


Corrosion can be controlled by

- ❖ Corrosion can be controlled by preventing formation of galvanic cells. By retarding either the anodic or cathodic reactions the rate of corrosion can be reduced
 - This can be achieved in several ways. The commonly available methods for controlling corrosion are:
 - Changing the environment
 - Design and selection of suitable materials
 - Protective coatings:
 - **Metal coatings:** anodic and cathodic
 - **Surface conversion coatings:** anodizing, phosphating and chromating
 - **Paints and enamels**
 - **Vacuum coatings process (physical vapor deposition (PVD), metal spray and chemical vapor deposition (CVD))**
 - Cathodic protection
 - Anodic protection
 - Corrosion inhibitors

❖ What is Cathodic Protection?

- The principle involved in this method is to force the metal to be protected to behave like a cathode thereby corrosion doesn't occur
 - Cathodic protection is an electrochemical technique in which a cathodic potential is applied to a metal structure in order to prevent corrosion from taking place
 - The material to be protected is supplied with an external cathodic current
 - The electrochemical potential of the protected material is moved in a negative direction to the immunity area
 - The material is completely protected when it reaches the Protection Potential
 - Cathodic protection is a method of corrosion control that can be applied to buried and submerged metallic structures
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❖ **Cathodic protection can be applied in two ways:**

- Sacrificial anode or galvanic protection
- Impressed current cathodic protection

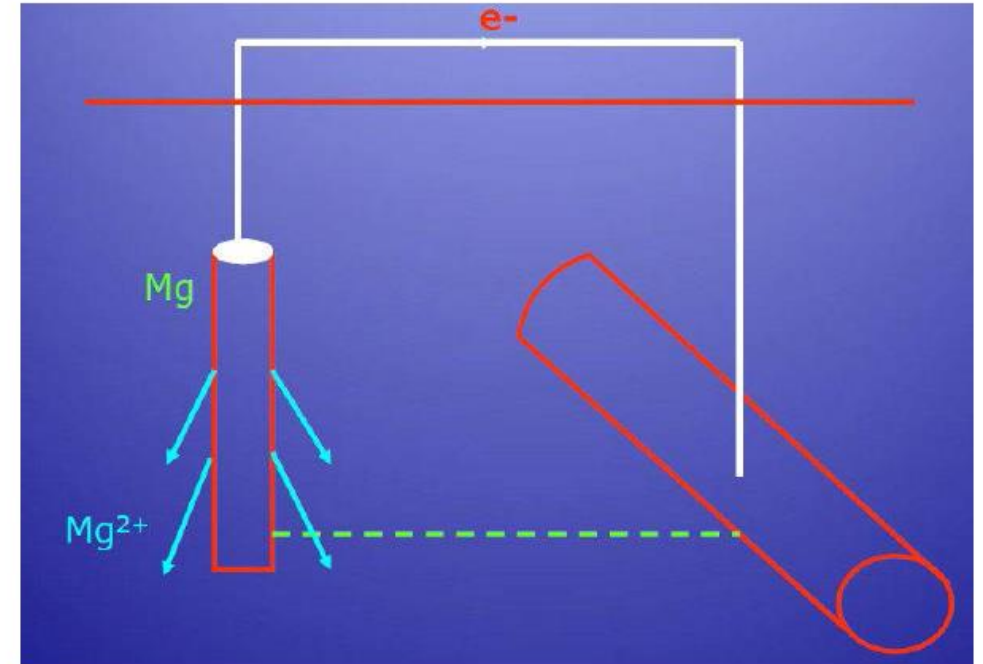
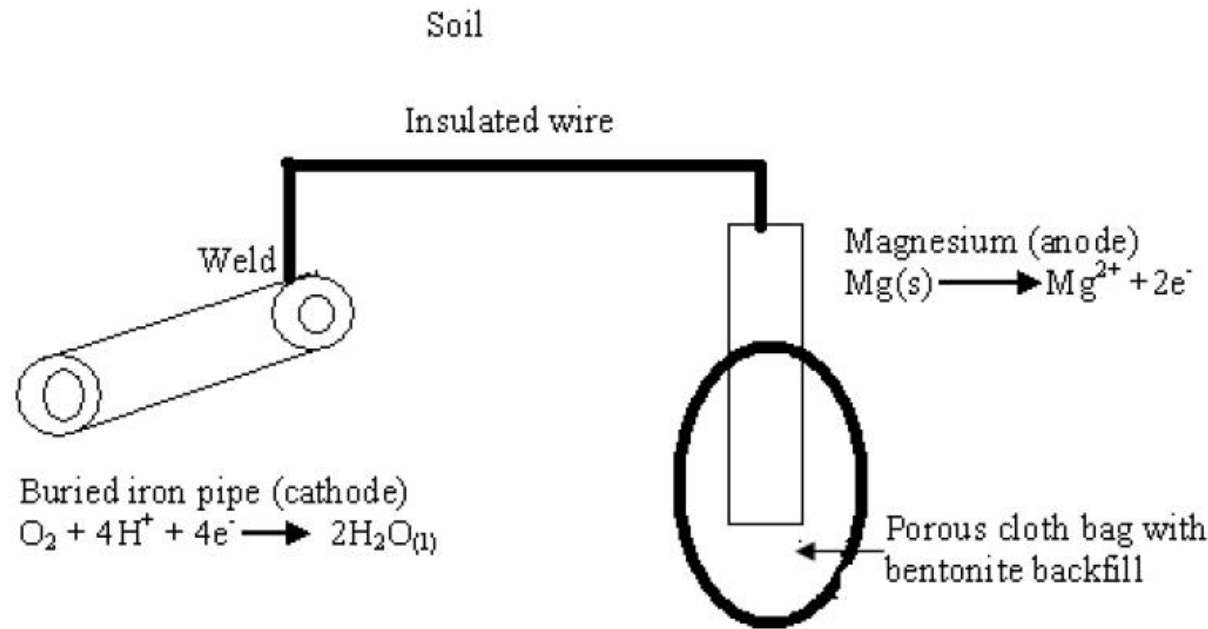
Cathodic Protection



❖ **Sacrificial anode/galvanic protection:**

- In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal implies the more active metal sacrifices itself and gets corroded slowly. While the parent structure which is cathodic is protected. The more active metal so employed is called “**sacrificial anode**”
- Whenever the sacrificial anode is consumed completely, it is replaced by a fresh one. Metal commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Sacrificial anodes are used for the protection of buried pipe lines underground cables, marine structures, ship hulls, water tanks etc
- The method involves the use of sacrificial anode in contact with metal structure being protected usually made of **Fe, Cu or brass**
- In this method, the metal structure is protected by connecting it with a piece of more anodic metal (active metal) from the galvanic series
- The active metal behaving as anode gets corroded thereby sacrificing itself
- Metals like Mg, Zn, Al are more active or more anodic and provide electrons to the metal being protected thereby converting the anodic sites on the metal structure to cathodic sites

❖ Sacrificial anode or galvanic protection



Bentonite is an absorbent aluminium phyllosilicate clay consisting mostly of montmorillonite $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$

Sacrificial anode or galvanic protection

❖ Advantages:

- No external power is required
- Easy to install
- Minimum of cathodic interference problems
- Anodes can be readily added
- Minimum of maintenance required
- Uniform distribution of current

❖ Disadvantages:

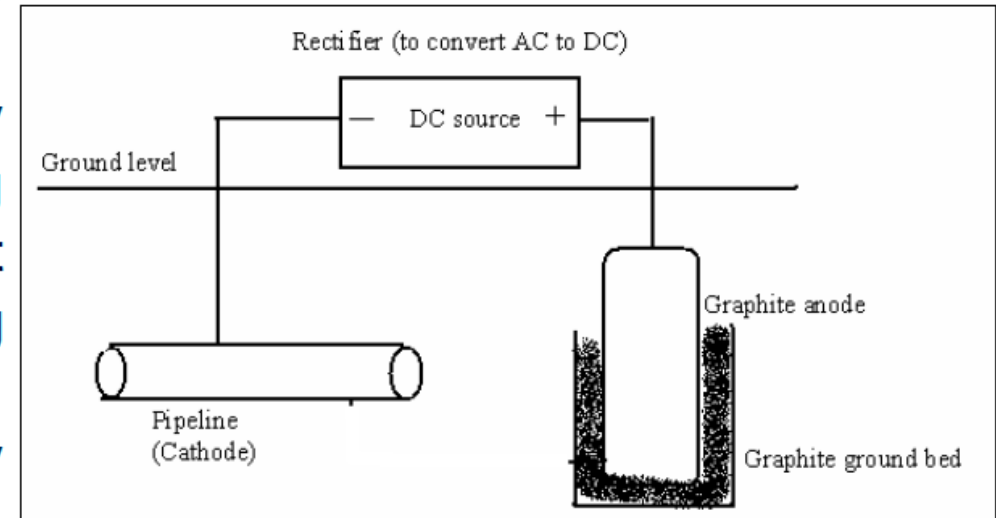
- More than one anode is required some times
- It does not work properly in high corrosive environment
- Sacrificial anode must be replaced periodically as and when it is consumed

Impressed current cathodic protection (ICCP)

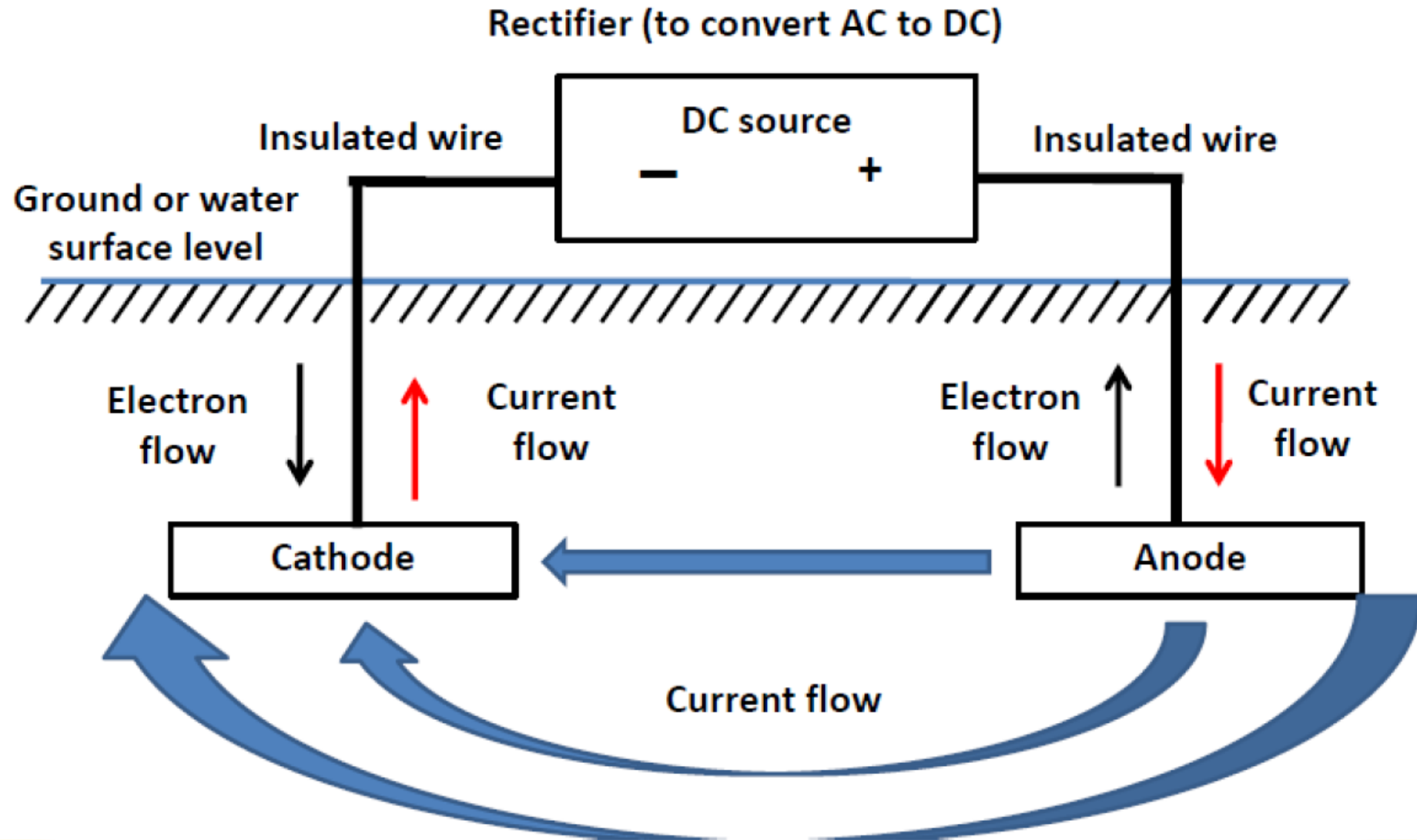
- The metal structure being protected is connected to an insoluble metal anode (lower in the galvanic series: stainless steel, Pt or even graphite). Early anodes were made from scrap steel but most modern ICCP systems use lead silver alloy, titanium or niobium.
- When an impressed current from a DC current source (like battery or rectifier) is applied in the direction opposite to the corrosion current, the metal structure being protected now behaves as cathode and hence protected. The insoluble metal behaves as anode.
- Exposed surface area or length of the anode determines how many square feet of cathode like steel it can protect.
- A buried pipeline is connected to the negative terminal of a rectifier or battery (power supply) and the anode to the positive terminal.
- Both terminals must be well insulated; otherwise, current leakage (stray-current) occurs and the structure may not be protected adequately

Impressed current cathodic protection (ICCP)

- The significance of the cathodic protection setups shown in the following figure is that the current flows from the rectifier to the inert anode (graphite or platinum coated titanium) through the soil (electrolyte) to the cathode.
- When this method is used in soil, the anode is usually in a “back-fill” (coke or gypsum) or conducting grounding bed so as to increase the electrical contact with the protected cathode through the surrounding soil.
- For structures immersed in seawater, the anodes may be platinum-coated titanium or high-silicon cast iron.
- The purpose of the rectifier is to convert alternating current (ac) to uniform direct current (dc).
- Applications: protection of ship-hulls, river dam gate, steel bridge, large buried oil or water pipes, transmission towers, etc.



Impressed current cathodic protection (ICCP)



Metallic Coatings

- ❖ The surface of the base metal coated with another metal (coating metal) is called metallic coatings. Metallic coatings are broadly classified into anodic and cathodic coatings
- ❖ **Anodic coatings:**
 - The metal used for the surface coating will be more anodic than the base metal which is to be protected
 - For example, coating of Al, Cd and Zn on steel surface are anodic, because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially
 - The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected

❖ Cathodic Coatings:

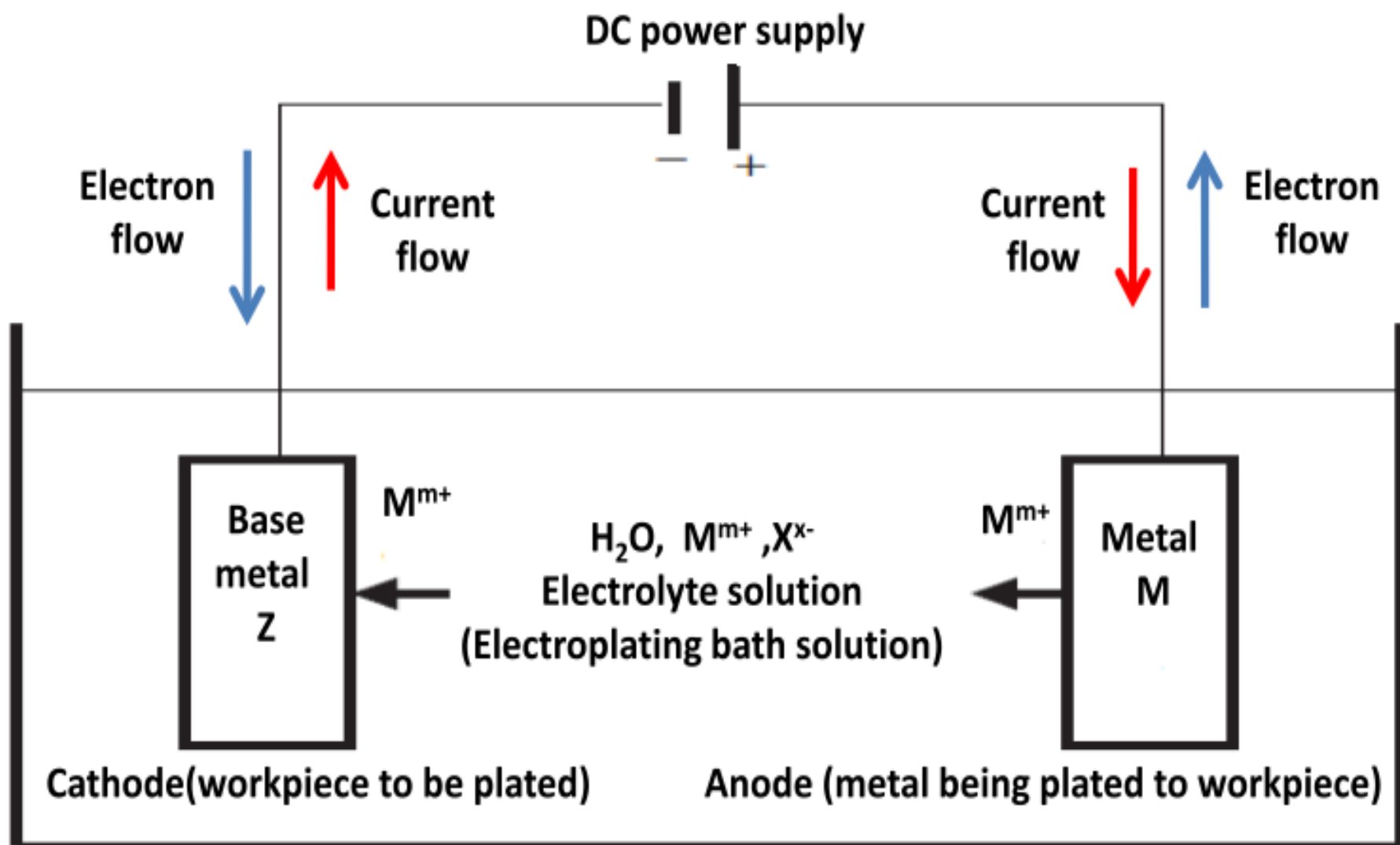
- ❑ Cathodic coatings are obtained by coating the base metal with more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as it now behaves as cathode having higher corrosion resistance than the base metal due to cathodic nature.
- ❑ Cathodic coating protects the base metal only when the coating is uniform and free from pores.
- ❑ The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

Electroplating

- It is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal
- Electroplating is done for improving
 - a) corrosion resistance
 - b) wear resistance
 - c) chemical resistance
 - d) surface hardness
 - e) appearance
- Both ferrous and non-ferrous metals are plated with Ni, Cr, Cu, Zn, Pb, Al, Ag, Au, Sn etc.
- Electroplating is mainly used in automobile, aircraft, refrigerator, chemical and electrical appliances etc.

Theory of Electroplating

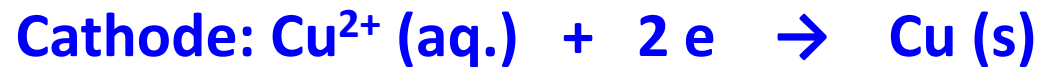
- The base metal to be plated is made cathode of an electrolytic cell, whereas the anode is either made of the coating metal itself or an inert material of good electrical conductivity
- If the anode is made of coating metal itself in the electrolytic cell, during electrolysis, the concentration of electrolytic bath remains unaltered.
- Since the metal ions deposited from the bath on cathode (Base metal) are replenished continuously by the reaction of free anions with the anode.
- If the anode is made of an inert material like graphite, electrolyte should be added continuously to maintain the concentration of the coating metal ions in the bath.



Electroplating metal M onto metal Z

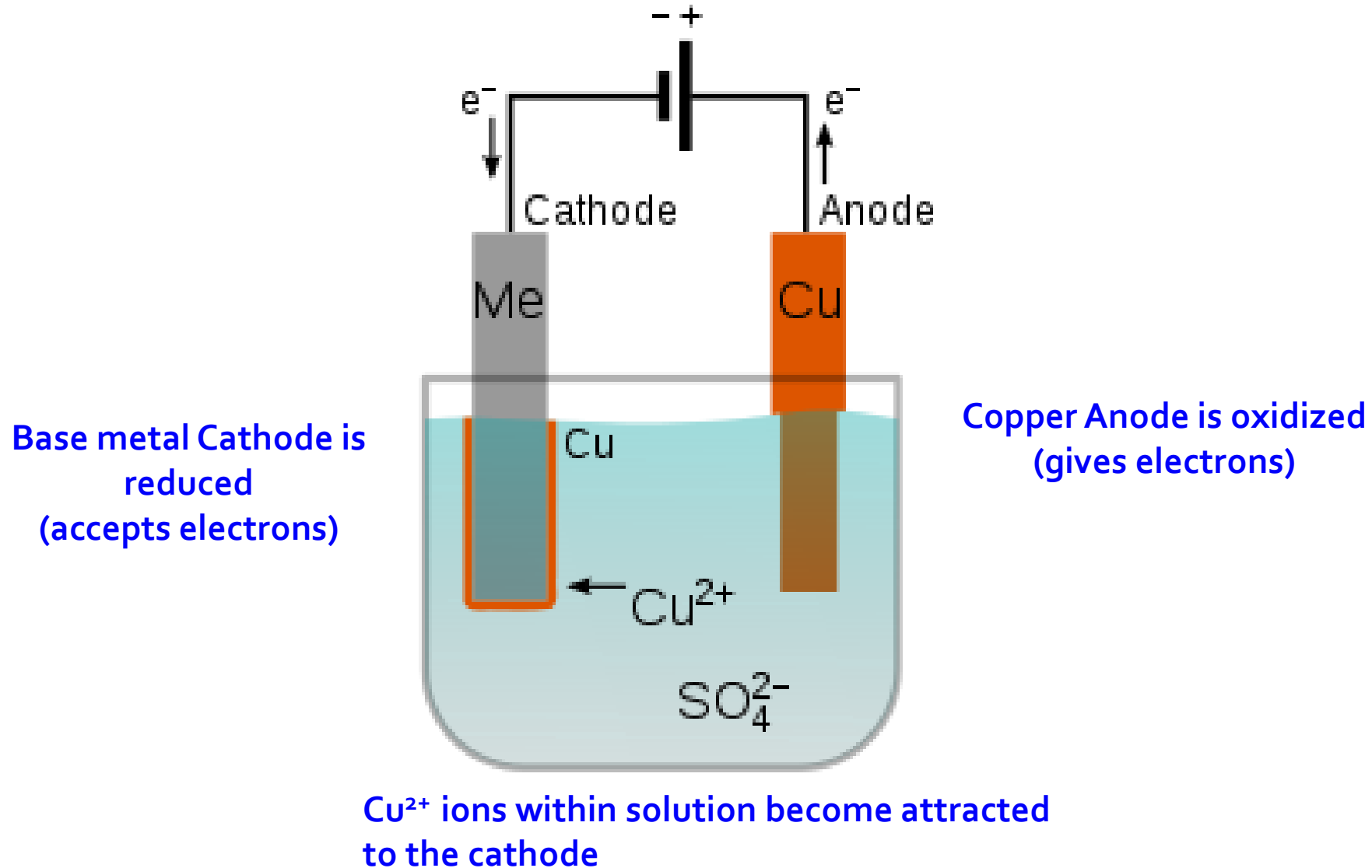
Electroplating Process

- Electroplating of Copper onto a base metal
 - Base metal (object) is treated with dil. HCl or dil. H₂SO₄ to remove oxide layers.
 - Object to be coated acts as cathode. Copper foil is taken as the anode. Copper sulphate is used as an electrolyte.
 - When a direct current is passed from an external source, the copper ions migrate towards cathode and get deposited over the surface of base metal (object) in the form of a thin layer.



- Low temperature, medium current density, low metal ion concentration are maintained for better electro-plating.
 - Temperature: 20-40 °C (bright and smooth surface)
 - Current density: 20-30 mA/cm²
 - Copper sulphate : 0.44 Molar solution

Electroplating of Copper



Important Factors of electroplating

- Cleaning of the article is essential for strong adherence of the electroplating:
 - Scraping, grinding, sand blasting, wire brushing, solvent cleaning and acid pickling are used for surface cleaning.
 - A well cleaned and properly pre treated surface of any material to be electroplated is necessary for obtaining the coating of long life.
- Concentration of the electrolyte is another important factor:
 - Low concentration of metal ions will give uniform coherent deposition.
 - To maintain low conc. of metal ions, complexing agents are added to the electrolyte.

- Thickness of the deposition should be optimised to get a strong and adherent deposition:
 - For corrosion protection multiple coatings are given to get impervious coating without any discontinuity.
 - For decorative purpose, thin coating is given.
- Current density
 - Current density is the current per unit area of the article being plated (amps cm^{-2}).
 - The C.D should be maintained at optimal level to get uniform and adherent deposition.
- Additives to electrolytic bath
 - Additives to electrolyte are added in small quantities to get strong adherent deposition.
 - Commonly used additives are gelatin, glue, glycine, boric acid etc. and brighteners for bright plating.

■ pH of the bath:

- For a good electrodeposit, the pH of the bath must be properly maintained. For most plating baths, pH ranges from 4 to 8

■ Method of Electroplating:

- Method depends upon the type of metal to be electroplated, the size and type of article to be electroplated
- Its main objectives and economics are also considered

■ Throwing power:

- It is the ability of electrolytic cell to give a deposit of uniform thickness over the entire cathode area.
- Maximum throwing power can be attained when cathode has regular shape.
- If the cathode has irregular shape then agitating the solution to minimize local electrolytic resistance.

Plating bath solution

- It is a **highly conducting salt solution** of the metal which is to be plated.
- However, **non-participating electrolytes** are added to the bath solution to **increase the conductivity** and the throwing power.
- The level of the plating **bath should cover completely the cathode** and sufficient area of anode.
- Heating if required is provided by heating coils or hot gases.
- Air sparger or nitrogen sparger is employed to introduce convection current in the plating bath solution.
- It should possess sufficient throwing power. Hence **mixture of two or more electrolytes are used** for electrolytic bath.
- It should be good conductor and highly soluble.
- It should not undergo hydrolysis, oxidation, reduction and other chemical changes.

Objectives of electroplating

- Electroplating is mainly used in automobile, aircraft, refrigerator, chemical and electrical appliances etc.
- On Metals:
 - To increase the corrosion/chemical/wear/heat resistance of the electroplated metal.
 - To improve surface properties (surface hardness, electrical conductivity, thermal conductivity, optical reflectivity).
 - To increase the decorative value of the metal.
- On Non-Metals(plastics, wood, glass, etc.):
 - To decorate the surfaces.
 - To make the surface conductive(by depositing a metal film).
 - To improve optical performance.
 - To increase strength.

Electroless plating

- Electroless plating is the controlled autocatalytic deposition of a metal on a substrate (conductor/Nonconductor) from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy
- This process is also called autocatalytic plating, since it takes place on catalytic surface.
- The metallic ions (M^+) are reduced to the metal with the help of reducing agents (R^-). When the metal (M) is formed, it gets plated over a catalytic surface.



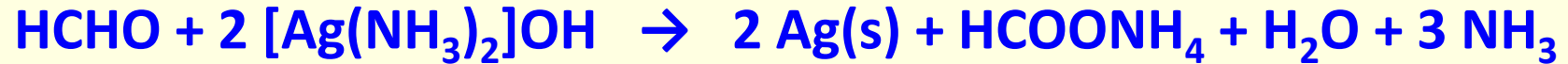
- Typically, sodium hypophosphite is used as a reducing agent. Also, formaldehyde, hydrazine, borohydride, amine boranes, and their derivatives could be utilized

■ Surface preparation

- Before applying electroless plating, the surface of the object should be activated.
- Pre-treatment and activation of the surface is performed by treatment with organic solvents or alkali, followed by acid treatment
- For metals having no catalytic activity should be treated with palladium chloride - HCl solution.
- For non-conductors like plastic, glass or PCB, the surface is activated by treating them with stannous chloride solution containing HCl followed by dipping in palladium chloride - HCl solution

Examples of electroless plating

- Silver coating on mirrors can be obtained by the using formaldehyde as reducing agent



- When sodium hypophosphite is used, the coating will also contain phosphorus. Example, nickel coating



- Electroless plating of copper on PCB. It is done by reduction of alkaline solution containing Cu^{2+} ion stabilized by EDTA. Here formaldehyde acts as reducing agent



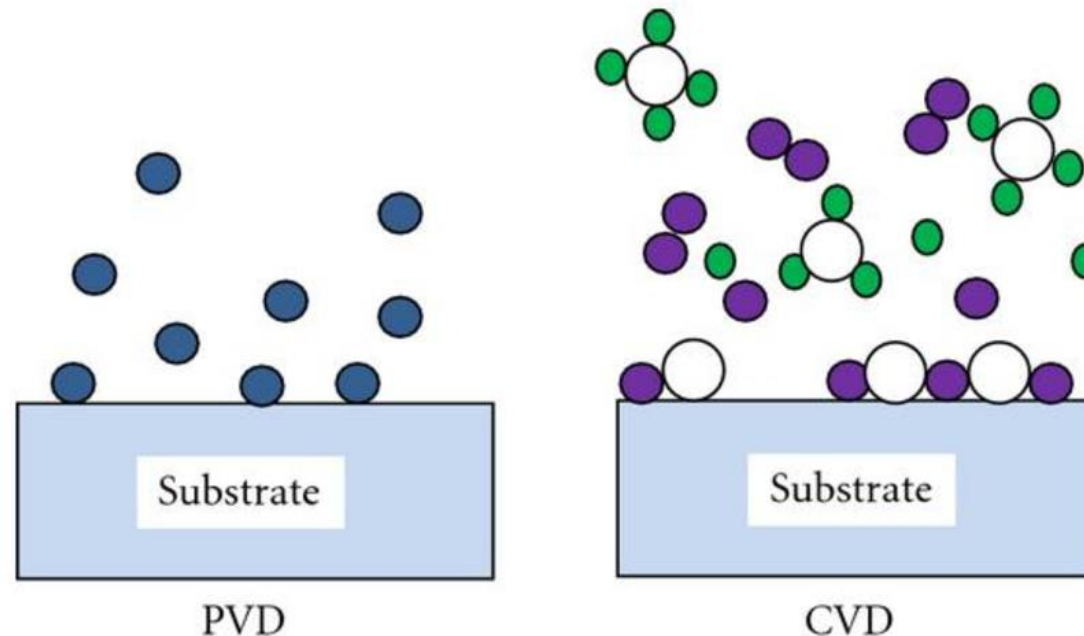
- **Advantages of electroless plating:**
 - **Electrical energy is not required.**
 - Even intricate parts (of irregular shapes) can be plated uniformly.
 - There is flexibility in plating volume and thickness.
 - The process can plate recesses and blind holes with stable thickness.
 - Chemical replenishment can be monitored automatically.
 - **Plating on articles made of insulators (like plastics) and semiconductors can easily be carried out.**
 - It is a **pore free coatings** with very high hardness, corrosion resistance and wear resistance values.

Differences between electroplating and electroless plating

	Electroplating	Electroless plating
Driving force	Electric current	Autocatalytic reduction reaction
Electrodes	Separate anode and cathode	Catalytically active surface
Applicability	Deposition can't be made on non-conductors such as plastics, ceramics etc.	Deposition can be made on non-conductors such as plastics, ceramics etc.
Throwing power	Low	High
Nature of deposit	Pure metal	Metal contaminated with reducing agents and oxidizing agents
	Levelers are added.	Levelers are not required.

Thin film coatings or Industrial coatings

- It is the **technology of applying a very thin film** of material between a few nanometers to about 100 micrometers.
- 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 thin film coating process produces coating thickness in the range **1 to 10 μm** .
- 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

■ **The process involves following steps:**

- Evaporation of the material to be deposited by a high energy source such as an electron beam or ions. This evaporates atoms from the surface
- Transport of the 'vaporized' atoms from the target to the substrate to be coated;
- Reaction between the metal atoms and the appropriate reactive gas (such as oxygen, nitrogen or methane) during the transport stage to form the metal oxides, nitrides, etc
- Deposition of the coating at the substrate surface. More the time, higher the coating thickness
- Rotary evaporation is performed to ensure uniform coating

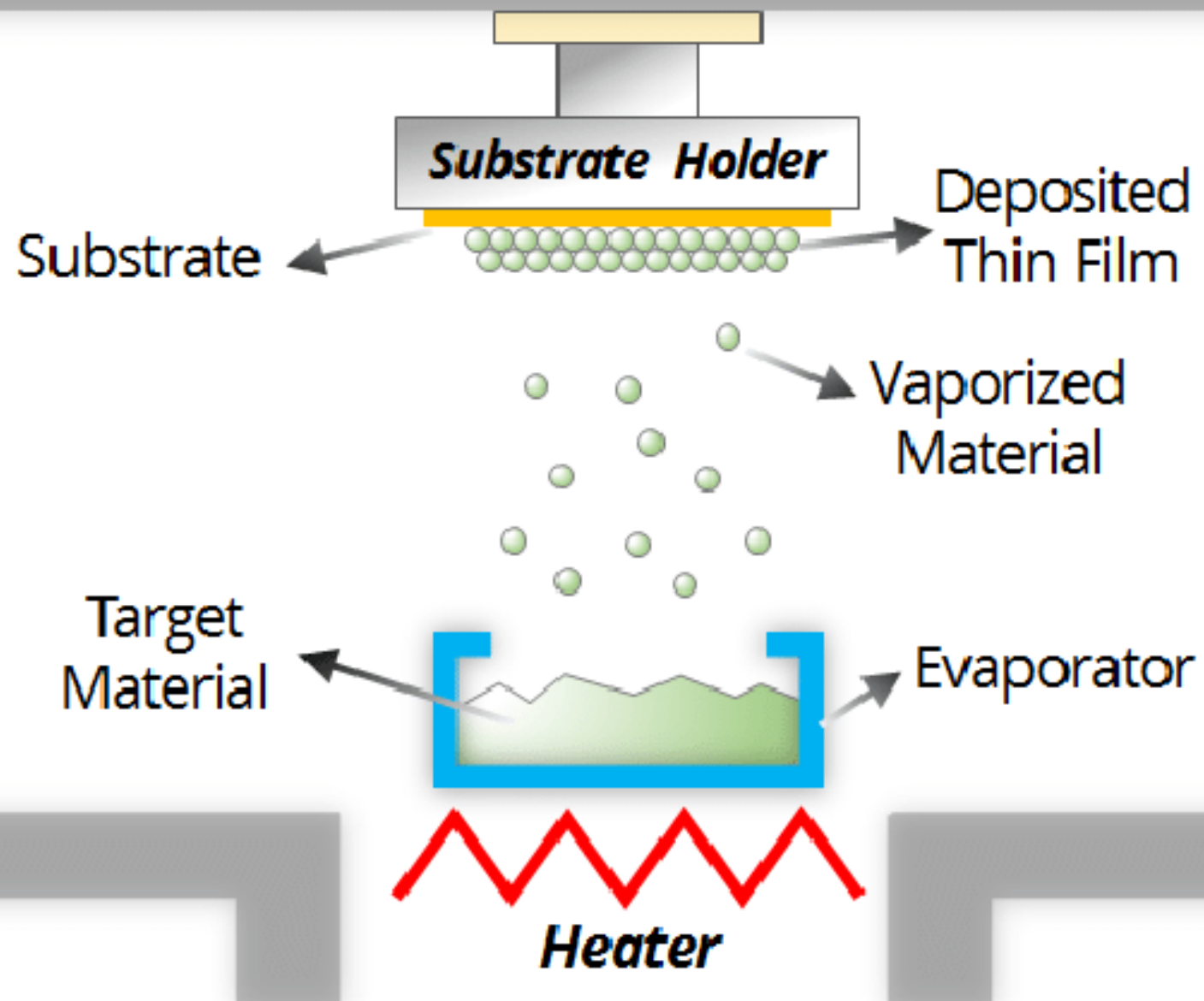
Types of Physical Vapor Deposition

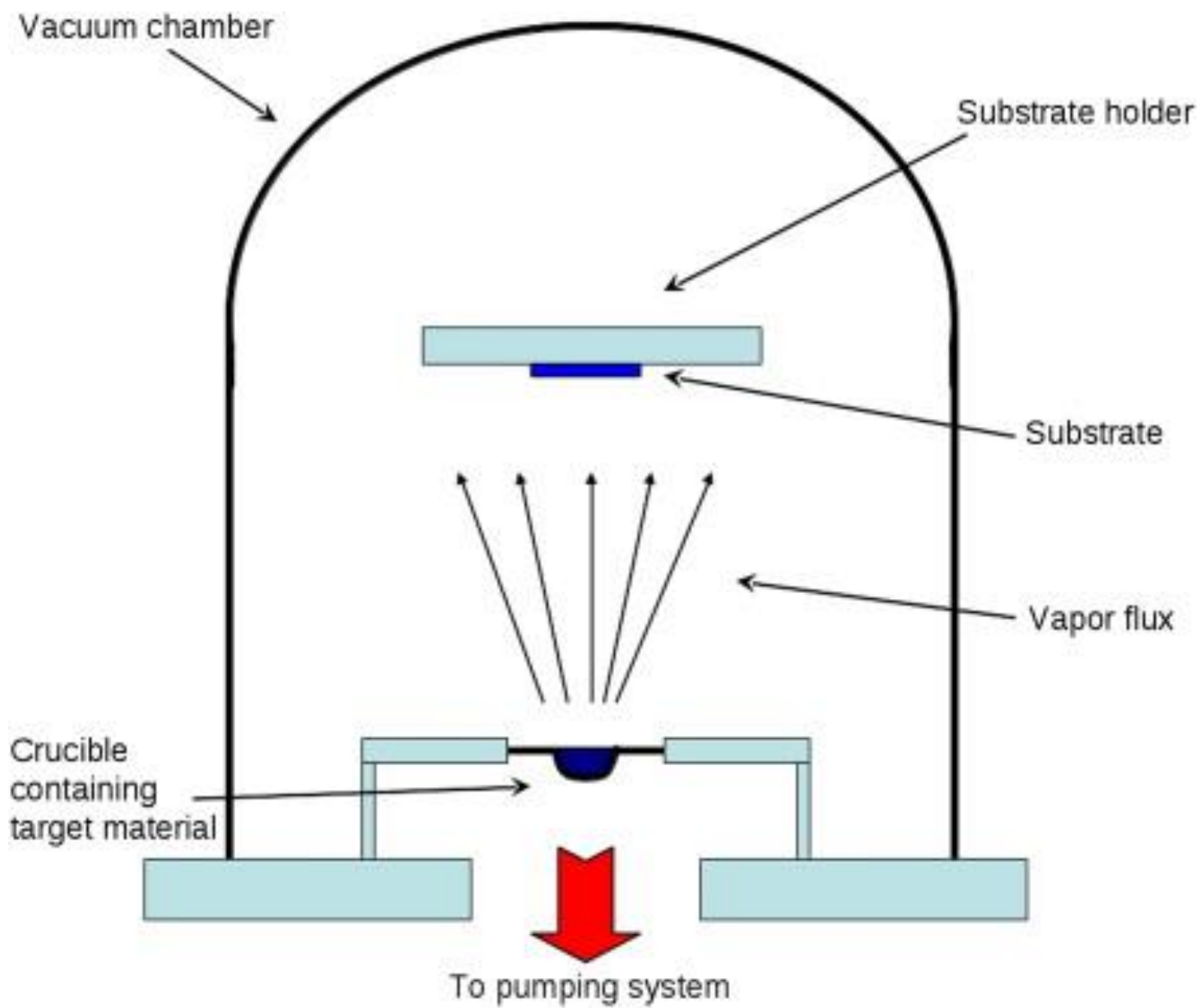
- There are three main types of PVD:
 - Thermal evaporation (vacuum thermal evaporation).
 - Sputtering
 - Ion plating
- All these three processes are performed under vacuum.
- Vacuum evaporation is also known as vacuum deposition
- Material used for coating is thermally vaporized and then proceeds by 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.

Thermal evaporation method

- 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 and electric arc
- The other common heat source is an electron beam or E-Beam Evaporation where an electron beam is aimed at the source material to evaporate it and enter the gas phase
- 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
- There is no chemical bonding between the coatings and substrates is established.
- When the coating materials hit the substrate, it is physically deposited as layers or atom by atom or molecules by molecules.

Vacuum Chamber





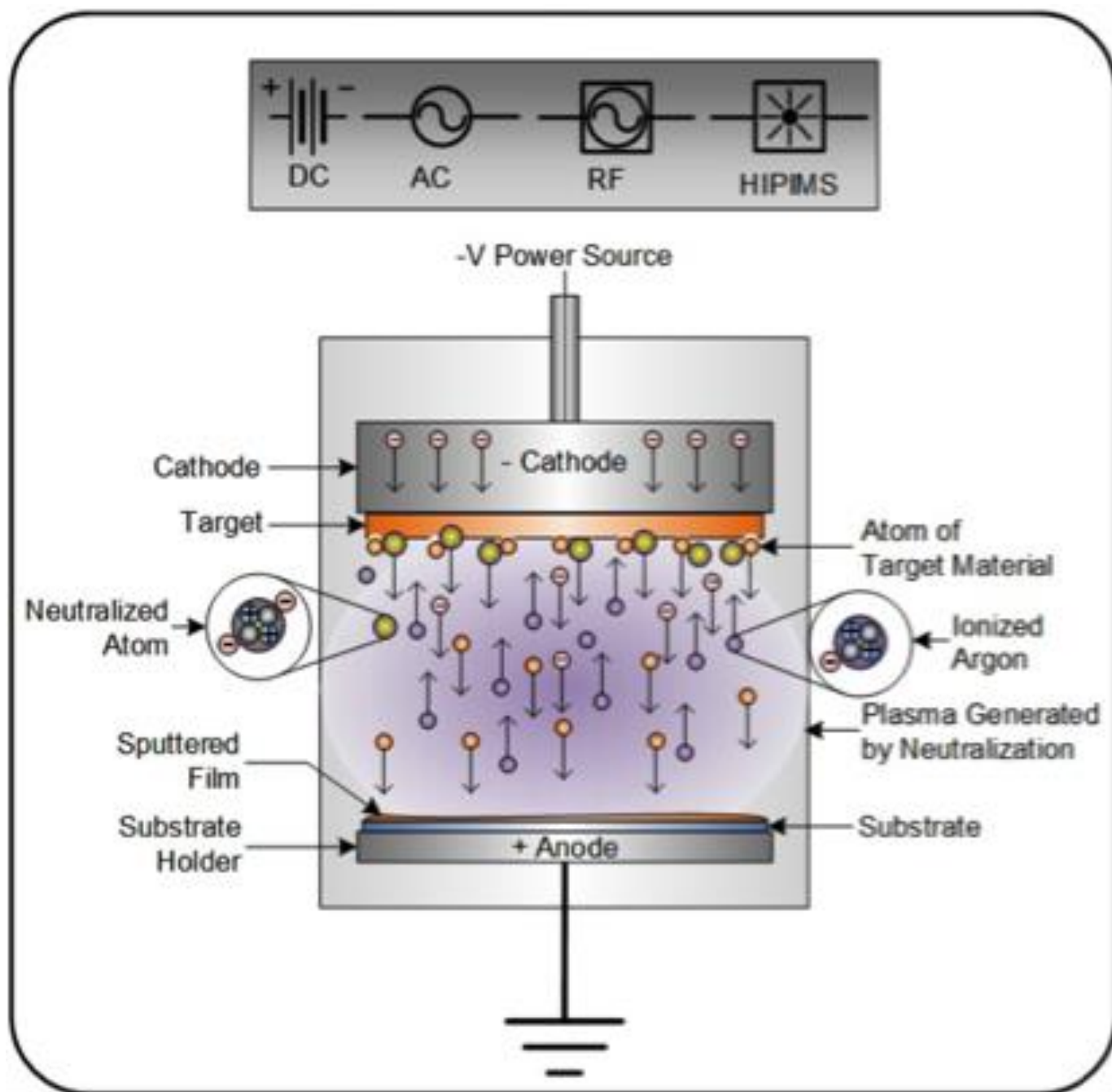


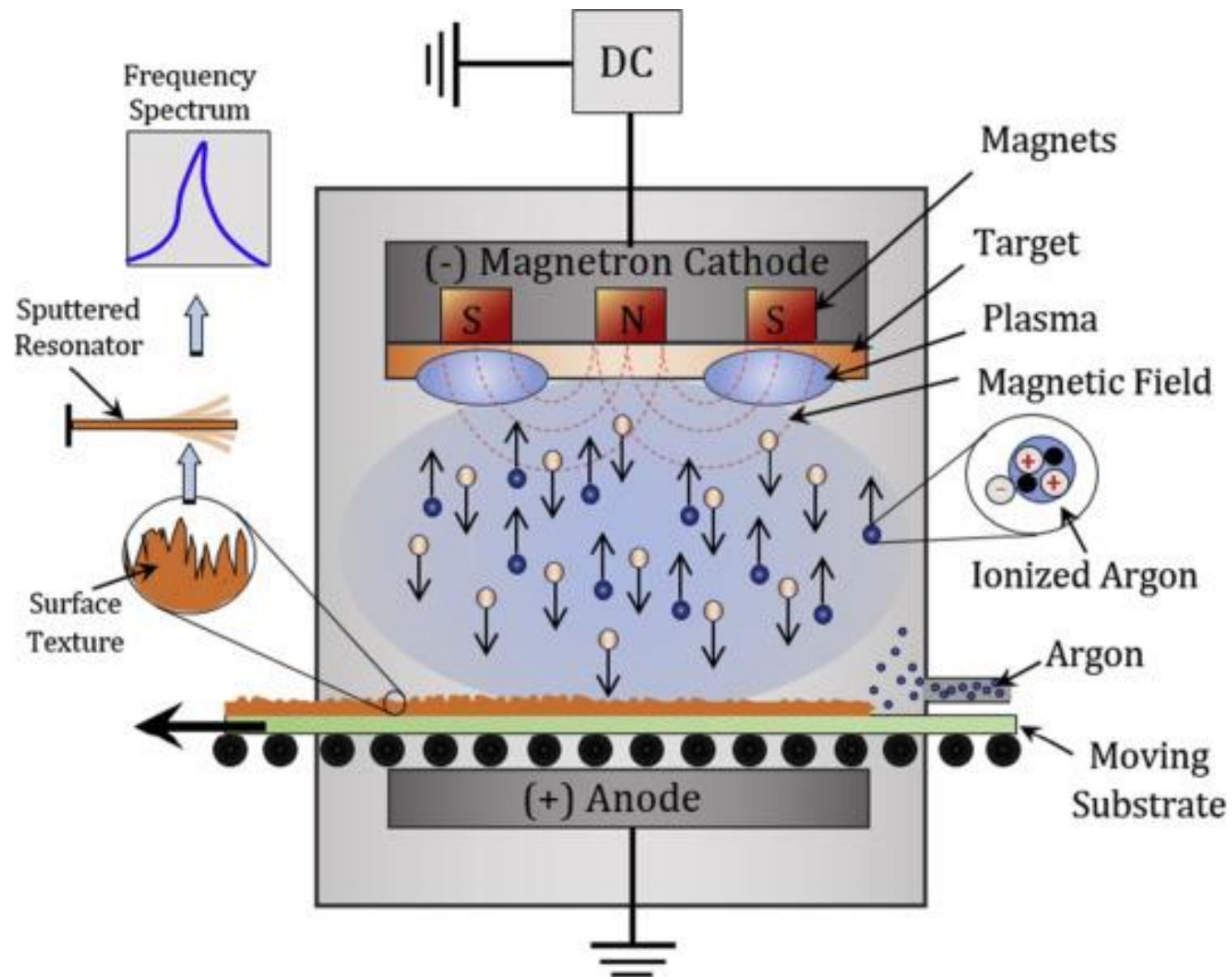
- **Al and Au are quite usable** in thermal evaporation system with heated crucible. They can be melt in crucible and generate enough quantity of vapours.
- **W and Ti are not suitable** due to their low vapour pressure.
- Typical **deposition rates** in industry is around **0.5 $\mu\text{m}/\text{min}$ ($\sim 8 \text{ nm}/\text{s}$, for Al)**

Sputtering Method

- Sputtering involves the electrical generation of a plasma between the coating species and the substrate
- 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.
- For efficient momentum transfer, the atomic weight of the sputtering gas should be close to the atomic weight of the target
- So for sputtering light elements neon is preferable, while for heavy elements krypton or xenon are used.
- The exposed surface of the cathode, called the target, is a slab of the material to be coated onto the substrates
- The gas atoms lose electrons inside the plasma to become positively charged ions

- These ions then accelerated into the target and strike with sufficient kinetic energy to dislodge atoms or molecules of the target material.
- This sputtered material now constitutes a vapor stream, which traverses the chamber and hits the substrate, sticking to it as a coating or "thin film"
- **Types of Sputtering**
 - DC sputtering.
 - Magnetron sputtering.
 - Unbalanced magnetron.
 - Balanced magnetron.
 - Radio frequency (RF) sputtering.
 - Reactive gas sputtering.
 - Ion beam sputtering.
 - Pulse DC/AC sputtering.



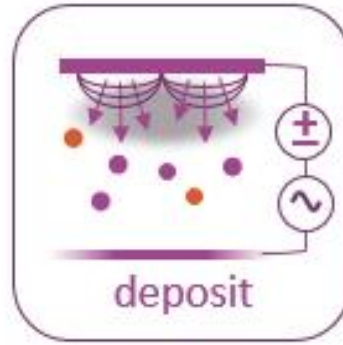


Magnetron sputtering

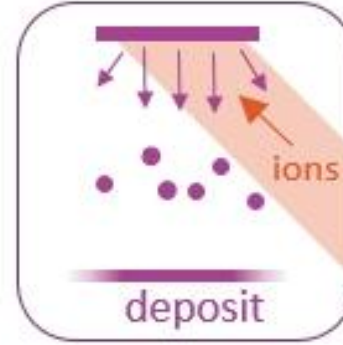
Evaporation



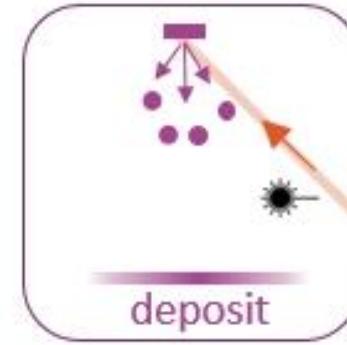
Magnetron sputtering



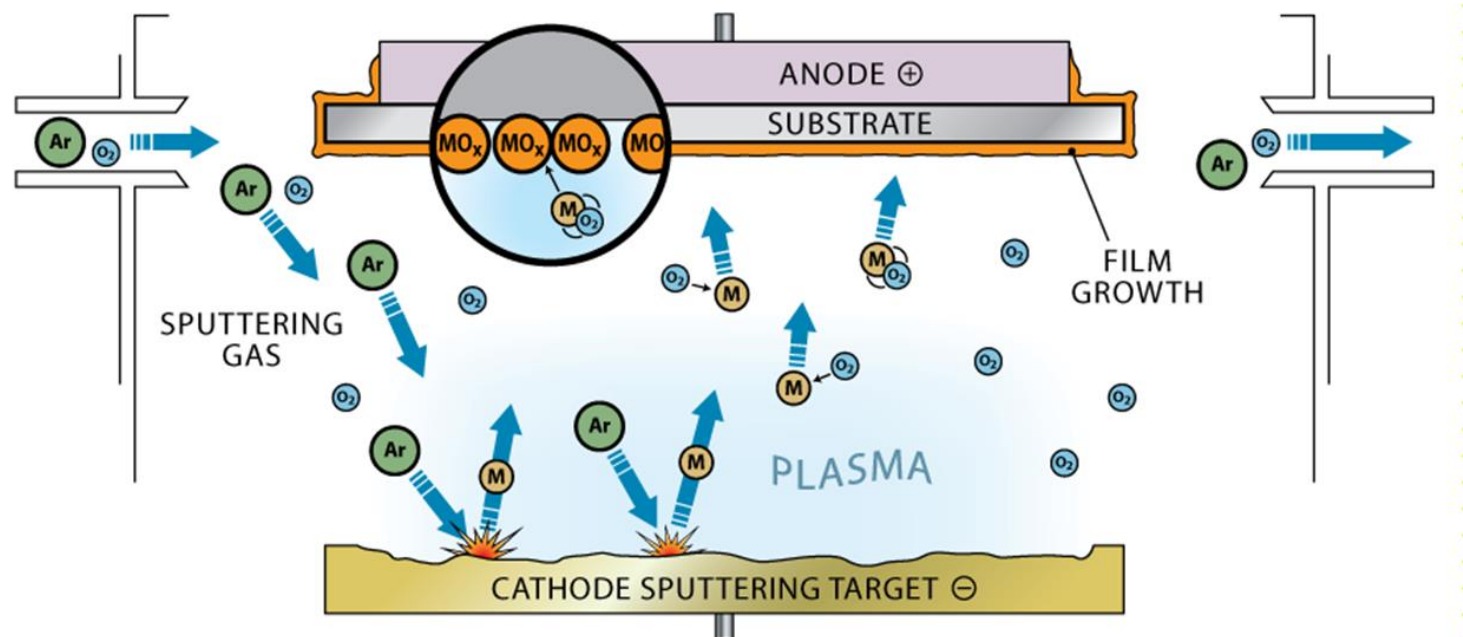
Ion Beam Deposition (IBD)



Pulsed Laser Deposition (PLD)



Reactive gas sputtering



■ Applications of Sputtering method:

- This method is used in **VLSI fabrication**
(Very-large-scale integration (VLSI) is the 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** (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. 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:

- 1) Sputtering can be achieved from large-size targets, simplifying the deposition of films with uniform thickness over large wafers;
- 2) Film thickness is easily controlled by fixing the operating parameters and simply adjusting the deposition time;
- 3) 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;
- 4) Sputter-cleaning of the substrate in vacuum prior to film deposition can be done;
- 5) Device damage from X-rays generated by electron beam evaporation is avoided.

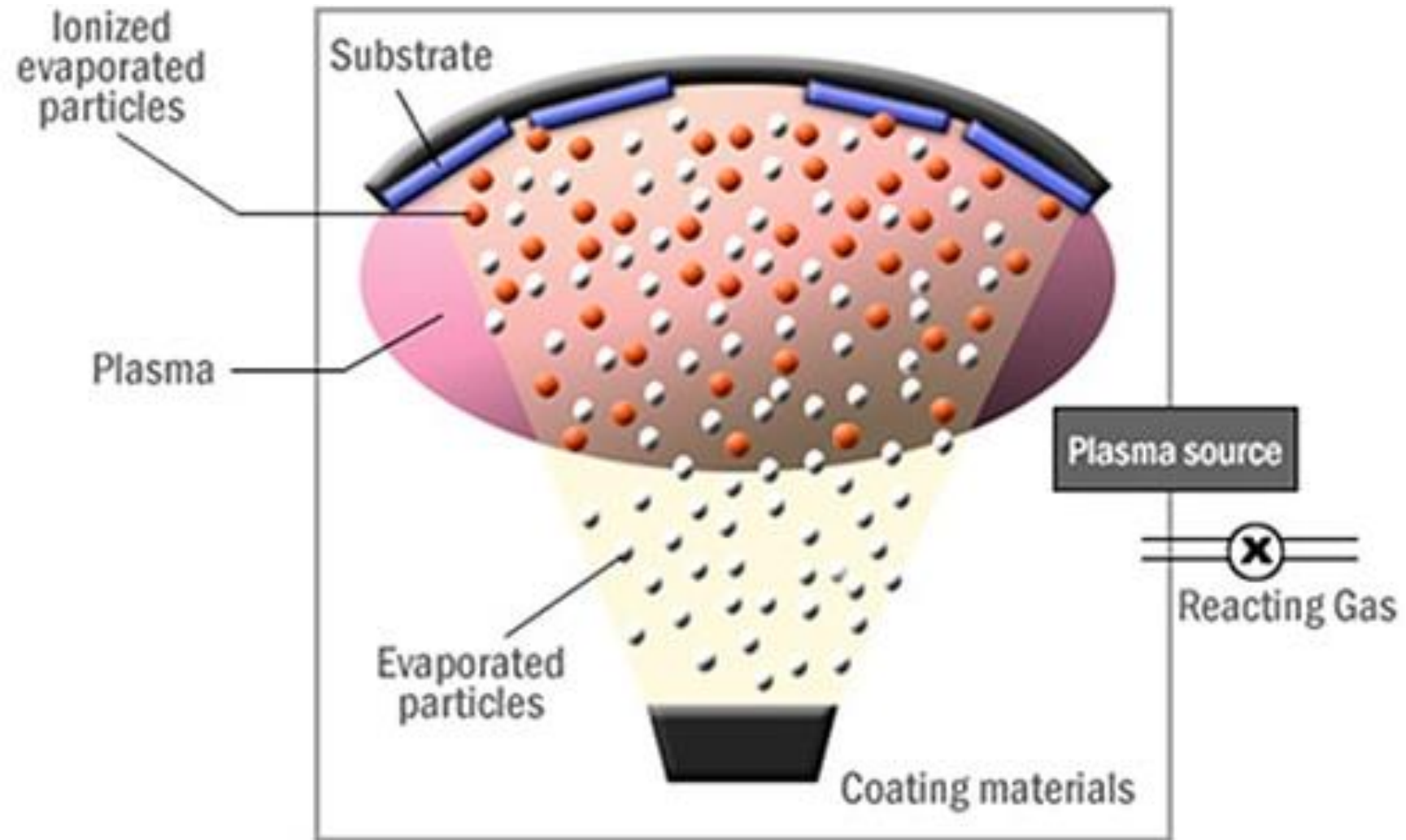
■ Disadvantages of Sputtering:

- 1) High capital expenses are required;
- 2) The rates of deposition of some materials (such as SiO_2) are relatively low;
- 3) Some materials such as organic solids are easily degraded by ionic bombardment;
- 4) 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.
- 5) The coatings are having very poor crystallinity.
- 6) Formation of holes inside the coating matrix due to very energetic hitting of target atoms.

Ion plating or Implantation method

- 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.

Ion plating



■ Advantages of PVD coating:

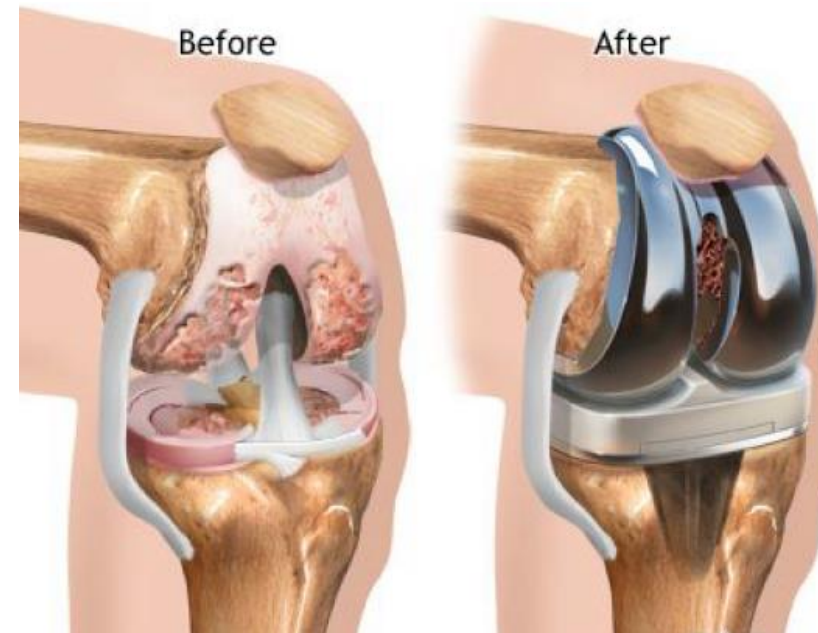
- Materials can be deposited with improved properties compared to the substrate material.
- Almost any type of inorganic material can be used as well as some kinds of organic materials.
- The process is more environmentally friendly than processes such as electroplating.

■ 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.

Applications of PVD methods

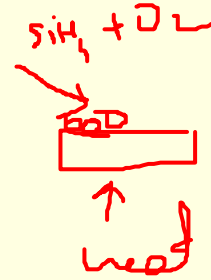
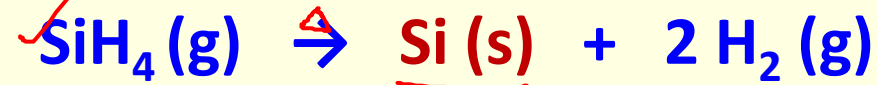
- This process is widely used to produce **decorative coatings on plastic parts** those are resembling shiny metal.
- Many **automobile parts are plastic with a PVD coating of aluminium.**
- A **polish coating** is applied over the decorative coating to provide corrosion protection.
- This process is 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.



Chemical Vapour Deposition (CVD)

- Chemical vapour deposition (CVD) is one of the most common processes used to coat almost **any metallic or 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

- The CVD process involves the **pyrolytic decomposition of a gaseous compound on the substrate** to provide a coating of a solid reaction product



Steps of the CVD process

1. Transport of reactants into the deposition chamber by forced convection.
2. Transport of reactants from the gas stream to the wafer surface by diffusion.
3. Reactants adsorption on the wafer surface.
4. Surface reaction (chemical decomposition, surface migration, etc).
5. By-products desorption from the wafer surface.
6. Transport of byproducts to the gas stream by diffusion.
7. Removal of byproducts away from the deposition chamber by forced convection.

