THIN FILMS & ALLOYS

> **Thin Films, Alloys:** [6 hours]
> Thin films: Method of preparation – Chemical and physical methods, Thermal evaporation in vacuum including sputtering, examples of application, Alloys, phase diagram, examples of Pb and Sn.

Thin films:

Thin films are thin material layers of thickness ranging from fractions of a nanometer to several micrometers. Thickness of thin film depends on the purpose for which it is prepared. The material on which thin film is coated is known as the substrate.

There are mainly two methods of preparation (i) Physical methods and (ii) Chemical methods.

Chemical deposition:

In chemical deposition, a fluid precursor undergoes a chemical change at a solid surface leaving a solid layer.

Example: The formation of soot on a cool object when it is placed inside a flame. Since the fluid surrounds the solid object, a deposition occurs on every surface, with out any regard to direction. Therefore, thin films formed by chemical deposition techniques tend to be conformal [comply with rules, standards or conventions] rather than directional.

Chemical deposition is categorized in to the following three types depending on the phase of the precursor.

1. **Plating: It uses liquid precursors**. The solution of a salt of a metal in water is used to deposit the film. Some plating processes are driven entirely by reagents in the solution [usually for noble metals], but electroplating is the most important commercial process used for plating.

2. **Chemical Solution Deposition** [CSD]: It uses a Liquid precursor. Usually a solution of organo-metallic powders dissolved in an organic solvent is used in the deposition process. This is relatively inexpensive, simple thin film process that is able to produce stoichiometrically accurate crystalline phases.

3. **Chemical Vapour Deposition** [CVD]: This process generally uses a gas phase precursor often a halide hydride of the element to be deposited. In the case of metal oxide CVD, an organo-metallic gas is used. Commercial techniques often use very low pressures of precursor gas. Plasma Enhanced CVD uses an ionized vapour or plasma as precursors. Commercially PECVD uses electromagnetic means [electric current, microwave excitation] rather than a chemical reaction to produce plasma.

Physical Vapour Deposition: In this method, physical processes such as high temperature vacuum evaporation or plasma sputter bombardment is used to form thin film on surfaces such as semiconductor wafers. Physical vapour deposition uses mechanical or thermo-dynamical means to produce thin film of solid. In this case, the material to be deposited is placed in an energetic, entropic environment, so that particles of material escape from the solid surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum chamber to allow the particles to travel as freely as possible. Since the particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

Different Physical vapour deposition processes in the order of increasing order of novel method are;

1. **Thermal Evaporative deposition:** In this method the material to be deposited is heated to a high vapour pressure by electrically resistive heating in 'low' vacuum.

2. **Electron beam physical vapour deposition:** In this method the material to be deposited is heated to a high vapour d\pressure by electron bombardment in "high" vacuum.

3. **Sputter deposition:** In this method a glow plasma discharge [usually localized around the target by a magnet] bombards the material sputtering some away as a vapour.

4. **Cathodic arc deposition:** In this method high power arc directed at the target material blasts away some into a vapour.

5. **Pulsed laser deposition:** In this method a high power laser ablates material from the target into a vapour.

> **Note:** An essential difference between PVD and CVD techniques is that in the first methods the material to be deposited already exists in pure solid form, while in the second method the material does not exist in pure solid phase originally, but it is synthesized in vapour phase of the solid to be deposited.

Thermal evaporation in vacuum:

In this method the material to be deposited is heated until it evaporates in a vacuum chamber. The material vapour finally condenses in the form of thin film on the cold substrate surface and on the inner walls of the vacuum chamber. The chamber is evacuated to a pressure of about 10^{-6} to 10^{-5} Torr, to avoid the reaction of vapour with the atoms of the residual gas. At such low pressures, the mean free path of vapour atoms is of the order of the dimensions of vacuum chamber, so these particles travel in straight lines from the evaporation source towards the substrate.

The schematic diagram of the technique used is as shown in figure (1)
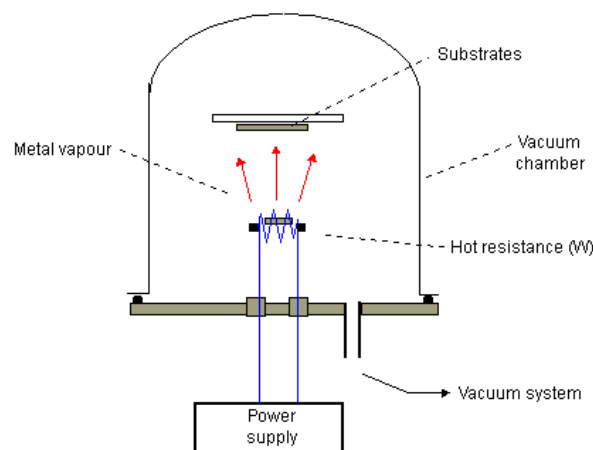
The material to be deposited is heated by means of an electric current passing through a filament or metal plate. Due to Joule's heating the material surrounding the filament melts and evaporates. The evaporated material condenses on the substrate. Heating is done also by using RF coil surrounding a graphite or BN crucible containing the material to be evaporated. This arrangement is simple and results are useful for depositing metals and some compounds with low fusion temperature such as Al, Ag, Au, SiO, etc.

Typical metals used as heating resistance are Tantalus [Ta], Molybdenum [Mo], and Wolfram [W] with vapour pressure practically zero at the evaporation temperature [1000 – 2000 ^{0}C]. While selecting the heating coil it is convenient to use such material for deposition that wets the metal filament. Due to proximity of material to the filament, evaporation occurs quickly.

Sputter deposition:

Sputtering is a technique used to deposit thin films of a material on to a substrate by first creating gaseous plasma [or a stream of electrons emitted from an electrons gun] and then accelerating the ions from this plasma [or electron] into some source material. The source material is eroded by the arriving ions [or electron] and via energy transfer the material is ejected in the form of either individual atoms or clusters of atoms or molecules. As these neutral particles are ejected they travel in a straight line and form a deposition on the surface they come in to contact.

Thin film deposition by sputter technique using an electron beam heating is as shown in the following figure (2)
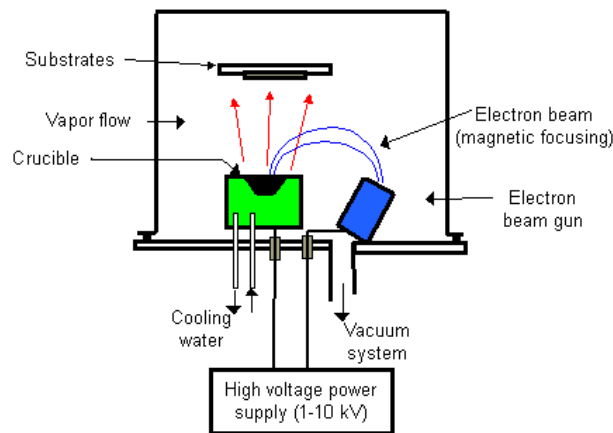
The electron beam generated by and electron gun is accelerated towards an anode by a high potential difference [kilovolts]. The crucible acts as anode or a perforated disc near the crucible act as the anode. A magnetic field is often applied to bend the electron trajectory so that the electron gun can be positioned below the evaporation line.

The focusing of electron on the material locally heats the material and causes it to evaporate with high density of evaporation power [several kW]. This allows to control the evaporation rate, from low to very high values and useful for depositing materials with high melting point [W, Ta, C, etc.].The crucible is cooled by circulating cold water to avoid contamination problems from heating and degasification.

Applications:

1. Thin films are used to produce thin film batteries.

2. Work is being done to use Ferromagnetic thin films for use as computer memory.

3. Ceramic thin films are widely used due to relative hardness and inertness. Such coatings are used to protect the substrate material against corrosion, oxidation and wear. The use of such coating on cutting tools can extend the life of these tools by several orders of magnitude.

4. Pharmaceutical industry uses thin films for drug delivery known as thin film drug delivery.

5. Sputtering with an inert gas is used to remove atoms from a material known as ion milling or ion etching.

6. Thin film deposition is used for decoration on glasses and precious metals. Such coating of variable thickness of the same material gives a decorative look to the painting as the colour reflected by thin film depends upon the thickness of thin film.

Alloy

An alloy is a partial or complete solid solution of two or more elements in a metallic matrix. Complete solid solution alloys give single solid phase microstructure, while partial solutions give two or more phases that may be homogeneous in distribution depending on thermal (heat treatment) history.

In other words, an alloy is a metal product containing two or more elements (i) as a solid solution or (ii) as an inter – metallic compound or as a mixture of metallic phases

Alloys have specific properties or production characteristics that are more attractive than those of pure metals. Some examples are; (i) Some alloys have high strength, (ii) Some alloys have low melting point, (iii) Some alloys are refractory with high melting temperature (iv) Some alloys are especially resistant to corrosion. (v) Some alloys have desirable magnetic, thermal and electrical properties. These properties arise because of both internal and electronic structure of alloys and inter-atomic forces of the alloys.

Example of some useful alloys:

1. Stainless steel: It is an alloy of Iron with 18% Chromium and 8% Nickel. It is resistant to corrosion.
2. Alloys used in bearings in machinery parts is an alloy of 70% Copper and 30% Lead.
3. Solder used for electrical circuitry is an alloy of 60% Tin and 40% Lead.
4. Dental alloy [amalgams] is an alloy of Silver – Mercury alloy containing minor amount of Tin, Copper and Zinc. [33%Ag, 32% Hg, 12%Sn, 2% Cr and < 1% Zn]. Dental gold alloy contain 80 – 90% gold, 3 – 12 % Silver & 2 – 4% Copper. For higher strength and hardness palladium and platinum [upto 4%] are added. Vitallium alloy used for dental bridge work has 27% Cobalt, 5.5% Chromium and 3% Molybdenum.
5. Fusible alloys are made from Lead, Cadmium, bismuth, Tin, Antimony and Indium.
6. Superconducting alloy Nb_3Sn has a critical temperature of 23 K. High temperature superconducting materials can be produced by using different elements in suitable proportions.
7. Gold ornaments are prepared using gold alloys. Pure gold is known as 24 karat [K]. 18 karat gold has 18/24 part of gold [75%]. 14 karat gold has 58.3% pure gold. Elements added to gold are Copper, Silver, Nickel and a little Zinc. Addition of these metals changes the colour of gold to red, yellow, greenish and white gold depending on the proportion of these elements taken.

Phase diagram:
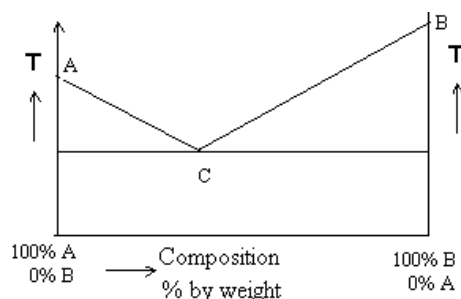
Phase diagram is a map or a graph of temperature versus composition of one of the constituent metals. As the composition of one metal increases, the composition of the second metal decreases and hence the extreme ends of the x – axis represented by the two ordinates indicate 100% of metal A and 100% of metal B.

In the study of phase diagram of any alloy the following definitions and their interrelation should be understood properly.

1. **Phase:** Phase is a homogeneous, physically distinct part of a system bounded by a surface and that can be mechanically separable from the other parts of the system.

Examples: (a) A gaseous mixture exists in a single phase. (b) Immiscible liquids such as water and kerosene form distinct layers and are physically separable from one another and hence they constitutes different phases (c) Completely miscible liquids such as water in alcohol or Benzene in Chloroform form one phase system

2. **Components:** The number of components of a system in equilibrium is defined as the number of independently variable constituents by means of which the composition of each phase can be expressed either directly or in terms of chemical equations.

   Examples:

   (i) Water exists in three phases. They are; Ice $\leftrightarrow$ liquid $\leftrightarrow$ vapour. However, the composition of each phase can be expressed in terms of H_2O. Hence, it is a one component system.

   (ii) Sulphur exists in 4 phases. They are rhombic, monoclinic, liquid and vapour sulphur. But the composition of each phase is expressed in terms of Sulphur only. Hence it is a one component system.

   (iii) Aqueous solution of Sucrose: This can be expressed by specifying the amount of sugar and water. Hence it is a two component system.

   The number of components in a system is given by the equation, **C = N – E.** Where N is the number of species, E is the number of independent equations relating concentration of N species and C is the number of components.

   Examples:

   (i) KCl – NaCl – H_2O system: In this case N = 3 [KCl, NaCl & H_2O], E = 0 and Hence C = 3-0 = 3 and hence it is a three component system.

   (ii) KCl – NaBr – H_2O system: In this case N = 5 [KCl, NaCl, NaBr, KBr & H_2O], E = 1 [KCl + NaBr = KBr + NaCl] and Hence C = 5 – 1 = 4 and hence it is a four component system.

3. **Degrees of Freedom:** [F] It is defined as the number of independent variables such as temperature, pressure and concentration [composition] which must be specified in order to define a system completely.

Examples:

   (i) **One component system with one phase:** The state of a pure gas can be specified by two variables P and T or P and V, since the third variable can be found from the equation of state.

   (ii) **One component system with two phases:** Water in equilibrium with its vapour: This system will have only one degree of freedom, because, at a given temperature, equilibrium vapour pressure can have only one fixed value. Thus, if the temperature is specified, the pressure becomes known automatically and vice versa. Hence it is a mono-variant system

   (iii) **One component system with three phases:** Ice, water and its vapour co-existing at the freezing point of water. It has zero degrees of freedom.. Just stating that the three phases co-exist defines the system completely

Note: F = 0, the system is invariant. F = 1, the system is uni-variant [mono-variant] and F = 3, the system is tri-variant.

Gibb's Phase Rule:

The number of degrees of freedom [F], the number of components [C] and the number of phases [P] are related to one another by Gibb's Phase Rule given below;

$$F = C - P + 2$$

One component system: C = 1, Minimum value for P = 1 and hence, F = 1 − 1+ 2 = 2. We can study the different phases of such system by considering a graph of P versus T..

Two component system: C = 2, Minimum value for P = 1 and hence, F = 2 − 1 + 2 = 3. We have three degrees of freedom. They are pressure, temperature and composition of the components in the system. We have to consider (i) the graph of P & T by keeping concentration constant (ii) the graph of T & C by keeping pressure of the system constant or (iii) the graph of P & C by keeping temperature constant. Of these graph, from the point of view of application, the second graph is very useful. Hence, the study of phases of a two component system is done by considering a graph of T versus Concentration of one of the component in terms of the other by maintaining pressure constant. Since, in drawing phase diagram, pressure is kept constant, the number of degrees of freedom of two component system reduces from 3 to 2 for a one component system. To take care of this, for two component system, Gibb's phase rule by reducing the constant term [2] in the phase rule by 1. Therefore the modified Gibb's phase rule applicable to two component system is given by, $F = C - P + 1$

Note: (i) For a two component system, with one phase, F = 2 [the system is bi-variant]

(ii) For a two component system with two phases, F = 1 [the system is mono-variant]

(iii) For a two component system with three phases, F =0 [the system is invariant]

Phase diagram of Lead – Tin system:

Lead – Tin alloy is an example of eutectic system and its eutectic phase diagram is as shown in the following diagram.
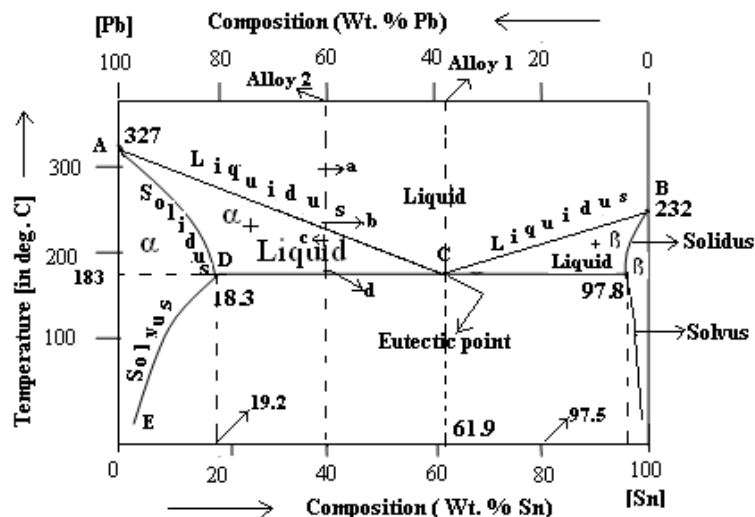
Pure lead melts at 327 ^{0}C. As tin is added to lead, the temperature at which the alloy melts decreases along the **Liquidus curve** represented by AC. Similarly, pure Tin melts at 232 ^{0}C and the addition of Lead decreases its melting point along the **liquidus curve** BC. Both the curve meets at a single point C, which represents the lowest melting point of the alloy. The point C corresponds to a temperature of 183 ^{0}C is known as eutectic temperature and at this temperature the alloy has a single melting point just like the pure metals. The composition corresponding to this temperature of

lowest melting point is known as eutectic composition and it has a value 61.9% Sn and 38.1% Lead. The alloy having eutectic composition is known as eutectic mixture.

In the region of limited solid solubility region, at each end of the lead – tin phase diagram, the solid formed has single phase designated as α and β phase respectively. 'α' phase is lead rich solid solution and can dissolve in solid solution a maximum of 19.2 wt % Sn at 183 ^{0}C. The beta phase is tin rich solid solution and can dissolve a maximum of 2.5 wt % Lead at 183 ^{0}C. As the temperature decreases below 183 ^{0}C, the maximum solid solubility of the solute elements decreases according to the **solvus line** in the phase diagram for alpha and beta phases.

When the liquid of eutectic composition is slowly cooled to the eutectic temperature, the single liquid phase transforms simultaneously in to two solid forms [solid solution α and β] and This transformation is known as **eutectic reaction,** represented by the following equation.

Eutectic temperature

Liquid [61.9% Sn] $\xrightarrow{\text{Cooling}}$ α [19.2% Sn] + β [97.5% Sn]

During eutectic reaction, the liquid, the two solid solutions α and β co-exist and are in equilibrium. Since the three phases can only be in equilibrium at one temperature, a horizontal thermal arrest occurs at the eutectic temperature in the cooling curve of an alloy of eutectic composition.

The composition to the left of eutectic point are called **hypoeutectic**, and the compositions to the right of eutectic point are called **hypereutectic**

Slow cooling of 60% Pb – 40% Sn alloy:

This alloy is in liquid state at 300 ^{0}C and as it is cooled, it remains in liquid state until the liquidus line is intersected at **b**. At this temperature solid solution α containing 12%Sn will begin to precipitate from the liquid. The first solid to form in this type of alloy is called **primary or pro-eutectic** alpha. The term pro-eutectic alpha is used to distinguish this constituent from the alpha that forms later by the eutectic reaction at 183 ^{0}C

As the liquid cools from 245 ^{0}C to slightly above 183 ^{0}C through the two phase liquid + alpha region of the phase diagram [point b to d], the composition of the solid α phase follows the solidus and varies from 12 % to 19.2 % of Sn at 183 ^{0}C. Similarly, the composition of liquid phase varies from 40 % Sn to 61.9 % Sn at 183 ^{0}C. At the eutectic temperature all the remaining liquid solidifies by the eutectic reaction.

Composition of different phases at the eutectic composition just below 183 ^{0}C:

Phase present	Alpha	Beta
Composition of phases	**19.2 % Sn**	**97.5 % Sn**
Amounts of phases	Wt% of alpha phase $=\left(\dfrac{97.5-61.9}{97.5-19.2}\right)\times100\%$ $=45.5\%$	Wt% of beta phase $=\left(\dfrac{61.9-19.2}{97.5-19.2}\right)\times100\%$ $=54.5\%$

Composition of different phases at 40 % Tin just below 183 ^{0}C:

Phase present	Alpha	Beta
Composition of phases	**19.2 % Sn**	**97.5 % Sn**
Amounts of phases	Wt% of alpha phase $$=\left(\frac{97.5-40}{97.5-19.2}\right)\times100\%$$ $$=73\%$$	Wt% of beta phase $$=\left(\frac{40-19.2}{97.5-19.2}\right)\times100\%$$ $$=27\%$$

Questions:

1. What is a thin film?
2. What is a substrate?
3. Mention one important difference between physical and chemical method of preparing thin film.
4. What is principle of thin film deposition by sputtering?
5. What is the principle of thin film deposition by thermal evaporation in vacuum?
6. Write a note on thin film deposition by thermal evaporation in vacuum
7. Write a note on thin film deposition by sputtering method.
8. Mention the applications of thin films.