivalent; that is, a plane with given Miller indices can be shifted about in the lattice simply by choice of the position and orientation of the unit cell.
15. A **direction** in a lattice is expressed as a set of three integers with the same relationship as the components of a vector in that direction ($[a, b, c]$ direction). Many directions in a lattice are also equivalent, depending only on the arbitrary choice of orientation for the axes. Such equivalent direction indices are placed in angular brackets $\langle \rangle$.
16. The basic crystal structure for many important semiconductors is the fcc lattice with a basis of two atoms, giving rise to the **diamond structure**, characteristic of Si, Ge, and C in the diamond form.

One of the simplest ways of stating the construction of the diamond structure is: The diamond structure can be thought of as an fcc lattice with an extra atom placed at $a/4 + b/4 + c/4$ from each of the fcc atoms.



(a)



(b)

Atom Packing Factor

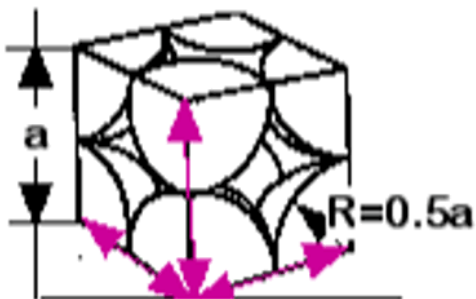
Atomic packing factor (APF) is the fraction of volume actually occupied by atoms in a crystal.

Atomic Packing Factor (APF)

$$\text{APF} = \frac{\text{Volume of atoms in unit cell}^*}{\text{Volume of unit cell}}$$

*assume hard spheres

For simple cubic structure. . .



contains $8 \times 1/8 =$
1 atom/unit cell

APF = 0.52 for simple cubic

$$\text{APF} = \frac{\text{atom/unit cell} \times \frac{4}{3} \pi (0.5a)^3}{a^3}$$

volume/atom

volume/unit cell

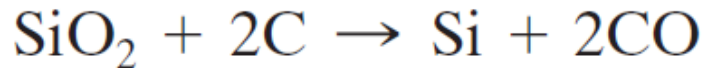
Bulk Crystal Growth

The progress of solid state device technology is depended not only on the development of device concepts but also on the improvement of materials.

The requirements on the growing of **device-grade semiconductor crystals** are more

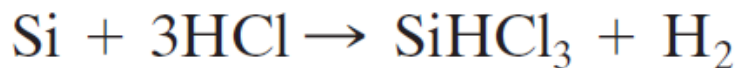
stringent than those for any other materials. Not only must semiconductors be available in large single crystals, but also the purity must be controlled within extremely close limits.

1. The raw material for Si crystal is silicon dioxide SiO_2 . SiO_2 reacts with C in a furnace at very high temperatures ($\sim 1800^\circ C$) to reduce SiO_2 according to the following reaction:

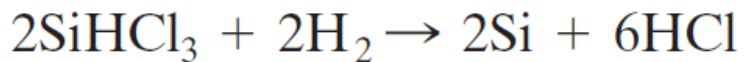


This forms **metallurgical grade Si** (MGS) which has impurities such as Fe, Al, and heavy metals at level of **parts per million** (ppm).

2. The MGS is refined further to yield semiconductor-grade or **electronic-grade Si** (EGS), in which the levels of impurities are reduced to **parts per billion** (ppb).



$SiHCl_3$ is then converted to **highly pure EGS** by reaction with H_2 ,



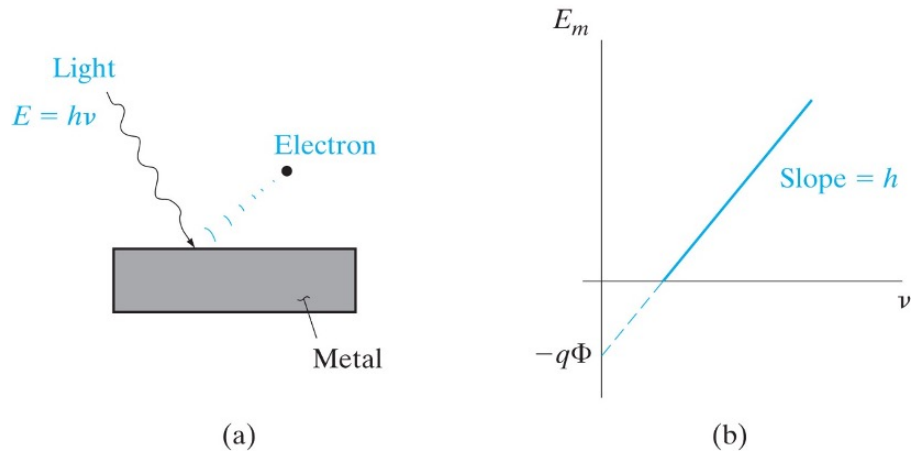
Next, step is to convert the high purity but still polycrystalline EGS to single-crystal Si **ingots** (a single crystal) or boules. This is done by a process commonly called the **Czochralski method**.

Atom and Electrons

The Photoelectric Effect:

The photoelectric effect is the emission of electrons when electromagnetic radiation, such as light, hits a material.

Planck indicated that radiation is emitted in discrete units of energy called **quanta**; the energy units were described by $h\nu$, where ν is the frequency of the radiation, and h is called **Planck's constant** ($h = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}$).

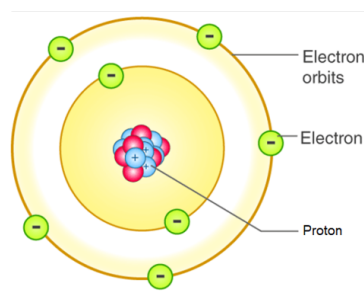


The electrons in the metal absorb energy from the light, and some of the electrons receive enough energy to be ejected from the metal surface into the vacuum. This phenomenon is called the photoelectric effect. \Rightarrow the **quantum nature of light** and electrons.

Atomic Structure

The model of the atom that we may use to understand the atom's general behavior is a simplified atomic model called the **shell model**, based on the **Bohr model**(1913).

- Electrons orbit nucleus in discrete quantized orbits with fixed radii
- Electron can be viewed as a charge contained within a spherical shell of a given radius
- An electron can jump from one orbital to another by losing (emission) or gaining (absorbing) energy



The mass of the atom is concentrated at the **nucleus**, which contains **protons and neutrons**. Protons are positively charged particles, whereas neutrons are neutral both have about the same mass.

The number of protons in the nucleus is the **atomic number Z** of the element.

The **electrons** are assumed to be orbiting the nucleus at very large distances compared to the size of the nucleus. There are as many orbiting **electrons** as there are **protons** in the nucleus.

The **shells** and **subshells** that define the whereabouts of the electrons are labelled using two sets of integers, n (principal number) and ℓ (orbital angular momentum quantum number).

The integers take the values $n = 1, 2, 3, \dots$, and $\ell = 0, 1, 2, \dots, n - 1$, and $\ell < n$. For each choice of n , there are n values of ℓ , so higher-order shells contain more subshells.

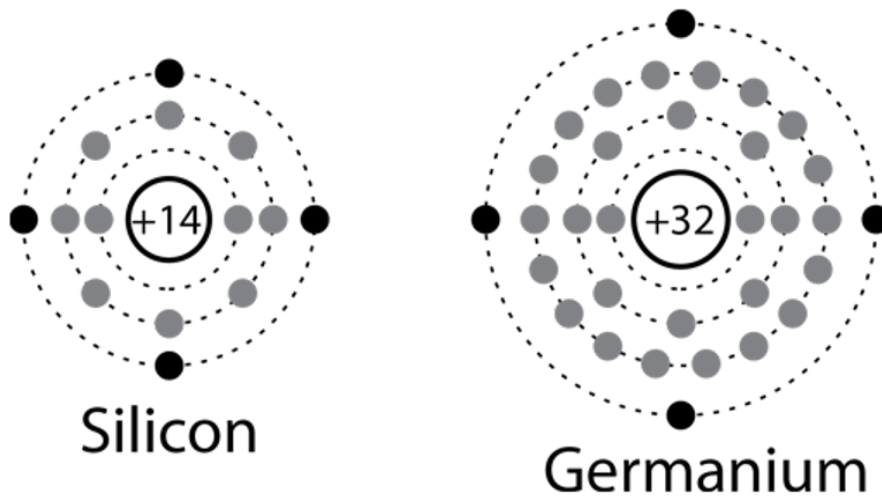
The shells corresponding to $n = 1, 2, 3, 4, \dots$ are labelled by the capital letters K, L, M, N, \dots , and the subshells denoted by $\ell = 0, 1, 2, 3, \dots$ are labelled s, p, d, f \dots .

The number of electrons a given subshell is: **$2(2\ell + 1)$**

Max no. of electrons in each shell is **$2n^2$**

Shell name	Subshell name	Subshell max electrons	Shell max electrons
K	1s	2	2
L	2s	2	2 + 6 = 8
	2p	6	
M	3s	2	2 + 6 + 10 = 18
	3p	6	
	3d	10	
N	4s	2	2 + 6 + 10 + 14 = 32
	4p	6	
	4d	10	
	4f	14	
O	5s	2	2 + 6 + 10 + 14 + 18 = 50
	5p	6	
	5d	10	
	5f	14	
	5g	18	

When a subshell is full of electrons, it cannot accept any more electrons and it is said to have acquired a **stable configuration**.

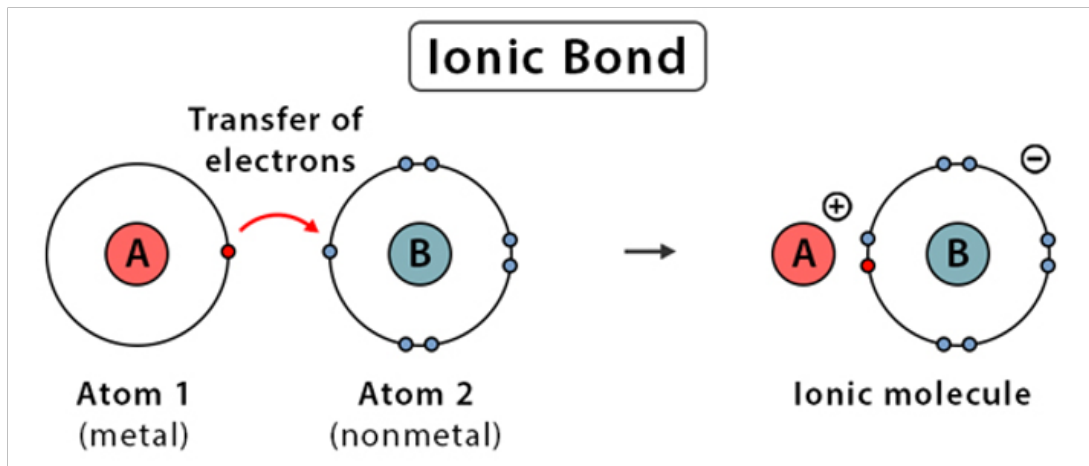


Energy Bands and Charge Carriers in Semiconductors

Bonding Forces in Solids:

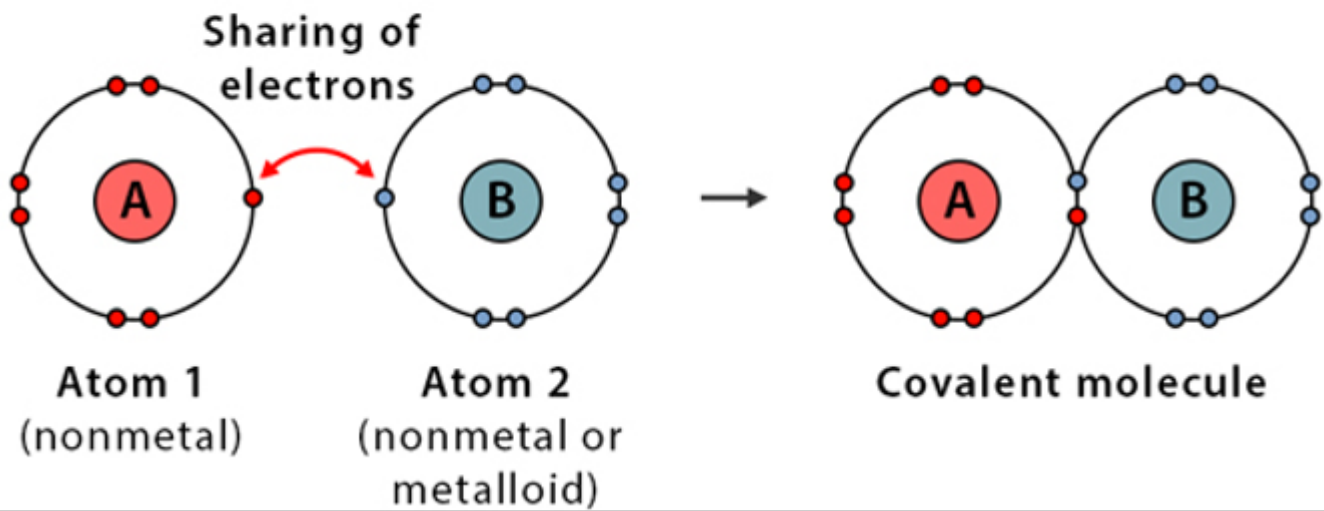
The interaction of electrons in neighbouring atoms of a solid serves the very important function of holding the crystal together. **For example**, NaCl are typified by **ionic bonding**.

In an **ionic bond**, one atom essentially **donates** an electron to stabilize the other atom. In other words, the electron spends most of its time close to the bonded atom.

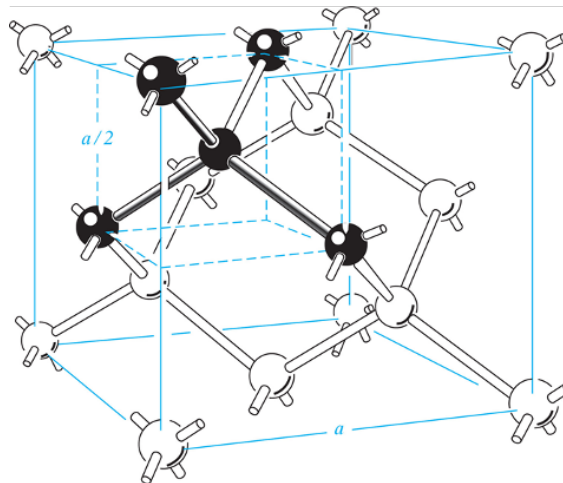


In a **covalent bond**, the atoms are bound by shared electrons.

Covalent Bond



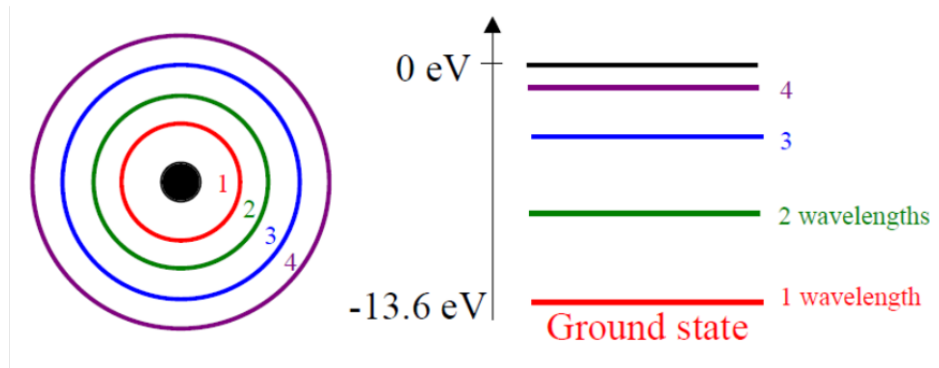
In a **diamond lattice**, each Si atom (with four valence electrons) is surrounded by four Si atoms that form four covalent bonds consisting of **shared electron pairs**, thereby forming an **octet** of electrons in the valence shell.



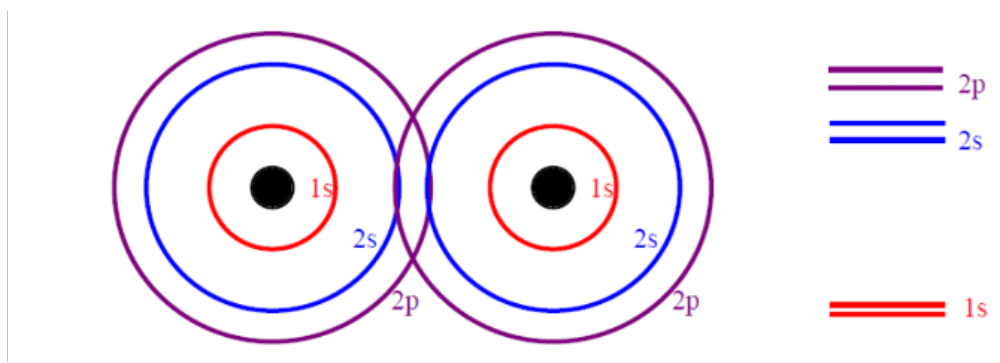
Energy Band Structures:

According to Bohr's theory, every shell of an atom contains a discrete amount of energy at different levels.

In solids, several bands of energy levels are formed due to the intermixing of atoms in solids. We call these set of energy levels as **energy bands**.



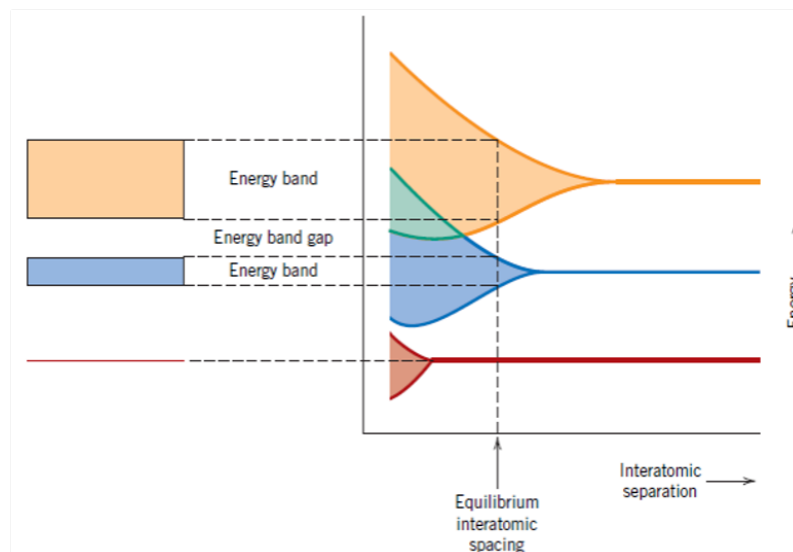
The interaction between two atoms when they are close together results in **splitting of the energy levels** in two.

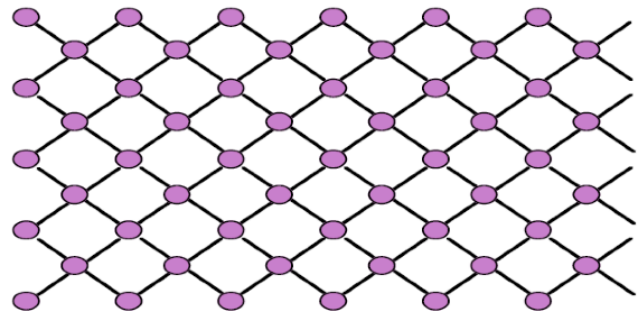
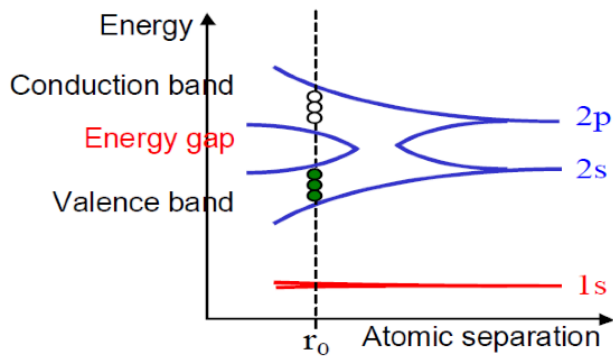


When atoms combine to form **substances**, the outermost shells, subshells and orbitals merge, providing a greater number of available energy levels for electrons to assume.

When large numbers of atoms are close to each other, these available energy levels form a nearly continuous band wherein electrons may move.

Equilibrium interatomic spacing will occur when the bond energy is a minimum. That is when the net forces (attractive force, repulsive force) between the two atoms is zero.





Diamond crystal

When the atoms are packed together in a crystal each energy levels splits in a band with large number of very closely packed states. The bands are separated by regions of forbidden energies for the electrons called *forbidden gaps* or *band gaps* E_g .

The last band completely full of electrons is called *valence band* E_V . The next band which may be either empty or partially filled with electrons is called *conduction band* E_C .

价带与导带：

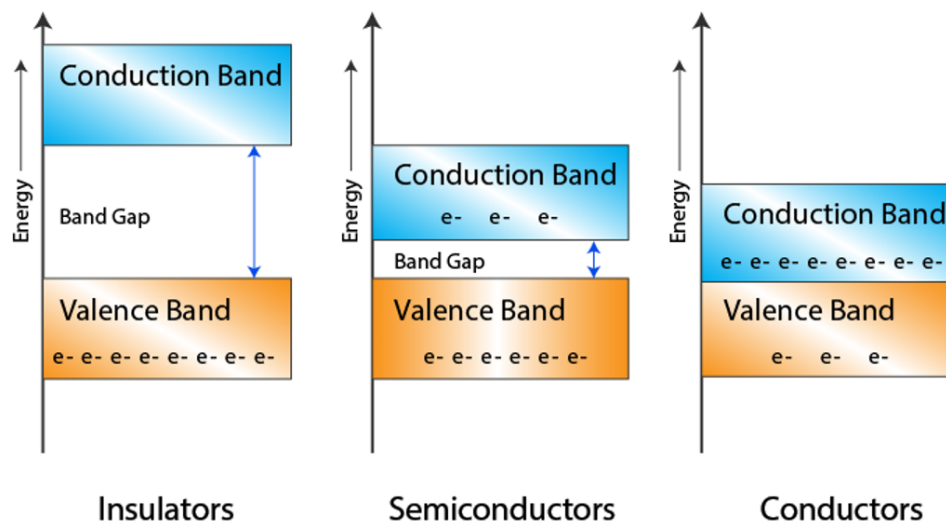
- 价带（Valence Band, EV）：在绝对零度下，被电子完全填满的最高能带。它对应于原子中最外层的价电子所形成的能带。在图中用红色区域标注。
- 导带（Conduction Band, EC：紧邻在价带之上的能带。在绝对零度下，该能带完全空着。电子可以在这里自由移动，从而导电。在图中用蓝色区域标注。

禁带（Band Gap, E_g ）：位于价带顶和导带底之间的能量区域。这个区域是电子不允许存在的“禁区”。禁带的宽度 E_g 是材料的核心属性，直接决定了材料的导电性（是导体、半导体还是绝缘体。

Valance Band (Ev)

The electrons in the **outermost shell** are known as **valence electrons**.

These valence electrons contain a series of energy levels and form an energy band known as the **valence band**.



Conduction Band (E_c)

The valence electrons are not tightly held to the nucleus due to which a few of these valence electrons leave the outermost orbit even at room temperature and become free electrons.

The free electrons conduct current in conductors and are therefore known as **conduction electrons**.

Forbidden Energy Gap (E_g)

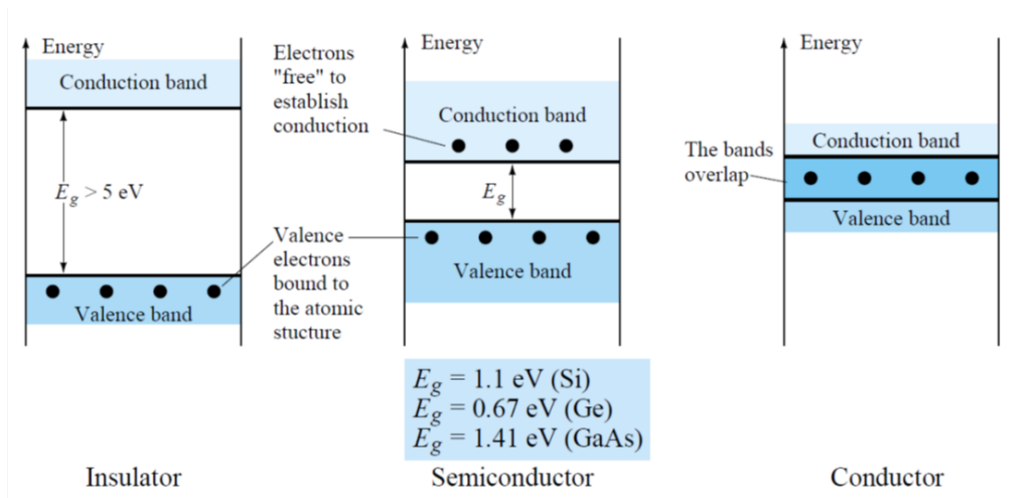
The gap between the valence band and the conduction band is referred to as the forbidden gap.

The forbidden gap doesn't have any energy and **no electrons stay** in this band.

Semiconductor materials at 0K have basically the same structure as insulators - a filled valence band separated from an empty conduction band by a band gap containing no allowed energy states.

The difference lies in the size of the **E_g** , which is much smaller in semiconductors than in insulators.

For example, the semiconductor Si has a band gap of about 1.1 eV compared with 5 eV for diamond.



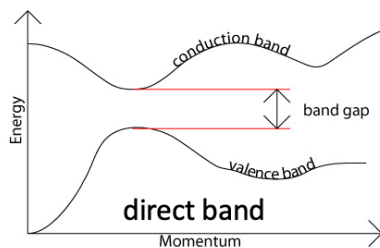
Direct and Indirect Band Gaps:

The band gap of a semiconductor can be of two basic types, a **direct** band gap or an **indirect** band gap.

The band gap is called direct if the crystal momentum (k-vector) of electrons and holes is the same in both the conduction band and the valence band; an electron can directly emit a photon.

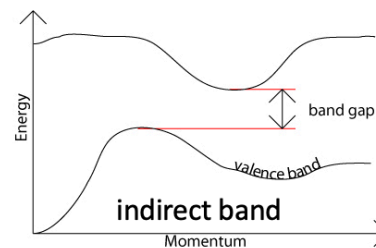
In a direct band gap semiconductor, the top of the valence band and the bottom of the conduction band occur **at the same value** of momentum.

In an indirect band gap semiconductor, the maximum energy of the valence band occurs at a **different value of** momentum to the minimum in the conduction band energy.



Gallium arsenide (GaAs)
Indium arsenide (InAs)

UESTCHN 3008 ED



Silicon (Si)
Germanium (Ge)

Compound Semiconductors:

In addition to group IV elements, compounds of group III and group V elements, and also group II and group VI elements are often semiconductors. The common feature to all of these is that they have an **average of 4 valence electrons per atom**.

Gallium arsenide, GaAs, is a compound semiconductor. In a compound semiconductor, doping can be accomplished by **slightly varying the ratio** of Ga atoms to As atoms. A

slight increase in the proportion of As produces **n-type doping**, and a slight increase in the proportion of Ga produces **p-type doping**.

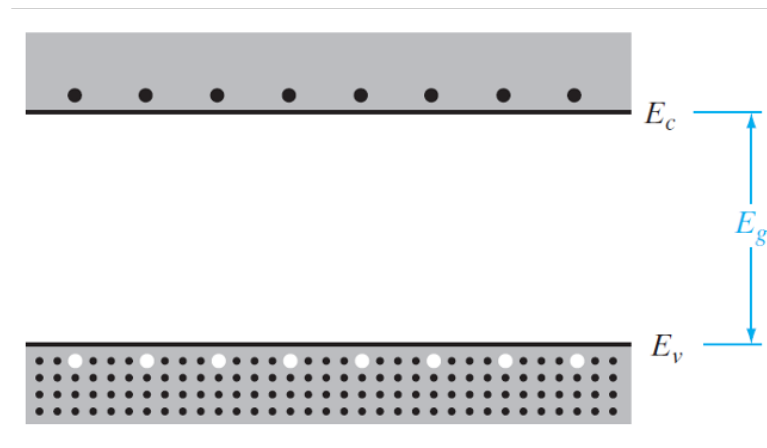
Charge Carriers in Semiconductors:

Semiconductor has a filled valence band and an empty conduction band at 0 K.

As the temperature of a semiconductor is raised from 0 K, some electrons in the valence band receive enough thermal energy to be **excited across** the band gap to the conduction band.

The result is a material with some electrons in an otherwise empty conduction band and some unoccupied states in an otherwise filled valence band as shown in Figure.

For convenience, an empty state in the valence band is referred to as a **hole**.

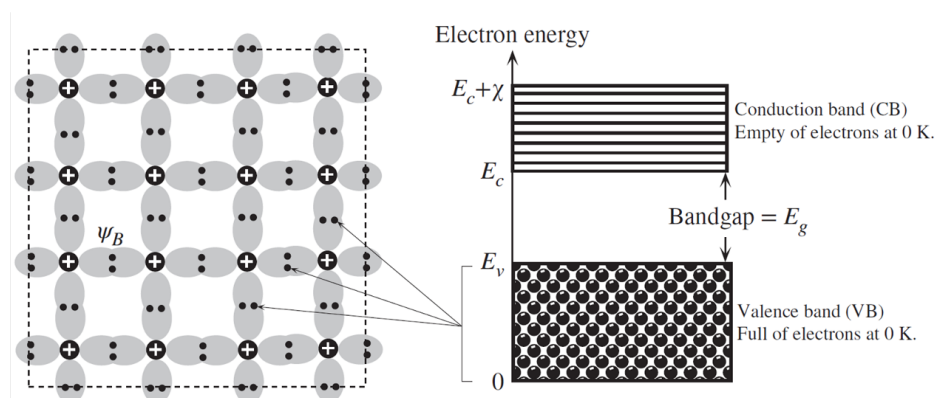


The CB is separated from the VB by an energy gap E_g , called the **bandgap**.

E_v marks the top of the VB and E_c marks the bottom of the CB.

The energy distance from E_c to the vacuum level, the width of the CB, is called the **electron affinity χ** .

The general energy band diagram shown here applies to all crystalline semiconductors with appropriate changes in the energies.

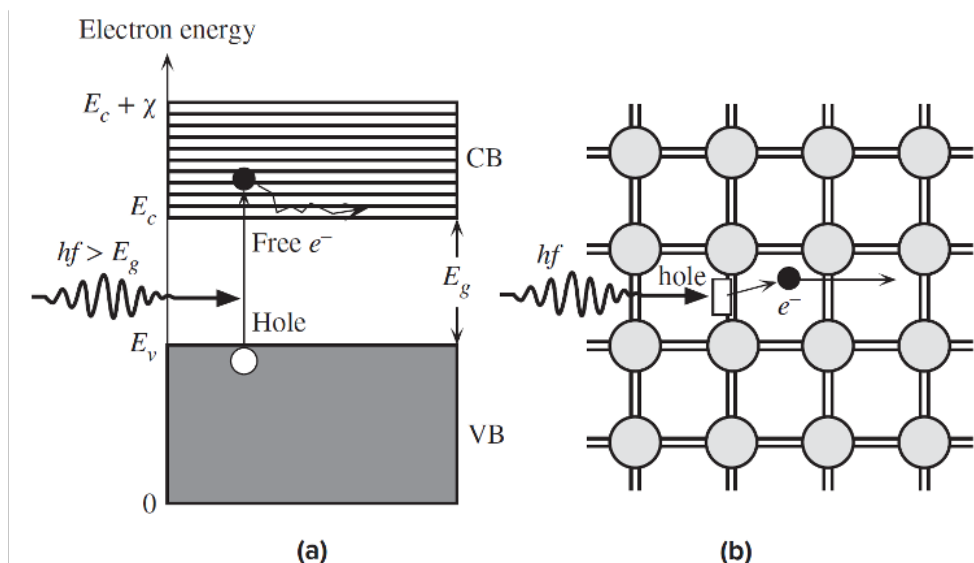


Holes and electrons are the types of charge carriers accountable for the flow of current in semiconductors.

The vacancy left behind by the missing electron in the bonding orbital is called a **hole**.

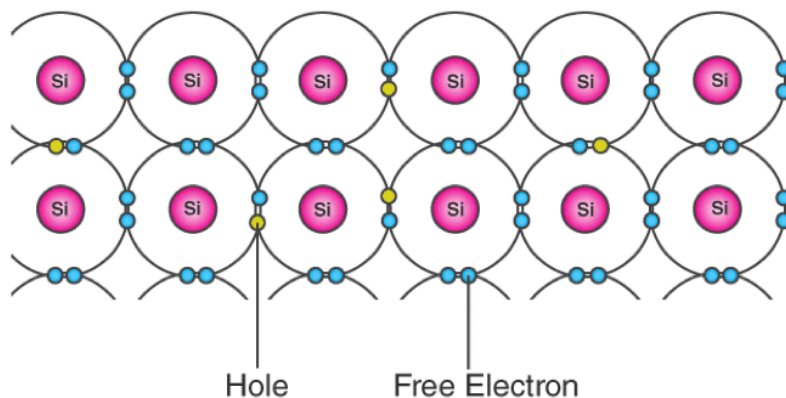
Electrons travel in the conduction band whereas holes travel in the valence band.

Since the holes experience stronger atomic force by the nucleus than electrons, thus holes have lower mobility.



As shown in bond model of electrons in silicon below. When one of the free electrons leaves the lattice position, it creates a hole.

This hole thus created takes the opposite charge of the electron and can be imagined as positive charge carriers moving in the lattice.



Concept of electrons and holes in semiconductors

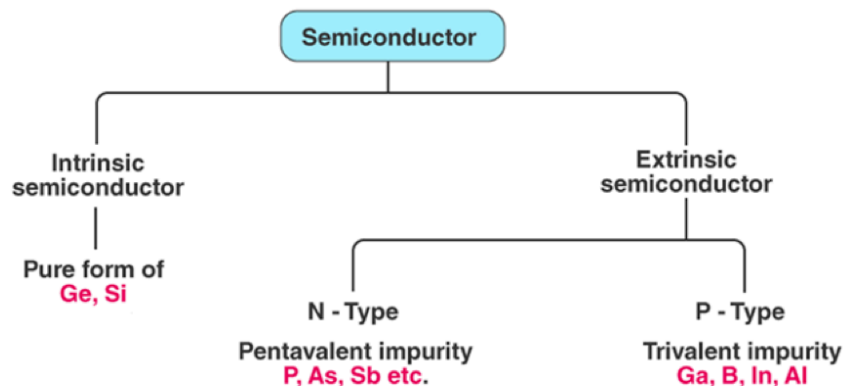
Properties of Semiconductors

- Semiconductor acts like an insulator at Zero Kelvin. On increasing the temperature, it works as a conductor.
- Due to their exceptional electrical properties, semiconductors can be modified by doping to make semiconductor devices suitable for energy conversion, switches, and amplifiers.
- Semiconductors are smaller in size and possess less weight.
- Their resistivity is higher than conductors but lesser than insulators.
- The resistance of semiconductor materials decreases with the increase in temperature and vice-versa.

Types of Semiconductors:

An **Intrinsic semiconductor** is a pure semiconductor crystal in which the electron and hole concentrations are equal. By pure we mean virtually no impurities in the crystal.

Germanium (Ge, $z = 32$) and Silicon (Si, $z = 14$) are the most common type of intrinsic semiconductor elements. They have four valence electrons(tetravalent).



Intrinsic semiconductor material is made up of only a single type of element.

The number of excited electrons is equal to the number of holes; $n = p$. They are also termed as **undoped** semiconductors or **i-type** semiconductors.

By introducing small amounts of impurities into an otherwise pure Si crystal is called Extrinsic semiconductor

The conductivity of semiconductors can be greatly improved by introducing a small number of suitable replacement atoms called Impurities. The process of adding impurity atoms to the pure semiconductor is called Doping.

An extrinsic semiconductor can be further classified into:

N-type (When a pure semiconductor is doped by pentavalent impurity (Phosphorus P,

Arsenic As, Antimony Sb, Bismuth Bi)

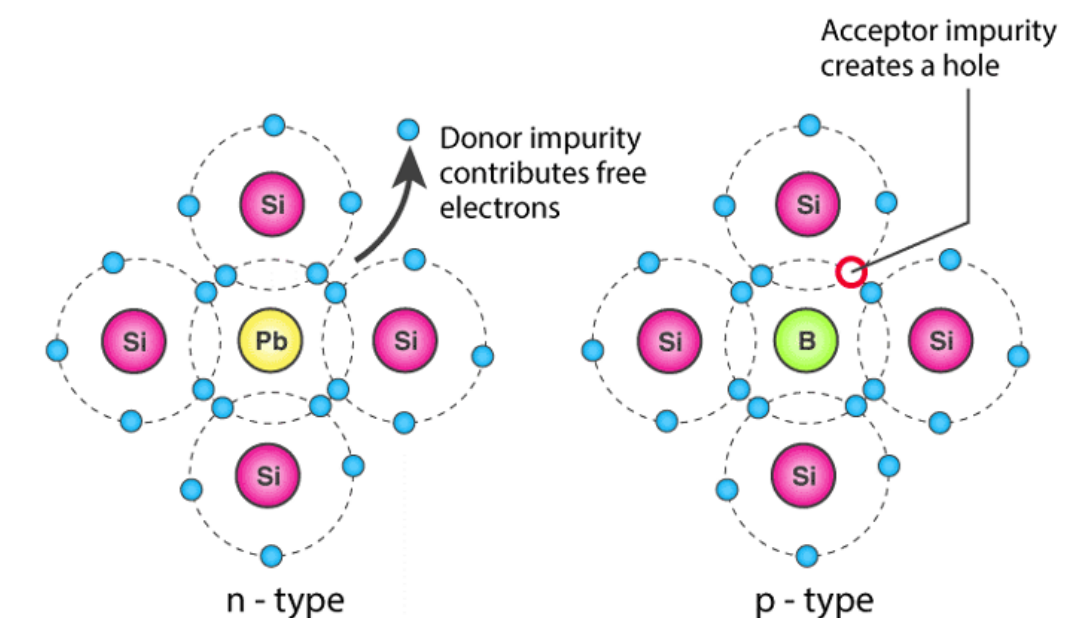
P-type (When a pure semiconductor is doped with a trivalent impurity (Boron B, Aluminium Al, Indium In, Gallium Ga)

Extrinsic semiconductors are doped with specific impurities. The impurity modifies the electrical properties of the semiconductor by **increasing** its conductivity.

Extrinsic semiconductors are also called **impurity semiconductors** or **doped semiconductors**.

In **N-type** semiconductor the fifth electron of the dopant is set free. Thus, the impurity atom donates a free electron for conduction in the lattice and is called **Donar**.

In **P-type** semiconductors there is absence of electron (hole) in the impurity. These impurity atoms which are ready to accept bonded electrons are called **Acceptors**.



Intrinsic Semiconductor	Extrinsic Semiconductor
Pure semiconductor	Impure semiconductor
Density of electrons = Density of holes	Density of electrons \neq Density of holes
Low electrical conductivity	High electrical conductivity

Only temperature dependence	Dependence on temperature as well as on the amount of impurity
No impurities	Trivalent impurity, Pentavalent impurity

Pauli exclusion Principle

The **Pauli exclusion principle** states that in a single atom every electron should have or be in its own unique state (singlet state). There are two salient rules that are:

Only two electrons can occupy the same orbital.

The two electrons that are present in the same orbital must have opposite spins or they should be antiparallel.

Helium



The Fermi Level

Fermi level is the term used to describe the **top of** the collection of electron energy levels at absolute zero temperature.

This concept comes from Fermi-Dirac statistics. Electrons are fermions .

So at absolute zero they pack into the **lowest available energy states** and build up a "Fermi sea" of electron energy states.

The Fermi level is the surface of that sea at absolute zero where no electrons will have enough energy to rise above the surface.

The distribution of electrons over a range of allowed energy levels at thermal equilibrium is

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}, k = 8.62 * 10^{-5} eV/K = 1.38 * 10^{-23} J/K$$

The function $f(E)$, the Fermi–Dirac distribution function, gives the **probability** that an available energy state at E will be **occupied by an electron** at absolute temperature T .

The quantity E_F is called the Fermi level, and it is an important quantity in the analysis of semiconductor behaviour.

For an energy E equal to the Fermi level energy E_F , the occupation probability of 1/2 of being occupied by an electron.

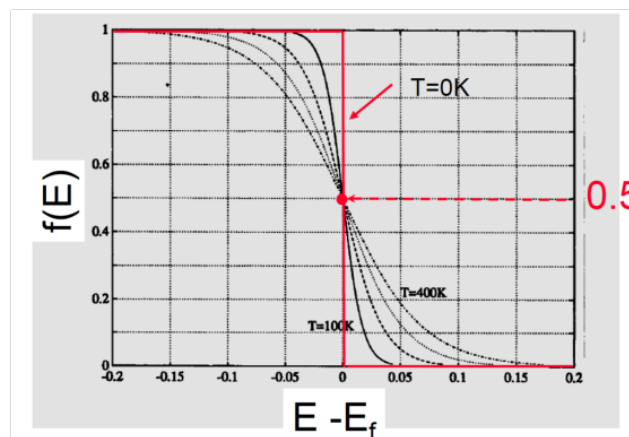
The symmetry of the distribution of empty and filled states about E_F makes the Fermi level a natural **reference point** in calculations of electron and hole concentrations in semiconductors.

Examination of $f(E)$ indicates that at 0 K the distribution takes the simple rectangular form as shown.

With $T = 0$ in the denominator of the exponent, $f(E)$ is $1/(1 + 0) = 1$

When the exponent is negative ($E < E_F$), and is $1/(1 + \infty) = 0$

When the exponent is positive ($E > E_F$). The rectangular distribution implies that at 0 K every available energy state up to E_F is filled with electrons, and all states above E_F are empty

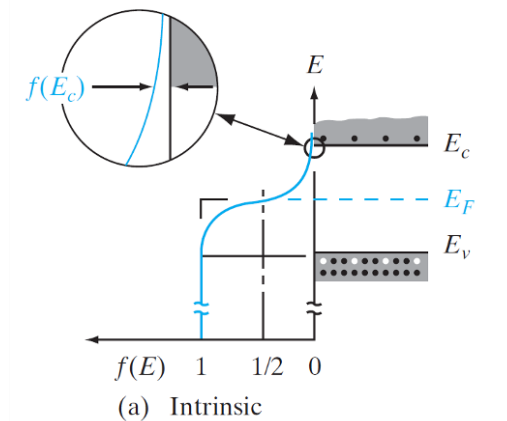


Fermi-Dirac distribution to semiconductors

For **intrinsic material** $n = p$, therefore, the Fermi level E_F must lie at the **middle of the band gap**.

Since $f(E)$ is symmetrical about E_F , the electron probability “tail” of $f(E)$ extending into the

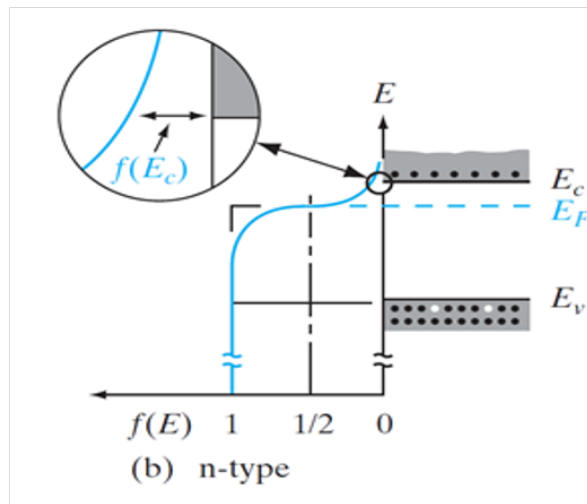
conduction band is symmetrical with the hole probability tail $[1 - f(E)]$ in the valence band. The distribution function has values within the band gap between E_v and E_c , but there are **no energy states available**, and no electron occupancy results from $f(E)$ in this range.



In **n-type material** $n > p$, thus in n-type material the distribution function $f(E)$ must lie **above its intrinsic position** on the energy scale as shown.

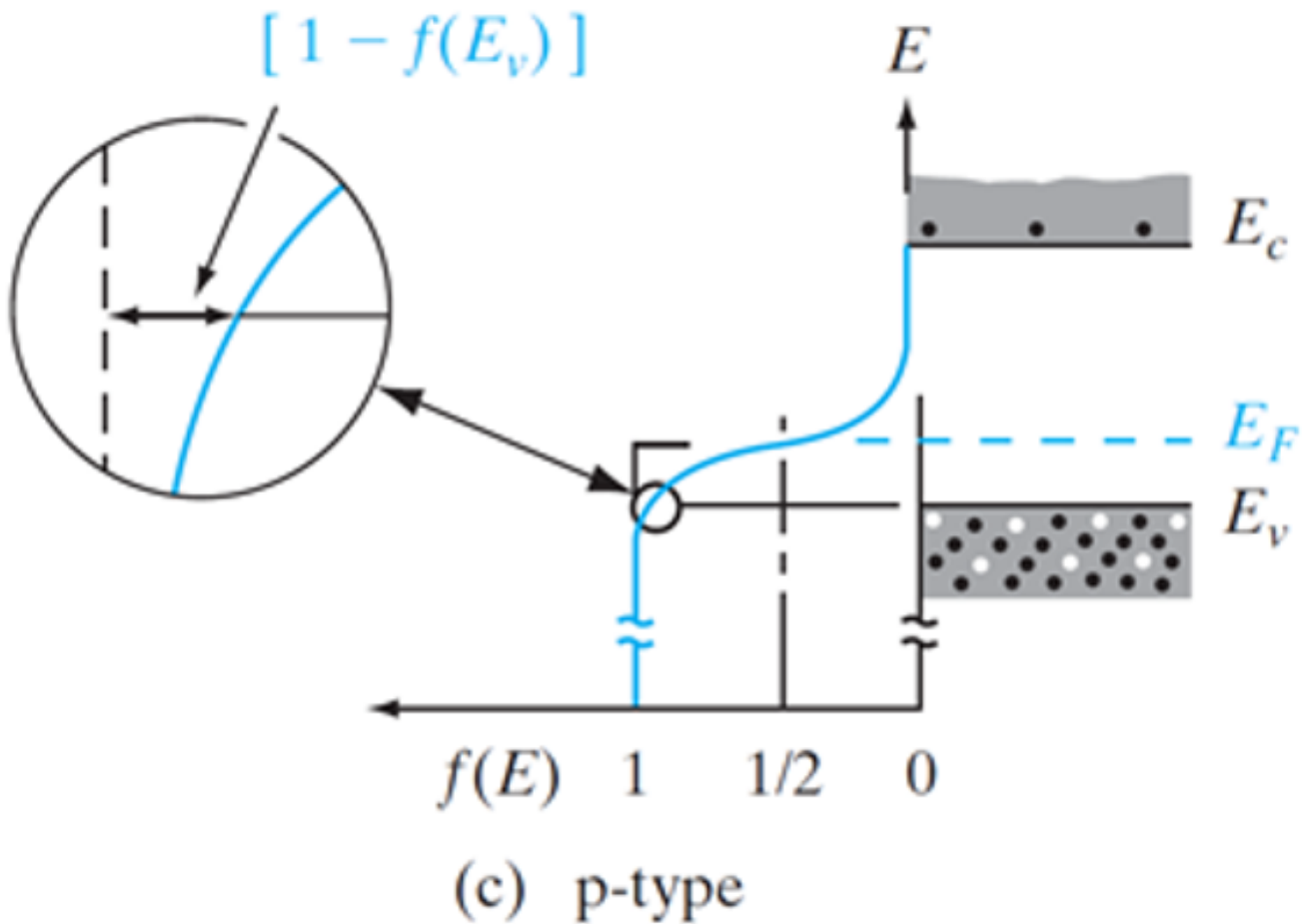
The larger concentration of electrons at E_c in n-type material implies a correspondingly smaller hole concentration at E_v .

The value of $f(E)$ for each energy level in the conduction band (and therefore the total electron concentration n_0) increases as E_F moves closer to E_c . Thus the **energy difference** ($E_c - E_F$) gives a measure of n .



For **p-type material** the Fermi level lies near the valence band such that the $[1 - f(E)]$ tail below E_v is larger than the $f(E)$ tail above E_c .

The value of $(E_F - E_v)$ indicates how strongly p-type the material is.



Electron and Hole Concentrations

The number of electrons per unit volume in the energy range dE is the product of the density of states and the probability of occupancy $f(E)$, the total electron concentration is the integral over the entire conduction band.

The concentration of electrons in the conduction band is given below. where $N(E)dE$ is the density of states in the energy range dE .

$$n_0 = \int f(E)N(E)dE$$

$N(E)$ is proportional to $E^{1/2}$, so the density of states in the conduction band increases with electron energy. Whereas, the Fermi function becomes extremely small for large energies. Thus $f(E)N(E)$ decreases rapidly above E_c , and very few electrons occupy energy states far above the conduction band edge.

Similarly, the probability of finding an empty state (hole) in the valence band $[1 - f(E)]$ decreases rapidly below E_v , and most holes occupy states near the top of the valence band

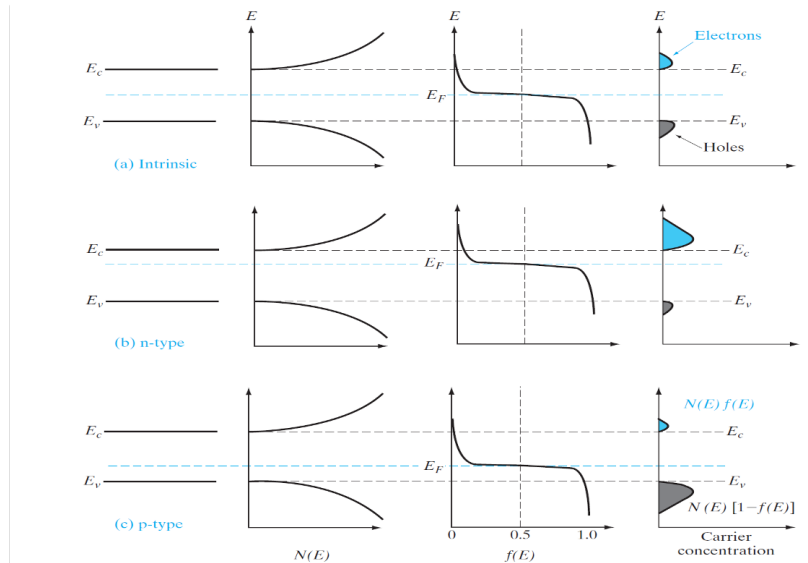


Figure 3-16 Schematic band diagram, density of states, Fermi-Dirac distribution, and the carrier concentrations for (a) intrinsic, (b) n-type, and (c) p-type semiconductors at thermal equilibrium.

Most used semiconductor materials

Silicon, germanium, and gallium arsenide are most used semiconductor materials.

Germanium was one of the earliest semiconductor materials used.

Germanium has largely fallen into disuse in favour of the current king of semiconductor materials-silicon.

Silicon is abundantly available in quartzite (hard, granular rock). Extraction, purification, and crystallization processes for silicon are both efficient and economical

Gallium arsenide is the second most common semiconductor in use today.

Gallium arsenide has some limitations, the compound is more difficult to manufacture in masse than silicon, and the chemicals used in gallium arsenide production are quite toxic.

Newest Innovations and Future

Research into new materials is ongoing, with some materials holding great promise for the future:

High-power gallium nitride could be used for more efficient, faster power conversions in electric grid systems due to its high critical energy field.

Antimonide-based and bismuthide-based semiconductors are seeing use in improved infrared sensors for the medical and military sectors.

Graphene has the potential to surpass silicon as an all-purpose semiconductor material, but widespread commercialization could be as long as twenty-five years away.

Pyrite could be used to replace the rare earth element cadmium telluride, which is widely used in solar cells but which has a limited supply. Pyrite is abundant, inexpensive, and nontoxic.

Applications of semiconductor materials

Products/components made	Reliant Industries
Bipolar transistors	Artificial intelligence
Diodes	Clean energy
Field-effect transistors	Communication
Integrated circuits	Computing
Light-emitting diodes (LEDs)	Health care
Metal-oxide semiconductor field-effect transistors (MOSFETs)	Internet of Things
Silicon-controlled rectifiers	Military