

## Engineering Chemistry Solved Important Questions

### UNIT-II

#### Chapter 4. Plating Techniques

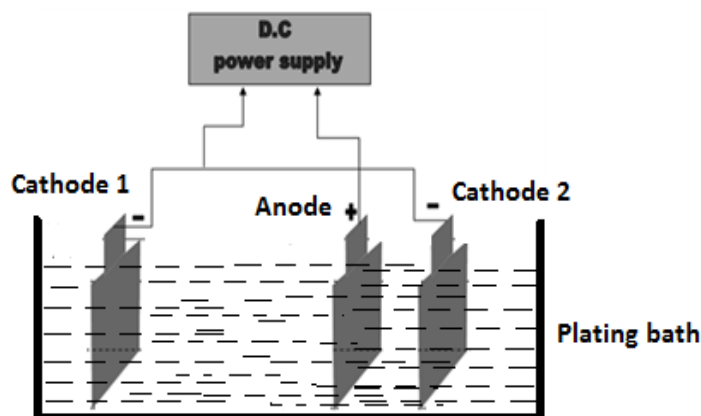
##### 1) Give the importance of plating techniques.

**Answer:** Plating technique finds extensive applications in variety of industries, extending to many electronics, engineering and metal processing companies as well as to both large and small specialist firms. The technological importance of plating technique is in imparting certain additional properties to the materials in addition to their intrinsic properties. So that, the utility of the materials is increased. Metal finishing imparts desirable surface characteristics such as,

1. Imparts higher corrosion resistance.
2. Imparts improved wear resistance.
3. Provides decorative appearance.
4. Increase abrasion and impact resistance
5. Improves chemical resistance.
6. Imparting thermal resistance/conducting surface,
7. Increase hardness and improved solderability.
8. Provides optical reflectivity or thermal conducting surface.
9. Manufacturing electrical and electronic components such as PCB, capacitors etc.
10. In electroforming of objects, in electro machining
11. In electro polishing and electrochemical etching.

##### 2) Explain the determination of throwing power of plating bath solution using Haring - Blum cell.

**Answer:** The ability of a plating bath solution to produce an even deposit is measured by its throwing power. It is difficult to get electric deposit with uniform thickness on the entire surface especially when the object is complex in nature. Throwing power of plating bath can be determined by using the **Haring-Blum cell**.



The cell contains plating bath solution whose throwing power is to be determined. The two cathodes are placed at markedly different distances  $d_1$  and  $d_2$  where  $d_1 > d_2$  from a single central anode and electroplating is carried out.

The weight of the metal plated on the two cathodes  $W_1$  and  $W_2$  are determined.  $W_1$  is for  $C_1$  and  $W_2$  is for  $C_2$ .

$$\% \text{ Throwing power of the bath solution} = \frac{(X - Y) \times 100}{(X + Y - 2)}$$

where,  $X = d_1/d_2$ ,  $Y = W_2/W_1$

When  $W_1 = W_2$  i.e., amount deposited is same irrespective of the placement of the electrode, then throwing power is considered very good (100 %). When the calculated throwing power is -100% then it is considered as very poor.

### 3) Discuss the process of gold plating using acid cyanide bath and mention its engineering applications.

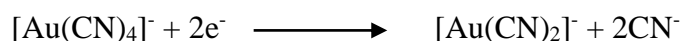
**Answer:** Gold plating was initially applied for decorative purposes on jewellery articles. But later it is found applications in the industries, for various purposes.

Plating bath used for electroplating of gold is generally called as cyanide bath because cyanide is used as complexing agent.

Constituents	Bath D (Acidic)
(1) Plating bath Solutions:	
(i) Potassium gold cyanide	6.0 – 18.0 g/dm <sup>3</sup>
(ii) Mono potassium dihydrogen phosphate g/dm <sup>3</sup>	20.0 g/dm <sup>3</sup>
(iii) Potassium citrate g/dm <sup>3</sup>	50.0 g/dm <sup>3</sup>

(2) pH	3 – 6
(3) Temperature	40 – 70 °C
(4) Current density	1 – 20 A/ft <sup>2</sup>
(5) Cathode efficiency	80 – 90 %
(6) Anode	Pt, Platinized Ti, Carbon
(7) Cathode	Object to be electroplated
(8) Leveler	Sodium allyl sulphonate

### **Reactions:**



Gold metal dissolves very fast in cyanides, therefore inert anode is used instead of pure gold metal.

$\text{AuCl}_3$  is periodically added to cyanide bath to maintain the concentration of  $[\text{Au}(\text{CN})_4]^-$ .

Concentration of gold ions should be minimum in plating bath to maintain a good, coherent deposit.

**Applications:** Gold deposit is a shiny deposit with good tarnish and corrosion resistance. It has good electrical conductivity, comparable with copper and silver, and has an ability to reflect IR radiation.

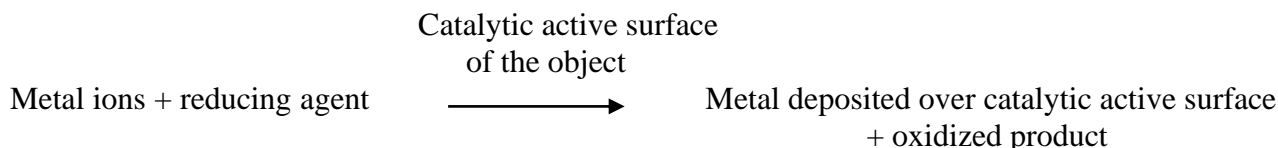
1. Used for decorative purposes in jewelers, watch cases, pen points, hallow ware, etc.,
2. In the electrical industry, printed circuits, contacts and connectors are gold plated.
3. In electronics, transistors and integrated circuit parts are gold plated.
4. In the aerospace industry, instrument coverings and external surfaces exposed to radiation in space are gold plated.
5. Reactors and heat exchangers in the conductor tube for desalination are gold plated, because of the high corrosion resistance nature of gold.
6. Because of its acid and corrosion resistance, it is used for decorative purpose especially in tombs of temples.

### **4) What is electroless plating? Mention the advantages of electroless plating over electro plating.**

**Answer:** It is a method of depositing a metal or alloy over a substrate (conductor or non-conductor) by controlled chemical reduction of the metal ions by a suitable reducing agent without using electrical

energy. The reduction of metal ions by the reducing agent is catalyzed by the metal atoms being plated. Therefore, electroless plating is also termed as autocatalytic plating.

The electroless plating process can be represented as,



### **Advantages of electroless plating:**

1. Does not require electrical power source.
2. It is applicable to conductors, semiconductors and non-conductors like plastics.
3. Electroless plating is less porous than electroplates and possess unique characteristic chemical, mechanical and magnetic properties.
4. Electroless plating baths have better throwing power and deposit a more uniform metal coating over an article irrespective of its shape or size.
5. Levellers are not required in electroless plating.
6. Electroless coating will be harder as compared to electroplating coating.
7. H<sub>2</sub> gas is not trapped.

### **5) What is electroless plating? Describe the electroless plating of copper in the preparation of PCB.**

**Answer:** It is a method of depositing a metal or alloy over a substrate (conductor or non-conductor) by controlled chemical reduction of the metal ions by a suitable reducing agent without using electrical energy.

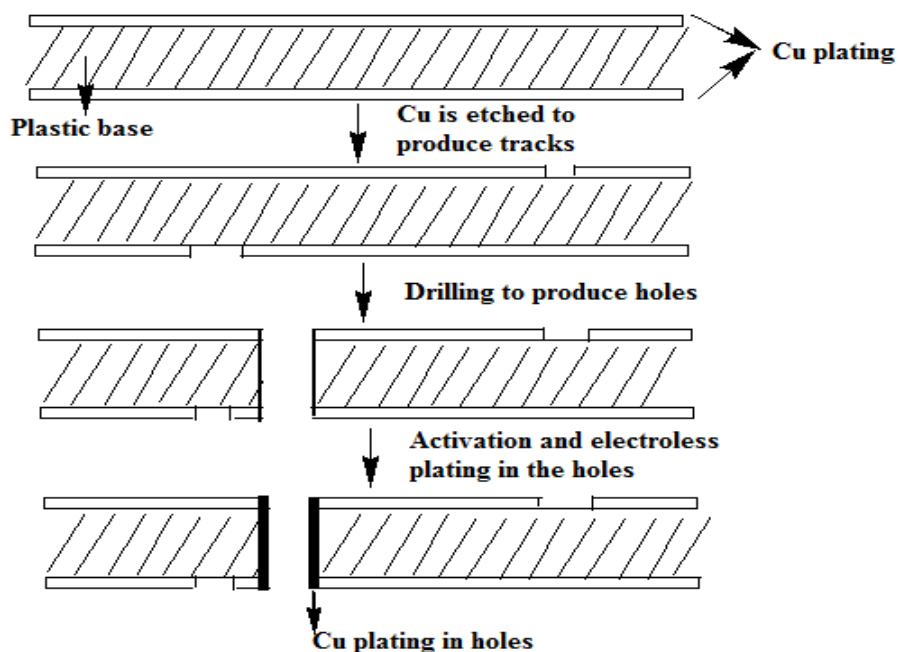
#### **Electroless plating of copper**

Electroless plating of copper on PCB's is carried out as follows.

Metal ion solution:	CuSO <sub>4</sub> .5H <sub>2</sub> O (12 g/L)
Reducing Agent:	Formaldehyde (HCHO, 8 g/L)
Buffer	Rochelle salt (sodium potassium tartarate, 14 g/L) + NaOH (12g/L)
Complexing agent:	EDTA (20g/L)
pH	11 -12
Temperature:	25 °C
<u>Reactions:</u>	
At Anode:	$2\text{HCHO} + 4\text{OH}^- \longrightarrow 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2 + 2\text{e}^-$

At Cathode:	$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$
Overall reactions:	$4\text{OH}^- + \text{Cu}^{2+} + 2\text{HCHO}^- \longrightarrow \text{Cu} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2$
Applications:	<ul style="list-style-type: none"> <li>• For Producing through – hole connections</li> <li>• Widely used for metalizing printed circuit boards</li> <li>• For plating on non conductors</li> <li>• For decorative plating on plastics.</li> <li>• As an undercoat/base for electroplating.</li> </ul>

**Preparation of printed circuit boards (PCB's):** The activated board is immersed in plating bath solution maintained at 25 °C. Plating is carried out at a rate of 1-5 µm/h, till 5-100 µm thickness is obtained. Selected areas are protected by a photo-resist or electroplated image and the rest of the copper is etched away to produce the circuit pattern. The connection between both sides of track is made by drilling hole followed by plating through holes by electro less plating. Double sided PCB's are commonly used because of feasibility of packing of more components in smaller space.



6) Calculate the throwing power of a plating bath in a Haring - Blum cell if the distances of the two cathodes from the anode are 6 cm and 5 cm and the quantities of metal deposited are 72 mg and 75 mg respectively. In the same cell if one of the cathode which was fixed at 6 cm was moved to 8 cm from the anode, calculate mass of metal deposited on the electrode.

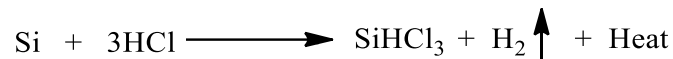
- 7) Calculate the percentage of throwing power of plating bath solution in a Haring - Blum cell if the distances between the two cathodes are 6.6 cm and 4 cm from the anode and the masses of the plating on the cathodes are 52 mg and 55 mg respectively.
- 8) The throwing power of an electrolyte in a Haring Blum cell is 75%. In an experiment, 68 mg of the metal was deposited at the nearest cathode kept at a distance of 4.8 cm from the cathode. At what distance must the cathode be kept if the metal deposited on it is 64 mg?

## Chapter 5. Wafer Technology

### 1) Explain with neat diagram, the manufacture of electronic grade silicon by CVD process.

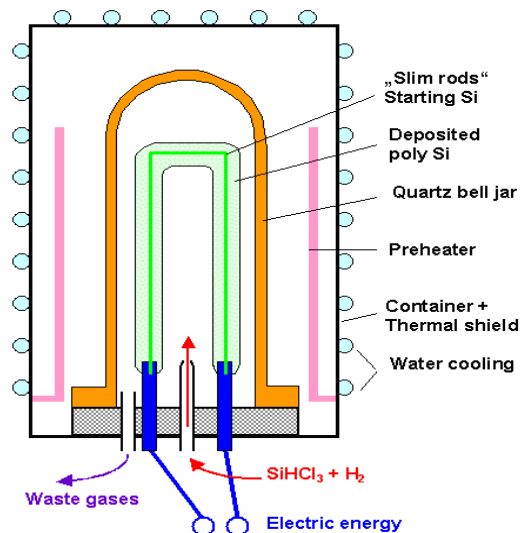
**Answer:** Electronic grade silicon (EGS) is one of the purest forms of silicon. It is approximately 99.99999999% pure form of silicon.

The metallurgical grade silicon (MGS) is solidified and pulverized (reduce particle size) to a fine powder. This powdered silicon is treated with anhydrous/dry HCl to obtain trichlorosilane and hydrogen as the products. The product mixture is subjected to fractional distillation to obtain pure trichlorosilane ( $\text{SiHCl}_3$ ).



This  $\text{SiHCl}_3$  is to be passed through a chamber of Chemical Vapor Deposition (CVD) to obtain EGS.

**Construction:** CVD technique is used for the production of polycrystalline silicon (grain size is 1  $\mu\text{m}$ -1 mm).



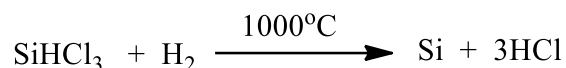
In a quartz bell jar, thin rods of silicon of 4 mm diameter are fixed to rod holders. The quartz bell has

an inlet through which reactants  $\text{SiHCl}_3$  and  $\text{H}_2$  to be supplied into the chamber. There is an outlet through which residual gases are taken out.

### **Working:**

#### **Reduction Reaction:**

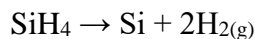
- The Si rods are heated from an external heating source to about  $1000^\circ\text{C}$ . By this sufficient conductivity is supplied through graphite electrodes and the vessel gets evacuated.
- At this stage, when the slim Si rods are at the reaction temperature, an optimized mixture of  $\text{SiHCl}_3$  and  $\text{H}_2$  is to be introduced into the chamber.
- To maintain the constant pressure, the reaction products are pumped out through outlet.
- At the elevated temperature, The  $\text{SiHCl}_3$  undergoes reduction to produce silicon and HCl. The silicon (polycrystalline) deposits over the T-shaped slim Si rod of 4mm diameter.



- The rods are cut and taken out from the CVD chamber. They have purity of 99.99999999% and are called EGS. The residual gas HCL is taken out through the outlet.

### **Pyrolysis:**

- Polycrystalline EGS can also be prepared by Pyrolysis of Silane at  $900^\circ\text{C}$  in the CVD reactor.



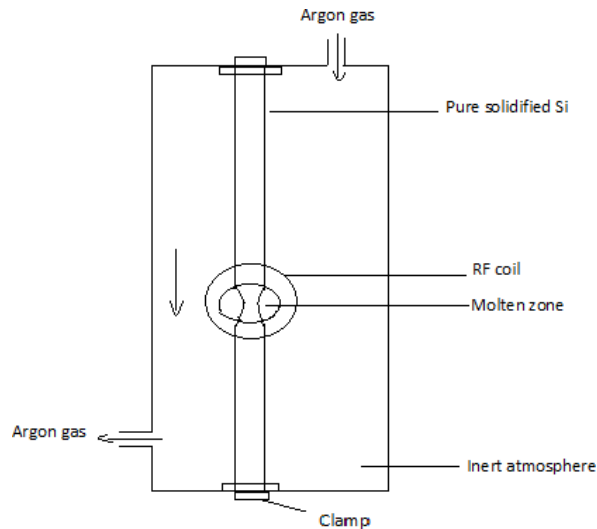
- This process helps in the production of low cost EGS and less harmful reaction products.
- Worldwide consumption of EGS is around 5000 tons per year

## **2) Describe the process of zone refining in the purification of silicon.**

**Answer:** Electronic grade silicon (EGS) obtained from CVD is to be subjected to zone refining to make sure that no solid impurities are carried on to the next process of making wafers.

**Zone Refining** is the unique method of obtaining 99.99999999% pure polycrystalline Electronic Grade Silicon with perfect and rigorous recrystallization.

**Principle:** When a solid is melted, the impurities tend to concentrate in the molten zone.



### **Procedure:**

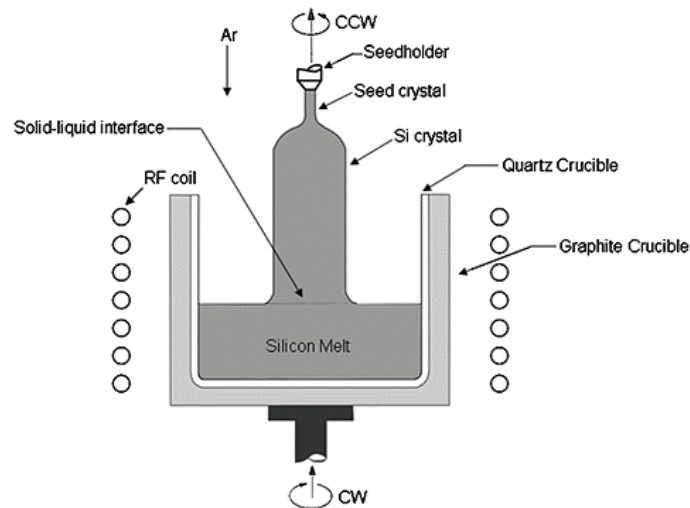
- A vertical zone refiner is used for the purification of EGS.
- The silicon rod is clamped vertically in an inert atmosphere of Ar.
- The Si rod is heated by a radio frequency (RF) coil at about 1000°C -1200°C.
- At this temperature, molten zone is created at the specific portion of Si rod where RF coil is held.
- The RF coil is slowly moved from top to bottom. As a result, the impurities are swept down with molten material due to gravity, while pure Si solidifies at the upper portion with perfect recrystallization. This is said to be one zone pass.
- Once RF coil is moved from top to bottom, it brings down most of the impurities to the lower part of the rod.
- This movement is repeated several times to ensure high purity. Once the process is done, we get two parts: purified upper part and unpurified lower part.
- The lower portion of the rod is cut and separated as it contains high concentration of impurities.
- The upper portion of the silicon rod is pure and polycrystalline which can be converted into monocrystalline silicon.
- From this technique, the impurity level can be reduced to 1 atom in every  $10^{12}$  atoms of silicon in parts per trillion ranges.

### **3) Discuss in detail the process of Czochralski crystal pulling technique in the production of single crystal silicon.**



**Answer:** Czochralski crystal pulling technique is a method used for the production of single crystal EGS from polycrystalline EGS.

**Principle:** In this technique single crystalline EGS is used as a seed to grow single crystal silicon from polycrystalline silicon. When the silicon melt is pulled out, the atoms of polycrystalline silicon solidify. It reproduces the same orientation and crystal structure as that of the used single crystalline EGS seed.



**Procedure:**

- A quartz crucible is placed on a crucible holder fixed with RF heating coil.
- Polycrystalline silicon material is taken into a quartz crucible.
- The crucible is heated using a RF power source in an inert atmosphere of krypton.
- When the silicon material melts, the temperature is lowered so that it is kept at the M.P. of the material (1500 °C).
- A single crystal of silicon is attached to the tip of a puller rod (seed holder) and is brought down into the molten silicon so that it just reaches the surface of the material.
- At the same time, the rod is rotated at the speed of 100 rpm and slowly lowered such that 25% of seed is immersed in the melt.
- The crucible is rotated in the opposite direction and simultaneously pulled out at the rate of 15 to 30 cm per minute.
- Initial pulling forms narrow neck of monocrystalline silicon rod. Once the neck is formed, the pulling rate is maintained at 1.5 – 5 cm per hour and the rotation at 100 rpm.
- As the melt is pulled out, it solidifies and has the same orientation and crystal structure as that of the seed.
- The process should be stopped when small amount of silicon melt is still remaining in the crucible as it contains high concentration of impurities.

- Finally, an intrinsic crystal of silicon of 5 cm diameter and 25 cm length is obtained. Such rod is called as **Ingot**. This crystal is then tested for its conductivity and cut into wafers of 0.25 mm thickness with the help of a diamond tipped saw.

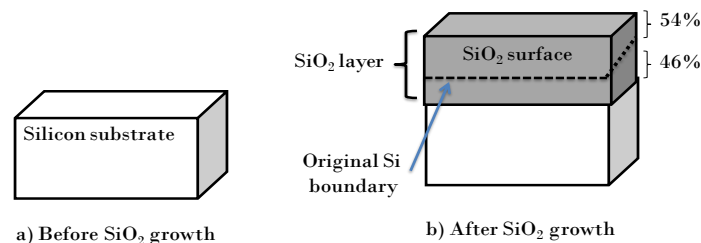
This technique is also used for the production of n or p-type of single-crystal silicon by doping with boron (p-type semiconductor) or phosphorous (n-type semiconductor) in the melt. Calculated amount of selected dopant must be added into the crucible so that dopant atom gets into silicon rod while it is being developed.

**Segregation Constant:** Segregation constant ( $K_0$ ) plays an important role in determining the amounts of dopants to be added. The  $K_0$  is defined as the ratio of concentration of impurities in the solid ( $C_s$ ) to the concentration of impurities in liquid state ( $C_l$ ) at equilibrium.

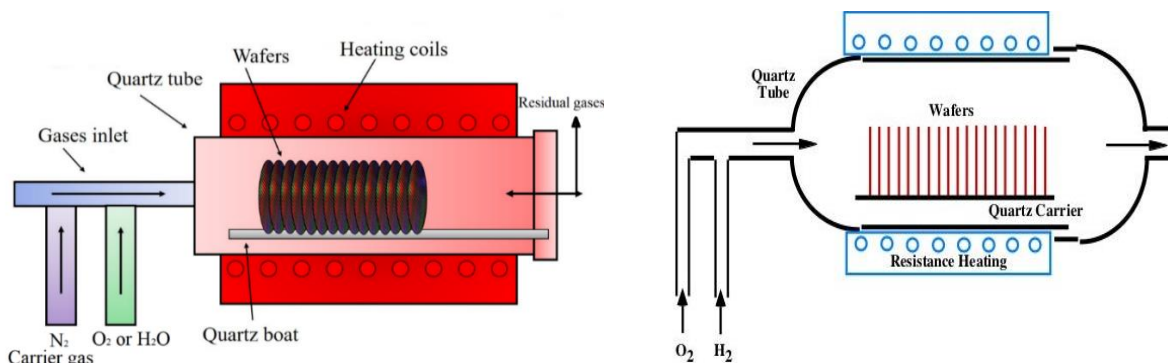
$$K_0 = \frac{C_s}{C_l}$$

#### 4) Describe the fabrication process of silicon wafers by thermal oxidation with relevant reactions?

**Answer:** Thermal Oxidation is a method of growing a  $\text{SiO}_2$  layer from a single crystal silicon wafer.



Thermal oxidation is required for, (1) masking the material 2) surface modification 3) biocompatibility 4) to act as a sacrificial layer.



**Fig. Thermal Oxidation System**

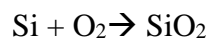
#### **Procedure:**

- Thermal oxidation is carried out in a thermal oxidation furnace system.

- It consists of a quartz furnace tube. Si wafers are placed vertically on quartz boat inside the quartz furnace tube in such a way that polished side of wafer is facing the inlet of quartz tube.
- One end of the quartz furnace tube is provided with an outlet to remove residual gases.
- The other end of the tube is provided with 2 inlets for sending in oxidizing agents i.e., oxygen (for dry oxidation) or water vapour (for wet oxidation) required for oxidation reaction.
- The quartz furnace tube is heated to a temperature of 900°C to 1200°C using resistance heaters/heating coils.
- Thermal oxidation proceeds in two ways depending on the nature of oxidizing agent used.

### **Dry Oxidation:**

- Dry oxidation takes place when dry O<sub>2</sub> is used as an oxidizing agent.
- The dry oxygen in its molecular form is diffused into the wafer at high temp of 900 °C to 1200°C and is made to react with it.
- The chemical reaction at the Si surface is,



- One molecule of oxygen results in the formation of one molecule of SiO<sub>2</sub>.
- As reaction proceeds, the thickness of SiO<sub>2</sub> increase. Decrease in the rate of reaction, decreases the rate of increase of thickness of SiO<sub>2</sub>.
- In dry oxidation, the rate pf oxide layer growth is very low. But its electrical properties are excellent. Dry oxidation results in SiO<sub>2</sub> layer of thickness less than 1.0 μm.

### **Wet Oxidation:**

- Here water vapour/steam is used as an oxidizing agent.
- This process takes place at a temp of 900°C to 1000°C.
- The steam is allowed through an inlet so that it reaches preheated silicon wafers. At high temperature, steam reacts with surface silicon atoms to form SiO<sub>2</sub> and hydrogen.



- Here, two molecules of water vapour are used to for one molecule of SiO<sub>2</sub>.
- As reaction proceeds, thickness of SiO<sub>2</sub> keeps increasing which decreases the rate of reaction and hence the rate of increased thickness of SiO<sub>2</sub> decreases.
- H<sub>2</sub> produced by this reaction diffuses rapidly through the growing oxide and leaves the system at the gas oxide interface.
- Wet oxidation is much faster than dry oxidation. It is suitable for making thick oxide greater than 1μM. But it suffers from more structural defects.

- Due to more quantity of  $\text{SiO}_2$  produced which results in further increased thickness of  $\text{SiO}_2$  layer. This is because,
- When  $\text{SiO}_2$  is grown on Si wafer, thickness of Si decreases as Si is consumed during oxidation.
- In the beginning,  $\text{O}_2$  & Si react to form  $\text{SiO}_2$ . Once oxide layer is formed, further oxidation occurs at Si-  $\text{SiO}_2$  interface, but not on top of oxide.
- Oxide growth rate slows down with increase in oxide thickness because the oxidizing agent should move through the growing oxide layer in order to reach the Si surface.
- The interface produced by thermal oxidation is not exposed to atmosphere, minimizing the impurities. The oxide films thus formed are used in making both simple and complex semiconductor devices, in integrated circuits etc.

## 5) Explain with neat diagram the process of diffusion for the development of silicon wafers of known dopant concentration.

### Answer:

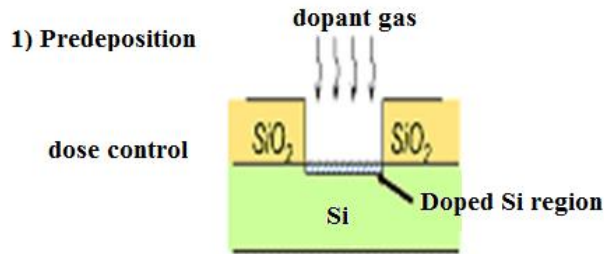
**Principle: Diffusion** is a process of selective doping of 'B' or 'P' atoms into semiconductor Si wafer.

- **Doping** means the introduction of impurities into the semiconductor wafer to change its conductivity.
- The specific area of silicon where dopants are to be introduced is precisely marked and  $\text{SiO}_2$  is etched from that area because impurities like B, P etc. do not diffuse through  $\text{SiO}_2$ .

The Si wafer ready for diffusion process is carried out in two steps. 1) Pre-deposition and 2) Drive in.

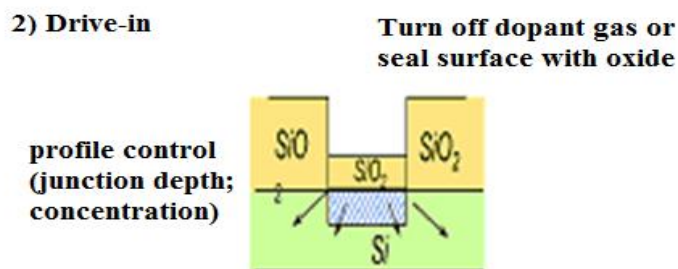
### **Pre-Deposition**

- i) In Pre-deposition, a high concentration of dopant atoms in vapour form is introduced on the Si surface at  $1000^\circ\text{C}$ .
- ii) At  $1000^\circ\text{C}$ , the dopant atoms penetrate through the silicon surface and get concentrated near the surface. This occurs due to the loss of energy at given temperature.
- iii) This process of dopant atom concentrating near the surface of wafer is also called as "Constant source deposition".
- iv) At this high temperature, the bonds in Si are broken and impurity atoms diffuse into the Si wafer because of the concentration gradient and replaces Si atoms in the bond.
- v) This process produces a shallow, heavily doped layer. This is also known as **constant source diffusion**.



### Drive-In

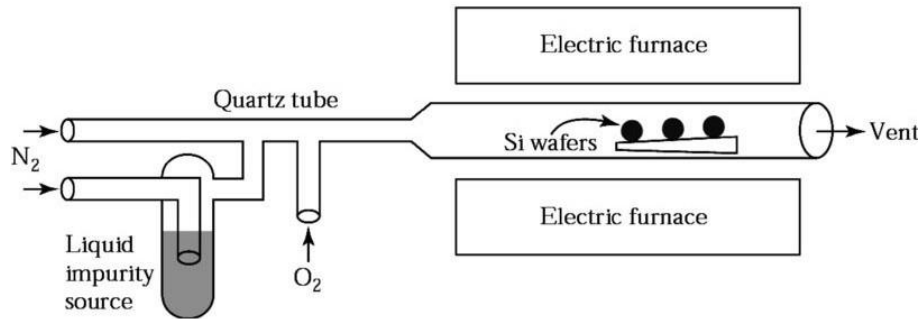
- i) After the desired amount of dopant is deposited on Si wafer during pre-deposition, the dopant source is removed during drive in process.
- ii) During drive-in process, the impurities are diffused deeply into the Si wafer.
- iii) For drive-in process the supply of impurity is stopped and the temperature raised to 1250°C.
- iv) As the dopant source is removed after pre-deposition, the total amount of impurities in the wafer remains constant during drive-in process.
- v) This reduces the surface concentration and increases the junction depth.
- vi) This process is done at higher temperature of 1100°C to 1250°C.
- vii) At high temperature of 1100°C, these impurities diffuse into Si wafer and their concentration reduce at the surface.
- viii) The diffusion depth is decided by the precise control of temperature and time of diffusion.
- ix) In drive-in, the dopant atoms are rich inside the silicon wafer. This is also called as **constant dose diffusion**.



After the doping is done only nitrogen gas is supplied to flush out any impurities left in the quartz tube and also to bring down the temperature so that silicon wafers can be taken out.

### Process

**Diffusion process** is carried out in an open tube diffusion reactor/furnace.



**Fig. Open tube diffusion system**

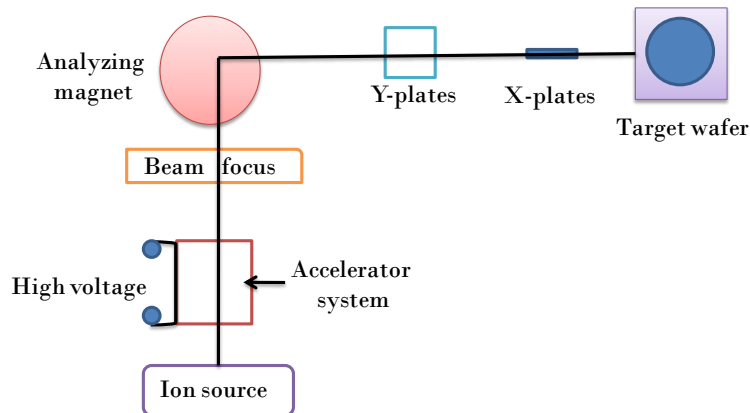
- It consists of a quartz tube inside of which movable quartz boat is present which acts as a carrier.
- Wafers are arranged on the quartz boat in series in order to have uniform doping on all wafers.
- Impurities are introduced into the furnace in vapour form using nitrogen & oxygen as carrier gases.
- Oxygen gas is introduced first to restore  $\text{SiO}_2$  (the place where it was over etched) and to oxidize any of the impurities which are carried away by nitrogen.
- After  $\text{O}_2$ , nitrogen gas is passed through dopant solution (diborane or phosphine) which will carry the dopant atoms to the surface of silicon wafer.
- Boron (acceptor impurity), & phosphorous (donor impurity) are two common sources of dopants/impurities for diffusion in silicon wafer. They have high diffusion rate in silicon, low diffusion rate in  $\text{SiO}_2$ .
- Quartz boat furnace is heated by means of electric furnace to a temperature of  $1000^\circ\text{C}$  when pre-deposition takes place. After pre-deposition, the supply of impurity is stopped by stopping nitrogen in liquid dopant and the temperature is increased to  $1100^\circ\text{C}$  to  $1250^\circ\text{C}$  and the drive-in process begins and driving the impurities deeply into the Si semiconductor.
- The diffusion depth is decided by the precise control of the temperature and time of diffusion.

## 6) Describe the technique of ion implantation used for doping process with neat diagram.

**Answer:** It is an alternate method of doping in which selected area of the wafer surface is bombarded with high energy (10,000 eV) impurity ions. For this selective doping technique, it is not mandatory to have any masking layer on the silicon surface.

- The dopant atoms are converted into highly concentrated tiny beam. These high energy ions can penetrate into the Si semiconductor.
- The faster the ions 'shot' at the wafer, the deeper they penetrate. On entering the wafer, due to collision with electrons and nuclei of silicon atoms, they lose their energy and stop penetration.

A simplified setup for ion implantation process is shown in the figure.



### **Procedure**

- Ion source consists of the dopant 'B' or 'P' material within a strong electric field.
- The strong electric field separates the dopant atoms into respective ions forming charged gaseous plasma.
- These charged ions are then induced to wanted velocity by controlling of high voltage in the accelerator system.
- Later, these charged high velocity ions are focused into a narrow beam of high velocity ions having current of the order of 1 mA.
- The beam is turned through  $90^\circ$  by using an analyzing magnet. The unwanted impurities in the beam are removed in analyzing magnet.
- The magnetic field in the analyzing magnet is set up in such a way that only the desired dopant turns through right angle ( $90^\circ$ ) and the unwanted impurities having different mass from that of the desired material are turned by different angle and are screened out by 'Y' plates.
- The focused beam of dopant ions is then passed through 'X' scanning plates which helps in proper implantation of ion beam over the target silicon wafer.
- The ion beam is moved over the target wafer up and down, as the implantation has to be done bit by bit.
- The depth of penetration of any particular type of ion will increase with increasing accelerating voltage.
- After the ion implantation process, the silicon wafer is subjected to annealing process at a temperature of  $800-1000^\circ\text{C}$  for period of 20 to 30 minutes to restore any mechanical damage on silicon wafer.

### **Advantages**

- The depth of the doping levels can be precisely controlled, because both the accelerating voltage and the ion beam current are electrically controlled outside the apparatus.
- Highly pure dopants can be added.
- Uniform doping over the silicon surface is possible.

- Doping area can be precisely defined since the spread of the directed ion beam is very little.
- As it is a low temperature process, the movement of impurities is less within the Si wafer.

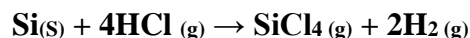
## 7) Explain with neat diagram a typical vapour phase epitaxial growth system.

### Answer: Procedure:

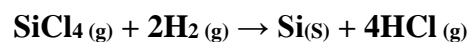
- The silicon wafers are placed in a boat shaped graphite crucible and kept in a long cylindrical quartz tube with inlet and outlet for gases.
- The reactive gases are introduced into the reaction chamber based on the selection of semiconductor material and the dopant atoms.
- The system is heated by RF coil to a temperature of 1200°C. At this temperature, semiconductor formation takes place and grows on the silicon semiconductor substrate.
- The byproduct gases like H<sub>2</sub> and HCl are vented away from the quartz tube.
- The thickness of the layer varies from 3 to 30 microns. This type of epitaxial growth is called as vapour phase epitaxial growth.

### Steps involved in vapour phase epitaxial growth:

- Hydrogen gas is passed to purify the reactor of any impurities.
- HCl gas is passed for vapour phase etching of silicon semiconductor wafer surface at a temperature of 1150°C to 1250°C for 3 minutes. Thin region of damaged Si is removed from the silicon wafer surface by means of HCl etching.



- Vapours of H<sub>2</sub> and SiCl<sub>4</sub> are passed into the reaction chamber for producing **silicon on silicon** epitaxial layer. This process of epitaxial growth is known as **chemical vapour deposition** as all the chemicals introduced and that take part in the reactions are in the form of gaseous state.

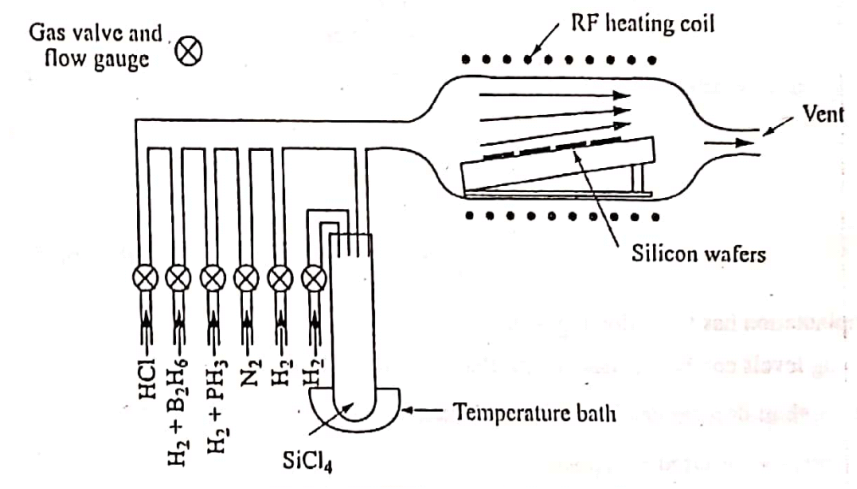


- H<sub>2</sub> and Diborane (B<sub>2</sub>H<sub>6</sub>) are supplied for p-type epitaxial layer growth on silicon wafer.
- H<sub>2</sub> and Phosphene (PH<sub>3</sub>) are supplied for n-type epitaxial layer growth on silicon wafer.
- Once the growth is completed, the dopant atoms and silicon flows are eliminated and temperature is reduced by shutting the power off.
- H<sub>2</sub> gas is passed to purify the reactor of any impurities left out in the reactor.
- As the reactor cools down to ambient temperature, the H<sub>2</sub> flow is replaced by N<sub>2</sub> flow so that the reactor may be opened up safely.

### Advantages of using SiCl<sub>4</sub> as source



- $\text{SiCl}_4$  is non-toxic, inexpensive and easy to purify.
- The reaction of  $\text{SiCl}_4$  and the formation of Si takes place only on the Si surface and not on boat or reaction chamber walls.



## 8) Explain with neat diagram different lithographic steps involved in selective diffusion over a wafer.

**Answer:** Photolithography is a process of transferring geometric shapes or images on a mask to the surface of a silicon wafer by the use of UV light and a photo resist.

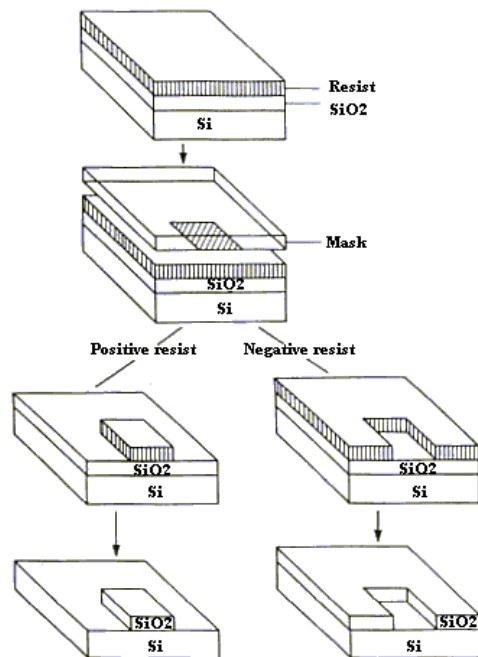
The steps involved in the photolithographic process are as follows:

### 1) Wafer Cleaning and Barrier Formation

In the first step, the wafers are chemically cleaned to remove any traces of organic, ionic, and metallic impurities. After cleaning, silicon dioxide, which serves as a barrier layer, is deposited on the surface of the wafer.

### 2) Photo resist Application (Spinning)

A drop of **light-sensitive liquid** called photoresist is applied on the surface of the oxidized silicon wafer. The wafer is then accelerated rapidly to a rotational velocity in the range **3000 to 7000 RPM for 30-60 seconds**. The spinning spreads the solution in a thin, nearly uniform coat and spins out the excess liquid. The thickness of the coat so obtained is in the range **5000 to 10000 Å**.



### **3) Prebake**

The silicon wafers coated with photo resist are now put into an oven at about 80°C for about 30-60 minutes to remove solvents in the photo resist and to harden it into a semisolid film.

### **4) Mask Alignment and Exposure**

A mask or "photomask" is a square glass plate with a patterned emulsion of metal film on one side. The mask is aligned with the wafer, so that the pattern can be transferred onto the wafer surface. Once the mask has been accurately aligned with the pattern on the wafer's surface, the photoresist is exposed through the pattern on the mask with a high intensity UV light. The exposure time is generally in the range 3-10 seconds and is carefully controlled such that the total UV radiation, and then developed in a developer.

### **5) Post bake**

After development and rinsing, the wafers are postbake in an oven at a temperature of about 150°C for about 30-60 minutes to further strengthen the remaining resist on the wafer. The photo resist adheres better to the wafer and make it more resistant to the hydrofluoric acid (HF) solution used for etching of the silicon dioxide.

### **6) Oxide Etching**

The remaining resist is hardened and acts as a convenient mask through which the oxide layer can be etched away to expose areas of semiconductor underneath. These exposed areas are ready for impurity diffusion.

For etching of oxide, the wafers are immersed in or sprayed with a hydrofluoric acid solution. This solution is usually a diluted solution of typically 10:1,  $\text{H}_2\text{O}:\text{HF}$ , or more often a 10:1  $\text{NH}_4\text{F}:\text{HF}$  solution. The HF solutions will etch the  $\text{SiO}_2$  but will not attack the underlying silicon, nor it will attack the photo resist layer to any considerable degree. The wafers are exposed to the etching solution to remove the  $\text{SiO}_2$  completely in the areas of the wafer that are not covered by the photo resist.

### **7) Photoresist Stripping**

Following oxide etching, the remaining resist is finally removed with a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  and with the help of scratch process. Finally washing and drying completes the required window in the oxide layer. The figure below shows the silicon wafer ready for next diffusion.

**5)** A silicon crystal is to be grown by Czochralski process and is to contain  $5 \times 10^{15}$  boron atoms per  $\text{cm}^3$ . Given:  $K_0 = 0.8$  for boron in silicon, atomic weight of B = 10.81g/mole, density of Si =  $2.33\text{g/cm}^3$ , Avogadro number =  $6.023 \times 10^{23}$  atoms/mole.

- a. Determine the initial concentration of boron atoms in the melt to produce the required density.
- b. If initial amount of silicon in the crucible is 50 kg, how many grams of boron should be added?

**6)** Define segregation constant ( $K_0$ ). A semiconductor crystal with acceptor concentration,  $N_A$  is  $2 \times 10^{16}$  atoms/ $\text{cm}^3$  must be obtained by Czochralski crystal pulling technique. What weight of Boron must be added to the melt if it contains 10 Kg of Si?

Given:  $K_0 = 0.8$  for Boron in Si;

Atomic weight of B = 10.81g/mole, Density of Silicon =  $2.33 \text{ g/cm}^3$ ,

Avogadro number =  $6.023 \times 10^{23}$  atoms/mole

**7)** A silicon crystal is to be pulled from the melt and doped with phosphorus. If Si weight is 1 Kg, how many grams of phosphorus should be introduced to achieve a donor concentration of  $2 \times 10^{15}$  atoms/ $\text{cm}^3$  during initial growth?

Given:  $K_0 = 0.32$  for P in Si;

Atomic weight of P = 30.97g/mole, Density of Si =  $2.33\text{g/cm}^3$ , Avogadro number =  $6.023 \times 10^{23}$  atoms/mole.

**8)** Determine the ratio of silicon consumed to the thickness of grown  $\text{SiO}_2$  layer over the wafer. If  $\text{SiO}_2$  layer of  $1000 \text{ }^\circ\text{A}$  is to be grown, what would be the thickness of used silicon? Given:

Atomic weight of Si = 28.09 g/mol. Density of Si = 2.33 g/cm<sup>3</sup>.

Molecular weight of SiO<sub>2</sub> = 60.08 g/mol.

Density of SiO<sub>2</sub> = 2.20 g/cm<sup>3</sup>.

**9)** Determine the ratio of Si consumed to the thickness of grown SiO<sub>2</sub> layer over the wafer. If 100 °A thick Si is used for the process, what would be the thickness of SiO<sub>2</sub> grown? Given: Atomic weight of silicon = 28.09 g/mol. Density of silicon = 2.33 g/cm<sup>3</sup>. Molecular weight of SiO<sub>2</sub> = 60.08 g/mol. Density of SiO<sub>2</sub> = 2.20 g/cm<sup>3</sup>.

**10)** Calculate the increase in thickness of Silicon wafer during the process of oxidation, if 50 °A thick Si is used for the process. Given: Atomic weight of Si = 28.09 g/mol. Density of Si = 2.33 g/cm<sup>3</sup>. Molecular weight of SiO<sub>2</sub> = 60.08 g/mol. Density of SiO<sub>2</sub> = 2.20 g/cm<sup>3</sup>.

**11)** Phosphorus is implanted in n-type silicon sample with a uniform doping concentration of 5 x 10<sup>16</sup> atoms/cm<sup>3</sup>. If the beam current density is 2.5 µA/cm<sup>2</sup> and the implantation time is 8 minutes, calculate the implantation dose.

## Chapter 6. Material Chemistry

**1) Define liquid crystals and explain the classification of liquid crystals with examples.**

**Answer:** Liquid Crystal state may be defined as any state of matter where the molecules are orientationally ordered but yet are in dynamic motion.

### Classification of Liquid Crystals

Liquid crystals are classified into two main categories, viz,

- (i) Thermotropic liquid crystals and
- (ii) Lyotropic liquid crystals

**1. Thermotropic liquid crystals:** The class of compounds that exhibit liquid crystal behaviour on variation of temperature alone are referred to as Thermotropic Liquid crystals.

The temperature ranges at which some liquid crystals are stable are:

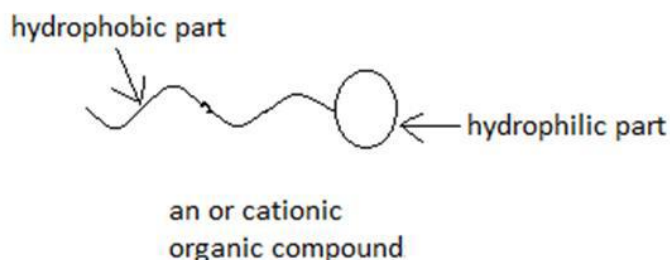
Compound	Solid	Liquid Crystal	Liquid
(i) Cholesteryl benzoate		145.5°C	178.5°C

(ii) p-azoxy phenetole	137°C	167°C
(iii) p-azoxy anisole (PAA)	116°C	135°C
(iv) p-methyl benzylidene – p' - n butyl aniline (MBBA)	21°C	47°C

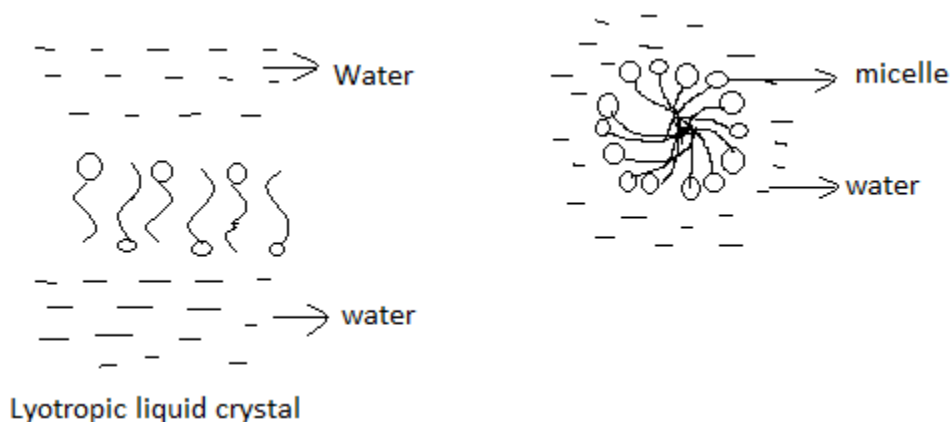
The liquid crystal state can be observed by carefully raising the temperature of a solid or by lowering the temperature of a liquid.

2. **Lyotropic liquid crystals:** Lyotropic liquid crystals are obtained by mixing the two components and increasing the concentration of one of the components till liquid crystal phase is observed.

e.g., Soap molecules (Soap - water mixture) and phospholipids (phospholipids water mixture)



Lyotropic liquid crystals are typically obtained from amphiphilic compounds comprising of both lyophilic (solvent attracting) and lyophobic (solvent repelling) ends in the same molecule. In the presence of a solvent, lyophobic ends come together while lyophilic ends are directed towards solvent forming 'micelles'.



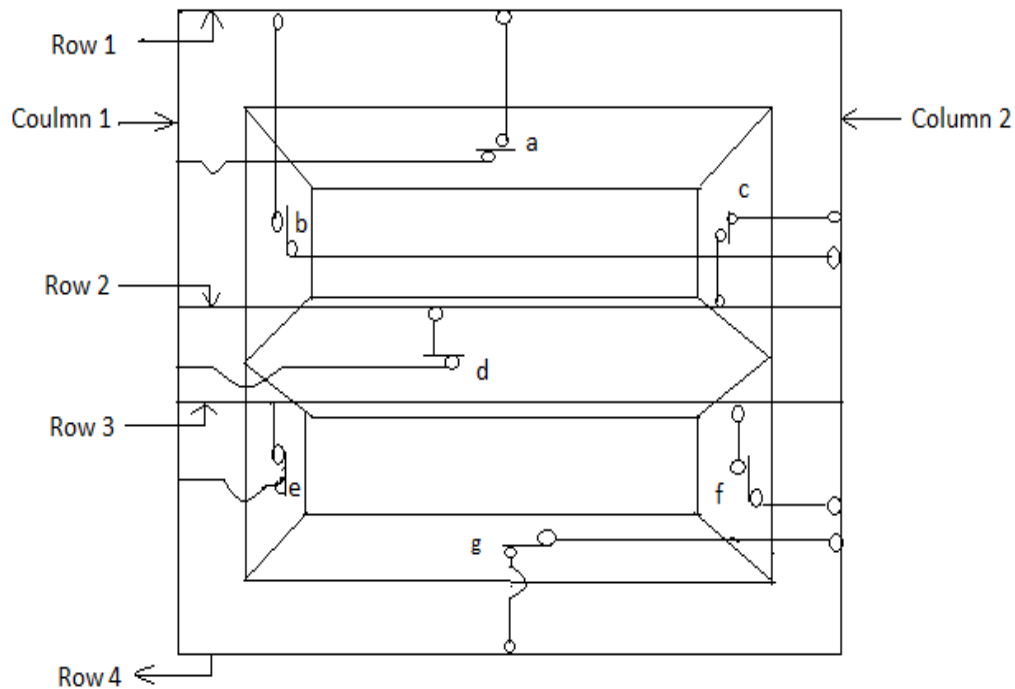
The formation of micelles takes place only beyond a certain concentration (50 to 100 molecules of amphiphilic compound) of the solution called, critical micelle concentration (CMC). When the concentration of the solution is increased beyond CMC, the micelles swell or increase in size and eventually coalesce to form liquid crystals phase.

**2) Explain the process of liquid crystal display with respect to 139.**

**Answer: Seven segment LCD for a digit:**

Each row is connected to two segments and each column is connected to three or four segments a, b, c, d, e, f and g are LCD cells.

The voltage is applied to rows and columns for operations I to VII to activate and brighten Liquid Crystals ‘a’ to ‘g’ respectively.

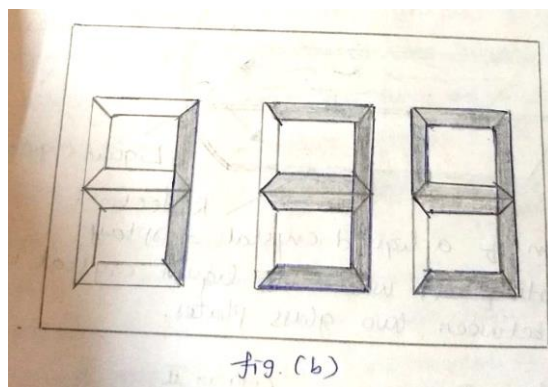


“Seven segment LCD for a digit; each row is connected to two segments and each column is connected to three or four segment; a, b, c, d, e, f & g are LCD cells”

When voltage is applied to a particular row and corresponding column, the respective liquid crystal in that area gets brightened according to the table given below.

Voltage applied to: Rows	Area where LC gets activated and brightened	
	Columns	
	C1	C2
R1	a	b
R2	d	c
R3	e	f
R4		g

### Display of Number 139



- For example, to get a number 139 on the display an electric field is applied between row 2 and column 2 ('c') and between row 3 and column 2 ('f') to give **1** on the display.
- For the second digit, an electric field should be applied to row 1 and column 1 ('a'), row 2 and column 2 ('c'), row 2 and column 1 ('d'), row 3 and column 2 ('f') and row 4 and column 2 ('g') to give **3** on the display.
- For the third digit, an electric field should be applied to row 1 and column 1 ('a'), row 1 and column 2 ('b'), row 2 and column 2 ('c'), row 2 and column 1 ('d'), row 3 and column 2 ('f') and row 4 and column 2 ('g') to give **9** on the display.
- In order to enhance the difference in the brightness between dark (turned OFF, voltage removed) and bright areas (turned ON, voltage applied), dyes are used.
- Dyes used in liquid crystal displays are called dichroic dyes and give desired colors to the displays with a good contrast.

### **3) Explain the process of fluorescence and phosphorescence with help of Jablonski diagram.**

#### **Answer:**

**Fluorescence:** When a beam of light is incident on certain substances, they emit visible light or radiations & they stop emitting light or radiations as soon as the incident light is cut off. This phenomenon is known as fluorescence. Such substances which emit radiations during the action of stimulating light are called fluorescent substances.

**Phosphorescence:** When a light radiation is incident on certain substances, they emit light continuously even after the incident light is cut off. This type of **delayed fluorescence is called phosphorescence** and the substances are called **phosphorescent substances**.

The phenomenon of fluorescence and phosphorescence can readily be followed by **Jablonski diagram**.

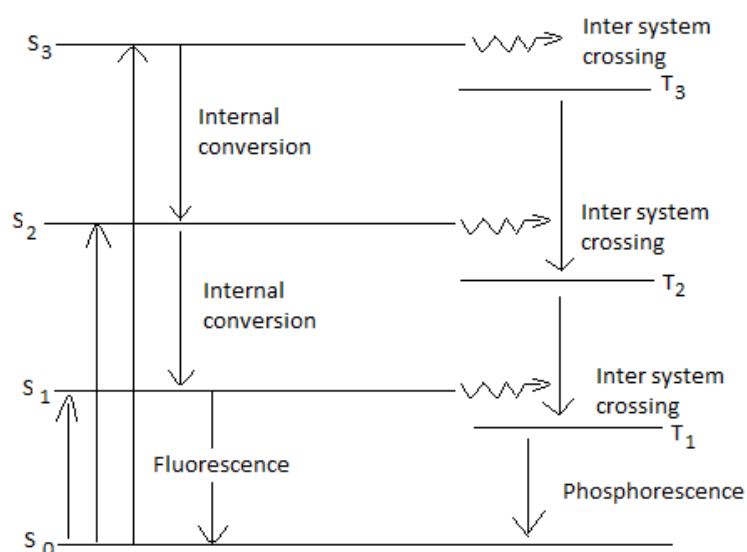
Since the electron can jump to any of the higher electronic states depending upon the energy of the photon quantum absorbed, it is possible to get a series of singlet excited states,  $S_n$  ( $n = 1, 2, 3, \dots$ ) & a series of triplet excited states  $T_n$  ( $n = 1, 2, 3, \dots$ ).

In other words,  $S_1, S_2, S_3$ , etc., are known as first singlet excited state, second singlet excited state, third singlet excited state etc., and  $T_1, T_2, T_3$  etc., as first triplet excited state, second triplet excited state and third triplet excited state, etc.

It has been shown quantum mechanically that a singlet excited state has higher energy than the corresponding triplet excited state. Accordingly, the energy sequence is:

$$ES_1 > ET_1; ES_2 > ET_2; ES_3 > ET_3$$

On absorption of light photon, the electron of the absorbing molecule may jump from  $S_0$  to  $S_1, S_2$  or  $S_3$  singlet excited state, depending upon the energy of the light photon absorbed, as shown in the following Jablonski diagram for various photo physical processes.



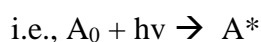
**Jablonski Diagram**

Radiative Transition: IC: Internal conversions; ISC: Inter system crossing;

Radiative Transition: FL: Fluorescence; PS: Phosphorescence.

For each singlet excited state ( $S_1, S_2, S_3$ , etc.,) there is a corresponding triplet excited state ( $T_1, T_2, T_3$ , etc.,)

The molecule whether in singlet or triplet excited state is said to be activated.



Where  $A_0$  is the molecule in the ground state and  $A^*$  is the molecule in the excited state. The activated molecule returns to the ground state by dispersing its energy through the following transitions.

- Spectroscopically the transition from  $S_1$  to  $S_0$  state is an allowed transition and occurs in about  $10^{-8}$  sec. The emission of radiation in this transition is called **Fluorescence**.



- The transition from  $T_1$  to  $S_0$  is rather slow as it is a forbidden transition spectroscopically and has longer life time of the order of  $10^{-3}$  sec to 20 sec or (longer) greater since the transition involves spin inversion which needs time for its occurrence. The emission of radiation in this transition is called **Phosphorescence**.
- Both fluorescent and phosphorescent radiations are of shorter frequencies than the exciting light. This is obvious because some part of light energy absorbed by the molecules is lost in the form of heat during the non-radiative transitions.

### **Characteristics of Fluorescence**

- 1) It is an instantaneous phenomenon, i.e., starts immediately re-emitting excess radiation within  $10^{-8}$  sec of absorption of light and stops as soon as the incident light is cut off.
- 2) It is stimulated by light of the visible or UV regions of the spectrum.
- 3) It is a general phenomenon and is exhibited by gases liquids and solids. No fluorescence will be observed in gases unless the pressure is low.

### **Characteristics of Phosphorescence**

- 1) It is a non-instantaneous phenomenon i.e., reemit excess radiation within  $10^{-3}$  to 20 seconds or longer. Thus, the life time of phosphorescence is much longer than fluorescence.
- 2) It is stimulated chiefly by UV and Violet parts of the spectrum.

### **Applications:**

The phenomena of fluorescence and phosphorescence find useful applications in the development of X - ray and TV screens, fluorescent tube lights, optical brighteners, in white dress materials, luminescent dials for watches, in quantitative and qualitative analysis of inorganic and organic substances and in the sample analysis of food, pharmaceutical and medical fields.

## **4) What are thermoelectric and piezoelectric materials and mention their properties and applications.**

### **Answer: Thermoelectric Materials**

Certain materials allow heat to be pumped from one place using electricity. While some materials allow electricity to be generated from heat. These materials are called **Thermoelectric, TE, Materials**.

The conversion of waste heat into electrical energy play an important role in our current challenge to develop alternative energy technologies to reduce dependence on fossil fuels and reduce greenhouse gas emissions.

### **Properties:**

The TE effect refers to a phenomenon by which either a temperature difference creates an electric potential called '**Seebeck effect**' or an electric potential creates a temperature difference called '**Peltier effect**'.

The Peltier effect is the basis for many modern-day refrigeration devices and Seebeck effect is the basis for TE power generation devices.

### **Applications**

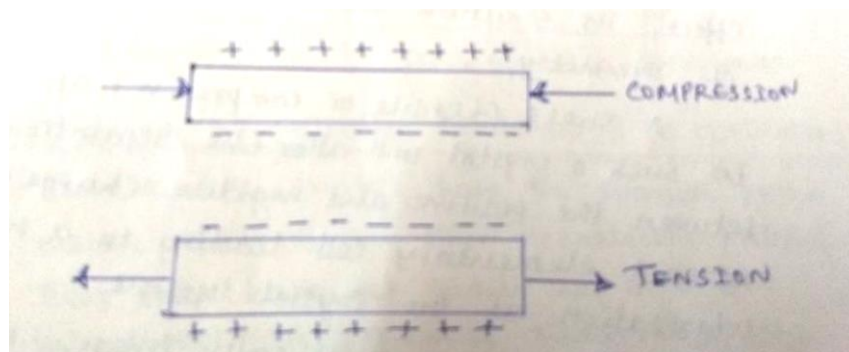
- 1) **Power Generation:** Nearly 90% of world's electricity is generated by thermal power stations, i.e., by heat energy, whose efficiency is around 30-40%, thereby dissipating enormous power in the form of heat to the environment. TE devices could convert this waste heat into useful electricity. TE devices also find applications in systems such as solar thermal energy.
- 2) **Refrigeration:** TE coolers or Peltier coolers don't require refrigerant fluids, such as CFCs which can have harmful environmental effects.  
TE refrigeration is an environmentally 'green' method of small-scale localized cooling in computers, IR detectors, electronics and opto-electronics.
- 3) **Novel applications:** Bio thermal batteries, power heart pace makers, power generation for deep-space probes via radioisotope - TE generators.

### **Piezo-electric Materials**

Materials when subjected to suitable force, produce electrical potentials linearly related to the mechanical strains. This effect is known as '**Piezo Electric Effect**'.

These same materials deformed when they were exposed to an electric field. This is known as '**inverse piezo electric effect**'.

Piezo electric effect is explained as:



The compression along the axis causes the upper surface to become +ve with respect to lower. If the material is subjected to a tension as a result of applied voltage or electric field along the axis, the polarity seems to be reversed.

Since piezo electric effect is reversible, all types of piezo-electric microphones will function as weak sources of sound when an alternating voltage is applied.

For a crystal to exhibit the piezo electric effect, its structure should have no centre of symmetry.

The common types of piezo electric substances are Rochelle 's salt, Ammonium dihydrogen phosphate, ADP, Lithium sulphate crystals and Barium titanate ceramic plates.

**Application:**

Piezo electric substances have been widely used in crystal microphones that must operate over a wide range of temperature. Piezo electric microphones are widely used in public system and for hearing aids. These are highly sensitive, low in cost and small in size. These respond to frequencies ranging from 20Hz to 40Hz.

April\_2022

15ECHB102

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**I Semester B.E. Examination  
(Common to All)  
Engineering Chemistry (15ECHB102)**

**Max. Marks: 100**

**Duration: 3 hours**

**Note:** i) Answer any TWO full questions from UNIT-I, any TWO full questions from UNIT-II and any ONE full question from UNIT-III.

**UNIT-I**

1. a. Explain the salient features of Molecular Orbital Theory and draw the MO diagram of  $H_2$  molecule and calculate its bond order. (07 marks)
- b. Explain the free radical mechanism of addition polymerization by taking ethylene as an example. (07 marks)
- c. An electrochemical cell consists of iron electrode dipped in 0.1 M  $FeSO_4$  and silver electrode dipped in 0.05 M  $AgNO_3$  solution. The standard reduction potential values of iron and silver are -0.44 V and 0.80 V respectively. Write the cell representation, cell reactions and calculate emf of the cell at 298 K. (06 marks)
2. a. Define single electrode potential. Derive Nernst equation for single electrode potential of an electrode. (07 marks)
- b. What are polymers? Explain the synthesis, properties and applications of polyurethanes. (07 marks)
- c. Define ion bond. The dipole moment of HCl molecule is 1.03D. For complete transfer of electrons, the charge on  $H^+$  and  $Cl^-$  ions would be equal to  $4.8 \times 10^{-10}$  esu. The length of HCl bond is  $1.275 \times 10^{-8}$  cm. Calculate the percentage of ionic character in HCl. (06 marks)
3. a. Describe the construction, working and applications of methanol-oxygen fuel cell. (07 marks)
- b. Explain the construction, working and applications of lead-acid battery. (07 marks)
- c. A polymer sample contains 2, 3, 4 and 5 molecules having molecular weights  $2 \times 10^5$ ,  $3 \times 10^5$ ,  $4 \times 10^5$  and  $5 \times 10^5$  respectively. Calculate the number average and weight average molecular weights of a polymer sample. (06 marks)

**UNIT-II**

4. a. Describe the electroless plating process of copper and its application in the preparation of PCB with neat diagram. (07 marks)
- b. Describe with neat diagram the fabrication process of thermal oxidation with relevant reactions. (07 marks)
- c. Explain the process of fluorescence and phosphorescence with the help of Jablonski diagram. (06 marks)
5. a. Discuss in detail the process of Czochralski crystal pulling technique in the production of single crystal silicon. (07 marks)
- b. What are liquid crystals? Explain the classification of liquid crystals with example. (07 marks)
- c. Determine the ratio of silicon consumed to the thickness of grown  $SiO_2$  layer over Si wafer. If  $SiO_2$  layer of 5000Å is to be grown, what would be the thickness of used Si? Given: Atomic weight of Si = 28.09 g/mole, Density of Si = 2.33 g/cm<sup>3</sup>, Molecular weight of  $SiO_2$  = 60.8 g/mole and Density of  $SiO_2$  = 2.20 g/cm<sup>3</sup>. (06 marks)



- 6 a. Describe with block diagram, the technique of ion implantation employed for the fabrication of n or p type Si wafers. (07 marks)
- b. Define throwing power. Explain the determination of throwing power of plating bath solution using Haring-Blum Cell.  $x = \frac{d_1}{d_2}$   $d_1 > d_2$   $\gamma = \frac{w_2}{w_1}$  (07 marks)
- c. A silicon crystal is to be pulled from the melt and doped with phosphorus. If Si weight is 1 kg, how many grams of phosphorus should be introduced to achieve a donor concentrations of  $2 \times 10^{15}$  atoms/cm<sup>3</sup> during initial growth?  
Given:  $K_0 = 0.32$  for 'P' in silicon; Atomic weight of 'P' = 30.97 g/mole; Density of Si = 2.33 g/cm<sup>3</sup>; Avogadro number =  $6.023 \times 10^{23}$  atoms/mole. (06 marks)

### UNIT-III

- 7 a. Explain the principle and methodology involved in potentiometry with respect to FAS. (07 marks)
- b. Discuss with neat diagram the working of double beam UV-Spectrophotometer. (07 marks)
- c. In the colorimetric estimation of copper, the optical density values for the series of solutions of concentrations  $1 \times 10^{-2}$ ,  $2 \times 10^{-2}$ ,  $3 \times 10^{-2}$ ,  $4 \times 10^{-2}$ ,  $5 \times 10^{-2}$ ,  $6 \times 10^{-2}$  &  $7 \times 10^{-2}$  moles/dm<sup>3</sup> are 0.08, 0.16, 0.25, 0.33, 0.42, 0.50 & 0.58 respectively. Verify Beer-Lamberts law with neat graph and calculate the amount of copper present in the supplied solution whose optical density is 0.21. (06 marks)
- 8 a. Discuss the determination of total hardness of sample of water by Na<sub>2</sub>EDTA method. (07 marks)
- b. Explain the determination of COD of a sewage sample. (07 marks)
- c. Define COD. 20 ml of sewage sample for COD is reacted with 25 ml of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution and the unreacted K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> requires 9.0 ml of 0.25 N FAS solution. Under similar condition, in blank titration 15.0 ml same FAS is used up. Calculate the COD of the sewage sample. (06 marks)