SOLID STATE PHYSICS - I

Thin film deposition techniques- Magnetic and electric properties

BY

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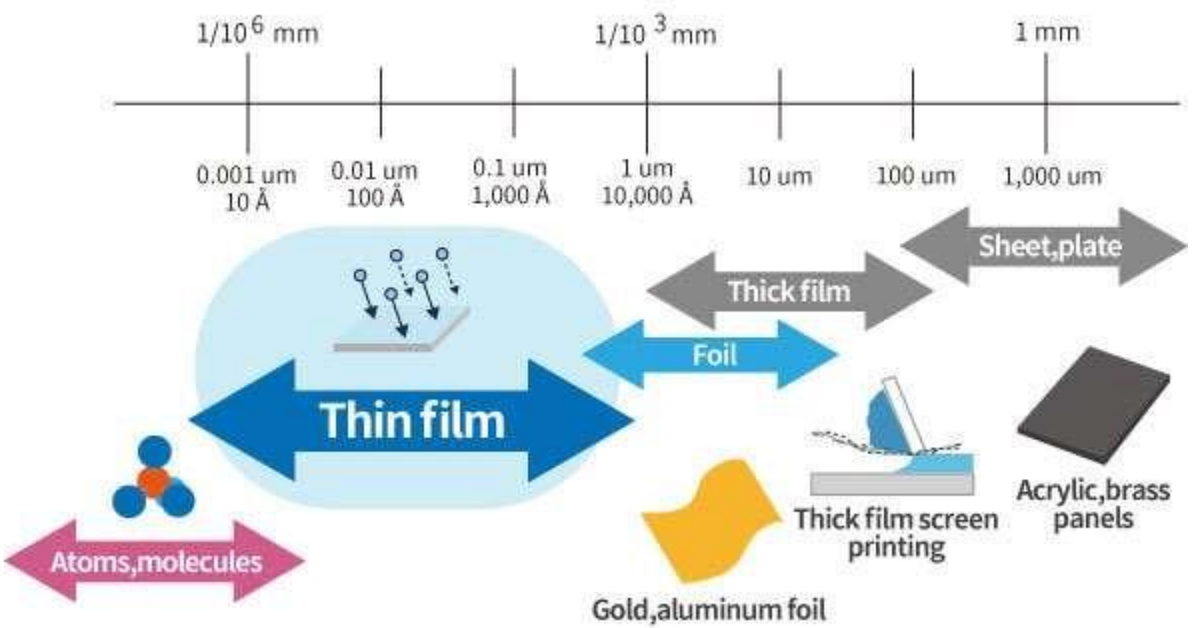
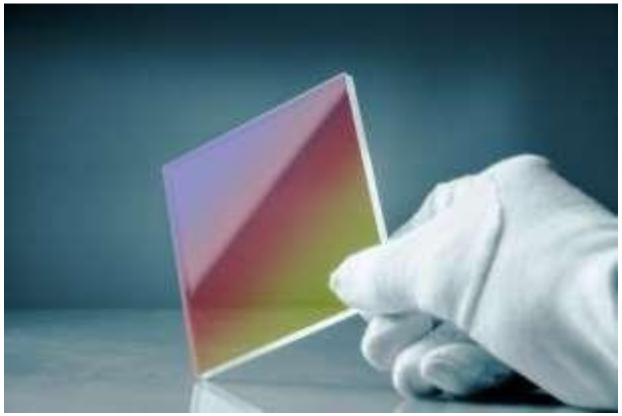
Thin film

A thin film is a layer of material of thickness ranging from fractions of a nanometer to several micrometers. The controlled synthesis i.e. deposition method of materials as thin films is a fundamental step in many applications. Small molecule thin-films are commonly fabricated by Physical methods like PVD, where under high vacuum (10^{-6} to 10^{-8} torr) the solid deposit material is heated above its sublimation temperature creating a vapour which then condenses on a target substrate.





Thin Films Deposition Process

Deposition of thin films on a substrate has several phases, including adsorption, surface diffusion, and nucleation, each depending on the material and the substrate properties, and deposition method and parameters. The interactions between adsorbates and the substrate surface determines the growth mode and the structure of the resulting thin film.

Physical Methods		Chemical Methods	
Evaporative	Sputtering	Gas Phase	Liquid Phase
▪ **Resistive heating**	▪ Glow discharge DC sputtering	▪ Chemical Vapour Deposition (CVD)	▪ Chemical Bath Deposition (CBD)
▪ **Flash Evaporation**	▪ Triode sputtering	▪ Laser CVD	▪ Modified-CBD (SILAR)
▪ **Electron beam evaporation**	▪ Getter sputtering	▪ Photo CVD	▪ Electrodeposition
▪ **Laser Evaporation**	▪ RF sputtering	▪ Plasma-Enhanced CVD	▪ Electroless deposition
▪ **Arc evaporation**	▪ Magnetron sputtering	▪ Metal Organo-CVD (MOCVD)	▪ Anodization
▪ **Radio Frequency (RF) heating**	▪ Face target sputtering		▪ Spray pyrolysis
	▪ Ion beam sputtering		▪ Liquid phase epitaxy
	▪ AC sputtering		▪ Sol-gel process
			▪ Langmuir-Blodgett (LB) technique

I. Physical methods of thin film deposition

Vacuum deposition apparatus: Vacuum systems, substrate deposition technology, substrate materials, substrate cleaning, masks and connections, multiple film deposition,

Thermal Evaporation methods: Resistive heating, Flash evaporation, Arc evaporation, laser evaporation, electron bombardment heating,

Sputtering: Introduction to sputtering process and sputtering variants, glow discharge sputtering, Magnetic field assisted (Triode) sputtering, RF Sputtering, Ion beam sputtering, sputtering of multicomponent materials

- Thin Film Deposition can be achieved through two methods: **Physical Vapor Deposition (PVD) or Chemical Vapor Deposition (CVD)**
- Physical Vapor Deposition (PVD) comprises a **group of surface coating** technologies used for decorative coating, tool coating, and other equipment coating applications.
- It is fundamentally a vaporization coating process in which the basic mechanism is **an atom by atom transfer of material from the solid phase to the vapor phase and back to the solid phase**, gradually building a film on the surface to be coated.
- Physical evaporation is one of the oldest methods of depositing metal films.
- Aluminum, gold and other metals are heated to the point of vaporization, and then evaporate to form to a thin film covering the surface of the substrate.

Vacuum system

- Deposition by vacuum evaporation is quite simple
- Need of vacuum environment in which sufficient amount of heat is supplied to the material for evaporation process
- Condensation of material on a substrate at suitable temperature
- Steps involved in deposition of film

1. Transition of solid/liquid to gaseous state
2. Transport of vapour to substrate from source
3. Condensation of vapour on substrate

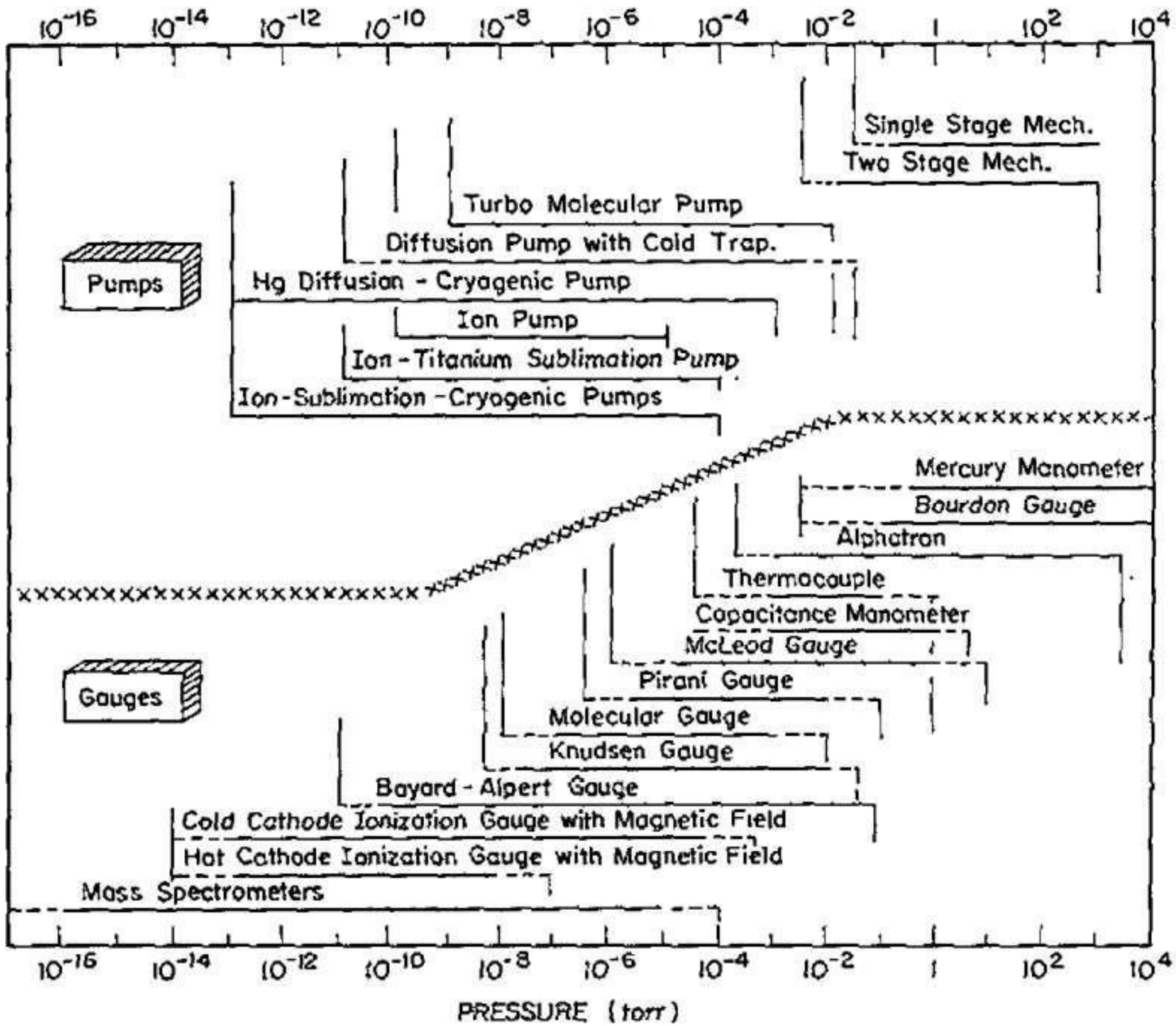
- Distance between source and substrate should be 10-50 cm for quality film

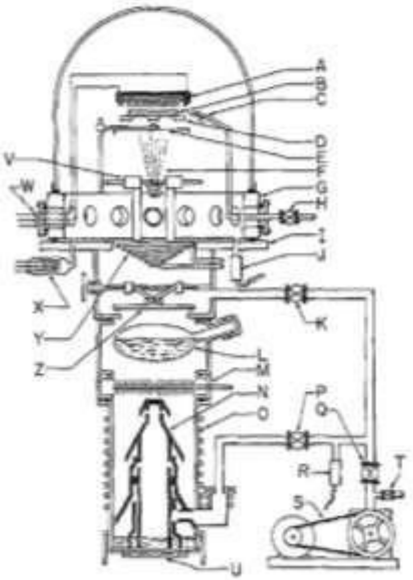
- All film deposition takes place under vacuum or very carefully controlled atmosphere.
- The degrees of vacuum and units is shown below:
- **Rough vacuum: 1 bar to 1 mbar**
- **High vacuum: 10^{-3} to 10^{-6} mbar**
- **Very high vacuum: 10^{-6} to 10^{-9} mbar**
- **Ultra-high vacuum: $< 10^{-9}$ mbar = vacuum in space**
- **1 atm = 760 mm = 760 torr = 760 mm Hg = 1000 mbar= 14.7 p.s.i**
- **1 torr = 1,33 mbar**

Vacuum deposition apparatus: Vacuum systems

- ✓ The **performance of a vacuum system with a chamber or bell jar** is the single most important consideration for vacuum deposition techniques.
- ✓ **Structure and properties of a film**, depending on the material, may be influenced profoundly by the **ultimate vacuum and residual gases and their partial pressures.**
- ✓ It is therefore necessary to employ as good a vacuum condition as possible.
- ✓ The ultrahigh-vacuum (uhv) range below 10^{-8} Torr is easily accessible with recent advancements in vacuum technology and is being adopted increasingly

The various types of pumps, their ultimate pressure, and the various types of gauges employed to measure pressure are summarized

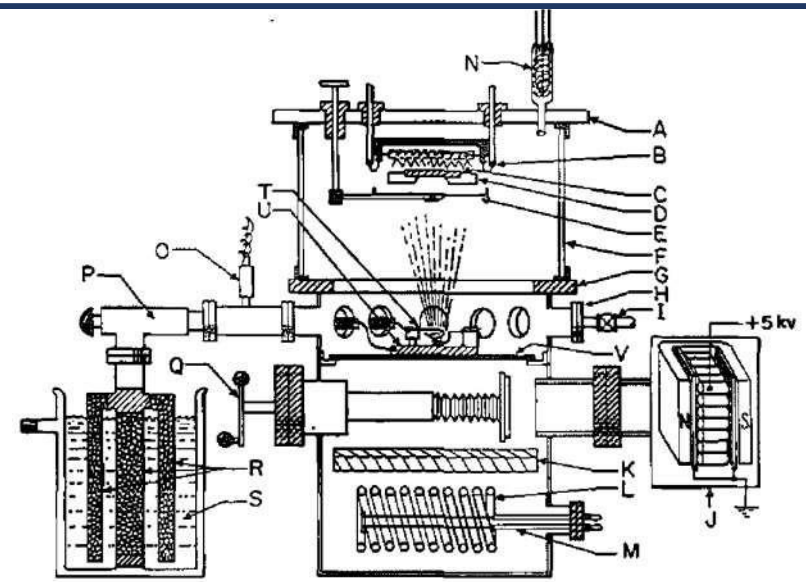




Diffusion pump bell jar:

Simple and cheap

10^{-6} to 10^{-7} Torr



Getter ion pump bell jar:

10^{-12} Torr

Selective towards reactive gases

- The ultimate pressure in an evaporator depends not only on the **pumps employed** but also on the **rate of desorption of the evaporator hardware and degassing of the evaporant.**

Substrate-deposition Technology

Substrate material:

- **Nature and surface finish** of the substrate are extremely important
- Glass, quartz, and ceramic substrates - for polycrystalline films
- Single-crystal substrates of alkali halides, mica, MgO, Si, Ge - used for epitaxial growth
- The most commonly used glass slides as substrates are of **Pyrex**, is **non-crystalline** and has a composition of

80.5% - $Si0_2$,

12.9% - B_20_3,

3.8% - Na_20,

2.2% - Al_2O_3

0.4 % - K_2O

- **Soft glass, Pyrex, and quartz surfaces** exhibit large (several microns) smooth areas

Substrate Cleaning:

- Glass substrates must be **thoroughly cleaned before deposition**, and a variety of procedures exist for this purpose.
- The gross contaminants are first removed by a **lukewarm, ultrasonically agitated, ionic detergent.**
- A hot detergent solution may produce **nonuniform etching** of soda-lime glasses.
- The glass is then rinsed thoroughly several times in deionized water and later subjected to a vapor degreaser using pure alcohol.
- The cleaned glass may be stored immersed in pure alcohol and occasionally agitated ultrasonically. Before use, the glass is dried by blowing with dry nitrogen.

- Additional methods for cleaning glass and cleaved surfaces **utilize heat and electron and ion bombardment**
- **Fire polishing or even heating to near the softening point** produces a clean glass surface.
- An efficient method to remove contaminants and oxide layers from a substrate is to sputter the surface by ionic bombardment.
- An atomically smooth surface can be realized by sputtering if it is preceded by degassing and extended annealing.
- It must be noted that low bombardment energies (~0.5 kV) and low current densities (~100 μA/cm2) should be used to prevent surface damage.
- Glow discharge should be confined to the surface for cleaning.

Masks and connections:

- By laying a suitable mask over the substrate during deposition, films in some pattern or shape can be obtained.
- A **moving mask** may be used to grow films laterally.
- Resolution of the pattern is determined by the definition' of the mask and its proximity to the substrate.
- Instead of using masks during deposition, the required patterns may be **photoetched or cut with a microelectron beam**. This is, of course, an important area of technology for microelectronics.
- Electrical connections to thin films for measurements, or interconnections within thin-film circuits can be obtained in a variety of ways.

Multiple film deposition:

- Deposition of films of the same material on a large number of substrates, and a large number of different types of films on a variety of substrates during the same sequential process is commonly required for research and development applications.
- Batch coating is simple and can be performed by mounting substrates on a holder which may be continuously rotated or moved step by step.
- An arrangement for sequential coating is more versatile and more useful.

Evaporation:

- Evaporation is **very simple and convenient**, and is the most widely used
- One merely has to produce a vacuum environment in which a sufficient amount of heat is given to the evaporant to attain the vapor pressure necessary for evaporation, then the evaporated material is allowed to condense on a substrate kept at a suitable temperature.
- A vast number of materials can be evaporated in vacuum and caused to condense on a substrate to yield thin solid films.

- Deposition consists of three distinguishable steps.

1. Transition of the condensed phase (solid or liquid) into the gaseous state.

2. Traversal by the vapor of the space between the vapor source and the substrate (i.e., transport of vapor from the source to the substrate).

3.Condensation of the vapor upon arrival at the substrate (i.e., deposition of these particles on the substrate)

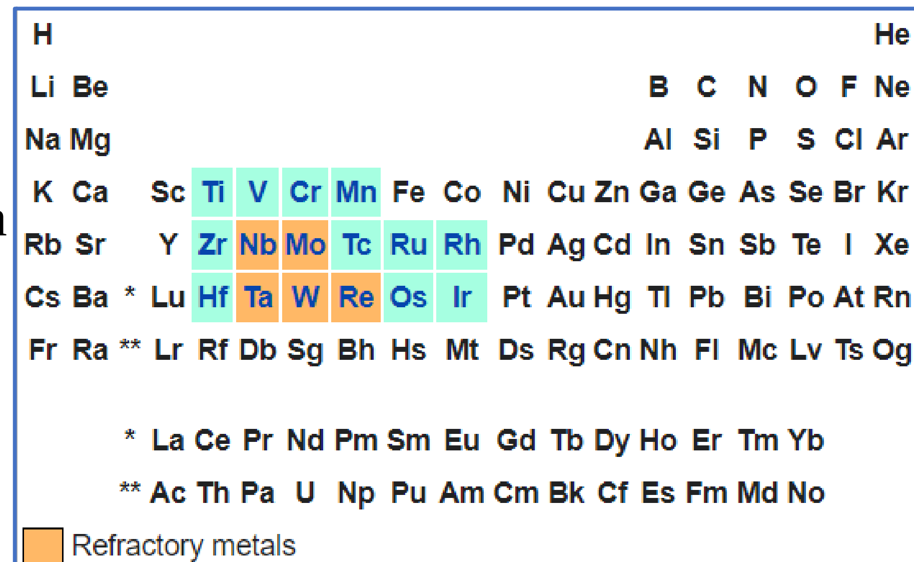
- To evaporate materials in a vacuum system, a container is required to support the evaporant and to supply the heat of vaporization while allowing the charge to reach a temperature high enough to produce the desired vapor pressure.
- To avoid contamination of the films deposited, the **support material itself must have negligible vapor and dissociation pressures at the operating temperature**.

- Rough estimates of the operating temperatures are based on the assumption that **vapor pressures of 10^{-2} torr** must be established to produce useful condensation rates.

- Materials commonly used are **refractory metals and oxides**.

Refractory metals:

- Refractory metals are a class of metals that are extraordinarily resistant to heat and wear.



- They all share some properties, including a melting point above 2000 °C and high hardness at room temperature.

- They are chemically inert and have a relatively high density

- The possibilities of **alloying and chemical reactions between the evaporant and the support materials must be taken into account** while choosing a particular support material.

- The shape of the support materials are used **depends very much on the evaporant.**

- The important methods of evaporation are

1. Resistive heating

2. Flash evaporation

3. Arc evaporation

4. Laser evaporation

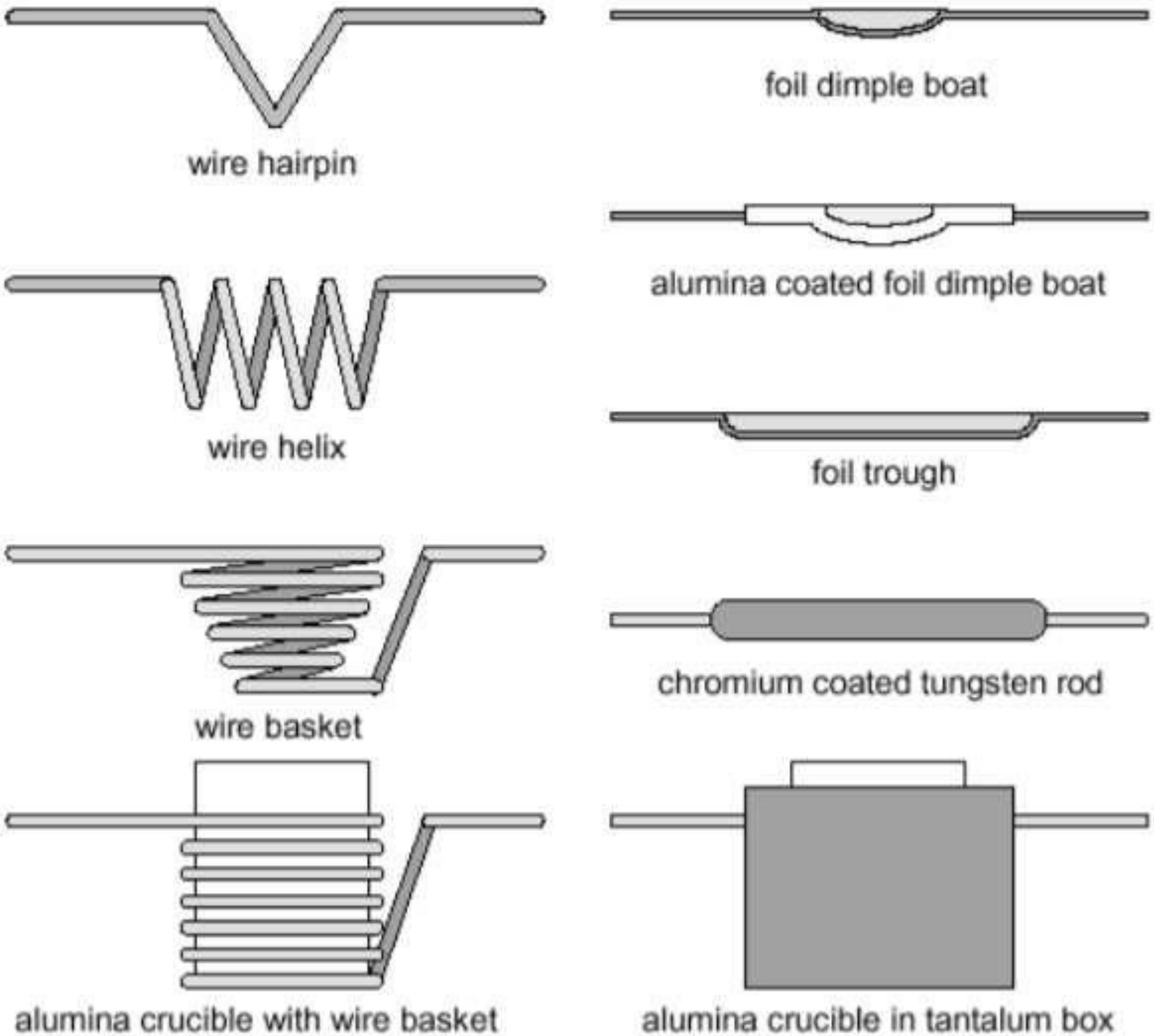
5. Electron beam evaporation

Two heating mechanisms are commonly used in evaporation: resistive heating and electron beam heating

Resistive heating:

- Materials in a boat of crucible are evaporated by heating with a filament.
- Common materials are W, Ta, Mo, C, and BN/TiB_2 composite ceramics.
- Vaporize materials at temperatures below about 1500°C.
- The material is to be evaporated is by giving **electrical resistance heating, resistive heating**
- Materials that can be deposited using this technique include aluminum, silver, nickel, chrome, magnesium, among many others.
- The simplest sources are in the **form of wires and foils** of different types

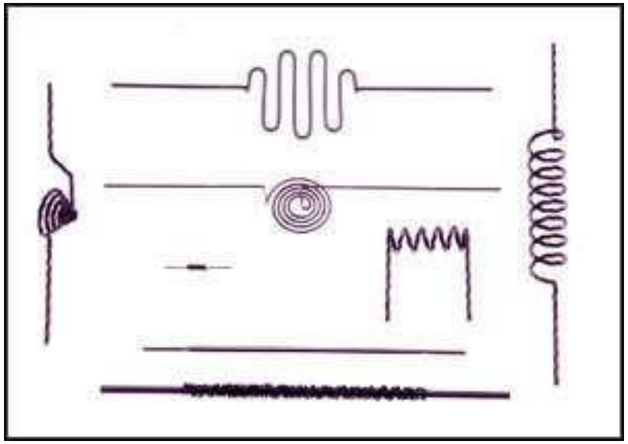
Resistance Heated Evaporation Sources



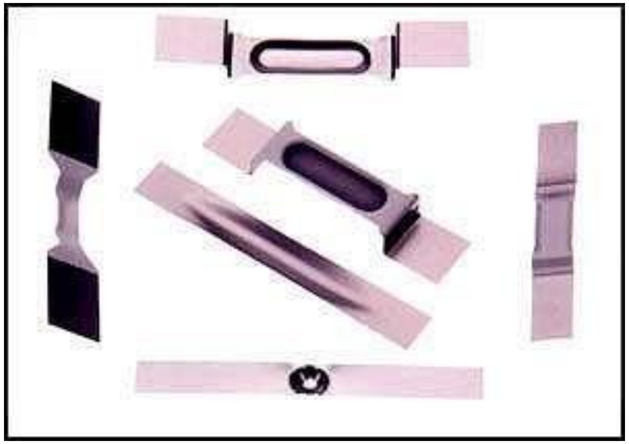
Electron beam:

- High energy electron beams are used (commonly referred to as e-beam heating) for refractory materials, an e-beam gun is accelerated to a high voltage (10–20 kV), electrostatically or magnetically collimated and focused, and impinged onto the surface of the materials to be evaporated.
- Advantage of e-beam evaporation over resistive heating is that the energy is transferred as heat only to melt the source locally instead of the entire crucible, and consequently there is less contamination from the crucible.

Popular heating "containers" for evaporation source

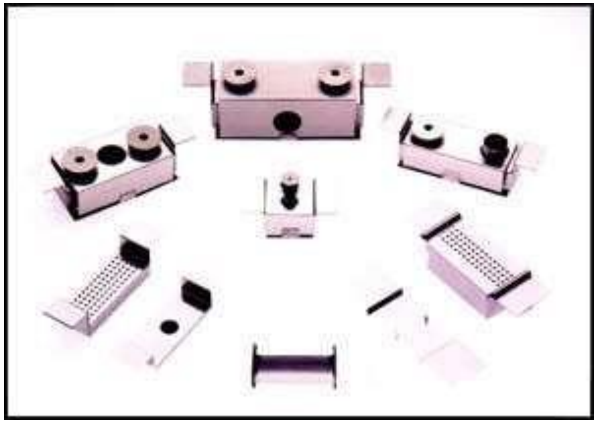


Resistors (put source rod inside coil)



Heating boat (open top)

Crucibles
(only choice for e-beam evaporator)



Box with small opening

Typical boat/crucible material

Refractory Metals		
Material	**Melting Point (^oC)**	**Temperature for 10-mtorr Vapor Pressure (P_e) (^oC)**
Tungsten (W)	3380	3230
Tantalum (Ta)	3000	3060
Molybdenum (Mo)	2620	2530
Refractory Ceramics		
Graphitic Carbon (C)	3799	2600
Alumina (Al_2O_3)	2030	1900
Boron Nitride (BN)	2500	1600

Considerations: thermal conductivity, thermal expansion, electrical conductivity, wetting and reactivity.

Graphite crucible is most popular, but avoid cracking the crucible due to stress/ temperature gradients (bad for materials that "wet" graphite such as Al and Ni).

Aluminum: tungsten dissolves in aluminum, so not quite compatible.

Comparison of thermal and e-beam evaporation

Deposition	Material	Typical Evaporant	Impurity	Deposition Rate	Temperature Range	Cost
Thermal	Metal or low melt-point materials	Au, Ag, Al, Cr, Sn, Sb, Ge, In, Mg, Ga CdS, PbS, CdSe, NaCl, KCl, AgCl, MgF_2, CaF_2, $PbCl_2$	High	1 ~ 20 A/s	~ 1800 °C	Low
E-Beam	Both metal and dielectrics	Everything above, plus: Ni, Pt, Ir, Rh, Ti, V, Zr, W, Ta, Mo Al2O3, SiO, SiO2, SnO2, TiO2, ZrO2	Low	10 ~ 100 A/s	~ 3000 °C	High

Thermal evaporation:

- Simple, robust, and in widespread use.
- Use W, Ta, or Mo filaments to heat evaporation source.
- Typical filament currents are 200-300 Amperes.
- Exposes substrates to visible and IR radiation.
- Contamination from heated boat/crucible.

Electron beam evaporation:

- More complex, but extremely versatile, virtually any material.
- Less contamination, less heating to wafer (as only small source area heated to very high T).
- Exposes substrates to secondary electron radiation.
- X-rays can also be generated by high voltage electron beam.
- Since x-rays will damage substrate and dielectrics (leads to trapped charge), e-beam evaporators cannot be used in MOSFET.

a. hairpin source and wire helix:

- Made of thin **tungsten/molybdenum wire**
- The **evaporants are fixed directly to the source** in the form of wire
- Upon melting, the evaporant wets the filament and is held by surface tension and deposite on the substrate. Multistrand filaments are generally used because they offer greater surface area than single-wire elements.

Drawbacks of sources:

(a) they can be used only for metals or alloys

(b) only a limited quantity of the material can be evaporated at a time

(c) the material to be evaporated should wet the resistive filament wire upon melting

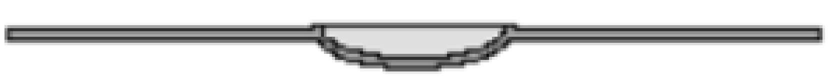
(d)Once heated, these elements become very fragile and will break if not handled carefully.

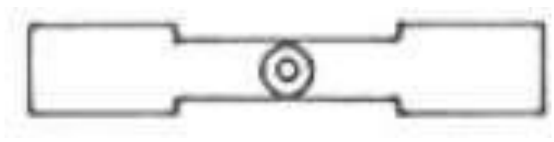
Advantages:

1. Simple and convenient technique
2. Less wastage of material
3. Free from pollution

b. Dimple foil:

- Dimpled foils fabricated from sheets of **tungsten, tantalum, or molybdenum**
- **0.005 - 0.015 in. thick**
- Most commonly used sources when only small quantities of the evaporant are available or needed.
- All three refractory metals become brittle after being heated in a vacuum, especially if alloying with the evaporant takes place.





c. Dimpled foil with oxide coating

- Oxide-coated metal foils are also used as evaporation sources.
- Here **Mo or Ta foils about 0.01 in. thick** are covered with a thick layer of alumina
- Operating temperatures up to **1900°C** are possible.
- The power requirements of such sources are much above those of uncoated foils due to the reduced thermal contact between the resistively heated metal and evaporant

d. Wire baskets

- Wire baskets are used to evaporate small chips of dielectrics or metal, which either sublime or do not wet the source material on melting.

e. crucible with wire spiral heater

- Crucibles of quartz, glass, alumina, graphite, beryllia, and zirconia are used with indirect resistance heating

Table: materials with appropriate temperatures required to produce vapor pressures of 10^{-2} torr and the suitable support materials

Material	Melting point (°C)	Temperature (°C) required to produce *Vp* = 10-2 torr	Wire or foil	Crucible	l
Ag	961	1030	W, Ta, Mo, Nb	Mo, Ta, C	Mo preferred
Al	660	1220	W, Ta	BN, graphite	Wets and cre with graphite
Al_2O_3	2030	1800	W, Ta	W, Ta	Oxygen-defic
As	817	300		Al_2O_3, C, BeO	Sublimes; to
Au	1063	1400	W, Mo	W, Mo, C, Al_2O_3	
B	2300	2100		C	
Ba	725	610	Mo, W, Ta		Does not allo
BaF_2	1280	1100	Mo, W, Ta		
Be	1280	1230	W, Mo, Ta	C	Toxic
Bi	271	670	W, Ta, Mo	Mo, Al_2O_3	
Bi_2O_3	817	1840		Al_2O_3	
Bi_2S_3	685 (decomposes)		W		Sulfur-defici
Bi_2Te_3	820		W, Ta, Mo		Reactive eva stoichiometri
Ca	850	600	W	Al_2O_3	
CaF_2	1360	1280	Ta, W, Mo	Ta, W, Mo	Sublimes
Cd	321	265	W, Ta, Mo, Fe, Ni, Nb	Mo, Ta, fused quartz	Sublimes; co vacuum syste
CdS	1750	670	W, Mo	Ta, W, graphite, quartz	Dissociates d
CdSe	1250	660		Mo, Ta, quartz,	

The main disadvantages of evaporation by simple resistive heating are

(a)The reaction of the evaporant material with the support crucibles

(b)The difficulty in attaining high enough temperatures for the evaporation of dielectrics (Al_2O_3, Ta_2O_5, TiO_2, etc.)

(c) Low rates of evaporation

(d) The dissociation of compounds or alloys upon heating.

2. Flash Evaporation

- Thin films of multicomponent alloys or compounds that tend to distill fractionally is that the chemical composition of the film obtained deviates from that of the evaporant - difficulty is best overcome in flash evaporation.
- Here small quantities of the material to be evaporated are dropped in powder form onto a boat hot enough to ensure that evaporation takes place instantaneously.
- The temperature of the boat should be high enough to evaporate the less volatile material fast.

- When a particle of the material evaporates, the component with the higher vapor pressure evaporates first, followed by components with lower vapor pressure.
- In practice, the feed of material is continuous, and there will be several particles in different stages of fractionation on the boat.
- Moreover, since no material accumulates on the boat during evaporation, the net result of these instantaneous discrete evaporations is that the vapor stream has the same composition as the source material.
- If the substrate temperature is not high enough to permit reevaporation to take place, stoichiometric compound or alloy films will be formed.

- The powdered material can be fed into the heated support using different arrangements (mechanical, electromagnetic, vibrating, rotating, etc.) for material feeding.

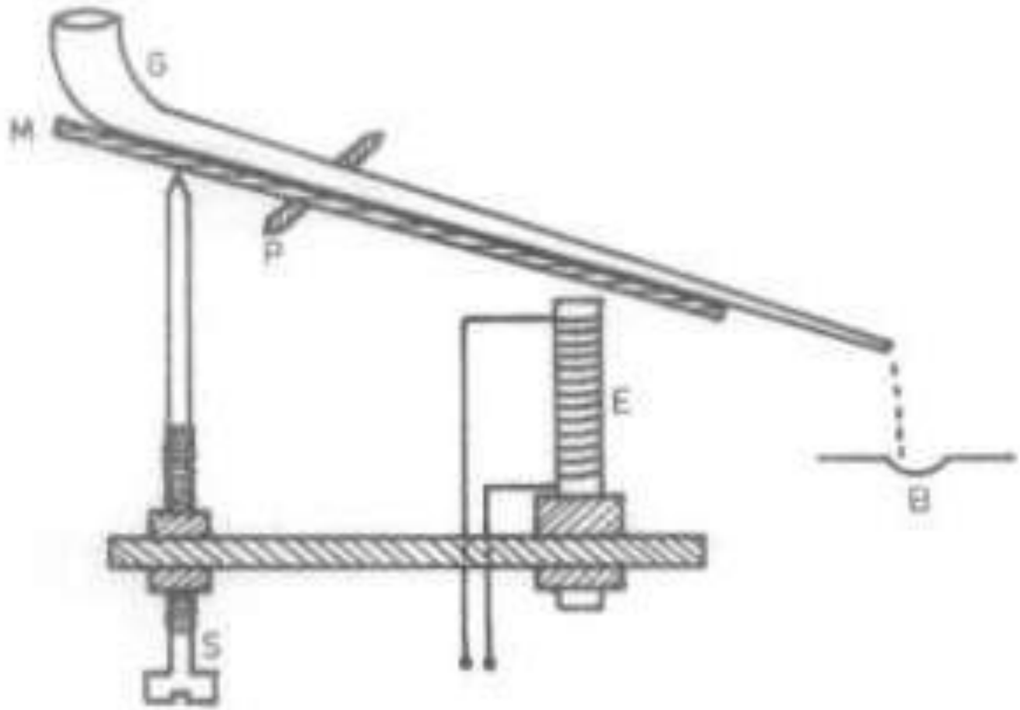


Figure 1.2
Schematic diagram of flash evaporator: M, mild steel plate; G, pipe-shaped glass tube; P, pivot; S, screw; E, electromagnet; B, heated molybdenum boat.

- The **mild steel plate**, which can be adjusted by screws on a pivot, is attracted by the electromagnet, and intermittent passage of the current through the coil makes the steel plate vibrate at a desired frequency.
- The **pipe-shaped glass tube** made of Corning glass serves to drop the powdered material onto a heated **molybdenum boat**. The whole system is enclosed in an aluminum cover and was used inside the vacuum system.
- The power to the winding of the electromagnet was fed from an astable multivibrator working at a frequency of 2 Hz.
- The starting material in the form of fine powder was taken in a stainless steel hopper and vibrated with the help of a vibrator.

- The powder dropped slowly onto a boat kept at about 1300°C and evaporated instantaneously. The lattice parameters determined agreed with those of the bulk.
- Flash evaporation has been very widely used for the preparation of cermet films, which are mixtures of metals and dielectrics.
- Their resistivity increases with the dielectric content, can be varied over a wide range, and possesses great stability at high temperature

3. Arc evaporation

- Arc evaporation to prepare thin films was first tried in a conventional vacuum evaporator by Lucas et al. to obtain thin refractory metal films.
- Electrodes of the metal to be evaporated were mounted on insulated supports in a vacuum system evacuated to a pressure of 10^{-5} torr; one of the rods was rotatable and the other was fixed.
- Using a standard welding generator, the voltage was applied between the electrodes, and the rotatable electrode was brought into contact with the fixed rod, held there until a hot spot appeared, and then moved away, thus drawing an arc.

- This resulted in the rapid deposition of the film of the electrode metals on the substrate placed close to the electrodes.
- Films of niobium, tantalum, vanadium, and stainless steel were obtained using this setup
- Their arrangement consisted of two electrodes in the form of rods facing each other and aligned along the axis of a helical filament
- One of the electrodes could be moved linearly to adjust the interelectrode gap by a gear system driven from outside the vacuum chamber by a servo motor.
- The electrode coil system was set in the vacuum chamber.

- The arc-type discharge is easily started by applying between the electrodes an input voltage of only about 1.52.5 kV, while simultaneously bombarding the electrodes with the electrons emitted from the filament.
- This achieved a steady state discharge of long duration, and the discharge power caused the electrodes evaporate.
- Thin films of conductive refractory materials (W, Ta, C) were prepared.
- The gas supply that sustains the plasma state came from the melting surface of the two electrodes

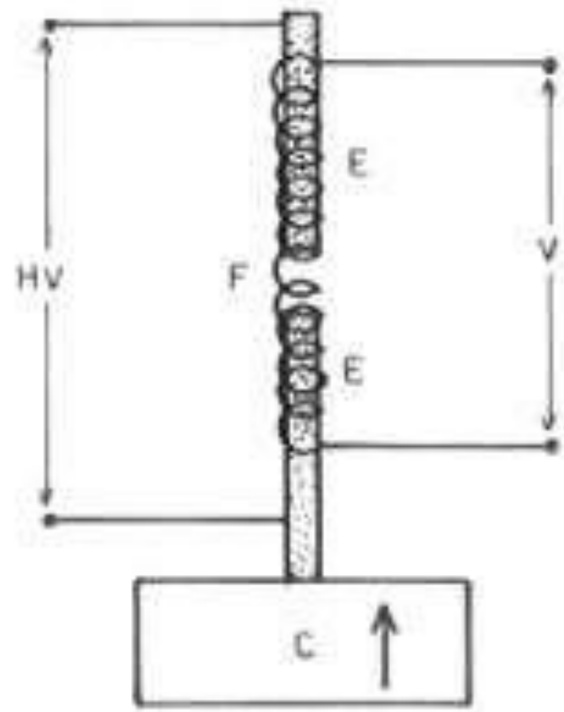


Figure 1.19
Schematic diagram of the electrode-filament arrangement for the vacuum arc method: C, gap control device; E, electrodes; F, helical filament.

4. Laser evaporation

- Lasers are used as the thermal source to vaporize the evaporant materials
- Laser evaporation is a high vacuum technique
- The source of power for evaporation is kept outside the vacuum system.
- The vaporized material is deposited onto substrates placed in front of the source material inside the vacuum chamber
- Many materials can be vaporized in a vacuum by a directed laser beam as the evaporation power source.
- They used a ruby laser external to the vacuum chamber and a lens focused the radiation from the ruby rod through a window in the bell jar onto the surface of the sample to be evaporated.

- Most of the films were evaporated from powdered materials placed in small inclined crucibles in the bell jar and deposited onto substrates placed 20 to 50 mm above the crucibles.
- Lateral motion of the lens allowed the focal spot to fall where desired on the surface of the material.

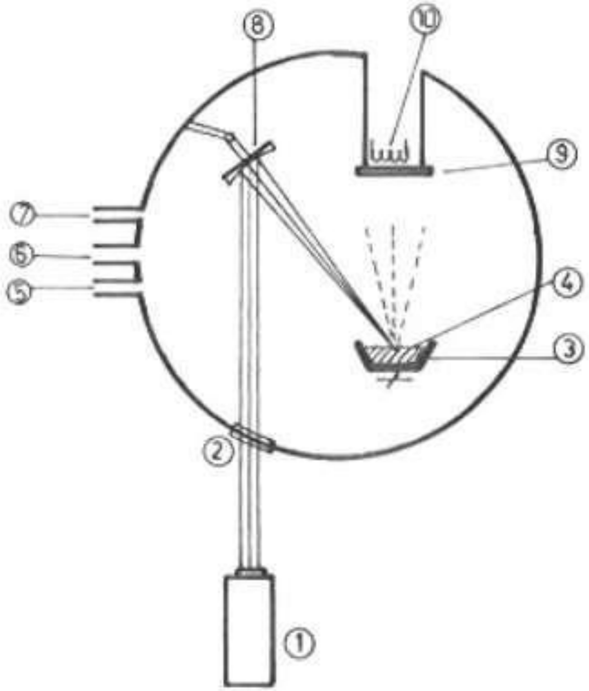


Figure 1.10
Schematic diagram of the laser evaporation system: 1, CO_2 laser; 2, ZnSe window; 3, Mo boat; 4, source material; 5, to pump; 6, to vacuum gages; 7, to mass filter; 8, concave mirror; 9, substrate; 10, infrared heater.

- Fujimori prepared carbon films using continuous wave (CW) CO_2 laser (80 W) as a heat source.
- The laser beam passed through a ZnSe window into the chamber and was reflected and focused by a Be-Cu concave mirror onto the source material in a molybdenum boat.
- Graphite and diamond, both in powder form, were used as source material.
- Unlike carbon, these powders are easy to evaporate because of their low heat capacity.
- The laser beam was scanned across the source by the rotation of the concave mirror as well as by the linear drive of the molybdenum boat.

Pulsed laser evaporation (PLE)

- The pulsed laser evaporation (PLE) technique for the preparation of SnO_2 film on GaAs and glass substrates using a high power pulsed laser.
- A train of pulses from an acousto-optically Q-switched Nd:YAG ((neodymium-doped yttrium aluminum garnet; Nd:$Y_3A_{l5}O_{12}$) laser was scanned by a pair of galvanometric mirrors, directed into the vacuum chamber, and finally focused onto the surface of the target (SnO2 pellets).
- The power densities of the laser pulses were in the 107 W/cm^2 range, pulsed laser frequency - 2000 Hz, pulse width - 200 ns, and the scan rates - 110 cm/s.
- Base pressure in the chamber was lower than 5×10^{-7} torr. The substrates were placed 2.5 in. above the surface.

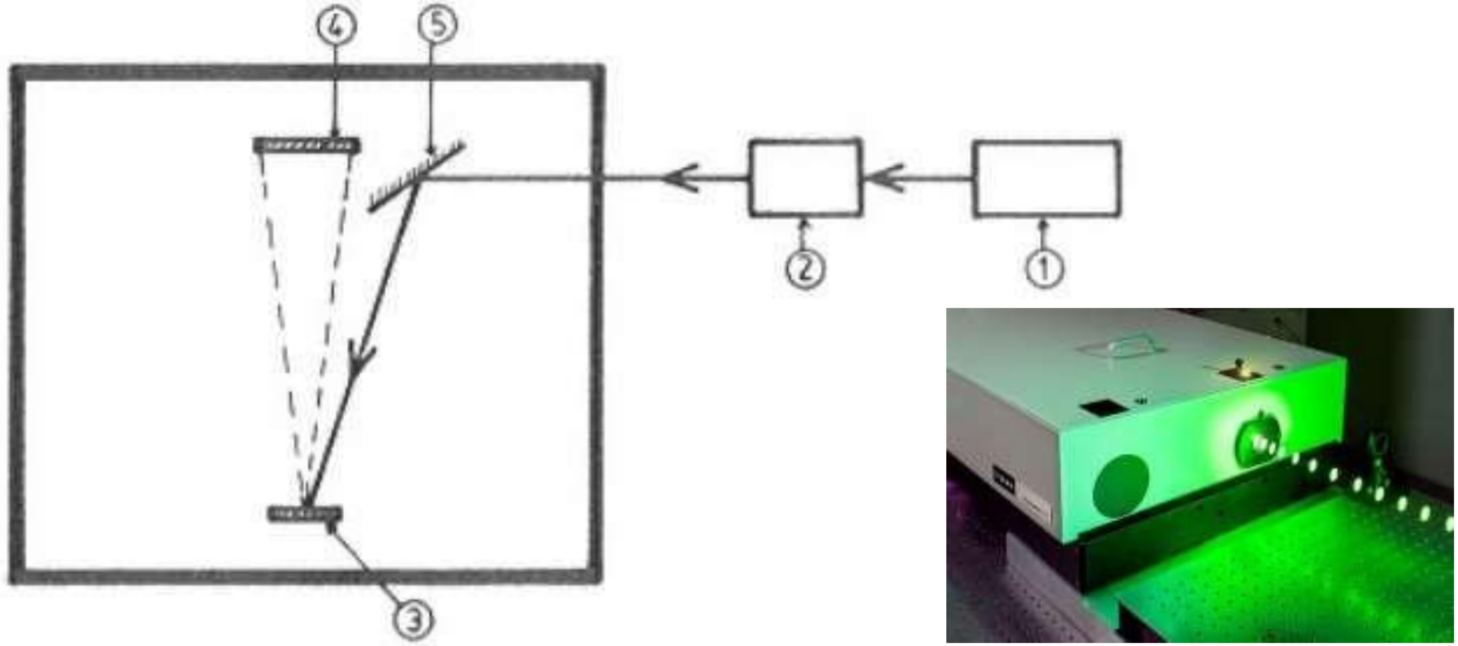


Figure 1.12
Schematic diagram of the pulsed laser evaporation system: 1, pulsed YAG laser; 2, scanner; 3, source; 4, substrate; 5, mirror.

Advantages of Laser Evaporation

1. Lasers are **clean and introduce minimal contamination** from the heat source.

2.Film contamination from the support material is reduced because of the surface evaporation characteristics of the beam.

3. With the high power densities obtained by focusing the laser beams, **high melting point materials can be vaporized at high deposition rates**.

4.Because of the small beam divergence, the laser and the associated **equipment could be kept far away**, an attractive feature in radioactive areas.

5.Simultaneous or sequential multisource evaporation can be done easily by directing the laser beam with external mirrors

3. Electron beam evaporation

- ✓ Disadvantages for instance, the reaction of the material with the support crucible, low evaporation rates, the vaporizaion of materials can be accomplished by electron bombardment .
- ✓ Here a stream of electrons is accelerated through fields of typically **510 k V** and focused onto the surface material for evaporation.
- ✓ The electrons lose their energy very rapidly upon striking the surface, and the material melts at the surface and evaporates.
- ✓ That is, the surface is directly heated by impinging electrons, in contrast to conventional heating modes.

- ✓ Because the material in contact with the support crucible remains solid, in effect the molten material is contained in a crucible of itself and the reactions are minimized.
- ✓ Direct heating allows the evaporation of materials from water-cooled crucibles, and these are very commonly used in electron beam (EB) evaporation.
- ✓ Such water-cooled crucibles are necessary for evaporating reactive and in particular reactive refractory materials, to avoid almost completely reactions with the crucible walls. This allows the preparation of high purity films because crucible materials or their reaction products are practically excluded from evaporation.

- ✓ By this type of heating any material can be evaporated, and the rate of evaporation varies from fractions of an angstrom per second to micrometers per second.
- ✓ The electron beam sources have been found to be versatile and reliable
- ✓ beam evaporators are used even for materials that can be quite easily and satisfactorily evaporated from an ordinary refractory metal boat.
- ✓ EB technology is rather expensive and complicated, and its use is not justified if the more easily controlled alternative electrical resistance heating is available.
- ✓ The method is of practical importance in certain cases requiring high purity films and in the absence of suitable support materials

- Electron beam guns can be classified into thermionic and plasma electron categories.
- In **thermionic**, the electrons are generated thermionically from heated refractory metal filaments, rods, or disks.

  In **plasma electron** type, the electron beams are extracted from a plasma confined in a small space.
- In thermionic systems, which feature a simple work-accelerated electron gun structure, there is a hot cathode in the form of a wire loop close to the evaporant, and the electrons converge radially on the work.

- The simplest is the **pendant drop configuration,** introduced by Holland.
- The metal to be evaporated should be in the form of wire or rod centered within the cathode loop.
- The tip of the rod melts, and the evaporation takes place from the molten tip and is deposited on the substrates located below the source.
- Because the drop of molten metal at the tip is held by surface tension, this method is limited to metals with high surface tension and vapor pressures greater than 10^{-3} torr their melting points.
- Careful control of the electric energy supplied is also necessary to avoid a temperature that too greatly exceeds the melting point.

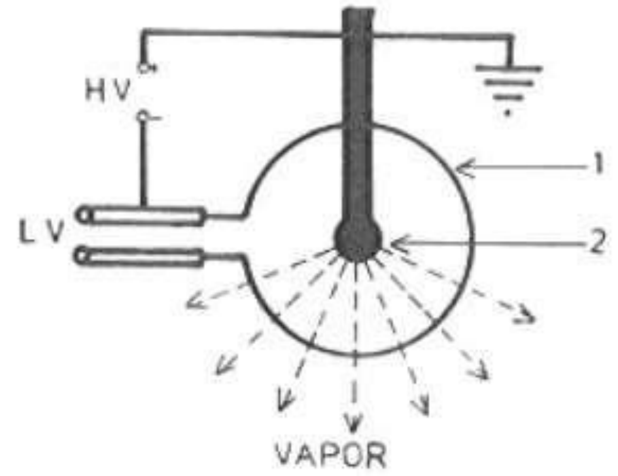


Figure 1.3
Work-accelerated electron gun structurependant drop configuration: 1, hot cathode; 2, pendant drop.

- Another class of thermionic system consists of self-accelerated electron guns that have a separate anode with an aperture through which the electron beam passes toward the work. Here the electron beam is focused by a negatively biased filament having a conical anode and magnetic lens.
- Focal spots a few millimeters in diameter are used to evaporate the materials.
- These guns operate at higher voltages, offer more flexibility, and are most commonly used. Telefocus guns have been used successfully to evaporate refractory metals such as Nb, which require temperatures higher than 3000°C.
- The telefocus guns have adequate power density on the evaporant even if the distance between the gun and the crucible is large.

- The path of the electron beam is a straight line, and therefore either the substrate or the gun must be mounted off to the side, unless the electron beam is bent through a transverse magnetic field.

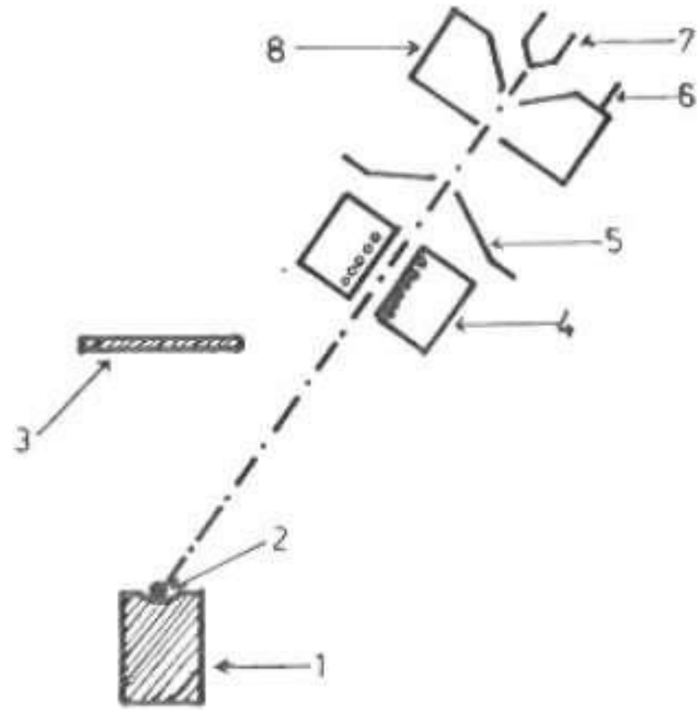


Figure 1.5
Self-accelerated electron gunelectrostatically and magnetically focused: 1, support; 2, evaporant; 3, substrate; 4, magnetic lens; 5, anode; 6, negative bias; 7, hot cathode; 8, filament housing.

- In this bent beam electron gun, the operating high tension (HT) voltage is 9 k V and currents up to 200 mA are used.
- By altering the HT voltage and the focusing current, the electron beam can be focused onto one or more supports situated between the pole pieces

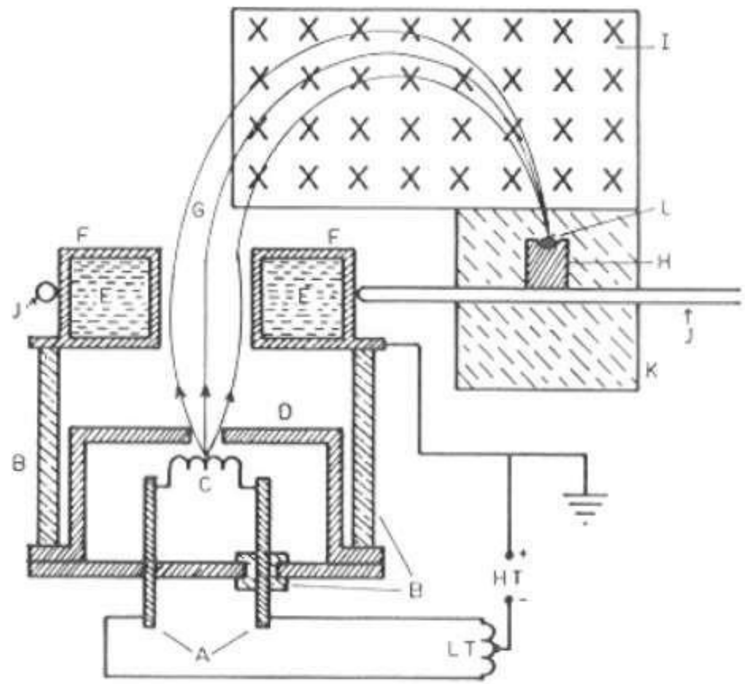
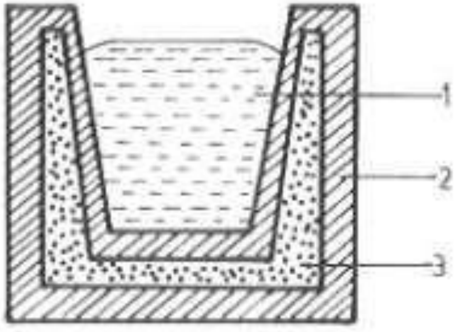


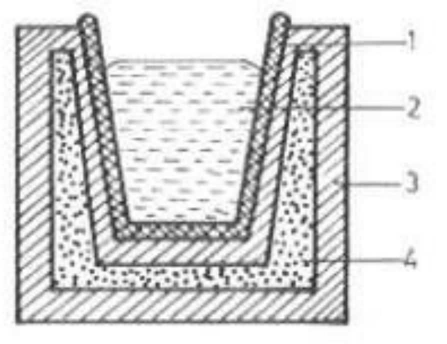
Figure 1.6
Schematic diagram of the bent-beam electron gun: A, L.T. electrodes; B, ceramic insulators; C, tungsten filament; D, shield; E, magnetic focusing coil; F, anode assembly; G, electron paths; H, copper hearth; I, extended pole pieces; J, water cooling tube; K. permanent U-magnet.

- To accommodate the evaporant for electron beam evaporation, crucibles of different types are used, depending on the required level of evaporation rate.
- Watercooled copper crucibles have been found to be useful in a wide range of applications.
- Crucibles of this type are used for the evaporation of refractory materials such as tungsten as well as for the evaporation of highly reactive material (e.g., Ti).



Water-cooled copper crucible: 1, evaporant; 2, copper crucible; 3, water cooling.

- When high power losses are to be avoided or when the evaporation rate at a given power level has to be increased, crucible inserts act as a heat barrier.
- The use of crucible inserts yields a more uniform temperature distribution over the molten pool and also a greater pool depth.
- The material selection depends on factors such as thermal conductivity, chemical resistivity to the hot evaporant, and high resistance to thermal shock.
- Ceramics based on Al_2O_3, graphite, titanium nitride, or boron nitride are used for crucible inserts.



Water-cooled copper crucible with inserts: 1, crucible inserts; 2, evaporant; 3, copper crucible; 4, water cooling.

- In the thermionic emission type of guns, the chamber pressure must **be limited to pressures of 10^{-4} torr** or less for reasonable beam control and cathode element life.
- But this limitation of 10^{-4} torr maximum operating pressure does not occur with the plasma electron beam source, which utilizes ionizable gas at a pressure of 10^{-3} torr or higher.
- The plasma electron beam can be used practically for the same purposes as thermally emitted electron beams.
- There are two types of plasma electron beam gun**: the cold hollow cathode guns and the hot hollow cathode (HHC) guns**.

- HHC has the advantage of being a low voltage, high current arc generating device and, when used to produce metallurgical coatings, the typical operating range has an arc current of 50200 A.
- The arc sends a beam of electrons to strike the evaporant material, and the beam is used to simultaneously evaporate and to ionize the material. Therefore this type of coating can be considered to be a variant of the ion plating.

Sputtering

- **Process of ejecting atoms from the surface by the bombardment of positive ions**

  \- **(cathode) sputtering**.

- The ejected atoms can be made to condense on a substrate to form a thin film.
- When a charged particle bombards the target surface, apart from the ejection of neutral atoms of the surface material, charged atoms and electrons are also emitted from the surface.
- The ejected neutral target atoms condense into thin films on the substrate.
- **Sputtering yield** - **the number of atoms ejected from the target surface per incident ion**.

- The sputtering yield depends on the **bombarded material, its structure and composition, the characteristics of the incident ion, and also the experimental geometry**.
- The sputtering yield has been determined for a number of metals bombarded with ions over a broad range of ion energy.
- According to **collision theory of sputtering**, the incident ion knocks atoms in the target from their equilibrium positions, thus causing these atoms to move in the material and to undergo further collisions, finally causing the ejection of atoms through the target surface.

- This mechanism is the **most universal** one and is applicable to the cathode sputtering process in general

- The main advantages of sputtering as a thin film preparation technique are:

(a) high uniformity of thickness of the deposited films

(b) good adhesion to the substrate

(c) Better reproducibility of films

(d)ability of the deposit to maintain the stoichiometry of the original target composition

(e) relative simplicity of film thickness control

Glow Discharge DC Sputtering

- Simplest arrangement is the glow discharge d c sputtering system
- A plate of the material to be deposited (target) is connected to negative voltage supply and the substrate facing the target is mounted on the adjacent anode
- Dc voltages of the order of 15 kV are applied across the electrode (current density, 110 mA/cm^2)
- A glow discharge is initiated by introducing a neutral gas such as argon into the vacuum chamber to provide a pressure of 10^{-1}-10^{-2} torr. When the glow discharge is started, the positive ions strike the target plate, removing mainly neutral atoms from the surface of the target, and these eventually condense as a thin film on the substrate.

- There are also electrons emitted from the target (cathode) by ion bombardment, and these are accelerated toward the substrate platform, where they collide with the gas atoms.
- These electrons help to maintain the glow discharge, as the ionized gas atoms in turn bombard the target and release more secondary electrons.
- If the gas pressure is too low or the cathode-anode spacing too small, the secondary electrons cannot undergo sufficient ionizing collisions before they hit the anode.
- On the other hand, if the pressure and/or separation is too large, the ions generated are slowed by inelastic collisions, and when they strike the target, they will not have enough energy to produce secondary electrons.

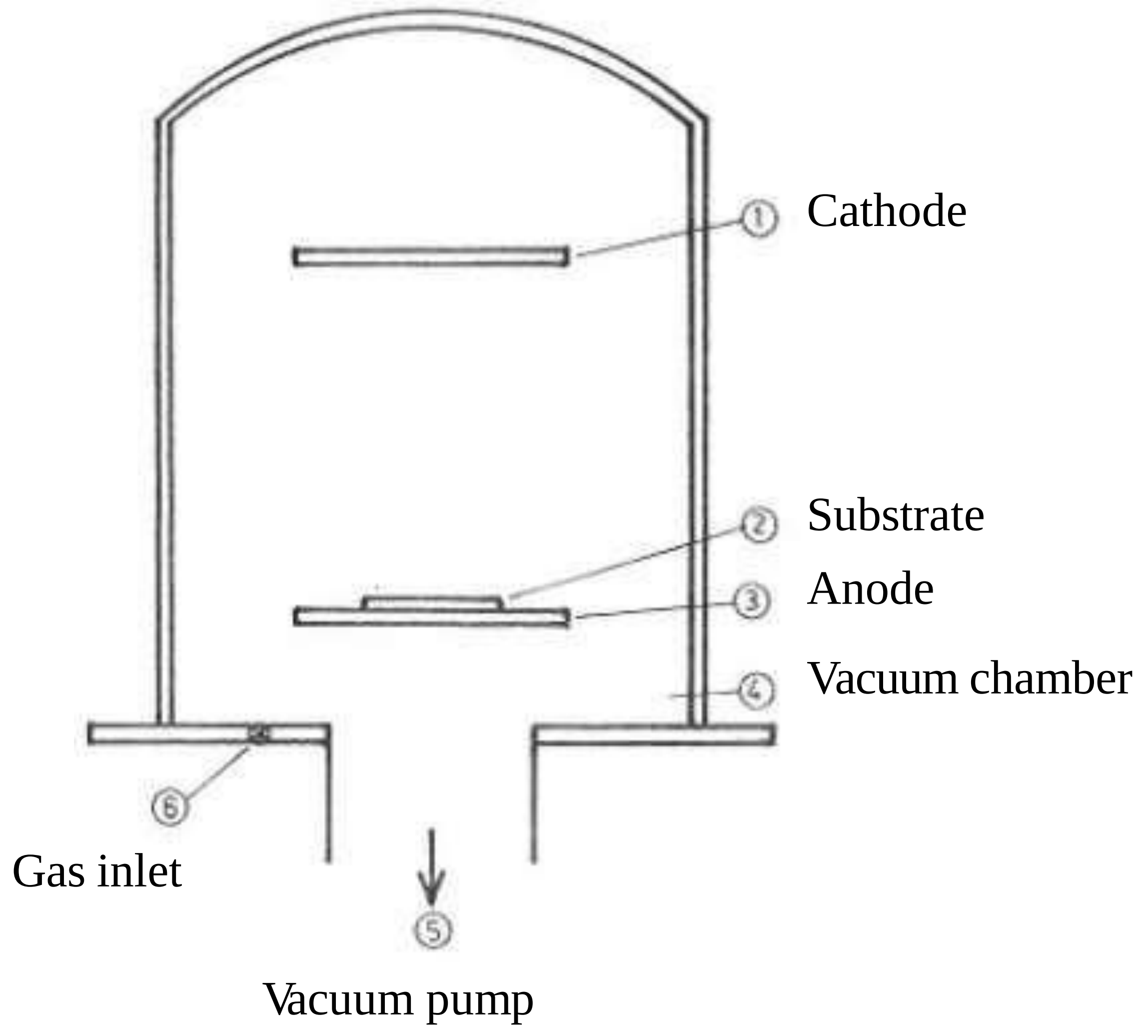
- In effect, the operation of a sputtering system requires the generation of a sufficient number of secondary electrons to replace these lost to the anode or to the walls of the vacuum chamber.

- The collision of the ejected atoms with the gas atoms in the plasma will cause the scattering of the former and reach the anode with random directions and energies.
- The probability of the sputtered material getting lost without striking the substrate thus increases with the cathode-substrate spacing.

- At constant P and V, the deposition rate is low at large distances from the cathode, the thickness distribution over the substrate showing a maximum at the center.

  Sputtering is a low temperature process, and less than 1% of the total applied power is used for the ejection of the sputtered material and secondary electrons.

- A considerable amount of energy is dissipated as heat at the cathode by the ions that strike it, and the cathode gets hot.
- The maximum temperature attained and the rate of rise of temperature depend on the glow discharge conditions.
- Although the sputtering yield for most materials increases with temperature, it is not generally advisable to set the cathode temperature rise beyond a tolerable level during sputtering because of the possible problems with outgassing.


Cathode
1
Substrate
2
Anode
3
Vacuum chamber
4
5
Vacuum pump
6
Gas inlet

- In glow discharge sputtering, the target, the substrate, and the depositing thin film are in the plasma atmosphere during deposition.
- The directionality of the beam allows the investigator to vary the angle of incidence of the beam on the target as well as the angle of deposition on the substrate

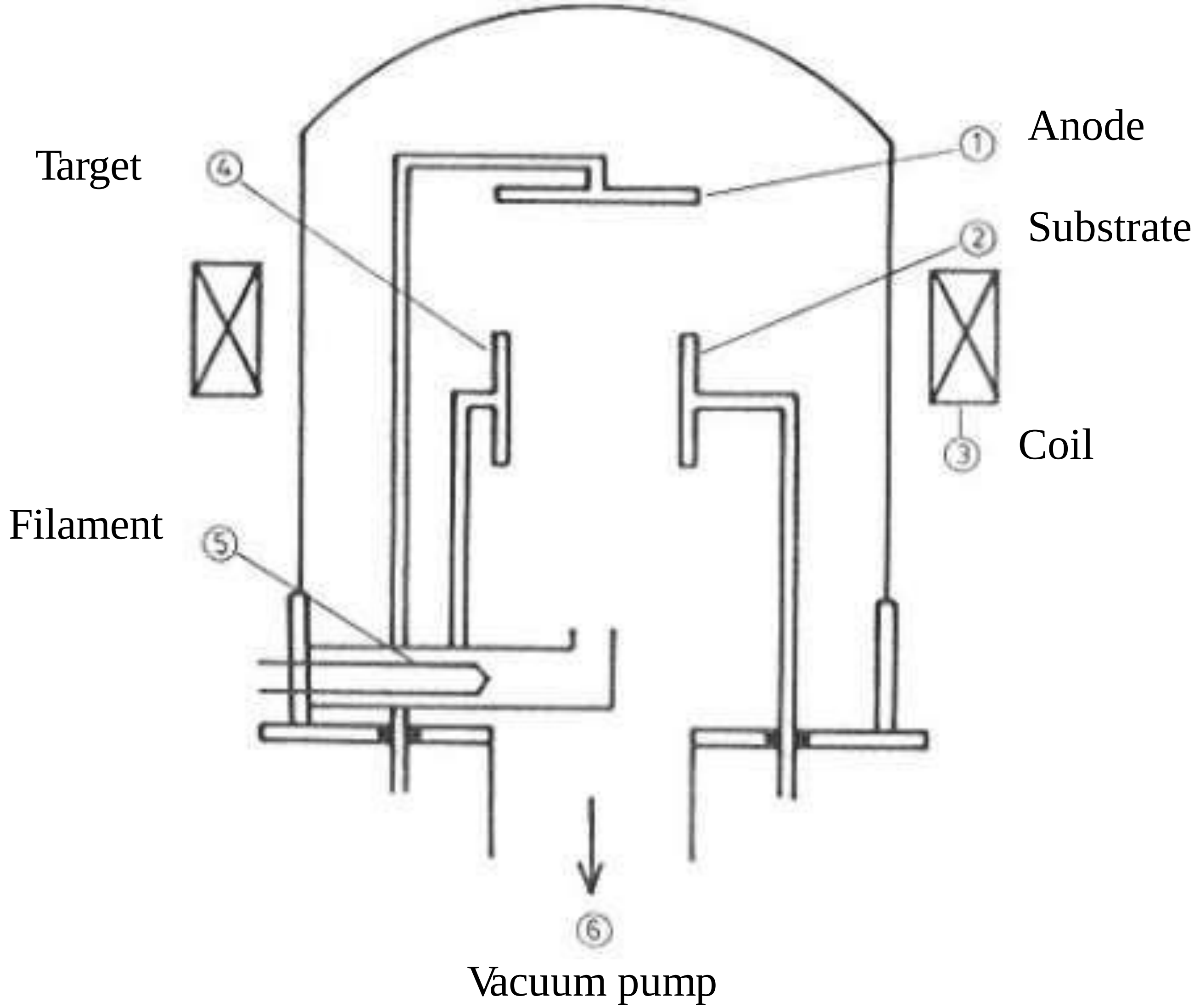
Triode Sputtering

- An alternative method to increase the ionization and sustain the discharge at low pressures is to supply additional electrons from a source other than the target cathode.
- Triode sputtering involves the injection into the discharge of electrons from an independent source by means other than the discharge itself.
- A hot cathode, which emits electrons through thermionic emission, is used to inject electrons into the discharge system.
- The thermionic cathode is usually a heated tungsten filament, which can withstand ion bombardment for long periods.

- The filament is placed in an elbow shown at the bottom of the bell jar, to protect the filament from any sputtered material.
- The plasma is confined between the anode and the filament cathode by a magnetic field provided by the external coil.
- Sputtering occurs when a high voltage negative potential with respect to the anode is applied to the target. Ions bombard the target as in diode glow discharge, and the target material is deposited on the substrate.

- The density of ions in the plasma can be controlled by adjusting either the electron emission current or the voltage used to accelerate the electrons.
- The energy of the bombarding ions can be controlled by varying the target voltage. Thus in a supported discharge like the triode discharge sputtering system, the ionization density is kept high by supplying extra electrons at the right energies from an additional electrode for efficient ionization.
- This method allows operation at much lower pressures ($< 10^{-3}$ torr) than in a conventional diode glow discharge system. The main limitation of this technique is the difficulty in producing uniform sputtering from very large flat targets.

- The plasma discharge was maintained by using a thermionic cathode and was confined in a water-cooled aluminum tube.
- A voltage of +90 V with respect to the ground was given for the auxiliary anode, and the anode current was approximately 6 A.
- Tungsten films were deposited at an Ar pressure of about 10^{-3} torr.


Anode
Target
④
①
Substrate
②
Coil
③
Filament
⑤
⑥
Vacuum pump

Radiofrequency Sputtering

- ✓ For deposition of thin films by sputtering, the **target should be a conductor**.
- ✓ In a conventional dc sputtering system, if an insulator is substituted for the metal target, a surface positive charge is built up on the front surface of the insulator during ion bombardment.
- ✓ This charge buildup can be prevented by simultaneously bombarding the insulator with both ion beam and electron beam particles.
- ✓ Here an rf potential is applied to the metal electrode placed behind the dielectric plate target. At rf potentials, the electrons oscillating in the alternating field have sufficient energies to cause ionizing collisions, and the discharge will be self-sustained.

- ✓ The high voltage at the cathode, which is essential in a dc glow discharge for the generation of secondary electrons, is no longer required here for the discharge to maintain itself.

- ✓ Since **the electrons, have much higher mobilities than ions**, many more electrons will reach the dielectric target surface

- ✓ The negative dc potential on the insulator target surface repels electrons from the vicinity of this surface, creating a sheath enriched in ions in front of the target.

- ✓ These ions bombard the target, and sputtering is achieved.

- ✓ At frequencies less than 10 kHz, such an ion sheath will not be formed, and **13.56 MHz frequency** is generally used for rf sputtering.
- ✓ It should be noted that since the applied rf field appears between the two electrodes, an electron escaping from the interelectrode space as a result of random collision will no longer oscillate in the rf field.
- ✓ Therefore these electrons will not get sufficient energy to cause ionization, hence will be lost to the glow.
- ✓ So a magnetic field is more important in rf sputtering than it is for the dc case.
- ✓ A grounded metal shield is placed close to the other side of the metal electrode to extinguish the glow on the electrode side and to prevent sputtering of the metal electrode.

- ✓ Thin films of quartz, aluminum oxide, boron nitride, mullite, and various glasses have been prepared using rf sputtering
- ✓ The physical appearance of an rf sputtering system is almost like that of a dc system.
- ✓ It is also important that in an rf system, adequate grounding of the substrate assembly be ensured to avoid undesirable rf voltages, which can develop on the surface.
- ✓ The use of rf sputtering for the deposition of thin films is of great interest because it enables more economical deposition onto substrates of large areas

Ion beam Sputtering

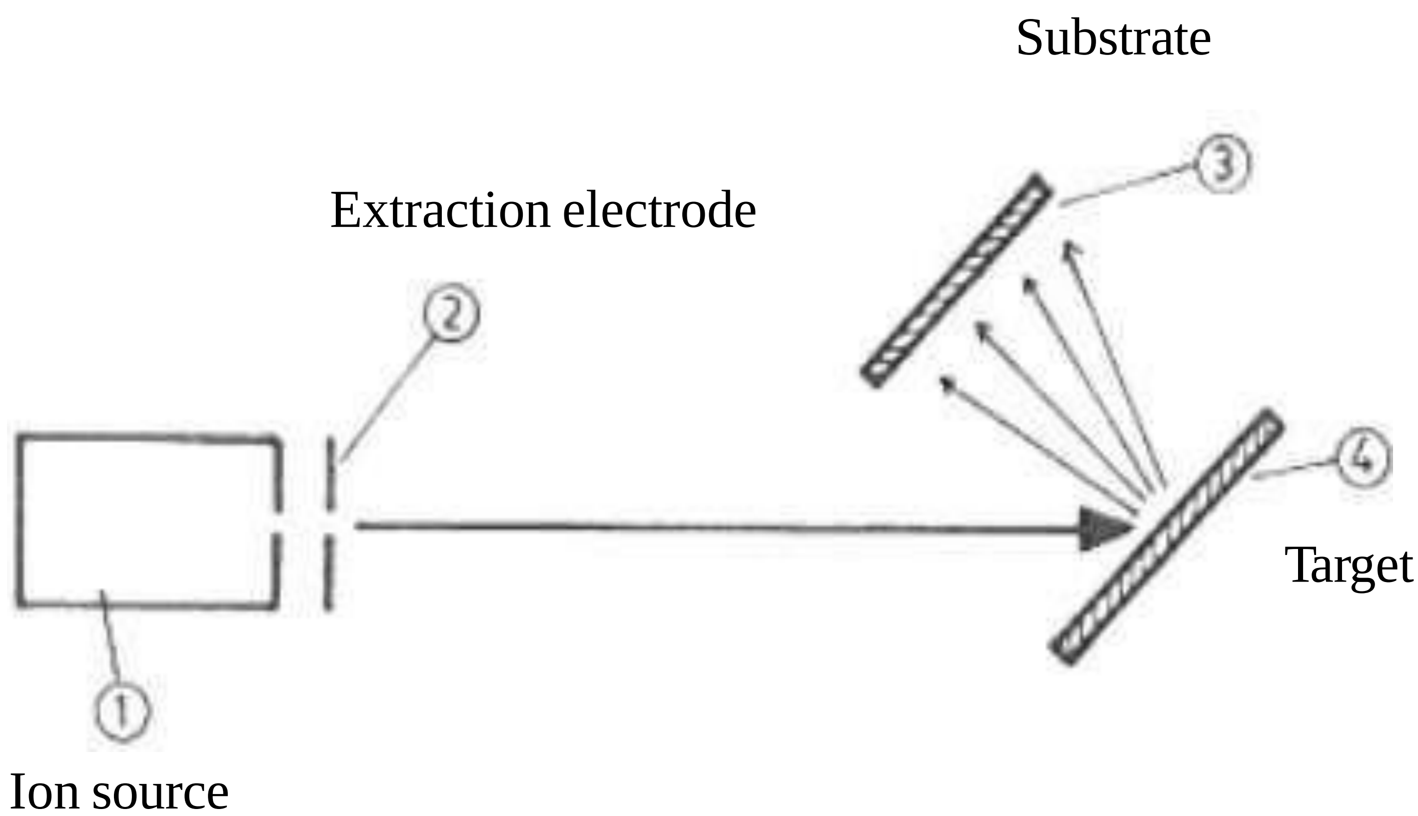
- In ion beam sputter deposition the ion beam generated at an ion source is extracted into the high vacuum by an extraction voltage and directed to a target of the desired material, which is sputtered and deposited on a nearby substrate.
- Ion beam sputtering allows greater isolation of the substrate from the ion production process, unlike the glow discharge sputtering. Advantages of ion beam sputtering:

1. The narrow energy spread of the ion beams enables us to study the sputter yield as a function of ion energy.
2. The process allows accurate beam focusing and scanning.
3. Changes in target and substrate materials are allowed, keeping beam characteristics constant.
4. Independent control of ion beam energy and current is possible

- ✓ The target and the substrate are independent of the acceleration electrode, and therefore the damage due to collision of ions is much less than in conventional sputter deposition.

- ✓ Also the influence of the residual gas is much less because the chamber can be kept at a low pressure, the ion source being independent of the chamber.
- ✓ Also, ion beam sputter deposition has become useful in the field of epitaxial growth of semiconductor films. It is possible to deposit a wide variety of materials, with the condensing particles having a kinetic energy exceeding 10 eV, in a high vacuum environment.
- ✓ This will lead to high surface diffusion rates, even at low substrate temperatures, a condition favorable for epitaxial diffusion.
- ✓ The main disadvantage is that the bombardment target area is small and the deposition rate generally is low. Also ion beam sputter deposition is not suited for depositions of uniform thickness over large substrate areas.

- ✓ The two most generally used types of ion source for ion beams sputter deposition are the Kaufman source and the duoplasmatron.
- ✓ The ion beam sputtering deposition technique has been used to prepare metallic, semiconductor, and dielectric films.
- ✓ The deposition of carbon films is shown in figure. The 99.999% pure graphite disk target (100 mm diameter) was bonded to the watercooled holder.
- ✓ An electron bombardment ion source with an ion beam diameter of 25 mm was used.
- ✓ The incident angle of the ion beam was about 30° to the target, and the substrate was placed near the target.
- ✓ At this position the ion beam sputtered the target and also grazed the substrate.


Substrate
Extraction electrode
Target
Ion source
1
2
3
4