

MODULE 1: CHEMISTRY OF ELECTRONIC MATERIALS

Conductors and insulators: Introduction, principle with examples, semiconductors- production of electronic grade silicon-Czochralski process (CZ) and float zone (FZ) methods.

Polymers: Introduction, Molecular weight - Number average, weight average and numerical problems, Conducting polymers – synthesis and conducting mechanism of polyacetylene. Preparation, properties and commercial applications of graphene oxide.

PCB: Electroless plating – Introduction, Principle of Electroless plating - copper in the manufacture of double-sided PCB.

Conductors and insulators

Conductors:

Conductors are the materials or substances which allow electricity to flow through them. They conduct electricity because they allow electrons to flow easily inside them from atom to atom. Also, conductors allow the transmission of heat or light from one source to another.

Examples:

- Material such as silver is the best conductor of electricity. But, it is costly and so, we don't use silver in industries and transmission of electricity.
- Copper, Brass, Steel, Gold, and Aluminium are good conductors of electricity. We use them in electric circuits and systems in the form of wires.
- Mercury is an excellent liquid conductor. Thus, this material finds use in many instruments.

Applications:

- Mercury is a common material in thermometer to check the temperature of the body.
- Aluminium finds its use in making foils to store food. It is also used in the production of fry pans to store heat quickly.
- Iron is a common material used in vehicle engine manufacturing to conduct heat.
- The plate of iron is made up of steel to absorb heat briskly.
- Conductors find their use in car radiators to eradicate heat away from the engine.

Insulators:

Insulators are the materials or substances which resist or don't allow the current to flow through them. In general, they are solid in nature. Also, insulators are finding use in a variety of systems. As they do not allow the flow of heat. The property which makes insulators different from conductors is its resistivity.

Examples:

- Glass is the best insulator as it has the highest resistivity.
- Plastic is a good insulator and it finds its use in making a number of things.
- Rubber is a common material used in making tyres, fire-resistant clothes and slippers. This is because it is a very good insulator.

Applications:

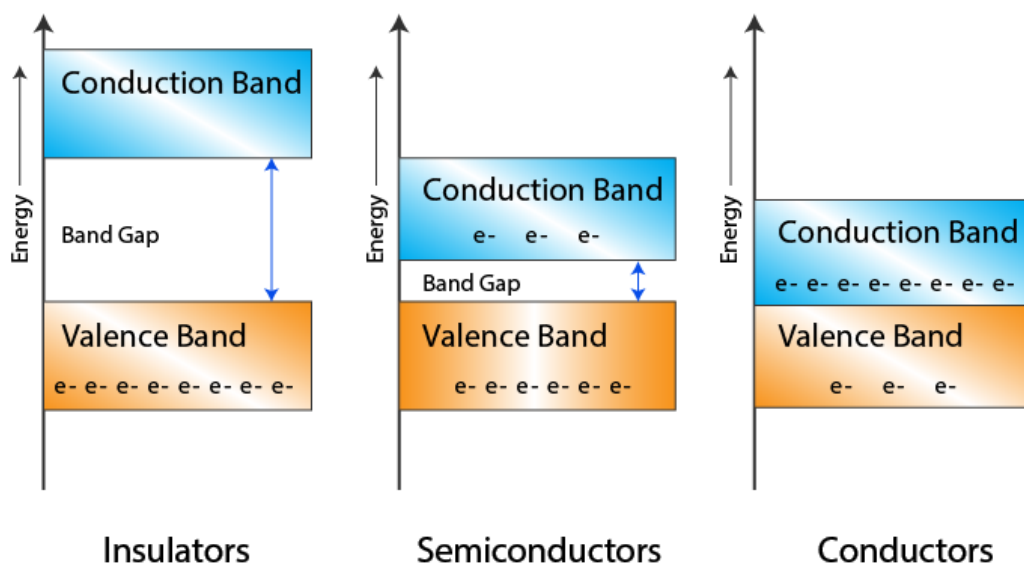
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Band Theory of conduction:

Conductors: According to band theory, a conductor is essentially a substance with its conduction bands and valence bands overlapping, permitting electrons to move freely between the valence band and the conduction band. In conductors, conduction band is only partially filled. This means there are spaces for electrons to move into conduction band and hence these materials act as conductors.

Semiconductors: In a semiconductor, the gap between the valence band and conduction band is smaller. The completely occupied valence band and the unoccupied conduction band classify semiconductors. As per band theory semiconductors will operate as insulators at absolute zero. Above this temperature there is sufficient energy available to move some electrons from the valence band into the conduction band and hence material acts as semiconductor. An increase in temperature increases the conductivity of a semiconductor because more electrons will have enough energy to move into the conduction band.

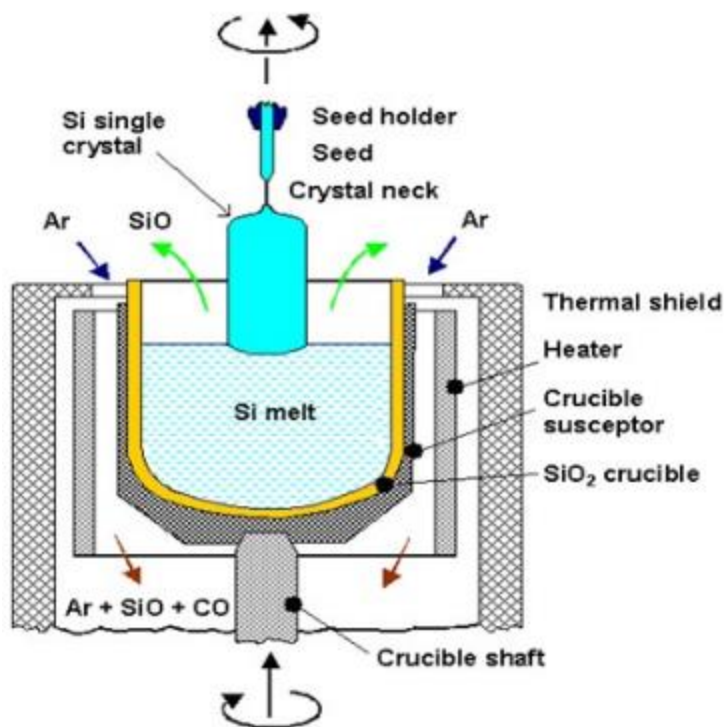
Insulators: An insulator has a large gap between the valence band and the conduction band. The valence band is full and no electrons can move up to the conduction band, hence these material can't conduct.



Production of electronic grade silicon: A silicon wafer is a thin piece of semiconductor which is used in fabrication process in integrated circuits. There are two different method to grow a single crystal.

1. Czochralski process (CZ)

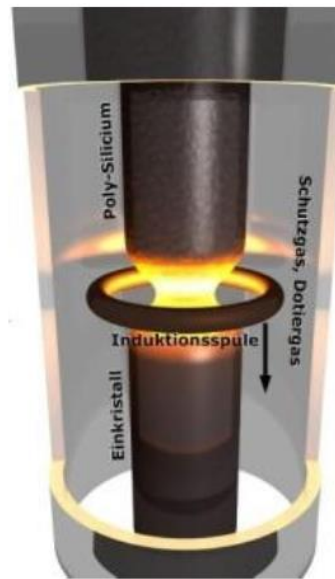
The Czochralski process, is a method of crystal growth used to obtain single crystals of semiconductors (e.g. silicon, germanium and gallium arsenide), metals (e.g. palladium, platinum, silver, gold), salts and synthetic gemstones. In this process high-purity polycrystalline silicon is placed in the quartz crucible and melted using a RF coil in an atmosphere of argon. The temperature is maintained at the melting point of the silicon (around 1,412 °C). Dopant impurity atoms such as boron or phosphorus can be added to the molten silicon in precise amounts to dope the silicon, thus changing it into p-type or n-type silicon, with different electronic properties. A rotating puller rod with a seed crystal at the bottom is lowered such that the seed crystal just touches the surface of molten silicon. A slight temperature drop initiates the crystallization of silicon on the seed crystal. The puller rod is pulled out at the rate of 1.5-5 cm/hour and simultaneously rotated at a speed of 100 rpm. As the rod is pulled away from the surface, silicon solidifies and a single crystal of silicon having the same crystal structure as that of the seed crystal is obtained. By precisely controlling the temperature gradients, rate of pulling and speed of rotation, it is possible to extract a large, single-crystal, cylindrical ingot from the melt.



2. float zone (FZ) method.

Float-zone silicon is a high-purity alternative to crystals grown by the Czochralski process. The concentrations of light impurities, such as carbon and oxygen, are extremely low in this method.

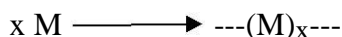
The float Zone (FZ) method is based on the zone-melting principle and was invented by Theuerer in 1962. The production takes place under vacuum or in an inert gaseous atmosphere. The process starts with a high-purity polycrystalline rod and a monocrystalline seed crystal that are held face to face in a vertical position and are rotated. With a radio frequency field both are partially melted. The seed is brought up from below to make contact with the drop of melt formed at the tip of the poly rod. A necking process is carried out to establish a dislocation free crystal before the neck is allowed to increase in diameter to form a taper and reach the desired diameter for steady-state growth. As the molten zone is moved along the polysilicon rod, the molten silicon solidifies into a single Crystal and, simultaneously, the material is purified.



Polymers

Polymers: They are macromolecules formed by the covalent linkage of a several small repeating units (monomers). Eg. Polyethylene, Polystyrene, Teflon etc. The properties of polymers are entirely different from those of its monomers. The fundamental chemical process by which the monomer units are converted into a polymer is called polymerization.

The process can be described as below:



where 'x' is the no. of repeating units in the polymer chain and is also called as degree of polymerization (DP).

If the chain have high degree of polymerization (>10,000) then the polymer formed is called a high polymer; and if 'x' is <10,000, then they are called as oligopolymers.

The building block of a polymerization reaction is called as a monomer unit. Eg. For the monomer unit polyethylene is ethylene.

Types of Polymers

There are many types of polymers including synthetic and natural polymers.

(i) Natural biopolymers

- Polypeptides in proteins - silk, collagen, keratin.
- Polysaccharides (Carbohydrate chains) - cellulose, starch, glycogen
- Nucleic acids - DNA and RNA

(ii) Synthetic polymers

- Plastics
- Elastomers - solids with rubber-like qualities
- Rubber (carbon backbone often from hydrocarbon monomers)
- silicones (backbone of alternating silicon and oxygen atoms).
- Fibers
- Solid materials of intermediate characteristics
- Gels or viscous liquids

Classification of Polymers

(i) Homopolymers: These consist of chains with identical bonding linkages to each monomer unit. This usually

implies that the polymer is made from all identical monomer molecules. These may be represented as : $-[A-A-A-A-AA]-$. Homopolymers are commonly named by placing the prefix poly in front of the constituent monomer name. For example, polystyrene is the name for the polymer made from the monomer styrene (vinylbenzene).

(ii) Copolymers: These consist of chains with two or more linkages usually implying two or more different types of monomer units. These may be represented as : $-[A-B-A-B-A-B]-$

Classification based on mode of polymerization

(i) Addition Polymers: The monomer molecules bond to each other without the loss of any other atoms. Addition polymers from alkene monomers or substituted alkene monomers are the biggest groups of polymers in this class. Ring opening polymerization can occur without the loss of any small molecules.

(ii) Condensation Polymers: Usually two different monomer combine with the loss of a small molecule, usually water. Most polyesters and polyamides (nylon) are in this class of polymers. Polyurethane Foam in graphic above.

Molecular wt. of Polymer:

Several properties of polymers depend on the size of the polymer chain. Polymers consist of a mixture of several unit of different chain length. Thus their average molecular wt. is considered.

Two types of average molecular wt. is known.

- (i) Number average molecular wt. (M_n)
- (ii) Weight average molecular wt. (M_w)

Number average molecular wt. (\bar{M}_n): It is the wt. or mass obtained when total mass of all molecules of the sample is divided by total number of molecules.

Eg. In a particular sample suppose,

N_1 molecules have molecular mass M_1 each

N_2 molecules have molecular mass M_2 each

N_3 molecules have molecular mass M_3 each and so on

Then, Number average molecular wt can be given by,

$$\bar{M}_n = \frac{N_1 M_1 + N_2 M_2 + N_3 M_3 + \dots + N_i M_i}{N_1 + N_2 + N_3 + \dots + N_i}$$

$$\bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

Weight average molecular wt. (\bar{M}_w): It can be expressed as follows,

$$\overline{M}_w = \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2 + \dots + N_i M_i^2}{M_1 N_1 + M_2 N_2 + M_3 N_3 + \dots + M_i N_i}$$

$$\overline{M}_w = \frac{\sum N_i M_i^2}{\sum M_i N_i}$$

Numerical problems

Q1. A polymer sample contains 200 molecules of molecular mass 2000, 300 molecules of molecular mass 3000, 500 molecules of molecular mass 5000. Calculate the number, average weight molecular mass of the polymer.

Solution

$$\begin{aligned}
 \overline{M}_n &= \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3} \\
 &= \frac{(200 \times 2000) + (300 \times 3000) + (500 \times 5000)}{200 + 300 + 500}
 \end{aligned}$$

$$= 3800000 / 1000$$

$$= 3800 \text{ g/mol}$$

$$\begin{aligned}
 \overline{M}_w &= \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3} \\
 &= \frac{[200 \times (2000)^2] + [300 \times (3000)^2] + [500 \times (5000)^2]}{(200 \times 2000) + (300 \times 3000) + (500 \times 5000)}
 \end{aligned}$$

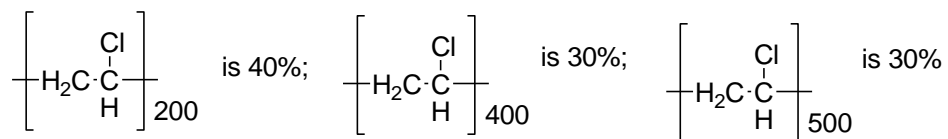
$$= 16000000000 / 3800000$$

$$= 4210.52 \text{ g/mol}$$

Ans. No average molecular wt = 3800 g/mol

Wt average molecular wt = 4210.52 g/mol

Q2. Calculate the number average and wt. average molecular wt. of polymer with the following composition :



Given , Atomic Wt of C = 12, Atomic wt of H = 1 and Atomic wt. of Cl = 35.5

Solution

$$\text{Molecular mass of 1} = [(12 \times 2) + (3 \times 1) + (35.5 \times 1)] \times 200 = 12500$$

$$\text{Molecular mass of 2} = [(12 \times 2) + (3 \times 1) + (35.5 \times 1)] \times 400 = 25000$$

$$\text{Molecular mass of 3} = [(12 \times 2) + (3 \times 1) + (35.5 \times 1)] \times 500 = 31250$$

$$\begin{aligned} \text{Mn} &= \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3} \\ &= \frac{(40 \times 12500) + (30 \times 25000) + (30 \times 31250)}{40 + 30 + 30} \\ &= 21875 \end{aligned}$$

$$\begin{aligned} \text{Mw} &= \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3} \\ &= \frac{[40 \times (12500)^2] + [30 \times (25000)^2] + [30 \times (31250)^2]}{40 \times 12500 + (30 \times 25000) + (30 \times 31250)} \\ &= 24821 \end{aligned}$$

Ans. No. average molecular wt = 21875

Wt average molecular wt = 24821

Q3. In a polymer sample, 25% of molecules have molecular mass of 25000 g/mol, 35% molecules have molecular mass of 35000 g/mol, and remaining molecules have molecular mass of 20000 g/mol, calculate the number average and weight average molecular masses of the polymer.

Solution:

$$\begin{aligned} \text{Number average molecular weight} &= \frac{N_1 M_1 + N_2 M_2 + N_3 M_3}{N_1 + N_2 + N_3} \\ &= \frac{(25 \times 25000) + (35 \times 35000) + (40 \times 20000)}{25 + 35 + 40} \\ &= 26500 \text{ g/mol} \end{aligned}$$

$$\begin{aligned} \text{Weight average molecular weight} &= \frac{N_1 M_1^2 + N_2 M_2^2 + N_3 M_3^2}{N_1 M_1 + N_2 M_2 + N_3 M_3} \\ &= \frac{(25 \times 25000 \times 25000) + (35 \times 35000 \times 35000) + (40 \times 20000 \times 20000)}{(25 \times 25000) + (35 \times 35000) + (40 \times 20000)} \\ &= 28113.20 \text{ g/mol} \end{aligned}$$

CONDUCTING POLYMER

Generally polymeric materials are poor conductor of electricity because of the non-availability of large number of free electrons in the conduction process. But π electrons in conjugated polymers can be easily removed or added to the polymeric chain in presence of impurities. So the phenomenon of conduction is observed in a number of conjugated polymers such as polyacetylene, polypyrrole, polythiophene and polyaniline, when doped with appropriate impurities. The polymers may be made either n-type i.e. free electron dominant, or p-type i.e. hole dominant depending upon the dopant used. However, unlike in semiconductors, the dopant atoms or molecules do not replace any of the atoms.

The conducting polymers are obtained by doping an oxidizing or a reducing agent into organic polymers with conjugated backbone consisting of alternating double and single carbon-carbon bonds. The important doping reactions are,

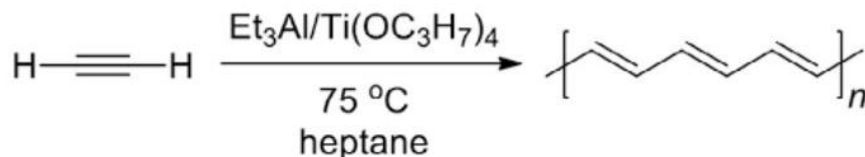
(i) Oxidative doping (p-doping): In this process, π -back bone of polymer is partially oxidized using a suitable oxidizing agent. This creates positively charged sites on polymer back bone, which are current carries for conduction. The commonly used oxidizing agent is I_2 in CCl_4 .

(ii) Reductive doping (n-doping): In n-doping, π -back bone of polymer is partially reduced by a suitable reducing agent. This creates negatively charged sites on polymer back bone. The commonly used reducing agent is sodium naphthalide in tetrahydrofuran.

(iii) Protonic Acid Doping: In this method charged species are prepared by protonation of the polymer. The protonation of the polymer is done by treating the polymer with an aqueous acid solution. Eg: conducting polyaniline is prepared by doping polyaniline polymer (Emeraldine Base) by conc. HCl or H_2SO_4 .

Synthesis of polyacetylene:

A variety of methods have been developed to synthesize polyacetylene, from pure acetylene and other monomers. One of the most common methods uses a Ziegler–Natta catalyst, such as $Et_3Al / Ti(OC_3H_7)_4$ with gaseous acetylene. This method allows control over the structure and properties of the final polymer by varying temperature and catalyst.

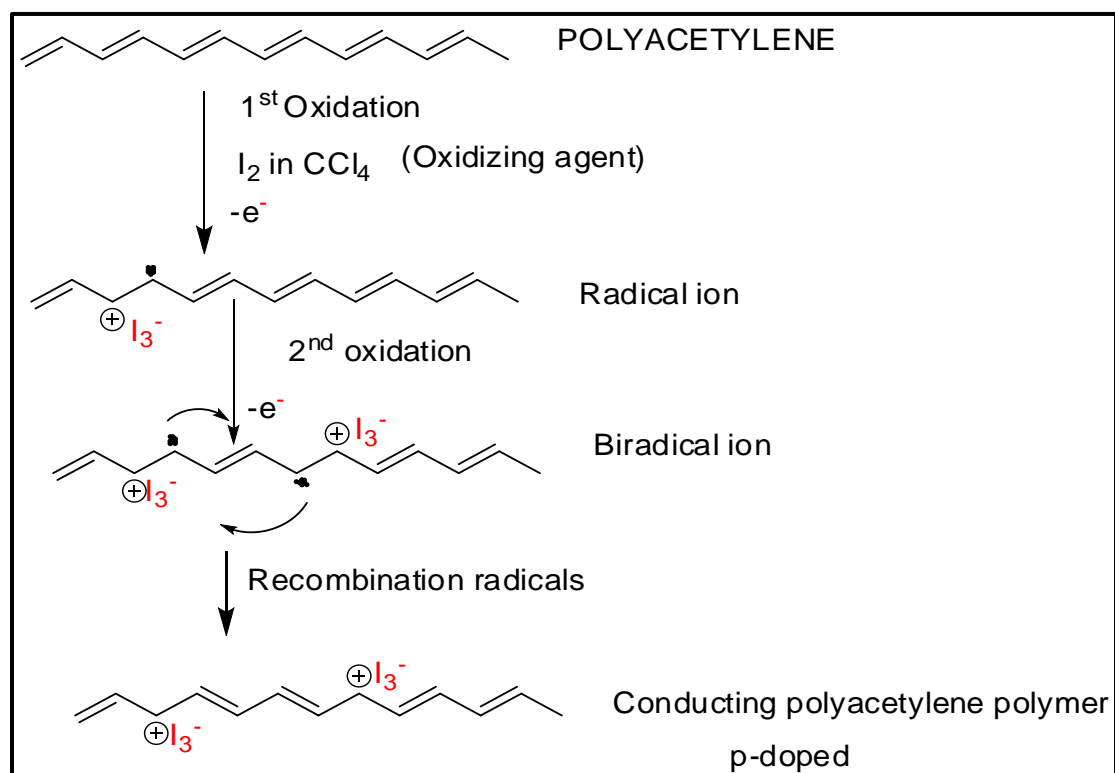


Mechanism of conduction in polyacetylene:

(i) By Oxidative doping (p-doping):

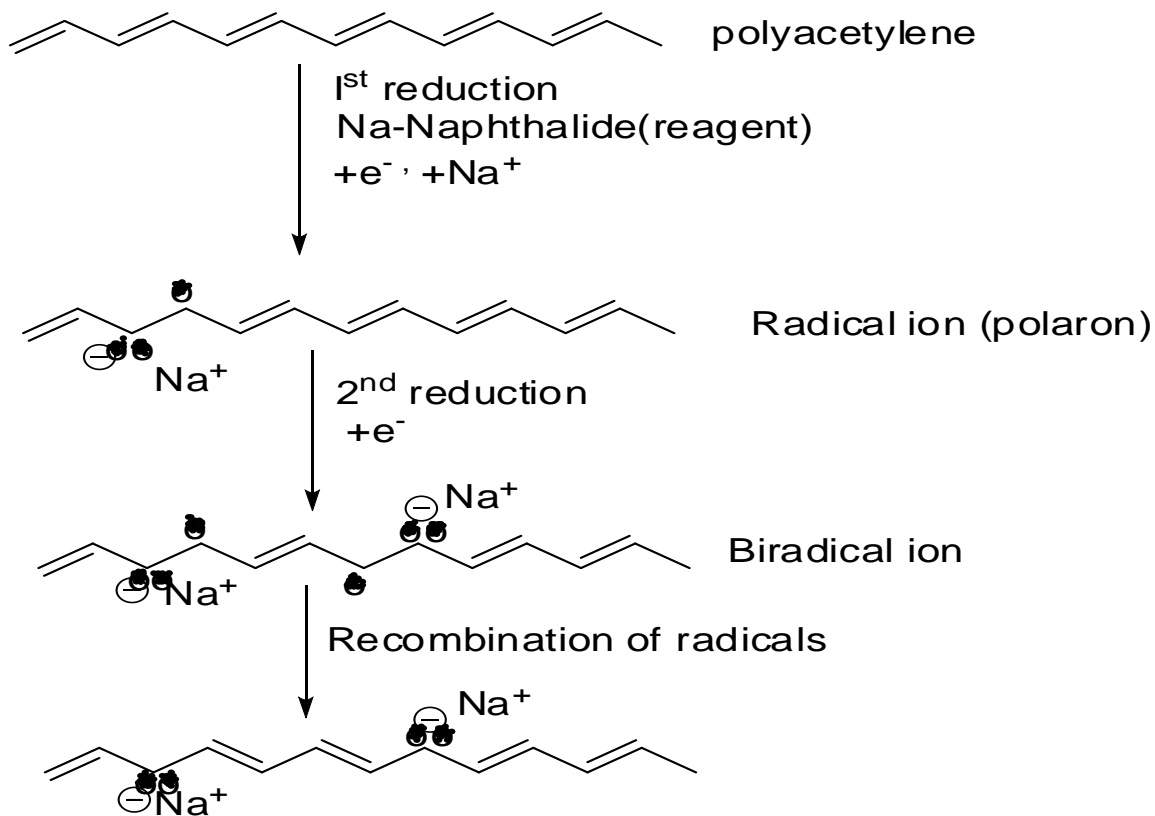
In this process, π -back bone of polymer is partially oxidized using a suitable oxidizing agent such as I_2 in CCl_4 . The removal of an electron from the polymer π -back bone leads to the formation of delocalized radical ion called polaron. A second oxidation of chain containing polaron produces bipolaron which on radical recombination yields two charge carries on each chain. The positive charge sites on the polymer chain are compensated by anion I_3^- formed by the oxidizing agent during doping. The delocalized positive charges on the polymer chain are mobile, not the dopant anions. Thus these delocalized positive charges are current carriers for conduction. These charges must move from chain to chain as well as along the chain for bulk conduction .

(v) On doping polyacetylene using I_2 in CCl_4 , the conductivity increases from $10^{-5} \text{ S cm}^{-1}$ to $10^3\text{-}10^5 \text{ S cm}^{-1}$.

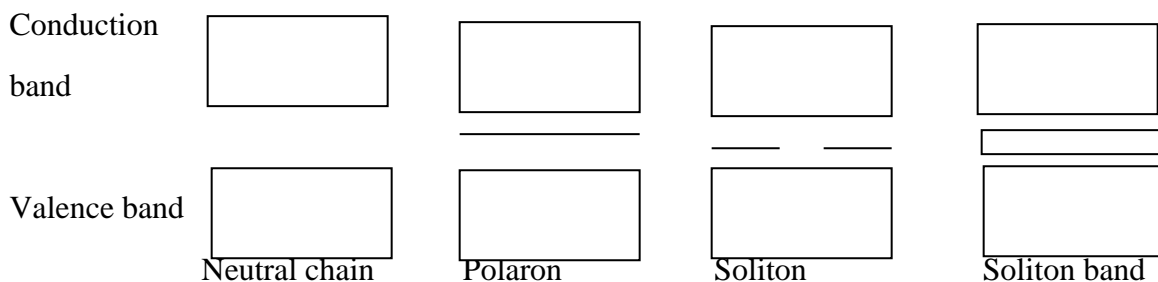


(2) By Reductive doping (n-doping)

In n-doping, π -back bone of polymer is partially reduced by a suitable reducing agent. This creates negatively charged sites on polymer back bone. The commonly used reducing agent is sodium naphthalide in tetrahydrofuran. The addition of an electron to the polymer back bone by using reducing agent generates a radical ion (polaron). A second reduction of chain containing polaron followed by recombination of radicals yields two charged ($-ve$) carriers on each chain. These charge sites on the polymer chain are compensated by cation (Na^+ ion) formed by the reducing agent.



If polyacetylene is heavily doped, polarons form pairs called solitons. In polyacetylenes the solitons are delocalized over 12 carbon atoms. Due to the formation of soliton, a new localized electronic state appears in the middle of the energy gap. When the doping is high, several charged solitons form soliton band. This band can later merge with edges of valence and conduction bands thus exhibiting conductivity.



Application of polyacetylene: .

The most extensively studied and is widely investigated computationally and experimentally for use in electronic devices such as light-emitting diodes, water purification devices, hydrogen storage, and biosensors.

Graphene Oxide

- Graphene oxide (GO) is a layered carbon structure with oxygen-containing functional groups ($=O$, $-OH$, $-O-$, $-COOH$) attached to both sides of the layer as well as the edges of the plane.
- As with any 2D carbon material, GO can also have either single layer or multilayer structure.
- A structure with one layer is graphene oxide; two layers of graphene oxide are referred to as a two-layered GO, GO with five to ten layers is called multi layered GO, and material with eleven or more layers is called graphite oxide.
- In contrary to graphene, GO is hydrophilic, and it is hence relatively simple to prepare a water- or organic solvent-based suspensions.
- Highly oxidized forms of GO are electric insulators with a bandgap of approximately 2.2 eV.
- Simplistically, GO is a monolayer sheet of graphite containing hydroxyl, carboxyl, and epoxy oxygen groups on its basal plane and edges, resulting in a mixture of sp^2 and sp^3 hybridized carbon atoms.

Properties of Graphene Oxide:

- The properties of graphene can be changed by the functionalization of graphene oxide. The chemically-altered graphene's could possibly be used in several applications.
- Graphene Oxide has a high surface area, and so it can be fit for use as electrode material for batteries, capacitors and solar cells.
- Graphene Oxide is cheaper and easier to manufacture than graphene, and so may enter mass production and use sooner.
- GO can easily be mixed with different polymers and other materials, and enhance properties of composite materials like tensile strength, elasticity, conductivity and more.

Synthesis of Graphene Oxide:

- There are several ways to prepare graphite oxide/graphene oxide. The most common way is to use an oxidizing agent in an acidic environment.
- In this procedure, phosphoric acid is mixed with sulphuric acid in the ratio 1:9 and potassium permanganate and graphite added in the ratio 6:1 in an ice bath.
- The mixture is then heated at $50^{\circ}C$ and stirred for 12 h
- After cooling down, the mixture is poured onto ice
- Finally, 30% H_2O_2 is added in order to remove the excess of potassium permanganate.

- Phosphoric acid works as a dispersive and etching agent, as well as a stabilizer of the oxidation process, which makes the synthesis of GO safe.
- This route produces a higher yield of GO with a higher level of oxidation and a more regular structure.

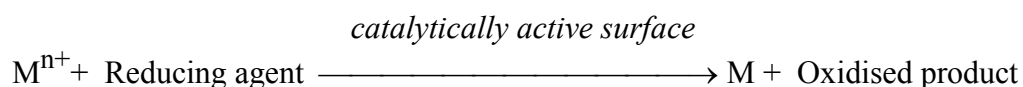
Applications of Graphene Oxide:

- Air pollution caused by the industrial release of harmful gases such as CO₂, CO, NO₂, and NH₃.
- GO can be employed in catalysis for converting polluting gases during industrial processing.
- The approach of GO application in this area can be divided into two paths: pollutant adsorption and conversion.
- The functional groups of few-layered GO composites exhibit unique adsorption behaviour towards different gases like acetone, formaldehyde, H₂S, SO₂, and NO_x can be adsorbed by GO-based composites.
- GO exhibits high adsorption ability towards Cd(II), Co(II), Au(III), Pd(II), Ga(III), and Pt(IV).
- Adsorption ability mainly depends on the synthesizing method. Multilayered graphene oxide nanosheets show a very high affinity towards Pb(II) ions, with a sorption capacity of about 842 mg g⁻¹ at 293 K.
- Small-molecule drug delivery seems to be another promising medical application of GO. Small molecules of drugs can be attached to a GO surface using pH-sensitive linkers.
- More over cancer targeting was successfully manifested as a codelivery of camptothecin (CPT) using folic acid conjugated nano GO (FANGO).

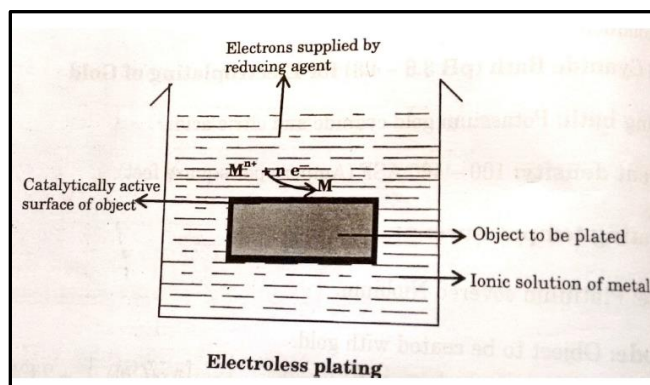
Electroless plating

Introduction: Electroless plating is the controlled deposition of a continuous film of a metal from its salt solution on a catalytically active surface of the substrate by a suitable reducing agent, without the use of electrical energy. The substrate may be a conductor like a metal or an alloy or a non-conductor like glass, plastic, ceramic etc.

The reducing agent converts metal ions (M^{n+}) to the metal (M) which gets plated over a catalytic surface. Schematically, it can be represented as,

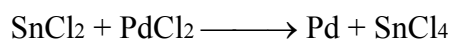


The driving force for electroless-plating is autocatalytic redox reaction on a pre-treated active surface. It is autocatalytic in nature. The metal atoms deposited are known to catalyse further deposition. However initial deposit of metal ion happens over catalytic surface.



An important aspect of electroplating is the **preparation of the surface of the object to get an active surface**. Pretreatment is done by one of the following technique. Some of the object surfaces are active by themselves. However, some others are to be activated by certain pre-treatment.

1. Al, Fe, Cu, Zn, brass, etc. can be plated directly.
2. Acid Treatment (Etching): Stainless steel need be activated by immersion into 1:1 H_2SO_4 .
3. Mg alloys are activated by electroplating a layer of Zn over it.
4. Non-metallic (non-conductors or insulators) plastics, glass, ceramic, quartz, etc. are sensitised by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$. Treatment with $SnCl_2$ leaves a thin layer of $SnCl_2$ and later treatment with acidified $PdCl_2$ leads to deposition of Pd.



Advantages of Electroless-plating:

1. Do not require any electrical power source & corresponding accessories.
2. It is applicable to conductors, semiconductors and non-conductors or insulators.
3. It exhibits high throwing power (only requirement for uniform deposit is that the solution should have an access to object surfaces). No levellers are required.
4. It gives harder coatings than conventional electroplating.
5. Electroless deposits are less porous than electrodeposits and possess unique chemical, mechanical and magnetic properties.

Limitations:

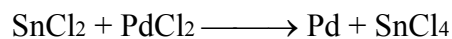
1. Deposits take pretty longer time durations even when thickness to be achieved is lesser.
2. Deposits are expensive because of chemicals & regulatory requirements.

Applications:

- 1) Metalizing PCBs, 2) Producing through-hole connections, 3) For plating on non-conductors.
- 4) As a base before electroplating

Electroless-plating of Copper on PCB

Activation of surface: The base of a printed circuit board is a plastic material such as epoxy or phenolic polymer or a glass fiber reinforced polymer composite. It is activated by treatment with acidified SnCl_2 and then with acidified PdCl_2 leads to deposition of Pd.



In the manufacture of double sided PCB, the board is clad on either side with thin electroformed copper foils. Then both sides of the copper clad board are printed with etch-resistant circuit patterns. Rest of the unprotected copper foil is etched (formation of tracks) away by using an acid. This leaves only the circuit patterns on both sides of the board. Electrical connection between the two sides of PCB is made by drilling a hole through the board. The hole is then activated & electroless plated with copper, as it can't be electroplated. The composition of the electroless plating bath & the procedure given below.

Constituents	Purpose
CuSO ₄	Provides metal ions
HCHO	Reducing reagent
Rochelle salt	Complexing agent
NaOH	Provides alkaline medium
EDTA	Exaltant & complexing agent
pH	11.0
Temperature	25°C

Following reactions takes place during the process:

Reactions:

Oxidation of reducing reagent : $2\text{HCHO} + 4\text{OH}^- \longrightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2\text{e}^-$

Reduction of metal ion over object surface : $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$

Overall reaction : $\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \longrightarrow \text{Cu} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2\uparrow$

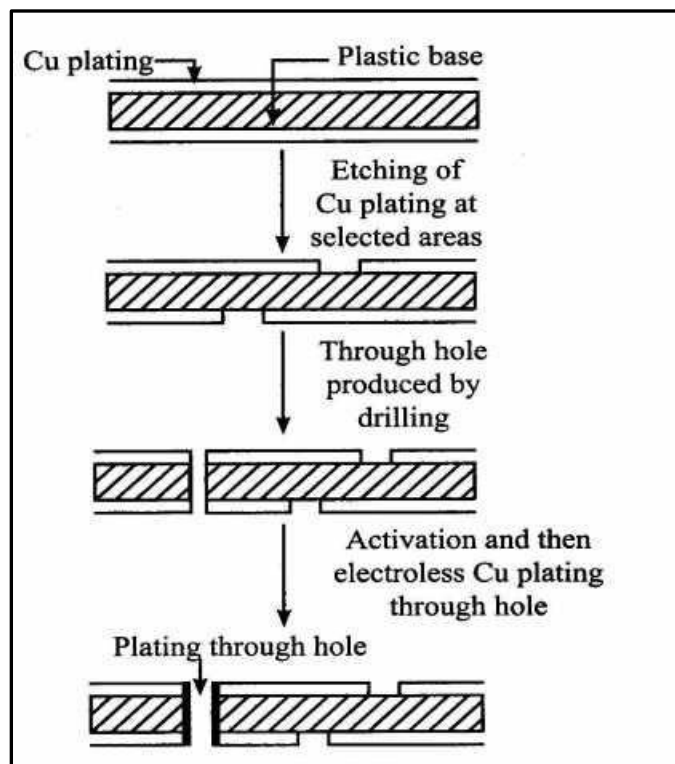


Fig: Electroless plating of Cu

