

ATRIA INSTITUTE OF TECHNOLOGYANAND NAGAR BANGALORE 24

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Electrical & Electronics Engineering Stream

(Chemistry group)

1 Course Title: Chemistry for EEE Stream

Course Code: 22CHEE12/22

CIE Marks 50 Course Type (Theory/Practical/Integrated) Integrated SEE Marks 50 Total Marks 100 Teaching Hours/Week

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.

What are Conductors?

Definition of conductor

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.

Metals, humans, earth, and animals are all conductors. This is the reason we get electric shocks! Moreover, the human body is a good conductor. So it provides a resistance-free path for the current to flow from wire to body.

Conductors have free electrons on its surface which allow current to pass through easily. This is the reason why conductors are able to conduct electricity.

Examples of Conductors

- 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 of Conductors

Conductors are quite useful in many ways. They find use in many real-life applications. For example,

- 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

Definition:

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.

Wood, cloth, glass, mica, and quartz are some good examples of insulators. Also, insulators are protectors. They give protection against heat, sound and of course

passage of electricity. Furthermore, insulators don't have any free electrons. It is the main reason why they don't conduct electricity.

Examples of Insulators

- 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.

Conductors, semiconductors and insulators

Solids can be categorised into conductors, semiconductors or insulators by their ability to conduct electricity. Electron band theory explains differences in conduction.

Classifying materials

Materials can be placed into three groups according to their electrical resistance:

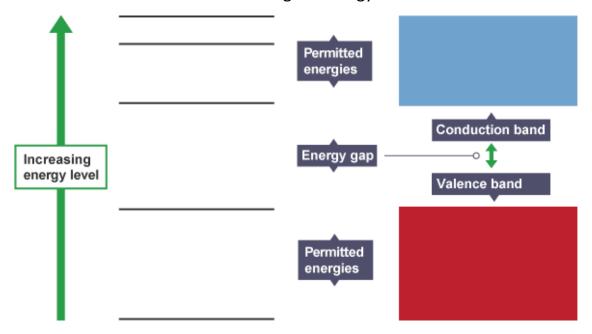
- conductors have a very low resistance
- semiconductors pure semiconductors have a very high resistance
- insulators have a very high resistance

This difference in conduction is explained by electron bands.

Band theory of conduction

• Electrons orbit the positive nucleus of an individual atom in permitted energy levels, as shown by the grey lines on the left of the diagram below.

- In a large collection of atoms, eg a metal wire or a semiconductor crystal, the energy levels become reorganised into two bands. This is shown on the right of the diagram:
- The valence band is the lower energy levels of electrons
- the conduction band is the higher energy levels of electrons



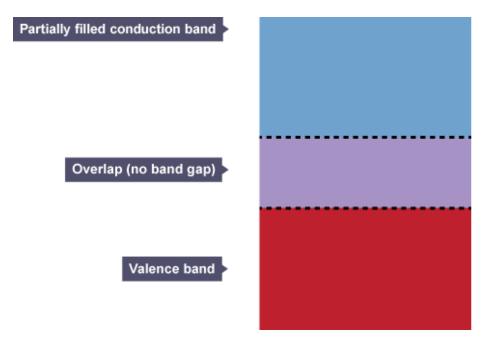
Electrons can't exist in the energy 'gap' between bands.

- Conduction is a movement of electrons in a solid. For conduction to occur there must be:
- Electrons free to move in the conduction band
- Spaces in energy bands for electrons to move into

Band theory and conductors, insulators and semi-conductors

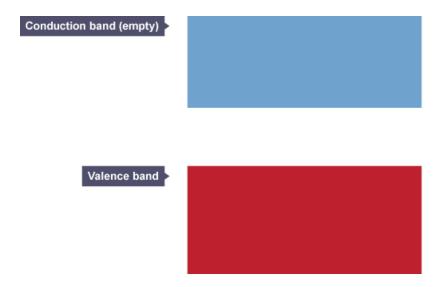
Conductors

 In a conductor there are no band gaps between the valence and conduction bands. In some metals the conduction and valence bands partially overlap. This means that electrons can move freely between the valence band and the conduction band. • The conduction band is only partially filled. This means there are spaces for electrons to move into. When electrons for the valence band move into the conduction band they are free to move. This allows conduction.



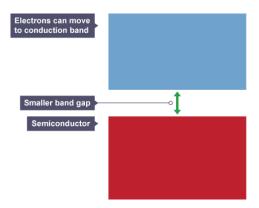
Insulators

- An insulator has a large gap between the valence band and the conduction band.
- The valence band is full as no electrons can move up to the conduction band. As a result, the conduction band is empty.
- Only the electrons in a conduction band can move easily, so because there aren't any electrons in an insulator's conduction band, the material can't conduct.



Semiconductors

- In a semiconductor, the gap between the valence band and conduction band is smaller. At room temperature there is sufficient energy available to move some electrons from the valence band into the conduction band. This allows some conduction to take place.
- An increase in temperature increases the conductivity of a semiconductor because more electrons will have enough energy to move into the conduction band.



The difference between insulators and semiconductors is due to a small amount of impurity added to a semiconductor which affects the energy bands. This process is called doping.

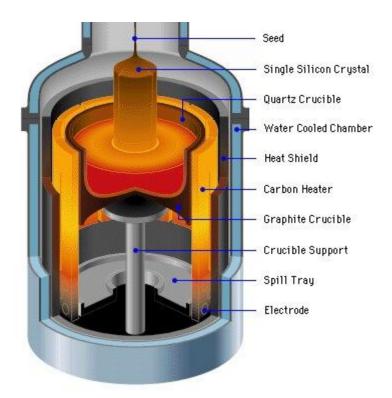
<u>Production of electronic grade silicon-Czochralski</u> process (CZ)

Introduction

- The vast majority of the commercially grown silicon is Czochralski silicon due to the better resistance of the wafers to thermal stress, the speed of production, the low cost and the high oxygen concentration that offers the possibility of Internal Gettering.
- The industrial standard crystals range in diameter from 75 to 200 mm, are typically I m long.

Process production electronic grade silicon

- (1) The Czochralski method is named after J. Czochralski, who determined the crystallisation velocity of metals by pulling mono- and polycrystals against gravity out of a melt which is held in a crucible.
- (2) A schematic diagram of a Czochralski-Si grower, called puller, is shown below fig:
- (3) Schematic setup of a Czochralski crystal puller



- (4) The puller consists of three main components:
- a) A furnace, which includes a fused-silica crucible, a graphite susceptor, a rotation mechanism (clockwise as shown), a heating element, and a power supply;
- b) A crystal-pulling mechanism, which includes a seed holder and a rotation mechanism (counter-Clockwise); and
- c) An ambient control, which includes a gas source (such as argon), a flow control and an exhaust system.
- (2) The Czochralski method begins by melting high purity polysilicon (SGS) with additional dopants as required for the final resistivity in the rotating quartz crucible. A single crystal silicon seed is placed on the surface and gradually drawn upwards while simultaneously being rotated.
- (3)This draws the molten silicon after it which solidifies into a continuous crystal extending from the seed. Temperature and pulling speed are adjusted to first neck the crystal diameter down to several millimetres, which eliminates dislocations generated by the seed/melt contact shock, and then to widen the crystal to full diameter.
- (4) During the production process the quartz crucible (SiO_2) gradually dissolves, releasing large quantities of oxygen into the melt. More than 99% of this is lost

- as SiO_2 gas from the molten surface, but the rest stays in the melt and can dissolve into the single crystal silicon.
- (5) Another impurity, however with smaller concentrations, that is also introduced into the melt by the production process itself is carbon. The silicon monoxide evaporating from the melt surface interacts with the hot graphite susceptor and forms carbon monoxide that re-enters the melt.
- (6) As the crystal is pulled from the melt, the impurity concentration incorporated into the crystal (solid) is usually different from the impurity concentration of the melt (liquid) at the interface.
- (7) Oxygen is always the impurity with the highest concentration in CZ silicon. Typical oxygen and carbon concentrations are respectively. The solubility of O in Si is $\approx 10^{^{18}}$ cm⁻³ at the melting point but drops by several orders of magnitude at room temperature, hence there is a driving force for oxygen precipitation. Furthermore the high oxygen concentration can lead to the formation of unwanted electrically active defects.
- (8) These are oxygen related thermal double donors (TDD) and shallow thermal donors (STD) which can seriously change the resistivity of the material. However, oxygen has also good properties.
- (9) Oxygen acts as a gettering agent for trace metal impurities in the crystal (Internal Gettering) and it can pin dislocations which greatly strengthens the crystal. Oxygen precipitates in the wafer core suppress stacking faults, and oxygen makes the Si more resistant to thermal stress during processing.
- (10) This is the reason why CZ-Si is used for integrated circuit production, where there are many thermal processing steps.
- However, the most important property of a high oxygen concentration from the point of view of this work is the improved radiation hardness. The main problem for the application as detector grade material arises from the resistivity of CZ silicon.
- (11) Due to contamination with boron, phosphorus and aluminum from the dissolving quartz Crucible the highest commercially available resistivity is about l00 Ohmcm for n-type and only slightly higher for p-type material.
- Therefore standard CZ silicon is not suitable for detector production.
- (12) However, first experiments to compensate the natural p-type background doping by adding a small quantity of phosphorus to the melt have been performed.

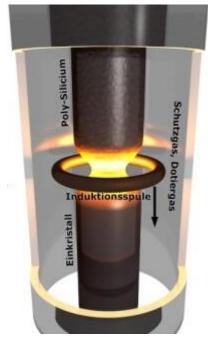
<u>Production of electronic grade siliconFloat zone silicon</u> (FIOAT-ZONE METHOD)

Introduction

- 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.
- Another light impurity, nitrogen, helps to control micro defects and also brings about an improvement in mechanical strength of the wafers, and is now being intentionally added during the growth stages.

The float zone method

- (a) The float Zone (FZ) method is based on the zone-melting principle and was invented by Theuerer in 1962.
- (b) A schematic setup of the process is shown in Fig.Schematic setup for the Float Zone (FZ) process



(1) 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.

- (2) 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.
- (3) As the molten zone is moved along the polysilicon rod, the molten silicon solidifies into a single Crystal and, simultaneously, the material is purified.
- (4) Typical oxygen and carbon concentrations in FZ silicon are below 5 10^{15} cm⁻³.FZ crystals are doped by adding the doping gas phosphine (PH₃) or diborane (B₂H₆) to the inert gas for n- and p-type, respectively.
- (5) Unlike CZ growth, the silicon molten Zone is not in contact with any substances except ambient gas, which may only contain doping gas. Therefore FZ silicon can easily achieve much higher purity and higher resistivity.
- (6) Additionally multiple zone refining can be performed on a rod to further reduce the impurity concentrations. Once again the effective segregation coefficient k plays an important role. Boron, for example, has an equilibrium segregation coefficient of $k_0 = 0.8$. In contrast to this phosphorus cannot only be segregated ($k_0 = 0.35$) but also evaporates from the melt at a fairly high rate.
- (7) This is the reason why on the one hand it is easier to produce more homogeneous p-type FZ than n-type FZ and on the other hand high resistivity p-type silicon can only be obtained from polysilicon with low boron content.

Polymers: Introduction, Molecular weight - Number average, weight average and numerical problems

Polymer introduction:

The word polymer is derived from Greek words, Poly (many) and meros (Parts or unit). A polymer is a large molecule formed by combining small molecules. The individual small molecules from which the polymer is formed are known as "Monomers "and the process by which the monomer molecule are linked to form big polymer molecule is called "polymerization"

Polymerization

$$nCH_2=CH_2$$
 \rightarrow $-(CH_2-CH_2-)_n$

Ethylene Polyethylene

The length of the polymer chain is specified by the number of repeat unit in the chain, the average number of repeat units in the chain is called "degree of polymerization" (n).

The polymers are generally called as "Plastics"

Polymerization is a process which allow monomer to combine and form polymer. The number of reactive site (bonding) available in a molecule for a particular reaction is called "functionality". Ethylene has functionality of two, acetylene has functionality of four.

Types of Polymers

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

Natural biopolymers

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

Synthetic polymers

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

Classification of Polymers

- 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]-

Polymers classified by mode of polymerization

- 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.
- <u>Condensation Polymers</u>: 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 weight - Number average, weight average and numerical problems

- In contract to the low molecular weight compound, polymer is usually a complex mixture of molecules of different molecular weights.
- The polymer are thus polydisperse and heterogeneous in composition. Therefore the molecular weight of a polymer is actually an average of the molecular weights of constituent molecules.
- Different averages are obtained depending on the method of measurement of the molecular weight.

Definition

The **number average molecular weight Mn** is obtained by the measurement of the colligative properties of a polymer by Osometry or end group analysis and is defined as

$$Mn = \sum Ni.Mi/\sum Ni$$

Where Ni is the number of molecules of molecular weight Mi

The weight average (MW) molecular weight is obtained from light scattering measurement and is defined as

$$Mw = \sum Ni.Mi^2/\sum Ni.Mi$$

To explain these molecular weight averages Example

Suppose there are 50 polymer molecules of molecular weight 10^2 , 200 polymer molecules of molecular weight 10^3 , and 100 molecules of molecular weight 10^4 . Then

Mn=
$$50X10^2+200X 10^3+ 100X10^4/ 50+200+100$$

= 3443 approx.
Mn= $50X10^4+200X10^6+100X10^8/ 50X10^4+200X10^3+100X10^4$
= 8470 approx.

Numerical problem 1

A polymer has the following composition 100 molecular mass 1000g/mol, 200 molecules of molecular mass 2000g/mol and 500molecular mass 5000g/mol.Calculate the number and weight average molecular weight. Solution:

Given M_1 =1000g/mol, N_1 =100: M_2 = 2000g/mol : N_2 = 200, M_3 = 5000g/mol, N_3 = 500

The number average molecular weight in given by

$$Mn = \sum Ni.Mi/\sum Ni$$
= 100X1000+200X2000+500X5000/ 100+200+500
=1X10⁵+4X10⁵+25X10⁵/800
=3.75X10³ g/mol

The weight average molecular weight is

$$Mw = \sum Ni.Mi^{2}/\sum Ni.Mi$$

$$= 100X1000^{2} + 200X2000^{2} + 500X5000^{2}/30X10^{5}$$

$$= 1X10^{8} + 8X10^{8} + 125X10^{8}/30X10^{5}$$

$$= 4.46X10^{3}g/mol$$

<u>Conducting polymers – synthesis and conducting mechanism of polyacetylene.</u>

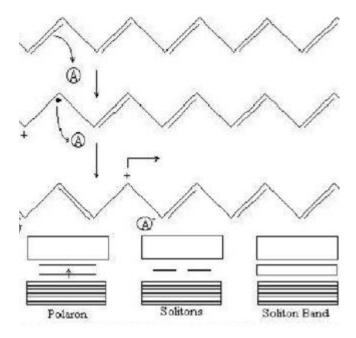
Synthesis of polyacetylene

 A variety of methods have been developed to synthesize polyacetylene, from pure acetylene and other monomers. • One of the most common methods uses a <u>Ziegler–Natta catalyst</u>, such as Et₃Al/Ti(OC₃H₇)₄, with gaseous acetylene. This method allows control over the structure and properties of the final polymer by varying temperature and catalyst.

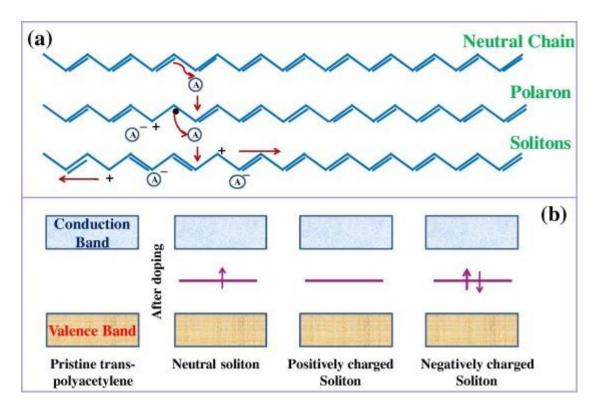
H——H
$$\frac{\text{Et}_3\text{AI/Ti}(\text{OC}_3\text{H}_7)_4}{75\,^{\circ}\text{C}}$$
 heptane

Mechanism of polyacetylene:

- (a) Polyacetylene consists of hundreds to thousands of carbon atoms linked by alternating single and double bond. Conductivity of pure oxyacetylene is about 4.4X10⁻⁵S/cm.
- (b) Upon doping with oxidizing agent like iodine, the conductivity increases to about 400 S/cm
- (c) When the oxidative dopart such as iodine is added, it takes away an electrons from the ∏ -back bone of the pollyacetylene chain and creates a positive centre (hole) on one of the carbon.
- (d) The other ∏- electron resides on the other carbon making it a radical. The radical ion formed is called Polaron. A dipolar on (soliton) is formed on further oxidation.
- (e) These radicals migrate and combine to establish a backbone double bond. As the two electrons are removed, the chain will have two positive centre (holes).
- (f) The chain as a whole is neutral, but holes are mobile and when a potential is applied the migrate from one chain as a whole is neutral but holes are mobile and when a potential is applied they migrate from one carbon to another and account for conductivity. This depicted by the sequence of reaction.



- (g) When a \prod bond is formed, valence (VB) and conduction bond (CB) are created. Before doping there is sufficient energy gap between VB and CB, so the electron remain VB and the polymer acts as an insulator.
- (h)Upon doping polarons and Solitons are formed which results in the creation of new localized electronic states that fill the energy gap between VB and CB.When sufficient soliton are formed, new mid gap energy band created which overlaps with valence and conduction bands allowing electrons to flow.



Application polyacetylene conducting polymer.

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 sp2 and sp3 hybridized carbon atoms.

Properties of GO:

- 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 grapheme oxide (Hammer method)

- 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 (Figure 3A).

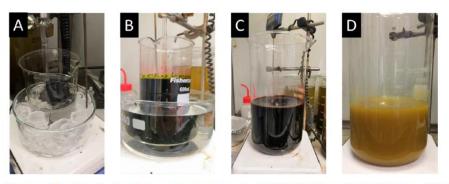


Figure 3. Photographs describing preparation process of GO by Tour's method: (A) before addition of potassium permanganate; (B) after oxidation; (C) after pouring on ice; (D) after addition of H_2O_2 .

Graphene oxide synthesis

- The mixture is then heated at 50°C and stirred for 12 h (Figure 3B). After cooling down, the mixture is poured onto ice (Figure 3C).
- Finally, 30% H₂O₂ is added in order to remove the excess of potassium permanganate (Figure 3D).
- 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

1. Environmental Applications of GO

- 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.

Removal of Toxic Gases

• The functional groups of few-layered GO composites exhibit unique adsorption behaviour towards different gases like acetone, formaldehyde, H₂S, SO₂, and NOx can be adsorbed by GO-based composites.

Water Purification

- 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. Multi-layered 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.

Medical and Biological Applications of GO

- 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

It is the deposition of the metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electricity.

Example Electroless plating with respect to copper, nickel etc.

CAS

Metal ion + Reducing agent → Metal plated + oxidized products.

Note: CAS: Catalytically Active Surface

Advantages of Electroless plating process

Electrical power and electrical contacts are eliminated.

Semiconductors and insulators like plastics, glass, quartz, wood, and thread can be plated.

Electroless plating baths having better throwing power.

Irregular shapes can be uniformly coated.

Electroless plating of copper

1. Pre-treatment and activation of surface

- The object (metal/non -metal/alloy) is degreased with organic solvent or alkali followed by acid treatment. Metals can be directly used along with a suitable reducing agent.
- An alloy (example- stainless steel) is dipped in hot solution containing 1:1 H₂SO₄, semiconductors and insulators like plastics, glass quartz, wood thread etc., followed by dipping in palladium chloride solution. When the object is dried, layer of palladium is obtained.

2. Electroless plating bath composition:

- * 1.2g /L of copper sulphate (Electro active metal)
- * 8g/L of formaldehyde (Reducing agent)
- *20 g/L of EDTA (Complexing agent and exalting)
- * 15 g/L of NaOH + 14 g/L of Rochelle's salt (buffer)
- 3.**pH**: 11.0
- 4.**Temperature** :25 °C

5. Reactions:

Cathode (**Reduction**)

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

Anode (Oxidation)

$$2 \text{ HCHO} + 4 \text{ OH}^- \rightarrow \text{HCOO}^- + 2 \text{ H}_2\text{O} + \text{H}_2 + 2\text{e}^-$$

Overall reaction

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

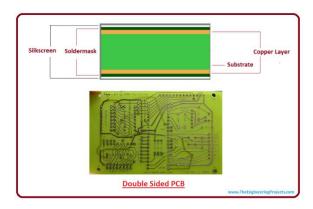
Applications

- 1. Copper plating is printed circuit board (PCB) etc.
- 2. For producing through-hole connection

- 3. For plating on non-conductors
- 4. As a base for subsequent conventional electroplating.
- 5. Applied on wave guides and for decorative plating on plastics.

Manufacture of double-sided PCB.

- Through hole connections are necessary when double sided printed circuit boards are fabricated.
- The electrical connection between two sides of the boards are fabricated.
- The electrical connections between two sides of board are made by drilling hole and the plating through holes by electroless plating.
- For the manufacture of double sided printed circuit boards, the plastic board is initially covered with copper with an etch-resistant pattern of the circuit or the tracking required on both the sides.
- On etching with suitable etchant the copper except below the printed pattern is etched away, leaving the circuit pattern.
- The connection between two sides is made by drilling hole followed by activation and plating through holes by electroless plating. The steps involved in the process is shown above fig.



Module 1: model VTU Question Bank

- 1) What are conductors and insulators? Explain the principle involved in conductors and insulators by taking an examples. (6 marks)
- 2) Mention the differences between conductors, semiconductors and insulators band theory? 6marks
- 3) What are semiconductors? Explain the production of electronic grade silicon by Czochralski (CZ) process. 7 marks
- 4) Explain the production of electronic grade silicon by Float Zone (FZ) method.7marks
- 5) What are conducting polymers? Explain the synthesis and conducting mechanism of polyacetylene. Mention its commercial applications. (7marks)
- 6) Explain the preparation, properties and commercial applications of graphene oxide (Hammer method) ? (7 marks)
- 7) Define electroless plating. Describe the electroless plating of copper in the manufacture of double-sided PCB? (6 marks)

Numerical problem

8) A polymer has the following composition 100 molecular mass 1000g/mol, 200 molecules of molecular mass 2000g/mol and 500molecular mass 5000g/mol.Calculate the number and weight average molecular weight. (6marks)