Classification of solids on the basis of conductivity

(i) Conductor Conductors are those substances through which electricity can pass easily, e.g., all metals are conductors.

(ii) Insulator Insulators are those substances through which electricity cannot pass, e.g., wood, rubber, mica etc.

(iii) Semiconductor Semiconductors are those substances whose conductivity lies between conductors and insulators. e.g., germanium, silicon, carbon etc.

Energy Bands of Solids

1. **Energy Band**

In a crystal due to interatomic interaction valence electrons of one atom are shared by more than one atom in the crystal. Now splitting of energy levels takes place. The collection of these closely spaced energy levels is called an energy band.

2. **Valence Band**

This energy band contains valence electrons. This band may be partially or completely filled with electrons but never be empty. The electrons in this band are not capable of gaining energy from external electric field to take part in conduction of current.

3. **Conduction Band**

This band contains conduction electrons. This band is either empty or partially filled with electrons. Electrons present in this band take part in the conduction of current.

4. **Forbidden Band**

This band is completely empty. The minimum energy required to shift an electron from valence band to conduction band is called band gap (Eg).

Depending on the Eg, solids are classified into three types.

a) Conductors

b) Insulators

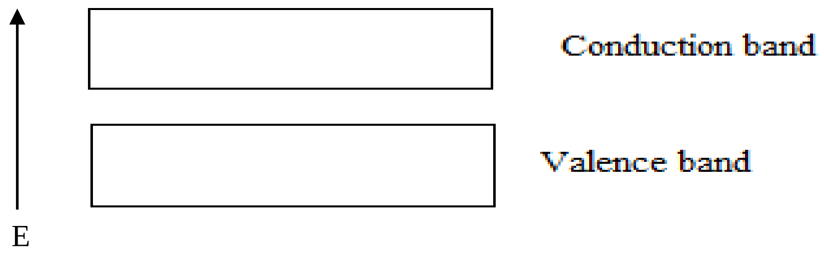
c) Semi-conductors

Conductors- In these materials, the energy gap is almost negligible.

a) When a potential is applied to the half-filled valence band, the free electrons get excited to the empty conduction band and they begin to conduct. Eg:- Na, Al etc.

b) In elements like Mg, conduction is mainly due to overlapping of filled valence band with higher empty band.

c) Electrical conductivity of a metals decreases with rise in temperature because of the increased thermal vibrations of metal atoms which causes scattering of the electrons. Hence their flow is obstructed.



Conductors

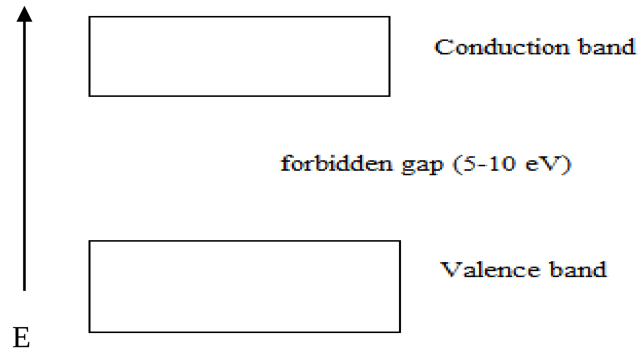
Insulators- In these materials, the energy gap is or order 5-10eV.

a) In insulators, the valence band electrons are tightly bound to their parent nuclei and require large amount of electric fields to remove electrons to conduction band.

b) They possess a complete valence band and completely empty conduction band.

c) Eg:- Diamond, glass, solid NaCl, Plastics, ceramics etc.

d) Electrical conductivity increases with increase in temperature. At room temperature, they act as best insulating materials. At higher temperatures, some of the valence electrons acquire sufficient energy to overcome the energy gap and enter the conduction band



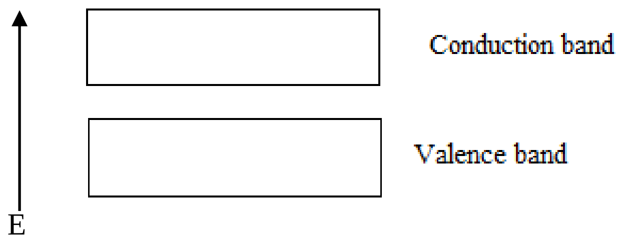
Insulators

Semiconductors- In these materials, the energy gap is of order of 1 eV.

a) Solids having electrical conductivity in between those of insulators and conductors are called semiconductors.

b) They have filled valence band, almost empty conduction band. Eg:- Si, Ge.

c) Electrical conductivity increases with increase in temperature. The probability of promotion of electrons from valence band to conduction band decreases with the energy gap and increases with temperature



Semiconducors

CLASSIFICATION OF SEMICONDUTORS

SEMICONDUCTORS

- Semiconductors are materials with electrical conductivities that are intermediate between those of conductor’s and insulators.
- They acts as insulators at very low temperature, but acts as sizable electrical conductors at room temperature.
- The width of band gap in semiconductors is intermediate to that of insulators and conductors.
- They are used for electronic purposes as they can carry an electric current by electron migration or hole propagation.
- The resistance of semiconductors decreases with increase in temperature- negative temperature coefficient of resistance.
- The resistibility is less than an insulator but more than a conductor.
- When a suitable metallic impurity e.g., arsenic, germanium, gallium, etc is added to a semi-conductor, its current conducting properties change appreciably.

Semiconductors are classified into the following types-

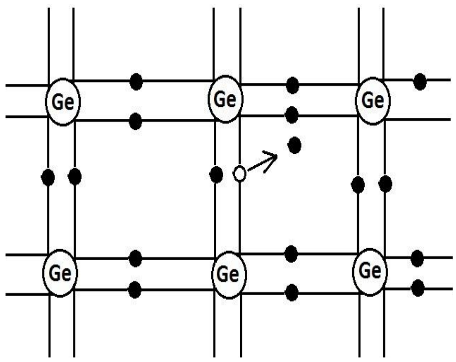
1. **Intrinsic semiconductors**
2. **Extrinsic semiconductors**
   a) **n-type semiconductors**
   b) **p-type semiconductors**
3. **Organic semiconductors**

1. **Intrinsic semiconductors**

These semiconductors are pure enough that impurities do not appreciably affect its electrical behavior. Elements like Silicon, germanium, selenium acts as intrinsic semiconductors which have four valence electrons in their atoms and their band gap is about 1ev.

Conduction Process:-

- When an electron from the valence band is ejected, a covalent bond is broken and a positively charged hole is left in the valence band.
- The hole travels to an adjacent atom by accepting an electron from the latter one.
- This forms a new covalent bond and breaks an existing covalent bond by filling up the previous hole and creating a new hole.
- When electric field is applied, electrons in the conduction band move to the anode and positively charged hole moves to cathode.
- Hence current is produced due to **simultaneous movement of conduction band electrons and valence bond holes** in opposite directions.

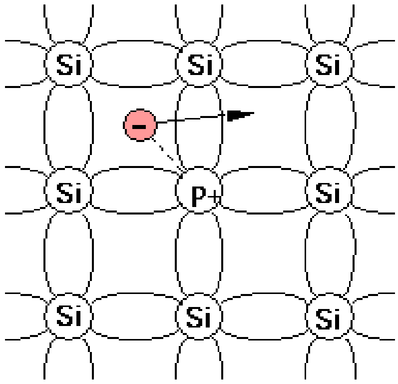


2. Extrinsic semiconductors-

Intrinsic semiconductors when added with extremely small amount of substitutional impurities (doping) are called extrinsic semiconductors. On adding a doping agent, the energy gap gets reduced and makes the electron flow easy from valence band to conduction band. The conductivity increases by 10,000 times.
Based on the doping agent added, extrinsic semiconductors are classified into two types:-

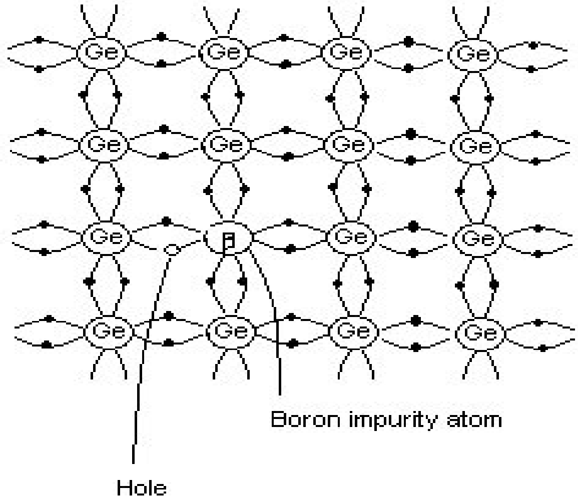
i) **n-type semiconductors-**

- These semiconductors contain a small quantity of a penta valent element impurity (like phosphorous, arsenic or antimony).
- The doping atom forms four covalent bonds with the surrounding four atoms of intrinsic semiconductor (Germanium, Silicon etc) with the help of its four valence electrons.
- The fifth excess electron remains loosely bound to the donor atom itself. It is easily excited from the valence band to conduction band on applying electric field.
- Thus conduction is due to movement of extra electron in an n-type semiconductor.



ii) **p-type semiconductors**

- They contain a small quantity of a trivalent element (like boron, aluminium).
- The three valence electrons present in the trivalent impurity forms three covalent bonds with the surrounding three of the four atoms. So that one bond in one of the four surrounding atom is left incomplete.
- This gives rise to a positive hole.
- On applying an electric field, a hole travels to an adjacent atom by acquiring an electron and establishes a new covalent bond, by breaking an existing covalent bond in the adjacent atom.
- Hence conductivity in p-type semiconductors is due to the movement of positive holes.



Union Carbide process

- **Production of solar grade silicon is done by Union carbide process**. It is developed by Union Carbide Chemical in USA. The steps are:
- In this process SiO_2 is treated with carbon in electric arc furnace at 1500-2000^oC to produce Silicon.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

- The molten silicon obtained is treated with O_2 and fresh silica as flux to remove impurities Al, Ca and Mg.
- Metallurgical grade silicon is treated with HCl at 300^oC to form trichlorosilane.

$$Si + 3HCl \xrightarrow{300^\circ c} HSiCl_3 + H_2$$

- Trichlorosilane is then passed through fixed bed columns containing ammonium ion exchange resin catalyst where trichlorosilane converts to silicon hydride.

Union Carbide process

$$6HSiCl_3 \xrightarrow{\text{Ammonium ion exchange resin}} 3H_2SiCl_2 + 3SiCl_4$$

$$3H_2SiCl_2 \xrightarrow{\text{Ammonium ion exchange resin}} SiH_4 + 2HSiCl_3$$

- The products are separated by distillation and trichlorosilane are recycled. The poly silicon is obtained through pyrolysis of SiH_4 in silicon seed rods mounted in a metal bell jar reactor.

$$SiH_4 \longrightarrow 2H_2 + Si$$