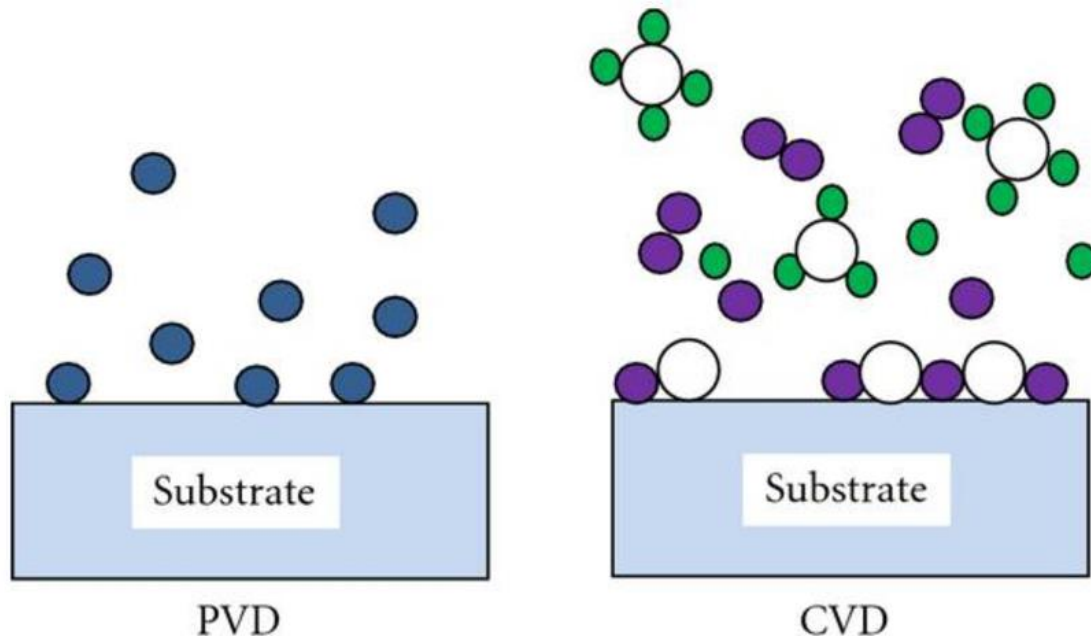


## IV. Physical Vapour Deposition (PVD)

### ➤ Thin Film Coatings or Industrial Coatings

- ❑ **Technology of applying a very thin film** of material between a few nanometers to about 100  $\mu\text{m}$ .
- ❑ Thin film deposition is usually divided into two broad categories
  - **Physical Vapour Deposition (PVD)**
  - **Chemical vapour Deposition (CVD)**



### ➤ Physical Vapour Deposition (PVD)

- ❑ **PVD** is a process used to produce a **metal vapour** that can be **deposited on electrically conductive materials** as a thin, highly adhered pure metal or alloy coating. This coating process produces coating thickness in the range **1 to 10  $\mu\text{m}$** .
- ❑ It involves **physically deposition atoms, ions or molecules** of a coating species on to a substrate.
- ❑ The process of thin film coating by means of PVD is to **apply electric current and voltage or bombardment of inert gas to ionize the desired material**. Once the material is ionized into vapor form it is the deposited on the desired substrate. PVD methods use **clean and dry vacuum deposition**.
- ❑ Coating is deposited over the entire object simultaneously, rather than in localized areas

## IV. Physical Vapor Deposition (PVD)

❑ There are three main types of PVD:

a. Thermal evaporation (vacuum thermal evaporation)

b. Sputtering and

c. Ion plating

❖ All these three processes are performed under vacuum.

Vacuum evaporation is also known as vacuum deposition

❖ Material used for coating is thermally vaporized and then proceeds by potential differences to the substrate with little or no collisions with gas molecules.

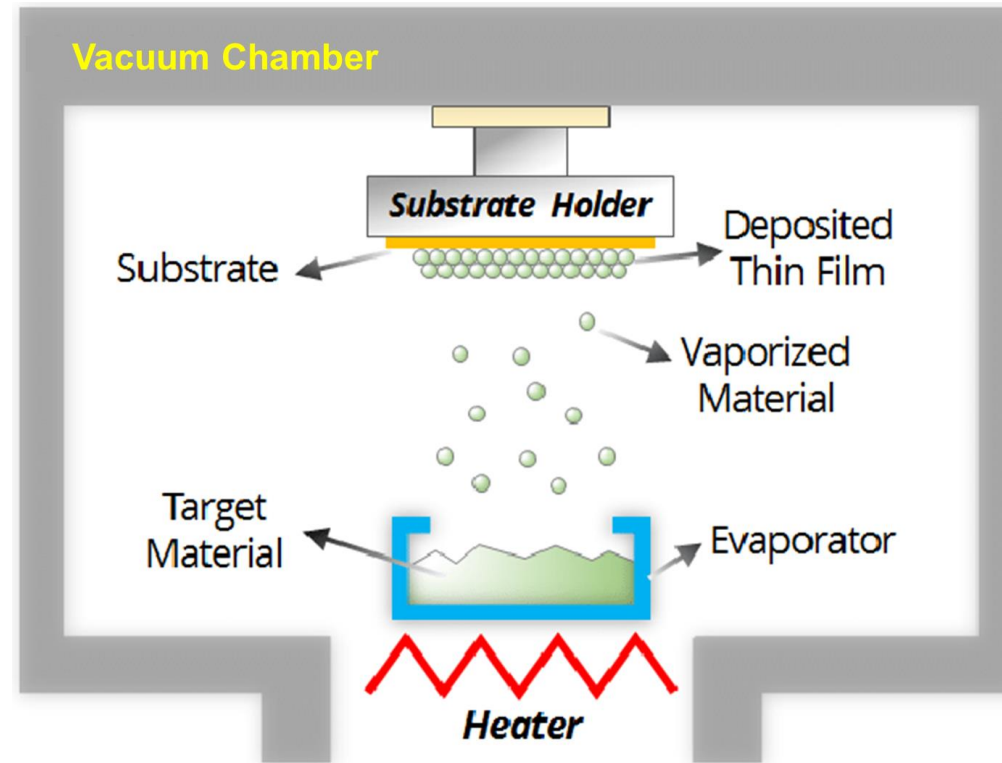
❖ Normal vacuum levels are in the medium to high vacuum range of  $10^{-5}$  to  $10^{-9}$  Torr.

a. Thermal evaporation

⇒ It uses the heating of a material to form a vapour which condenses on a substrate to form the coating.

⇒ Heating is achieved by various methods including hot filament, electrical resistance, laser beam, electric arc, electron beam

⇒ The surface to be coated needs to have a higher melting temperature than the coating metal and this limits the choice and make more complicated to mix the components



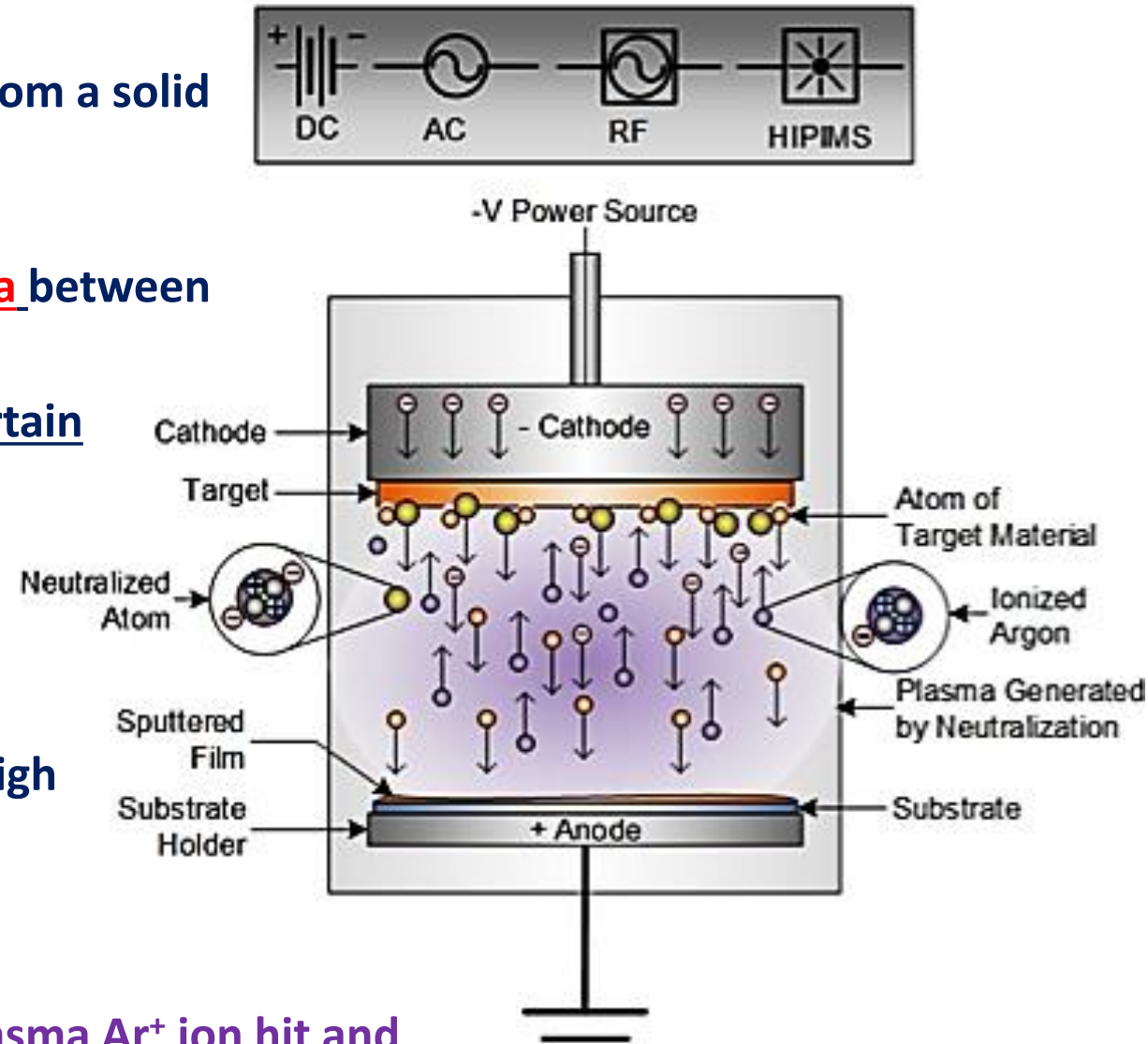
⇒ no chemical bonding between the coatings & substrates is established.

⇒ When the coating materials hit the substrate, it is physically deposited as layers or atom by atom or molecules by molecules.

## IV. Physical Vapor Deposition (PVD)

### b. Sputtering Method

- Sputtering is a process whereby particles are ejected from a solid target material due to bombardment of the target by energetic particles.
  - Sputtering involves the electrical generation of a plasma between the coating species and the substrate.
  - Plasma is a “state of matter similar to gas in which a certain portion of the particles are ionized”
  - In this method a **controlled gas, usually chemically inert argon**, is introduced into a vacuum chamber and **electrically energized to establish a self sustaining plasma**.
  - The argon ion ( $\text{Ar}^+$ ) will move toward to cathode with high speed and sputter the target material.
  - The target atom or molecular will be hit to substrate surface and condense as a film.
- # Instead of heat melting in evaporation method, the **plasma  $\text{Ar}^+$  ion hit and sputter the target** is the **main mechanism** in plasma sputtering method.



- The target atom is knocked out by  $\text{Ar}^+$  ion. The knock force is so big that it can accelerate target atom a high speed. With such velocity, the target atom can hit and attach to substrate surface deeply.
- The film density is good compared to thermal evaporation
- For efficient momentum transfer, the atomic weight of the sputtering gas should be close to the atomic weight of the target. For sputtering light elements neon is preferable, while for heavy elements krypton or xenon are used.

- ❑ Types of Sputtering:
  - ✓ DC sputtering.
  - ✓ Magnetron sputtering.
  - ✓ Radio frequency (RF) sputtering.
  - ✓ Reactive gas sputtering.
  - ✓ Ion beam sputtering.
  - ✓ Pulse DC/AC sputtering.

## ❑ Applications of Sputtering method:

- ☑ This method is used in VLSI fabrication (Very-large-scale integration: process of creating an integrated circuit (IC) by combining hundreds of thousands of transistors or devices into a single chip)
- ☑ Sputtering is used extensively in the semiconductor industry to deposit thin films of various materials in integrated circuit processing.
- ☑ Thin antireflection coatings ( $\text{MgF}_2$  and Fluoropolymers; mesoporous silica materials; titanium nitride and niobium nitride) on glass for optical applications are also deposited by sputtering.
- ☑ An important advantage of sputter deposition is that even materials with very high melting points are easily sputtered while evaporation of these materials in a resistance evaporator or Knudsen cell is problematic or impossible. Sputter deposited films have a composition close to that of the source material.



❑ Sputtering offers the following advantages over other PVD methods used in VLSI fabrication:

- I. Sputtering can be achieved from **large-size targets**, simplifying the deposition of thins with **unifrom thickness** over large wafers
- II. Film **thickness is easily controlled** by fixing the operating parameters and simply adjusting the deposition time
- III. **Control of the alloy composition**, as well as other film properties such as step coverage and grain structure, is more easily accomplished than by deposition through evaporation
- IV. **Sputter-cleaning of the substrate** in vacuum prior to film deposition can be done
- V. **Device damage from X-rays generated by electron beam evaporation is avoided.**

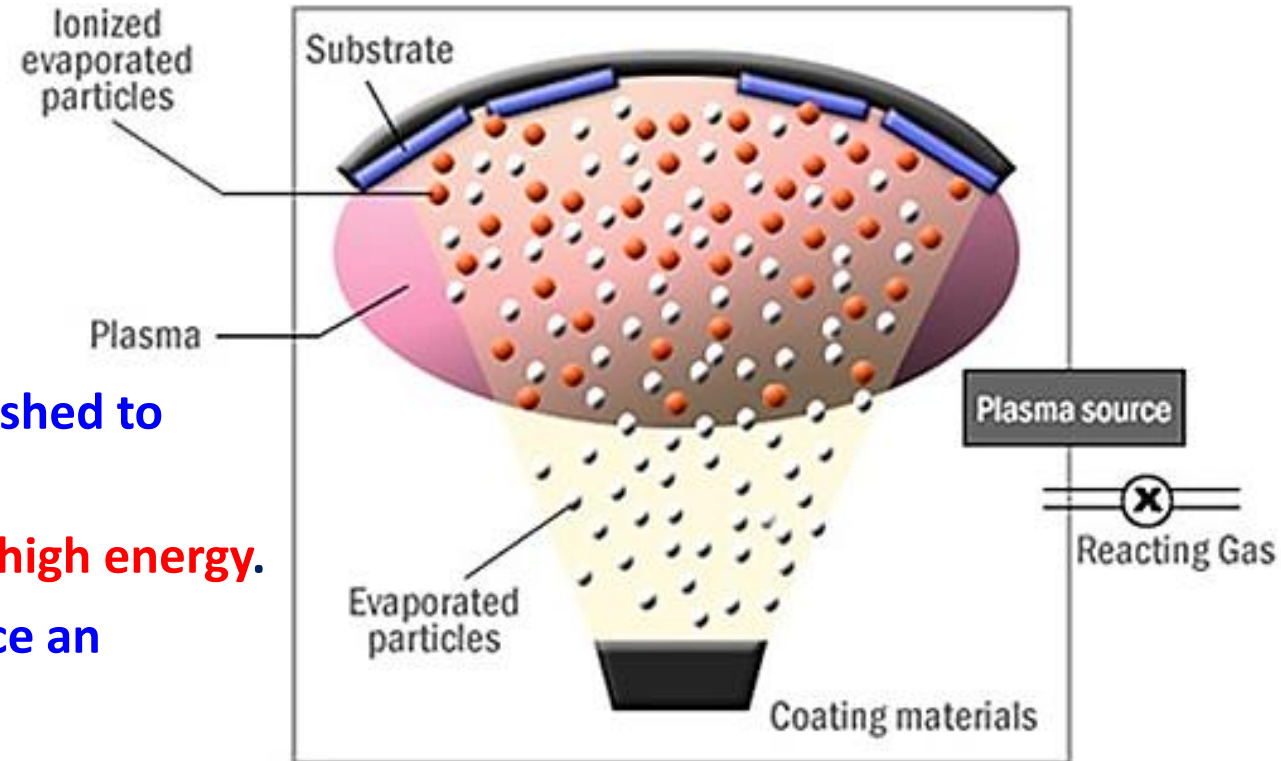
❑ Disadvantages of Sputtering:

- High capital expenses are required
- The rates of deposition of some materials (such as  $\text{SiO}_2$ ) are relatively low
- Some materials such as **organic solids are easily degraded** by ionic bombardment
- Sputtering has a **greater tendency to introduce impurities** in the substrate than deposition by evaporation because the former operates under a lesser vacuum range than the latter.
- The coatings are having **very poor crystallinity**
- **Formation of holes** inside the coating matrix due to very energetic hitting of target atoms.

## IV. Physical Vapor Deposition (PVD)

### c. Ion plating

- Ion plating is the **combination of thermal evaporation and sputtering methods**. sometimes called ion assisted deposition (IAD) or ion vapor deposition (IVD).
- Metal is evaporated thermally and plasma is established to ionize the evaporated species.
- Evaporated metal ions bombard the substrate with **high energy**.
- They physically implant into the substrate to **produce an extremely strong coating bond**.
- Sputter and ion plated coatings are used in design for very thin films for electrical, optical and wear-resistant applications.
- The wear properties of tools are greatly enhanced by hard thin film coatings.
- Sputtered coating processes produce **microscopic modules of diameter of several micrometers and they are called macros**.



## IV. Physical Vapor Deposition (PVD)

### ❑ Advantages of PVD coating:

- ✓ Materials can be deposited with improved properties compared to the substrate material.
- ✓ Almost any type of inorganic material can be used as well as some kinds of organic materials.
- ✓ The process is more environmentally friendly than processes such as electroplating.

### ➤ Applications of PVD methods

- ❖ This process is widely used to produce decorative coatings on plastic parts those are resembling shiny metal.
- ❖ Many automobile parts are plastic with a PVD coating of aluminium.
- ❖ A polish coating is applied over the decorative coating to provide corrosion protection.
- ❖ This process is also used to apply relatively thick (1 mm) coatings of heat resistant materials on jet engine parts
- ❖ PVD coating is widely used for artificial medical implants.

### ❑ Disadvantages of PVD coating:

- ≠ It is extremely difficult to coat undercuts and complicated surface features.
- ≠ High capital cost.
- ≠ Some processes operate at high vacuums and temperatures requiring skilled operators.
- ≠ Process emit large amounts of heat and hence require a cooling system.
- ≠ The rate of coating deposition is usually quite slow.



# V. Chemical Vapor Deposition (CVD)

❑ CVD is one of the most common processes used to coat almost **any metallic/ceramic compound**, including elements, metals and their alloys and inter-metallic compounds.

➤ The CVD process involves **depositing a solid material from a gaseous phase**

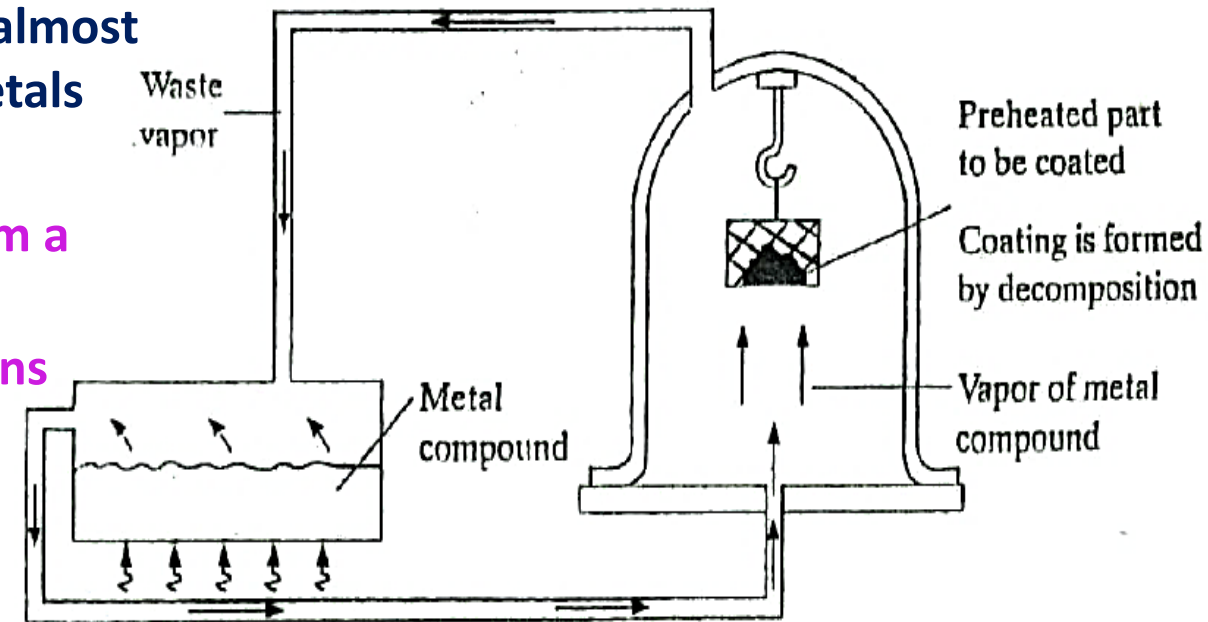
❑ Coating process uses **thermally induced chemical reactions at the surface** of a heated substrate, with reagents supplied in gaseous form

❑ Precursor gases are delivered into the reaction chamber. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase which are deposited onto the substrate.

❑ The **substrate temperature is critical** and can influence what reactions will take place

❑ A CVD apparatus will consist of following basic components

- Gas delivery system,
- Reactor chamber,
- Substrate loading mechanism,
- Energy source,



- Vacuum system,
- Exhaust system,
- Exhaust treatment systems,
- Process control equipment



# V. Chemical Vapor Deposition (CVD)



## ❑ Applications of CVD

- **Gas delivery system:** For the supply of precursors to the reactor chamber
- **Reactor chamber:** Chamber within which deposition takes place
- **Substrate loading mechanism:** A system for introducing and removing substrates, mandrels etc
- **Energy source:** Provide the energy/heat that is required to get the precursors to react/decompose.
- **Vacuum system:** A system for removal of all other gaseous species other than those required for the reaction/deposition.
- **Exhaust system:** System for removal of volatile by-products from the reaction chamber.
- **Exhaust treatment systems:** In case exhaust gases may require treatment or conversion to safe/harmless compounds.
- **Process control equipment:** Gauges, controls etc to monitor process parameters such as pressure, temperature and time.

- ❖ **Coatings:** Coatings for a variety of applications such as wear resistance, corrosion resistance, high temperature protection, etc.
- ❖ **Semiconductors and related devices:** Integrated circuits, sensors and optoelectronic devices
- ❖ **Optical Fibers:** For telecommunications.
- ❖ **Dense structural parts:** To produce components that are difficult/uneconomical to produce using conventional fabrication techniques.
- ❖ **Composites:** Preforms can be infiltrated using CVD techniques to produce ceramic matrix composites such as carbon-carbon, carbon-silicon carbide and silicon carbide-silicon carbide composites.
- ❖ **Powder production:** Production of novel powders and fibres
- ❖ **Nanomachines**
- ❖ **CVD is also used to produce synthetic diamonds**

# V. Chemical Vapor Deposition (CVD)

## ❑ Advantages:

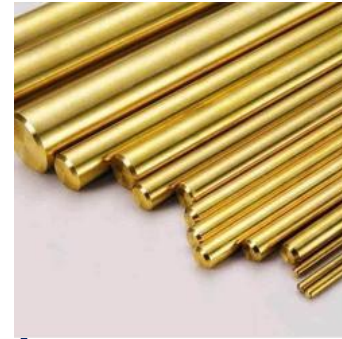
- ✓ CVD coatings are typically fine grained and of high purity.
- ✓ Harder than similar materials produced using conventional ceramic fabrication processes. CVD coatings are **used to make explosion or shatter resistant glasses.**
- ✓ The main advantage of CVD process over PVD is that it is not line of sight. All surfaces in the reaction chamber get coated.

## ❑ Disadvantages:

- ≠ Separate process and reaction must be developed for each coating.
- ≠ Some of the gases are toxic and dangerous.
- ≠ Greatest disadvantage is temperature of the substrate should be very high at 700°C. At this temperature, many metals (substrates) soften.

PVD	CVD
Deposition occurs by condensation	Deposition occurs by chemical reaction
The material introduced onto the substrate is introduced from solid form.	The material introduced onto the substrate is introduced from gaseous form.
Atoms are moving and depositing on the substrate.	The gaseous molecules will react on the substrate,
PVD coating is deposited at a relatively low temperature(around 250°C~450°C).	CVD uses high temperature in the range of 450°C~1050°C.
PVD is suitable for coating tools that are used in applications that demand a tough cutting edge.	CVD is mainly used for depositing compound protective coatings.
High capital cost	Low capital cost
Coating thickness up to 20 micrometers	Coating thickness 3-5 micrometers
Directional : It can be used for lift-off.	Poor directionality: Good for step coverage.

- ❑ Alloy is a homogeneous substance formed by mixing two or more elements, at least one of them being a metal
- ❑ Types: Alloys are of three types.
  - Formed by two or more metals; eg. Cu-Zn (Brass)
  - Formed between a metal & a non-metal; eg. WC
  - Formed between mercury & another metal; eg. Zinc amalgam



## ❑ Characteristics of alloys:

- ⇒ Hardness and tensile strength of the alloy is higher
- Tensile strength of Fe 10 fold increases by alloying with 1% Carbon
- ⇒ Melting points of alloys is generally lower
- Solder melts at 183°C; while Pb melts at 327°C and Sn melts at 232°C
- ⇒ Alloys are less conductive than pure metals
- Small quantity of impurities in copper will reduce its conductivity
- ⇒ Colour of alloy gets modified
- Red coloured copper & Silver white Zinc provide Yellowish brown brass
- ⇒ Chemical Properties are modified
- Dissolution of alloy in HCl is lower compared to its constituent metals
- ⇒ Corrosion resistances: Generally alloys are more resistant to corrosion than pure metals.
- Stainless steel (alloy of Fe, C, Ni & Cr) is not corroded by atmospheric conditions though pure Fe corrodes heavily in moist environment.

## ❑ Significance of Alloying

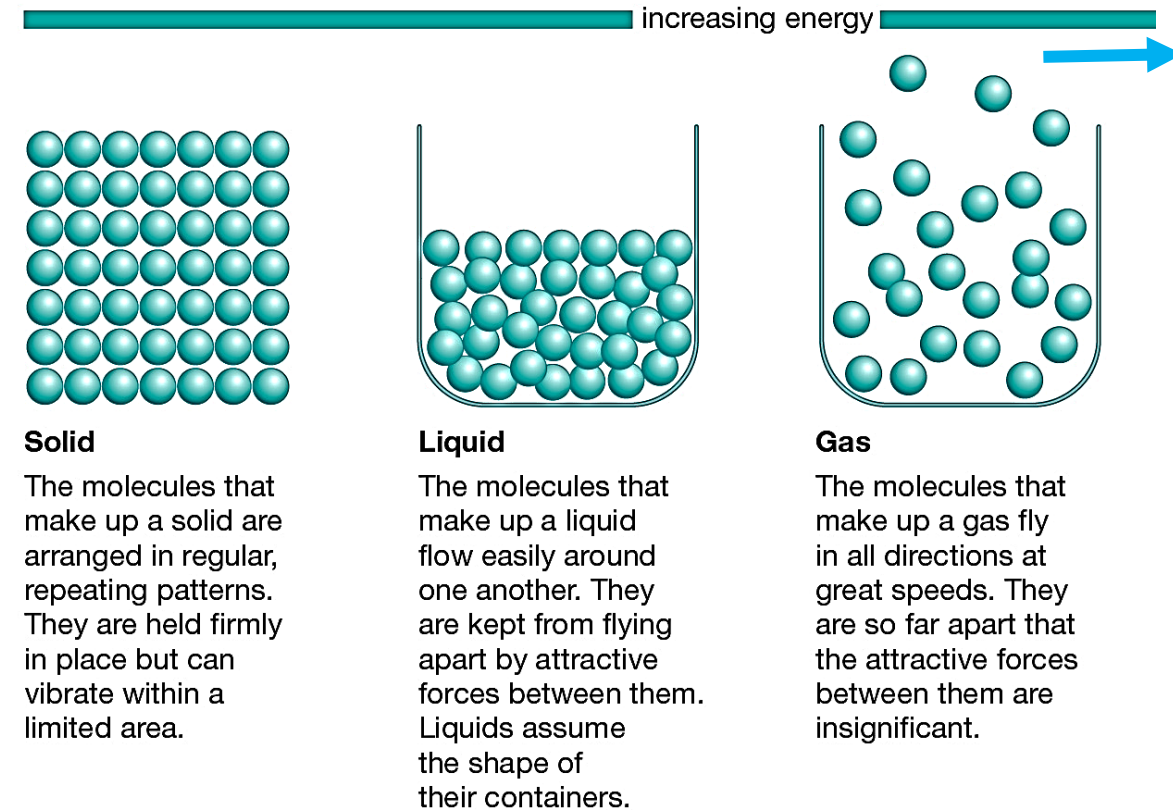
- The alloy coatings **bring quality, reliability and durability** for process vessel linings and pipe linings along with the surface protection of components and equipment **against extreme conditions such as high temperature, higher abrasion or high acidity surroundings.**
- Alloying Increases mechanical strength, reduce chemical reactivity, change electrical conductivity, increase corrosion protection

## ❑ Examples

- ✓ **Lead-Tin alloys – for soldering purpose**
- ✓ **Nickel alloys – for resistance to extreme corrosion & high temperature requirements.**
- ✓ **Copper-nickel alloys – for anti-fouling resistance.**
- ✓ **Iron-nickel alloys – for low thermal expansion**

## ❑ Basic concepts of Eutectic composition

### ➤ Phase

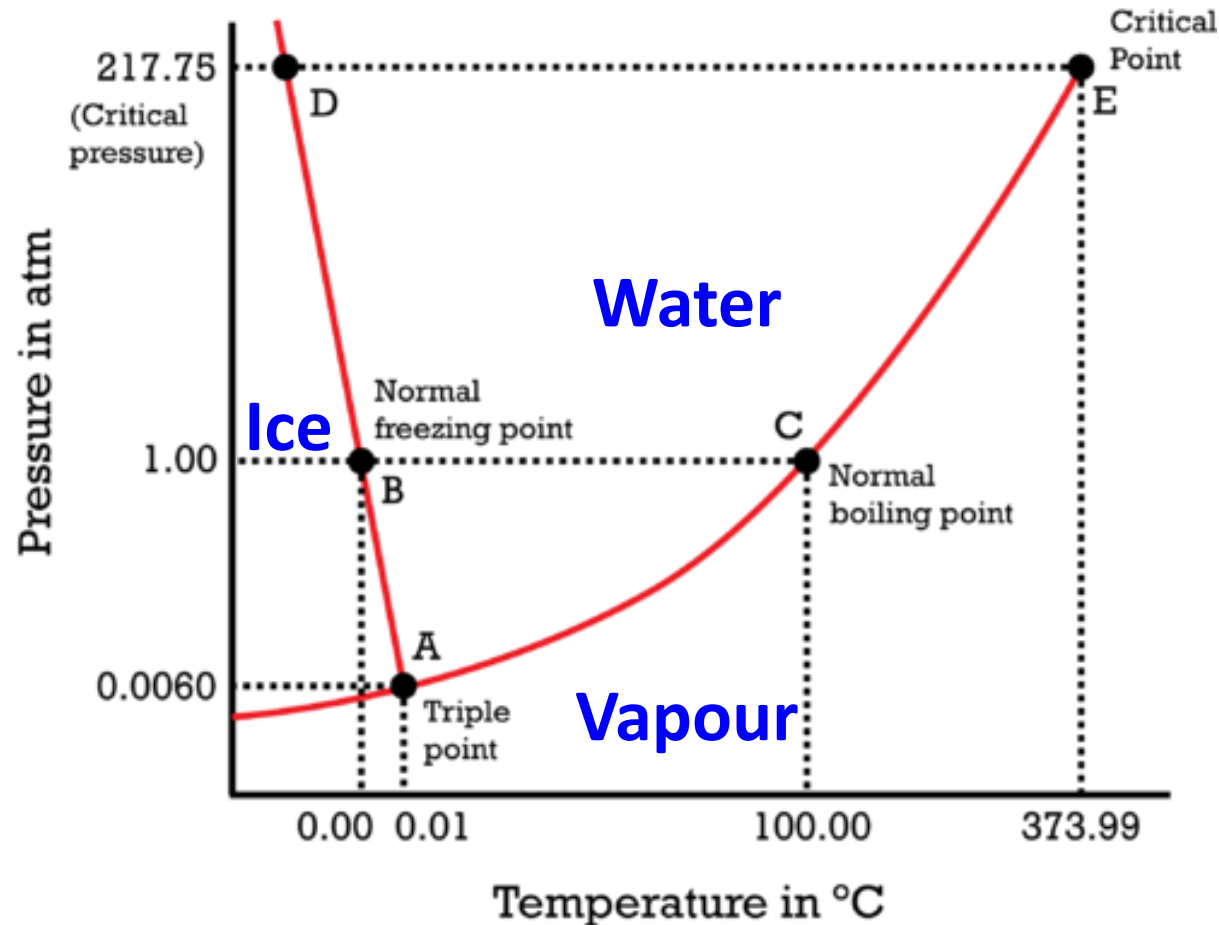


- When a phase in one form is altered to another form, a **phase change** is said to have occurred. Phase change generally occurs by addition/removal of thermal energy
- A heterogeneous system is defined as a system consisting of a number of phases in equilibrium



# Basic Concepts of Eutectic Composition

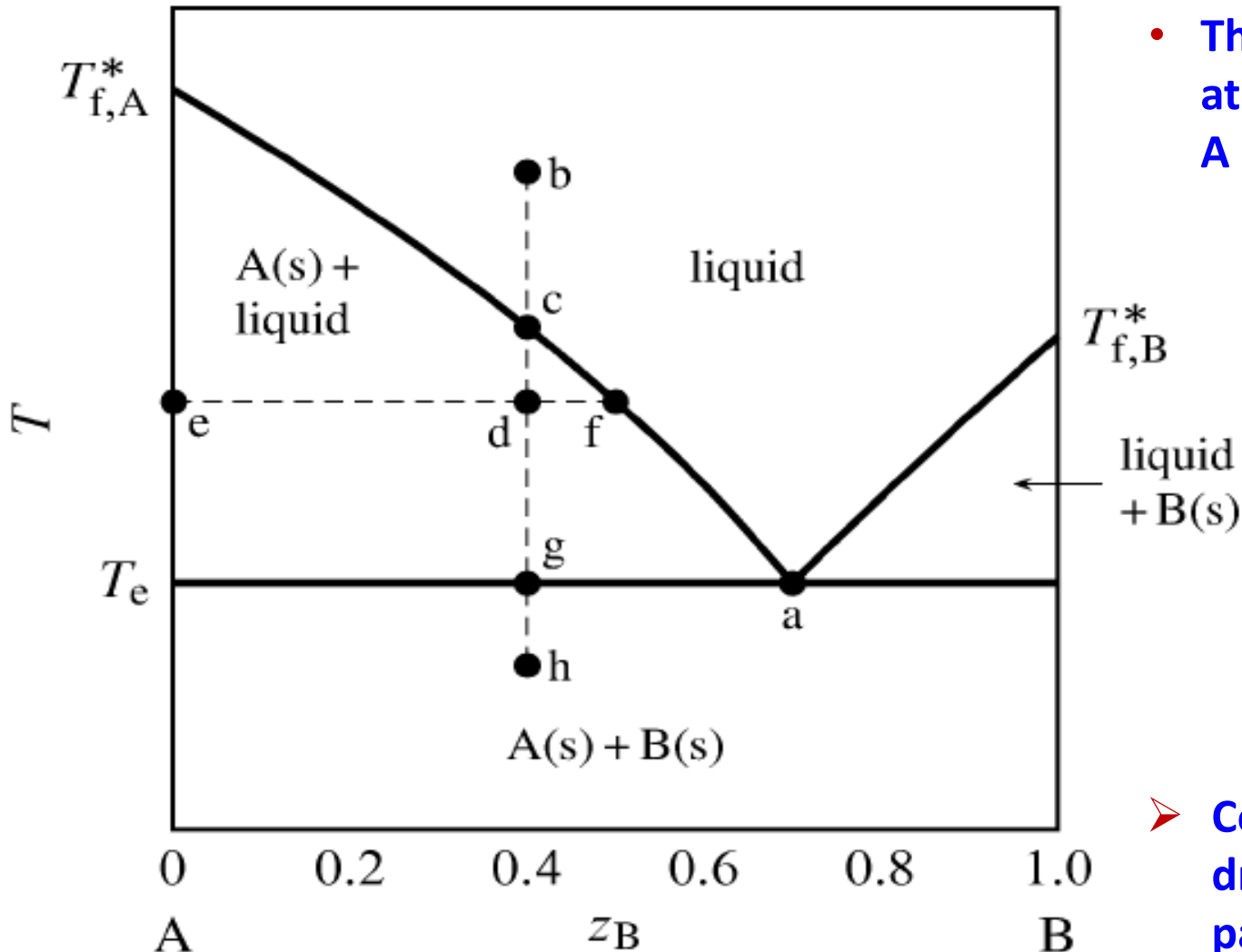
- A phase diagram is a type of chart used to show **conditions (pressure, temperature, volume)** at which thermodynamically distinct phases (such as solid, liquid or gaseous states) occur and coexist at equilibrium



- Generally the phases at equilibrium are studied under the conditions considering following variables
  - **Temperature & Pressure** or **Temperature & Composition**
- Phase diagram is one of the most succinct ways of presenting the physical changes of state that a substance can undergo.
  - ☑ For two component systems
    - **Temperature, pressure and composition** are required to define the system
    - This leads to 3-dimensional figures which cannot be explained on a paper. Hence one of the three variable to be kept constant.
    - The composition variable  $z_B$  is the mole fraction of component B in the system as a whole.
    - The measurement is carried out in an open vessel to keep the system under constant atmospheric pressure

# Basic Concepts of Eutectic Composition

- $T_{f,A}^*$  = freezing point of A
- $T_{f,B}^*$  = freezing point of B



- The curve  $T_{f,A}^*$  = FP of B to which A is being added
- The curve  $T_{f,B}^*$  = FP of A to which B is being added
- These two curves represent condition of temperature at which the liquid mixture is in equilibrium with solid A and solid B

Point 'a' = meeting point of the curves  $T_{f,A}^*$  &  $T_{f,B}^*$ . At this point three phases, solid A, solid B and the liquid mixture, are in equilibrium.  
 The point 'a' correspond to a temperature below which any liquid mixture of A and B will freeze as a whole. This is known as the **Eutectic Point**.  
 The composition at this point is the **eutectic composition**, and the **temperature here** (denoted  $T_e$ ) is the eutectic temperature

- Composition of any point, say d, can be obtained by drawing a horizontal line passing through the particular point to find where it cuts the curves  $T_{f,A}^*$  &  $T_{f,B}^*$