MODULE-1

Chemistry of Electronic Materials

Syllabus

[**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.

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

Conductors, Semiconductors and Insulators:

Conductivity of materials can be explained on the basis of band theory. According to this theory, there are three types of bands namely i) Conduction band ii) Valence band and iii) Forbidden gap
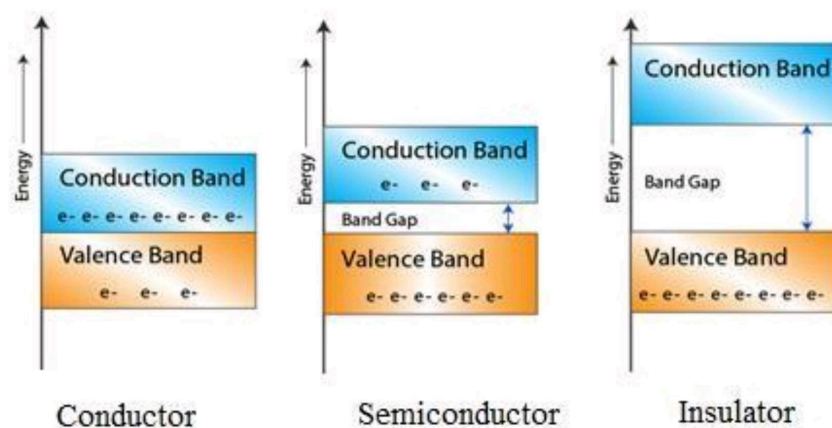
The band formed by a series of energy levels containing the valence electrons is called the Valence Band (VB).
- ➢ It is highest occupied energy band.
- ➢ It may be completely filled or partially filled with electrons.

The next higher permitted energy band is called the Conduction Band (CB).
- ➢ It is lowest unoccupied energy band.
- ➢ It may be empty or partially filled with electrons.
- ➢ The electrons can move freely in the conduction band and hence the electrons in conduction band are called conduction electrons.
- ➢ The energy gap between the VB and CB is called the Forbidden Energy Gap or Forbidden Band.
- ➢ It is formed by a series of non-permitted energy levels above the top of valence band and

below the bottom of the conduction band.
- ➢ It is the amount of energy to be supplied to the electron in VB to get excited into the CB.
- ➢ When an electron gains sufficient energy, it ejects from the valence band creating hole, which is supposed to behave as a positive charge.

Conductivity of a material depends on the available charge carriers (ionic) and their mobility, valency of ions and the temperature. It is based on Ohm`s law, which states that *"the current (I) flowing through a conductor is directly proportional to the applied potential (E) and inversely proportional to the resistance (R)"*.

$$i.e. \ I = E/R \quad or \quad E = I \ R$$

The reciprocal of resistance is called conductance.

$$i.e. \ C = 1/R$$

Conductors: A conductor or electrical conductor is a substance or material that allows electricity to flow through it. In conductors, electrical charge carriers (electrons or ions), move easily from atom to atom when voltage is applied and also, conduction band and valence band are overlapped. Therefore there is easy flow of electrons and thus they are good conductors of heat and electricity. Typically, metals, metal alloys, electrolytes and even some nonmetals, like graphite and liquids, including water, are good electrical conductors. Pure elemental silver is one of the best electrical conductors. Other examples include copper, steel, gold, silver, platinum, aluminium, brass, etc. Copper has the second-highest electrical conductivity of all metals (5.9×10^7 Siemens/m).

Insulators: Materials that don't allow electrical current or heat to pass through them are known as insulators. In insulators, due to a large forbidden gap between conduction and valence band, there is no easy flow of charge carriers. Therefore, they are bad conductors of heat and electricity. Most insulators are solids in nature. Ex:- wood, glass, quartz, plastic, etc. The electrical conductivity of polymer is in the range of 10^{-10} to 10^{-8} S/m.

Semiconductor: Any of a class of solids (such as germanium or silicon) whose electrical conductivity is between that of a conductor and an insulator. In semiconductors, because of small gap (forbidden gap) in between conduction band and valence band, there conductivity lies between that of conductors and insulators. However, their conductivity can be increased by increasing temperature or by adding dopants. The conductivity of Silicon is 16.7 S/m.

Preparation of Single Crystal Silicon: Silicon obtained by above process is polycrystalline. But for the fabrication of semiconductor device, silicon should be a single crystal. Czochralski and Float Zone methods are used to obtain single crystals.

Czochralski (CZ) process
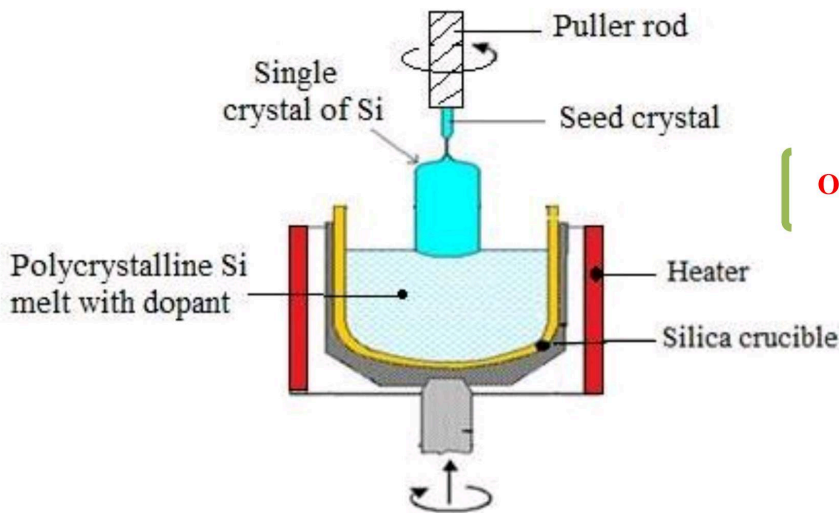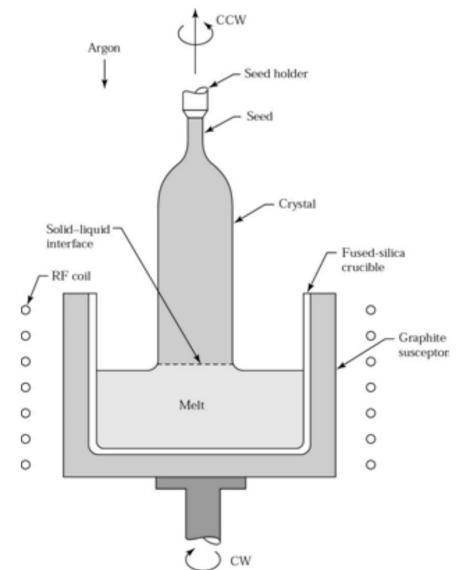
Czochralski method is used obtain single crystals of semiconductors (silicon, germanium), metals (palladium, platinum, gold), salts and synthetic gemstones. This method was invented by Jan Czochralski in 1915.

High-purity, semiconductor-grade silicon is melted in a quartz crucible at 1425 °C using RF coil. Dopant such as boron or phosphorus can be added to the molten silicon in precise amounts to obtain p-type or n-type silicon. A monocrystalline seed crystal fixed to the puller rod is rotated slowly at the rate of 50 rpm and dipped into the melt. Then the rod is slowly pulled upwards at the rate of 1.5 to 5 cm per hour and rotated simultaneously. By precisely controlling the temperature, rate of pulling and speed of rotation, it is possible to extract a large, single-crystal of silicon from the melt. This process is normally performed in an inert atmosphere, such as argon. (OR)

The float zone (FZ) method
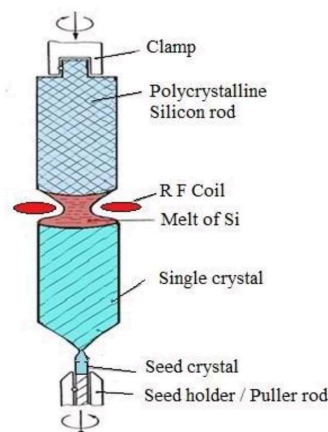
The float zone method is based on the zone-melting principle and was invented by Theuerer in 1962. In this process high purity silicon crystal with extremely low concentrations of impurities, such as carbon and oxygen, can be obtained. It is carried out in an inert atmosphere. The process starts with a high-purity polycrystalline rod fixed to the clamp and a monocrystalline seed crystal

fixed to the seed holder. They are held face to face in a vertical position and rotated as shown in the figure. Melt the feed rod using radio frequency heating coil and the seed crystal is brought up from below to make contact with the drop of melt formed at the tip of the poly silicon feed rod. The molten silicon solidifies into a single crystal and the material is purified simultaneously. The crystals are can be doped by adding the doping gas like phosphine (PH_3) or diborane (B_2H_6) to obtain n- and p-type, respectively. Unlike CZ method, in FZ method crystal is not in contact with any substances except dopant gas. Therefore crystal obtained in FZ process can easily achieve much higher purity and higher resistivity.

Polymers:

Polymers are macromolecules, formed by the combination of many smaller repeating molecules. These smaller molecules are termed as monomers. The word "polymer" is derived from Greek language poly means many, meros means molecules. "Deoxyribonucleic acid (DNA), ribonucleic acid (RNA) and proteins are macromolecules and are essential forms of life and hence polymers are linked to life. Cellulose, lignin, starch and natural rubber are other examples of natural polymers. Polypropylene, Polyester, PTFE, Polyethylene are the well-known synthetic polymers. They find applications in every possible field of human activity from personal care products like clothing, shoes to electrical and electronic appliances, packaging, utensils, automobile parts, coatings, paints, adhesives, tires and so on. Hence the synthetic polymers are more important to modern society in terms of their utility and the economic value that they signify.

The process of linking the repeating molecules is called polymerisation. It can be shown as,

$$nM \rightarrow --(M)_n--$$
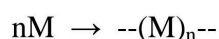
where, M is monomer

If a polymer is made of one type of monomer, it is called homopolymer. Ex- Polyethylene. If the polymer is made of different types of monomers, it is called copolymer, Ex- Phenol-formaldehyde resin. Number of times the monomer unit is repeated in a polymer is called degree of polymerisation. Higher the degree of polymerisation, higher will be the molecular mass.

Molecular Mass of Polymer:

The substances like water, ammonia, benzene, etc., are monodispersed in nature i.e., their molecules have same size whereas polymers contain molecules of different size depending on their chain length. Therefore polymers supposed to have average molecular mass. The average molecular mass can be calculated in two ways viz.

  i)   Number-average molecular mass (Mn)
  ii)   Weight-average molecular mass (Mw)

Number-average molecular mass (Mn): It is the ratio of total mass of all the molecules of a sample to the total number of molecules.

Ex;- in a polymer sample, Suppose

N_1 molecules have molecular mass M_1 each.
N_2 molecules have molecular mass M_2 each.
In general, N_i molecules have molecular mass M_i each.
Then,

Total mass of all the N_1 molecules = N_1M_1

Total mass of all the N_2 molecules = N_2M_2

In general, Total mass of all the N_i molecules = N_iM_i

So,

$$\overline{Mn} = \frac{Total\ mass\ of\ all\ the\ molecules}{Total\ number\ of\ molecules}$$

i.e. $$\overline{Mn} = \frac{N_1M_1 + N_2M_2 + ... + N_iM_i}{N_1 + N_2 + ... + N_i}$$

In general $$\overline{Mn} = \frac{\sum N_iM_i}{\sum N_i}$$

Weight-average molecular mass (Mw): It is the ratio of products of total mass of groups of molecules to the total mass of all molecules.

i.e. $$\overline{Mw} = \frac{Products\ of\ total\ mass\ of\ groups\ of\ molecules}{Total\ mass\ of\ all\ molecules}$$

$$\overline{Mw} = \frac{w_1M_1 + w_2M_2 + ... + w_iM_i}{w_1 + w_2 + ... + w_i}$$

Since, $w = N \times M$

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + ... + N_iM_i^2}{N_1M_1 + N_2M_2 + ... + N_iM_i}$$

In general $$\overline{Mw} = \frac{\sum N_iM_i^2}{\sum N_iM_i}$$

Polydispersity Index: It is the measure of number of molecular species having different sizes, equal to the ratio of weight average molecular mass to number average molecular mass.

i.e. $PDI = \dfrac{\overline{Mw}}{\overline{Mn}} \geq 1$, higher the value, greater is the polydispersity.

Numerical Problems:

1. In a sample of a polymer, 100 molecules have molecular mass 10^3 g/mol, 200 molecules have molecular mass 10^4 g/mol and 250 molecules have molecular mass 10^5 g/mol. Calculate the number average, weight average molecular mass of the polymer and PDI.

Solution, Given

$N_1 = 100$, $M_1 = 10^3$ g/mol,
$N_2 = 200$, $M_2 = 10^4$ g/mol,
$N_3 = 250$, $M_3 = 10^5$ g/mol

We have

$$\overline{Mn} = \frac{N_1 M_1 + N_2 M_2 + \ldots\ldots + N_i M_i}{N_1 + N_2 + \ldots\ldots + N_i}$$

$$\overline{Mn} = \frac{(100 x 10^3) + (200 x 10^4) + (250 x 10^5)}{100 + 200 + 250}$$

$$\overline{Mn} = 49272 g/mol$$

$$\overline{Mw} = \frac{N_1 M_1^2 + N_2 M_2^2 + \ldots\ldots + N_i M_i^2}{N_1 M_1 + N_2 M_2 + \ldots\ldots + N_i M_i}$$

$$\overline{Mw} = \frac{100 x (10^3)^2 + 200 x (10^4)^2 + 250 x (10^5)^2}{(100 x 10^3) + (200 x 10^4) + (250 x 10^5)}$$

$$\overline{Mw} = 92992 g/mol$$

$$PDI = \frac{\overline{Mw}}{\overline{Mn}} = \frac{92992}{49272} = 1.89$$

2. In a polymer sample, 20 % of molecules have molecular mass 12000 g/mol 30% molecules have molecular mass 20000 g/mol, remaining molecules have molecular mass 22000 g/mol. Calculate the number average, weight average molecular mass of the polymer and PDI.

Solution, Given

N_1 = 20, M_1 = 12000 g/mol,
N_2 = 30, M_2 = 20000 g/mol,
N_3 = 50, M_3 = 22000 g/mol

$$\overline{Mn} = \frac{N_1M_1 + N_2M_2 + ... + N_iM_i}{N_1 + N_2 + ... + N_i}$$

$$\overline{Mn} = \frac{(20x12000) + (30x20000) + (50x22000)}{20 + 30 + 50}$$

$$\overline{Mn} = 19400 g/mol$$

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + ... + N_iM_i^2}{N_1M_1 + N_2M_2 + ... + N_iM_i}$$

$$\overline{Mw} = \frac{20x(12000)^2 + 30x(20000)^2 + 50x(22000)^2}{(20x12000) + (30x20000) + (50x22000)}$$

$$\overline{Mw} = 20144 \ g/mol$$

$$PDI = \frac{Mw}{Mn}$$

$$= 20144 / 19400 = 1.03835 \ g/mo$$

3. A polymer sample contains
100 molecules with the formula $-(CH_3- CHCl)_{1000}$
200 molecules with the formula $-(CH_3- CHCl)_{2000}$
300 molecules with the formula $-(CH_3- CHCl)_{4000}$
Calculate the number average, weight average molecular mass of the polymer and PDI.

Solution,

Molecular mass of $-(CH_3- CHCl)- = 62.5$ g/mol

Therefore

$N_1 = 100$, $M_1 = 62.5$ x $1000 = 62500$ g/mol,
$N_2 = 200$, $M_2 = 62.5$ x $2000 = 125000$ g/mol,
$N_3 = 300$, $M_3 = 62.5$ x $4000 = 250000$ g/mol

We have

$$\overline{Mn} = \frac{N_1M_1 + N_2M_2 + ... + N_iM_i}{N_1 + N_2 + ... + N_i}$$

$$\overline{Mn} = \frac{(100x62500) + (200x125000) + (300x250000)}{100 + 200 + 300}$$

$$\overline{Mn} = 177083 g/mol$$

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + ... + N_iM_i^2}{N_1M_1 + N_2M_2 + ... + N_iM_i}$$

$$\overline{Mw} = \frac{100x(62500)^2 + 200x(125000)^2 + 300x(250000)^2}{(100x62500) + (200x125000) + (300x250000)}$$

$$Mw = 209558 g/mol$$

$$\underline{PDI} = \frac{Mw}{Mn} = \frac{209558}{17708} = 1.18$$

Conducting Polymers:

Organic Polymer that has delocalized pi electrons in their back bone and conduct electricity are called conducting polymers.

In polymer, electrons are localized and do not take part in conduction and also there a wide energy gap between valence band and conduction band. This makes polymer exhibit poor conductivity. But doping can delocalize the electrons responsible for conduction. The insulating polymer with conjugated backbone consisting of alternative double and single carbon-carbon bonds, can be converted into a conductor by doping it with either an electron acceptor such as I_2, $FeCl_3$ (oxidative dopant) or an electron donor such as sodium naphthalide (reductive dopant) or a protonating agent like HCl.

i) Oxidative dopant takes away electrons from the π-backbone of polymer and creates holes in the chain, resulting in the increase of conductivity of polymer. Ex- Polyacetylene

ii) Reductive dopant donates electrons to π-backbone of the polymer. These electrons are free to move along c-chain, resulting in the increase of conductivity of polymer. Ex- Polyacetylene.

iii) Protonating agent creates positive and negative charges in the polymer chain, resulting in the increase of conductivity. Ex- Polyaniline.

Polyacetylene

Synthesis:

Several methods have been developed to synthesize polyacetylene from pure acetylene and other monomers. One of the most common methods uses Ziegler–Natta catalyst, such as $Ti(OCH_3H_7)_4/Al(C_2H_5)_3$, with gaseous acetylene. Acetylene undergoes polymerisation in the presence of Ziegler-Natta catalyst to give polyacetylene.
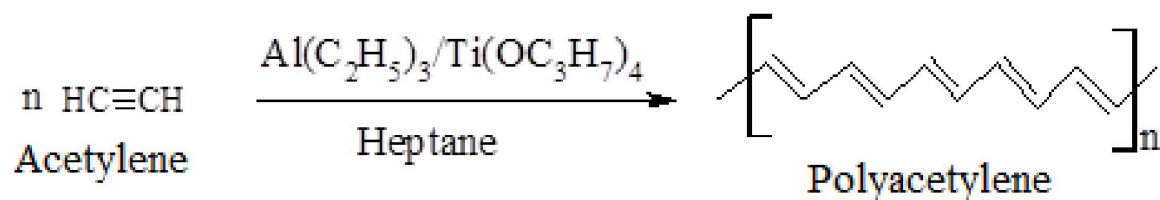
Mechanism of conduction in Polyacetylene

The conductivity of polyacetylene is 4.4×10^{-3} S/m. But the doped polyacetylene shows the conductivity of 4×10^4 S/m. When polyacetylene is partially oxidized with an oxidative dopant like I_2 in CCl_4, it takes away an electron from the π-backbone of polyacetylene chain producing a free radical and positive charge (hole). This combination of charge site and free radical is called **polaron**. This would create new localized electronic state in the energy gap. On further oxidation, a **bipolaron** is formed. If the polyacetylene chain is heavily oxidized, polarons condense pair-wise to form **solitons** which merge with the edges of conduction bond (CB) and valence bond (VB) exhibiting conductivity.
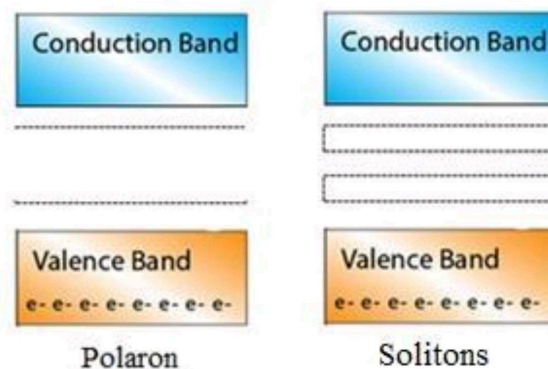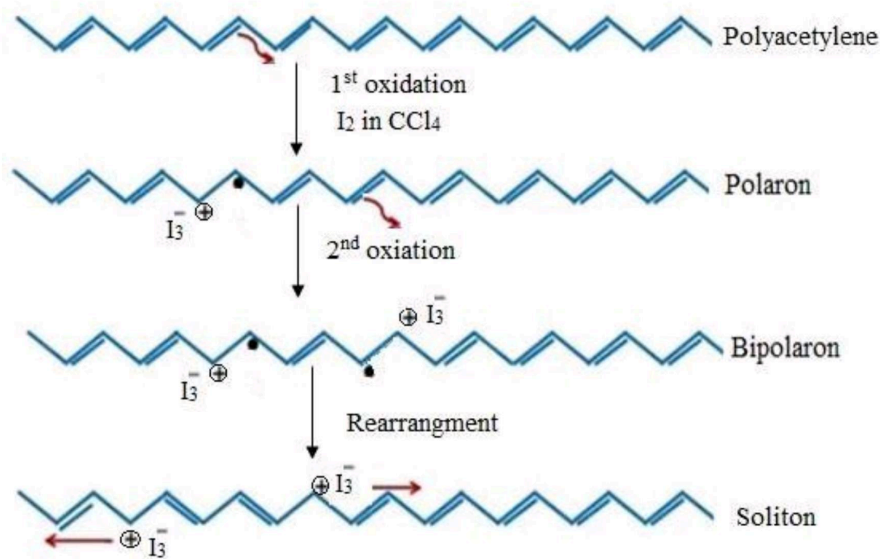
Graphene Oxide:

Graphene oxide (GO) is two-dimensional material formed by the oxidation of graphene. It is a single-atomic-layered material, when stacked together forms graphite oxide. It contains hydroxyl (-OH), alkoxy (C-O-C), carbonyl (C=O), carboxylic acid (-COOH) and other oxygen-based functional groups. These groups are attached to both the sides of a single graphite sheet and overcome the inter-sheet van der Waals force and enlarges the interlayer spacing and disturbs the sp^2 bond of graphene so reduces the conductivity of graphene oxide. It has been successfully used in several applications in electronics, conductive films, electrode materials and nano composites.

Synthesis:

Take 2g graphene and 2g of $NaNO_3$ (catalyst) in 50 ml of H_2SO_4 bath in 1000 ml volumetric flask kept in an ice bath (0-5 ^{o}C) with continuous stirring for 2 hours. Then add 6g $KMnO_4$ (oxidizing agent) very slowly at temperature kept below 15 ^{o}C. After some time, remove the ice bath and allow the mixture for stirring at 35 ^{o}C for 48 hours. Then dilute it with slow addition of 200 ml of water. Finally, treat the solution with 10 ml H_2O_2 to terminate the reaction and filter. After filtration, dry it in vacuum at room temperature to get powdered graphene oxide.
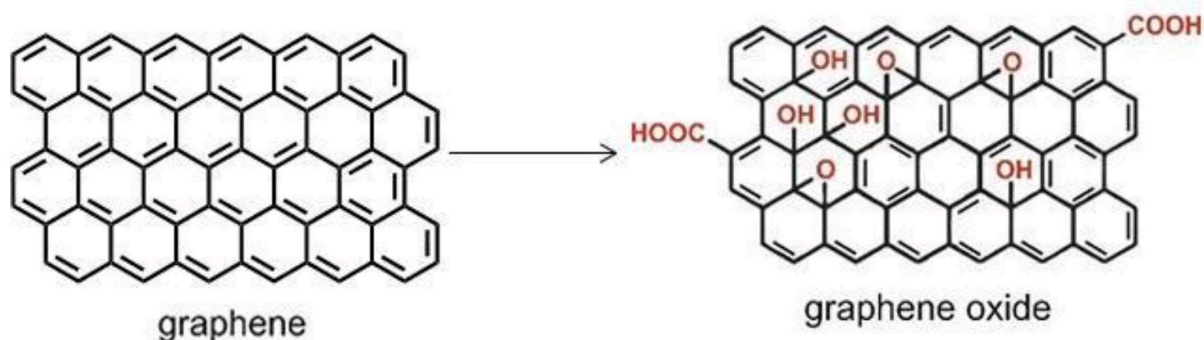
Properties:

> ➢ It is hydrophilic due the presence of hydroxyl, alkoxy, carbonyl, carboxylic acid groups.
> ➢ It can mix with matrix such as polymer and ceramic to improve their mechanical and electrical properties.
> ➢ It is hygroscopic and forms a strong hydrogen bond with water molecules.
> ➢ It has large surface area , so it is more reactive.
> ➢ It has low thermal conductivity (0.5-1 $Wm^{-1}K^{-1}$) as compare to graphite (3000-5000 $Wm^{-1}K^{-1}$).
> ➢ It has low electrical conductivity than graphene.

Applications:

- ➢ Graphene oxide can be used in coating technology,
- ➢ Graphene oxide papers can be used in desalination and reverse osmosis techniques to get pure water from saline water.
- ➢ GO can be used in the biomedical fields such as drug delivery, cancer therapy, bio-imaging and biosensor because of its biocompatibility nature.
- ➢ Nanocomposite of GO and silver (Ag) ions used for bacteria detection.
- ➢ GO can be as a bio-imaging tool for cancer cells.
- ➢ Reduced GO that can be produced from GO is used as a transparent electrode in polymer solar cells and LED.
- ➢ Reduced GO can be used as energy storage material in supercapacitors and in a lithium-ion batteries.
- ➢ Graphene Oxide-gold nanocomposites are good absorbents used for the removal of industrial dyes from aqueous atmosphere and aromatic pollutants.
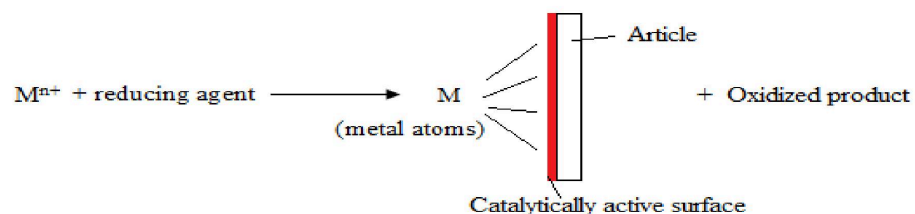
Metal finishing:

Metal finishing is the process of modification of surface properties of a material by coating a thin layer of metal or metal oxide or polymer. Material may be a metal or alloy or composite etc.
Electroplating: Electroplating is the process of deposition of metal on the surface of another metal by electrolysis.

Electroless plating

'Electroless plating is a process of deposition of metal from its salt solution over a catalytically active surface by a suitable reducing agent without using electrical energy'.

In electroless plating, the main driving force is auto catalyzed redox reaction. Reducing agent reduces the metal ions to atoms which will get deposited on the surface of article. Surface of article can be activated by treating with either dil. alkali or acid or $SnCl_2$ in presence of HCl followed by $PdCl_2$.

$$M^{n+} + \text{reducing agent} \longrightarrow \underset{\text{(metal atoms)}}{M} \quad \text{Article} \quad + \text{Oxidized product}$$
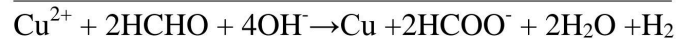
Catalytically active surface

Electroless plating of Copper: To prepare double sided printed circuit boards (PCBs):

The surface of the article to be subjected to electroless plating is cleaned thoroughly to remove the impurities. Insulators such as plastics, glass and quartz are activated by dipping first in stannous chloride ($SnCl_2$) in presence of HCl at 25^oC and then in palladium chloride ($PdCl_2$). Then, the electroless plating is done under the following conditions:

Plating bath composition:

Metal salt solution: $CuSO_4$ solution (12g/ L)
Reducing agent: Formaldehyde (8g/ L)
Complexing agent & Exultant: EDTA (20 g/L)
Buffer: NaOH (15g/L) + Rochelle salt (14g/L)
pH: 11
Temperature: 25^oC
Reactions:

$$Cu^{2+} + 2e^- \rightarrow Cu$$
$$2HCHO + 4OH^- \rightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$$
$$Cu^{2+} + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2$$

(Note: Formaldehyde and copper sulphate are need to be added to the plating bath periodically).

Process:
Activated plastic board on which circuit to be drawn is dipped in the electroless plating bath solution. Two sides of the plastic board is get coated with copper. Selected areas are protected and the copper in remaining area is etched away. Thus circuits are produced on either sides of the board. The connection between circuits of two sides is made by drilling hole followed by plating through-holes. The steps involved are shown below.
(Note: circuit shown only on one side of the board)
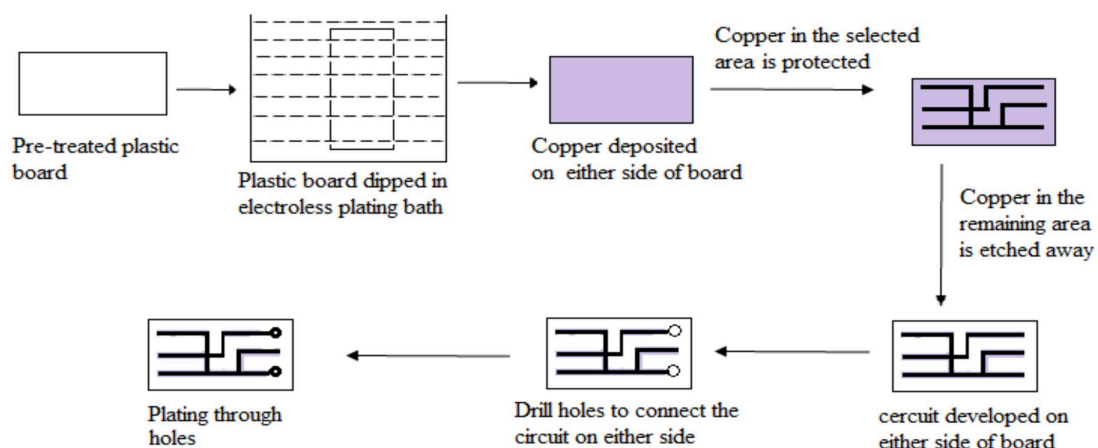
Electroless plating of copper

Distinguish between electroplating and electroless plating:

Property	Electroplating	Electroless plating
1. Driving force	Power supply	Autocatalytic redox reaction
2. Anodic reaction	$M \longrightarrow M^{n+} + ne-$ or	-----
	Metal salt $\longrightarrow Mn+ + Xy-+ ne-$	Metal salt $\longrightarrow Mn+ + Xy-+ ne-$
3. Cathodic reaction	$Mn+ + ne- \longrightarrow M$	$Mn++$ Reducing agent $\longrightarrow M +$ Oxidized product
4.Anode	Separate anode is required	Separate anode is not required
5.Cathode	Article to be plated (Pre-treated to remove impurities)	Article to be plated (Pre-treated to make the surface catalytically active)
6. Nature of deposit	Not satisfactory for complex surfaces and intricate parts	Satisfactory for all types of surfaces
7. Applicability	Only for conductors	For conductors, semiconductors and insulators.