VIVEKANAND COLLEGE, KOLHAPUR (AUTONOMOUS)

Presentation on

PHYSICAL VAPOUR DEPOSTION

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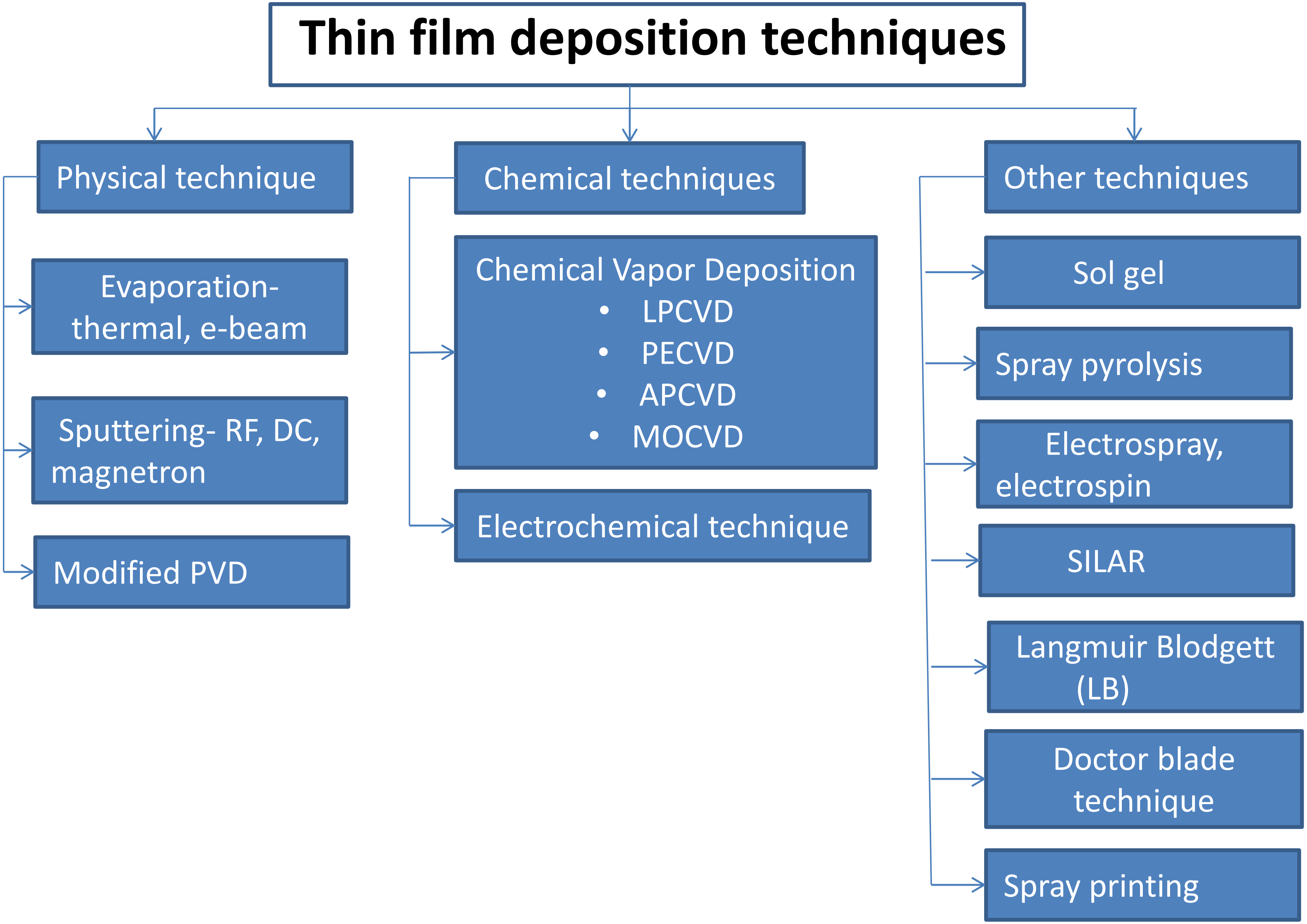
Introduction:

- **Thin film** is layer of material ranging from fraction of nanometer (monolayer) to few micrometer in thickness on any substrate.

Why need thin film?

- Adhesive coating- nonstick coating etc.
- Optical coatings (reflecting, antireflecting, UV absorbent coating, florescent coating)
- Protective coatings: anticorrosive coating, nonstick coating, hard coating –anti scratch coating,
- Waterproofing coating- waterproof paper, fabric.
- antimicrobial coatings.
- Conductive coating- PCB
- Insulating coatings.
- Catalytic coatings- self cleaning coatings.

Thin film deposition techniques



Physical technique

- Evaporation- thermal, e-beam
- Sputtering- RF, DC, magnetron
- Modified PVD

Chemical techniques

- Chemical Vapor Deposition
  - LPCVD
  - PECVD
  - APCVD
  - MOCVD
- Electrochemical technique

Other techniques

- Sol gel
- Spray pyrolysis
- Electrospray, electrospin
- SILAR
- Langmuir Blodgett (LB)
- Doctor blade technique
- Spray printing

Physical deposition techniques:

- It is physical technique, while deposition no any chemical reaction takes place

$$\text{A metal} \xrightarrow{\text{process}} \text{A metal film}$$

chemical deposition techniques:

- It is chemical technique, while deposition chemical reaction takes place

$$\text{AB material} \xrightarrow{\text{process}} \text{A metal film} + \text{B}\uparrow$$

What is physical vapor deposition ?

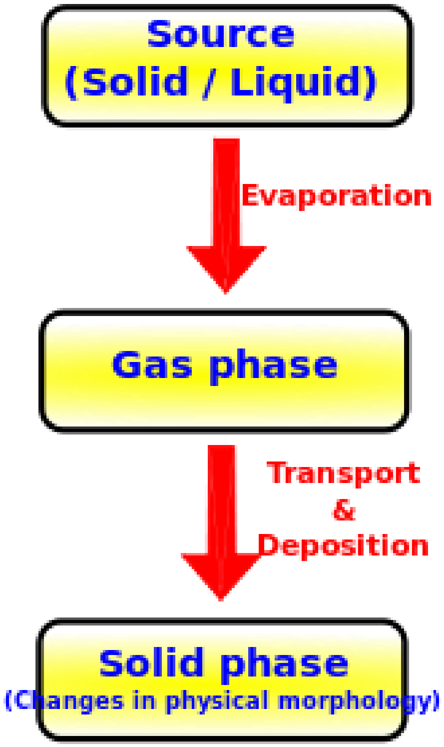
- **PVD** uses **physical** process (such as heating or sputtering) to produce a **vapor** of material, which is then **deposited** on the object which is called physical vapor deposition.

- PVD describes variety of vacuum deposition techniques.

1.Thermal evaporation (resistive heating, e-beam, pulsed laser etc.)

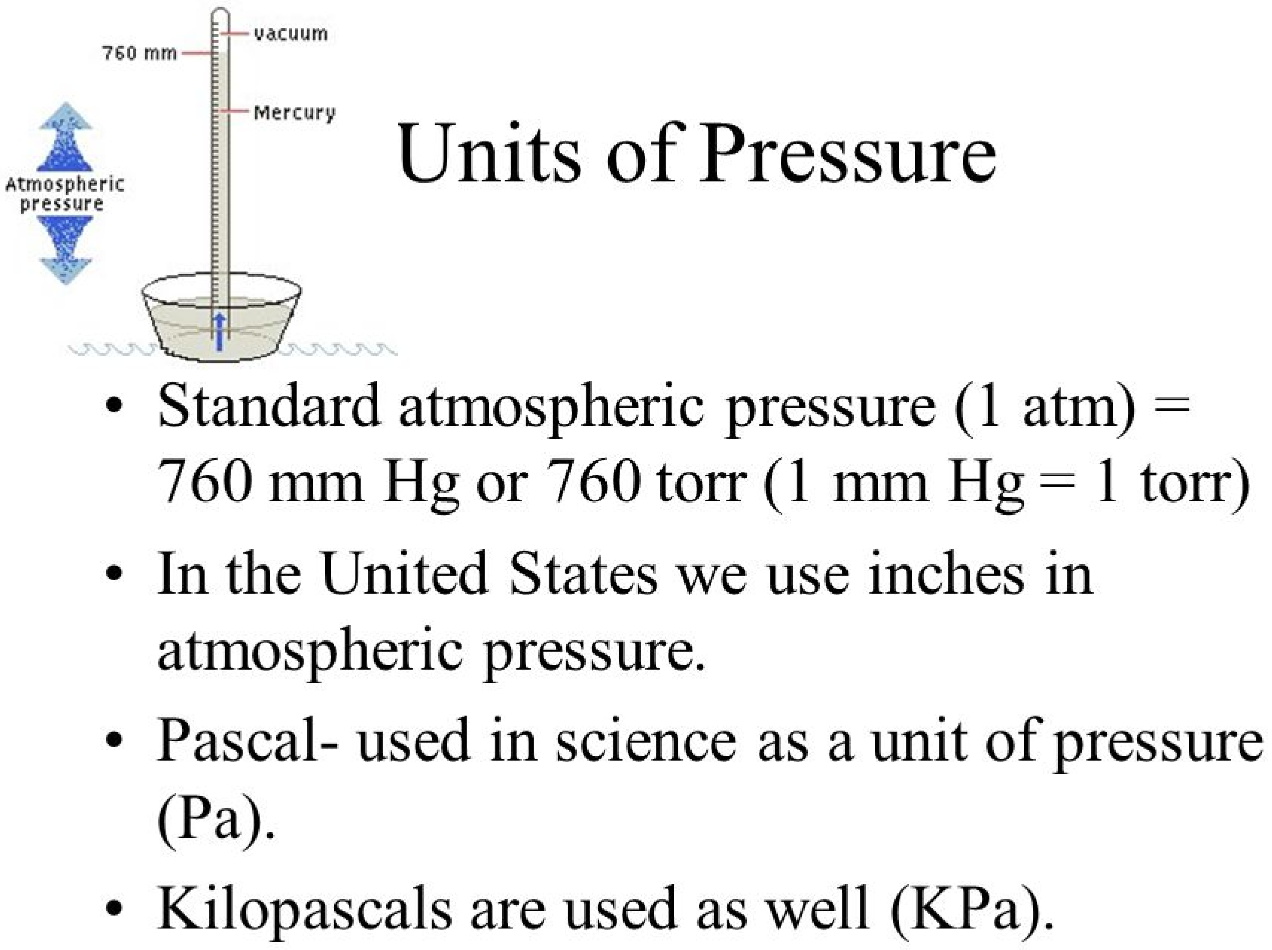
2. Sputtering (DC sputtering, DC magnetron, RF sputtering etc.)

Note: all PVD technique require vacuum



What is vacuum?

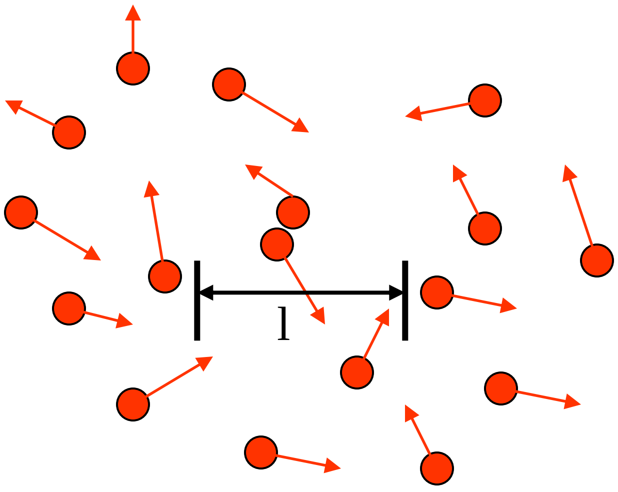
- Vacuum is the region with a gaseous pressure much less than atmospheric pressure.



Units of Pressure

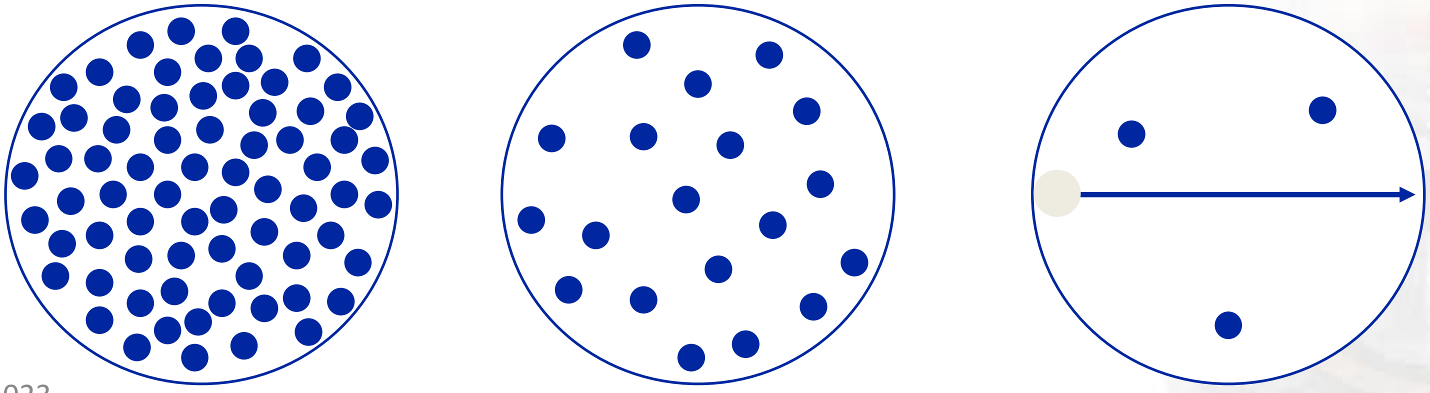
- Standard atmospheric pressure (1 atm) = 760 mm Hg or 760 torr (1 mm Hg = 1 torr)
- In the United States we use inches in atmospheric pressure.
- Pascal- used in science as a unit of pressure (Pa).
- Kilopascals are used as well (KPa).

Why do we need a vacuum?



l = Mean free path for air

- A vacuum provides a clean environment.
- Avoid possible contamination from other gases that may present in the atmosphere.
- Large mean free path for the air molecules.
- In case of vacuum evaporation it provides minimum solid angle for evaporation.
- Hence evaporated particles can move in a (straight) line over a large distance.



Vacuum ranges

Vacuum quality	Torr	Pa	Atmosphere
Atmospheric pressure	760	1.013×10^{5}	1
Low vacuum	760 to 25	1×10^{5} to 3×10^{3}	9.87×10^{-1} to 3×10^{-2}
Medium vacuum	25 to 1×10^{-3}	3×10^{3} to 1×10^{-1}	3×10^{-2} to 9.87×10^{-7}
High vacuum	1×10^{-3} to 1×10^{-9}	1×10^{-1} to 1×10^{-7}	9.87×10^{-7} to 9.87×10^{-13}
Ultra high vacuum	1×10^{-9} to 1×10^{-12}	1×10^{-7} to 1×10^{-10}	9.87×10^{-13} to 9.87×10^{-16}
Extremely high vacuum	$< 1\times10^{-12}$	$< 1\times10^{-10}$	$< 9.87\times10^{-16}$
Outer space	1×10^{-6} to $< 1\times10^{-17}$	1×10^{-4} to $< 3\times10^{-15}$	9.87×10^{-10} to $< 2.96\times10^{-20}$
Perfect vacuum	0	0	0

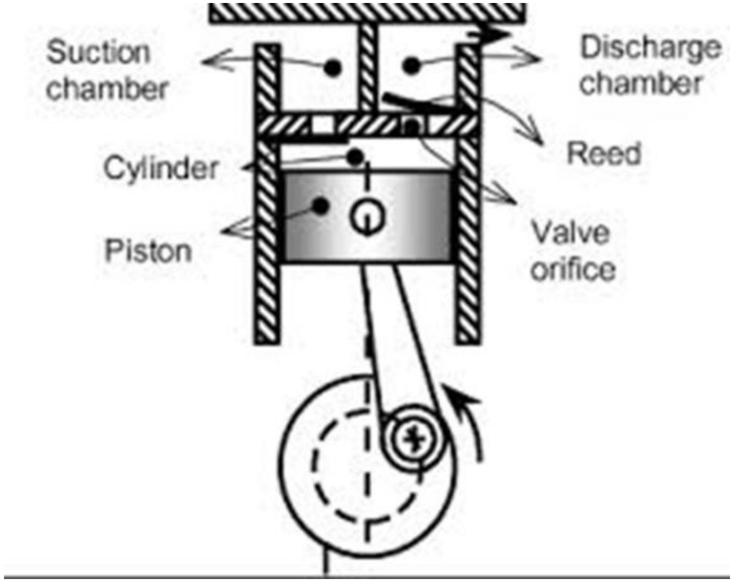
Generally, perfect vacuum does not exist or can not be achieved.

Type of Vacuum pumps

- Positive displacement pumps
  - Expand a cavity, seal, exhaust, repeat
  - Rotary mechanical pump

- Momentum transfer pumps (molecular pumps)
  - High speed liquids or blades to knock gasses around
  - Diffusion pump and turbo molecular pump

- Entrapment
  - Create solids or adsorbed gases.
  - Cryo-pumps and sputter ion pumps

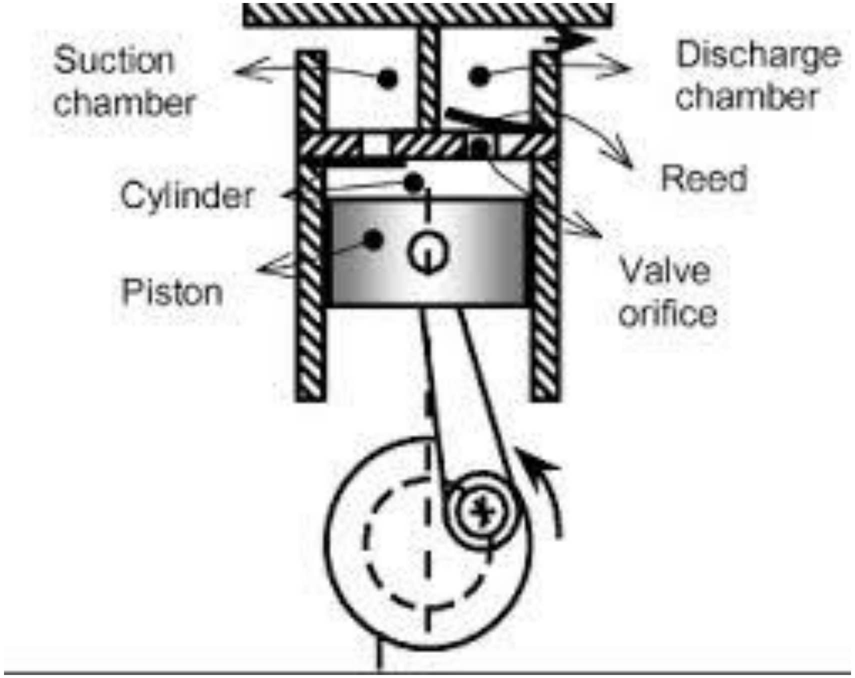


Compressor animation

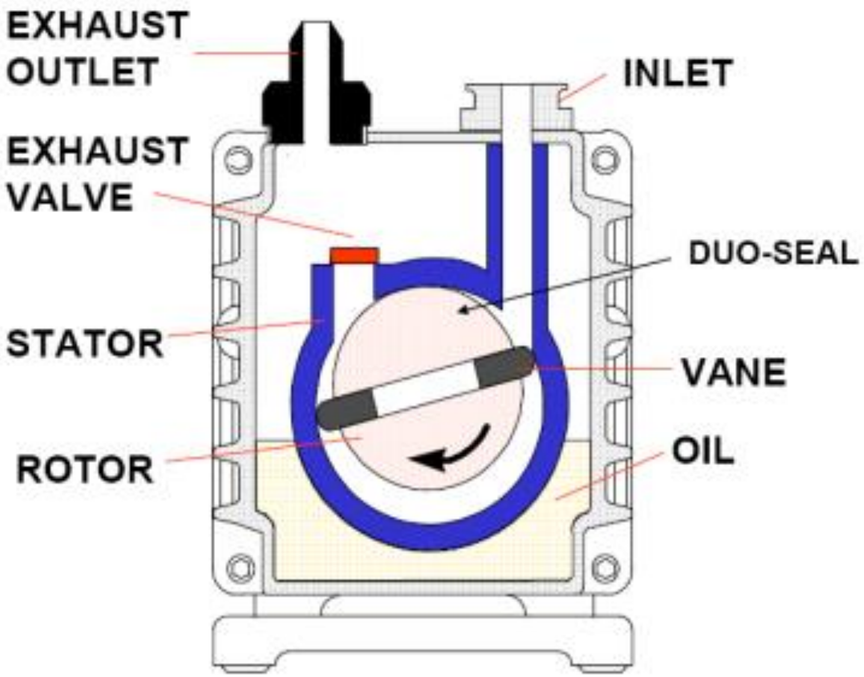
Vacuum pumps:

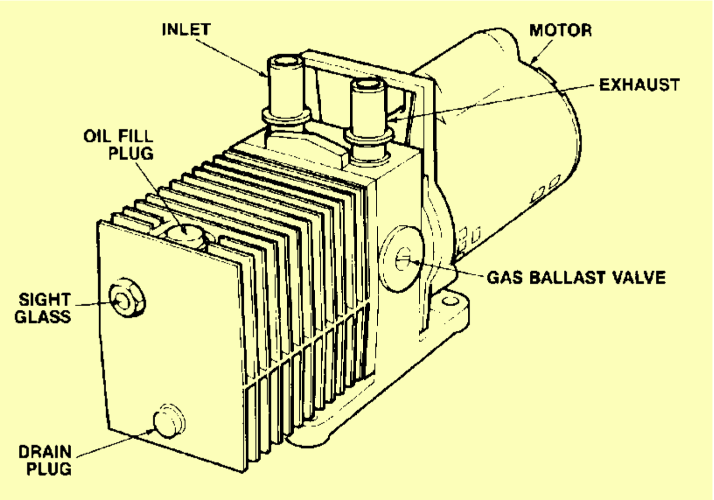
To produce vacuum, different types of vacuum pumps are required, which are as follows;

1. Rotary mechanical pump.
2. Turbo molecular pump
3. Diffusion pump
4. Cryo-pump
5. Sputter ion pump



Rotary vacuum pump





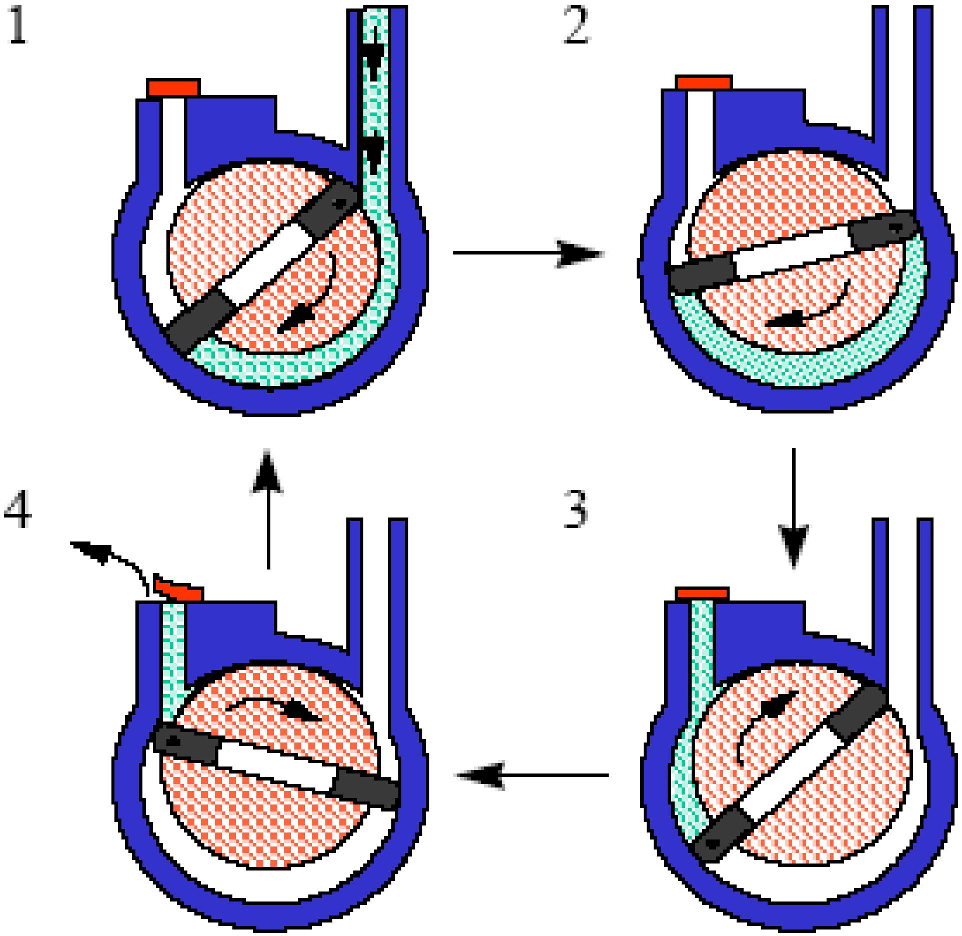
- **Rotor:** movable part of the system.
- **Stator:** fixed part and having cylindrical bore inside.
- **Center of axis of rotation** of stator is above the axis of cylindrical bore of stator by amount equal to difference in their radius.
- **Vanes:** two spring loaded movable vanes, connected at the center of the rotor slides opposite to each other.
- **Inlet:** connected to vacuum chamber
- **Exhaust outlet:** open to atmosphere.

Rotary vacuum pump

Vacuum limit:
ATP to 10^{-3} - 10^{-4} Torr

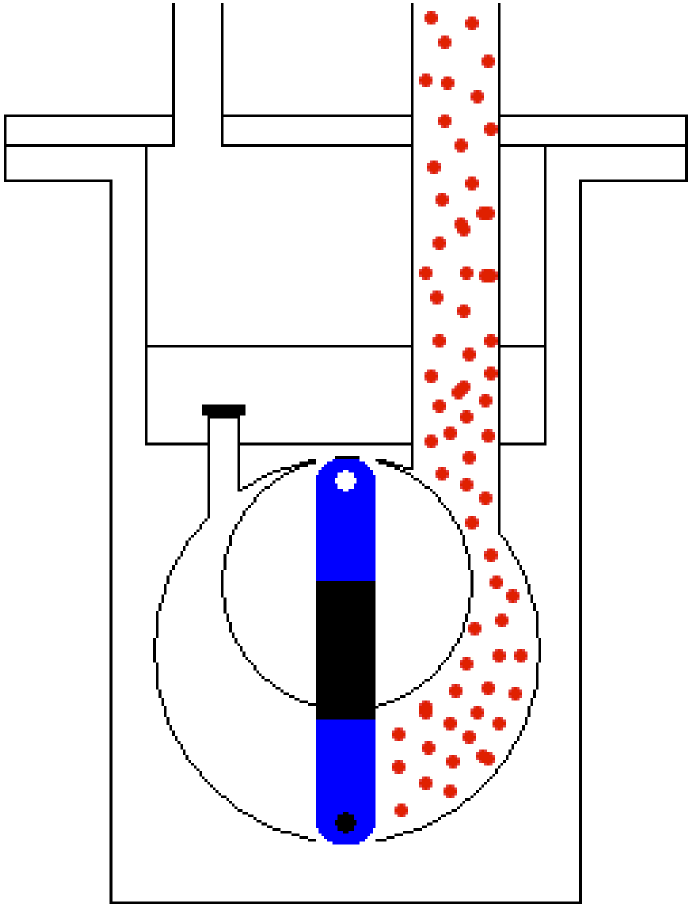
The Pumping Cycle

1 Inlet exposed
2 Trapped volume
3 Compression
4 Exhaust



Rotary vane animation.swf

How rotary mechanical pump work?



Pumping speed

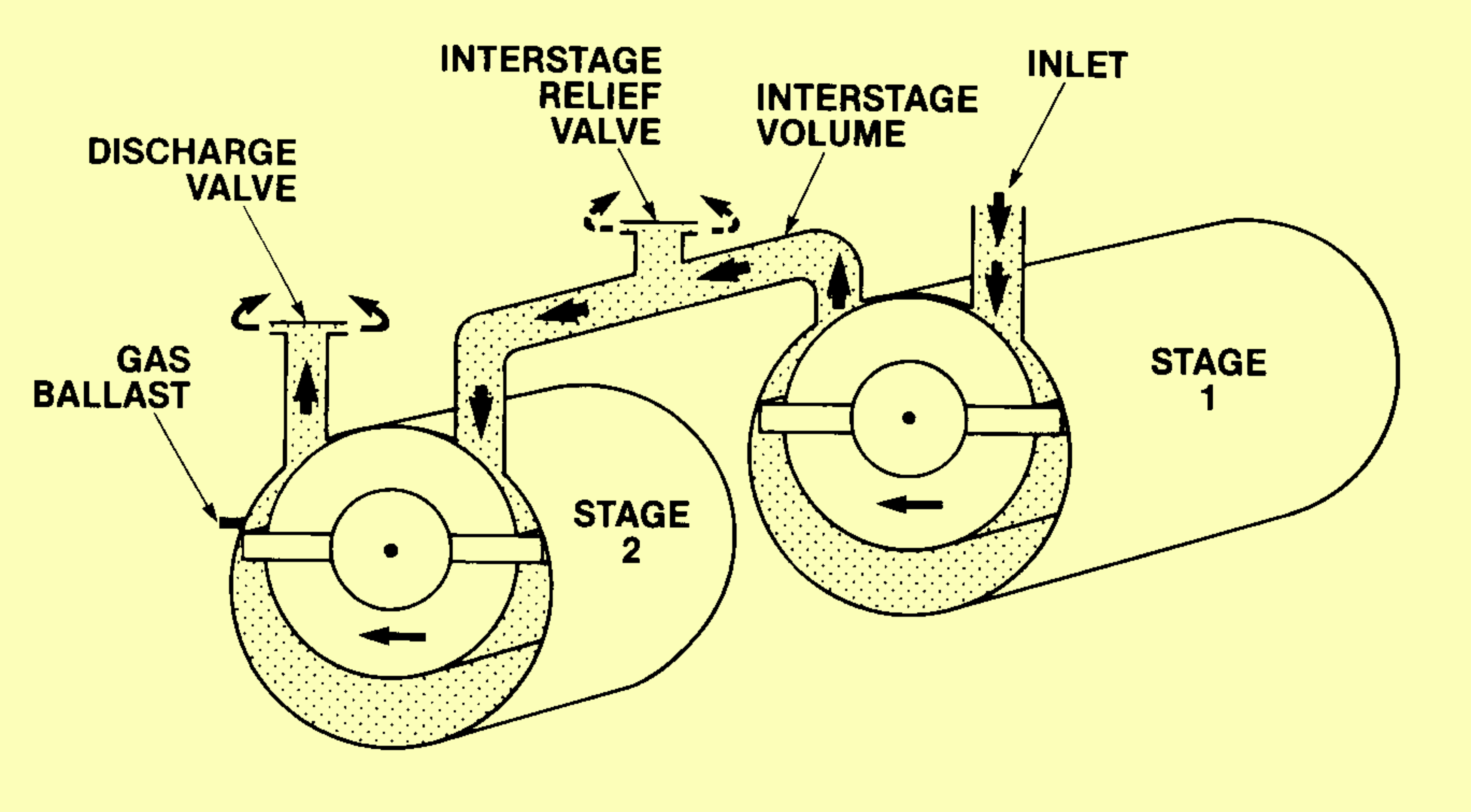
$$t = 2.3V/S \log p^0/p$$

t= time require to evacuate the chamber
V= Volume of chamber
S= pumping speed of the pump
P^0 = initial pressure
p= final pressure

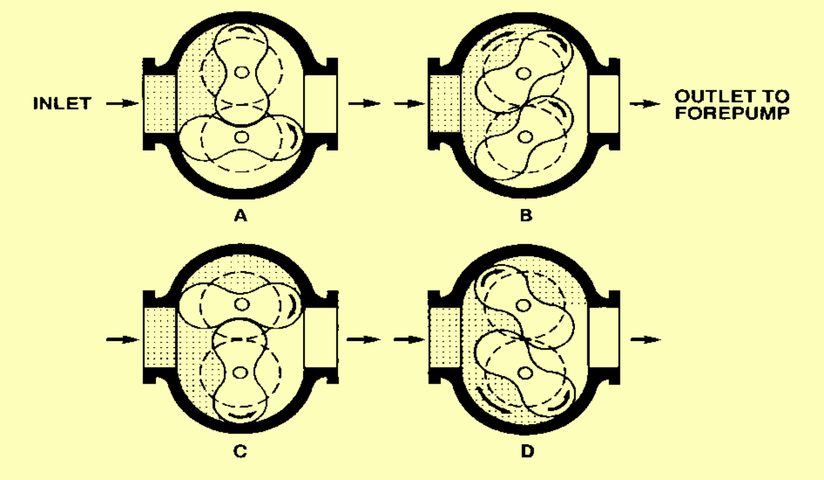
Limitation:

- Efficiency is low generally around 30%, better can go around 50%.
- Vacuum degree is low, that is not because of structural design but due to saturation of working fluid. Can achieve vacuum up to 10^{-3} to 10^{-4} torr

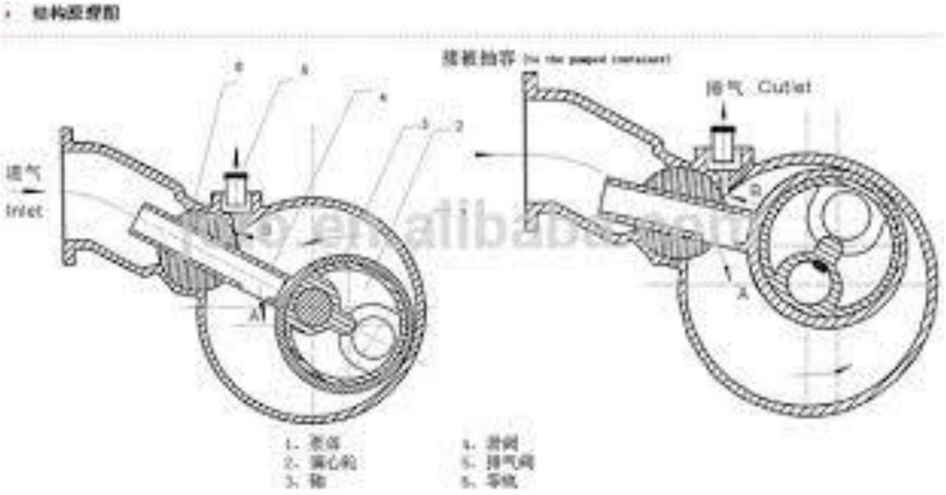
Dual stage rotary mechanical pump:



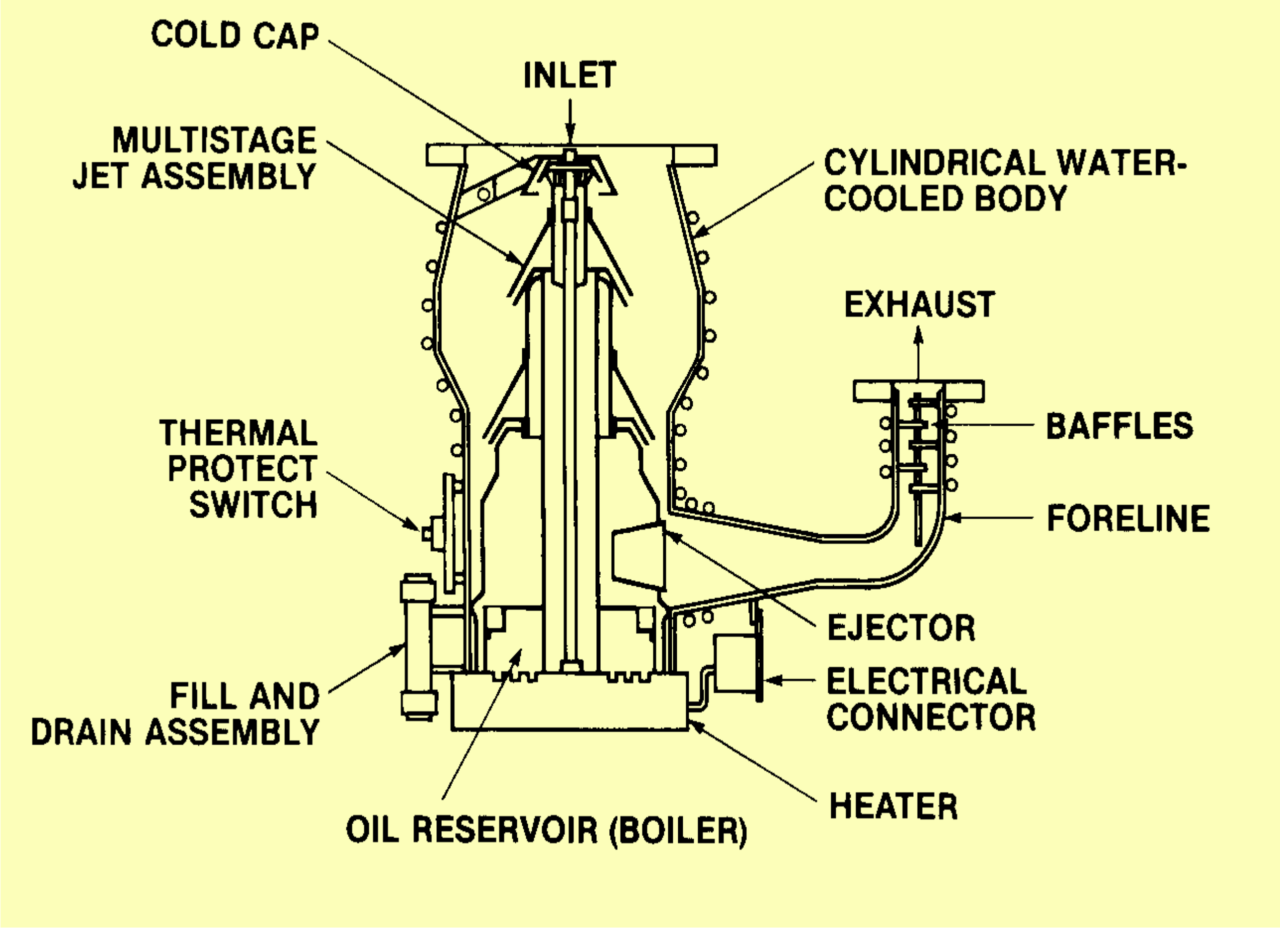
Blower/Booster Pump



Rotary piston pump

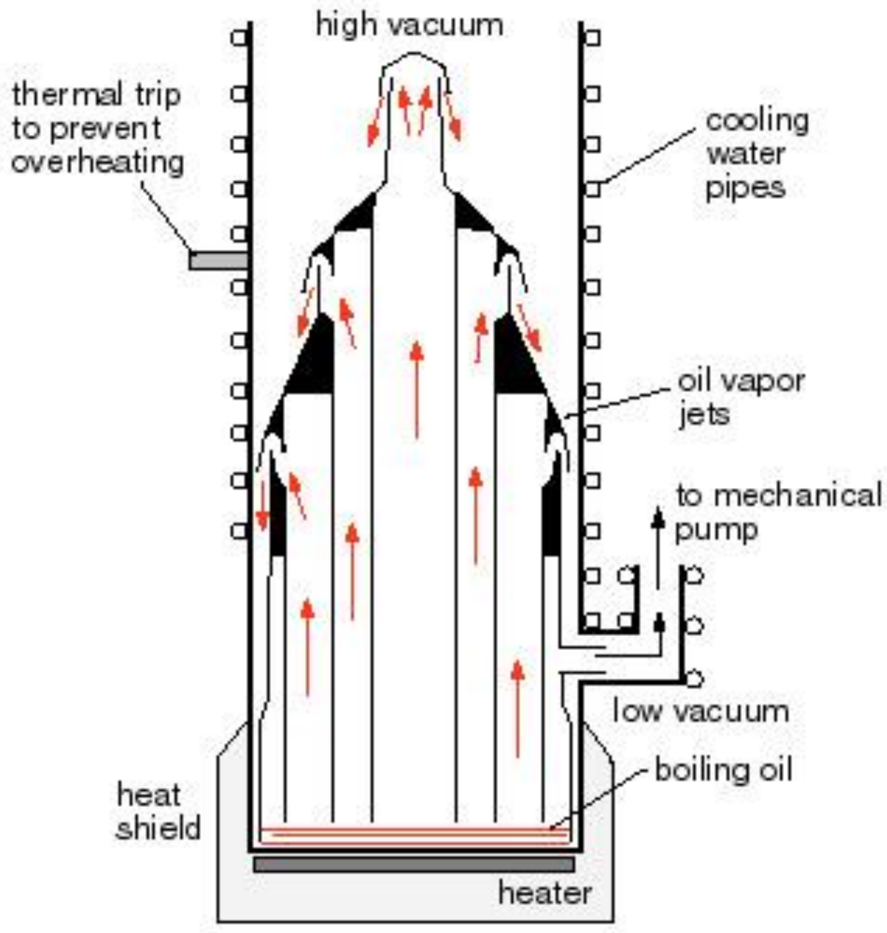


Diffusion pump:



PRINCIPLE: It has no moving part, it is moment transfer pump, the vapor come out from the jet gives momentum to the air molecule towards downward direction, which is evacuated by backing pump

Working:

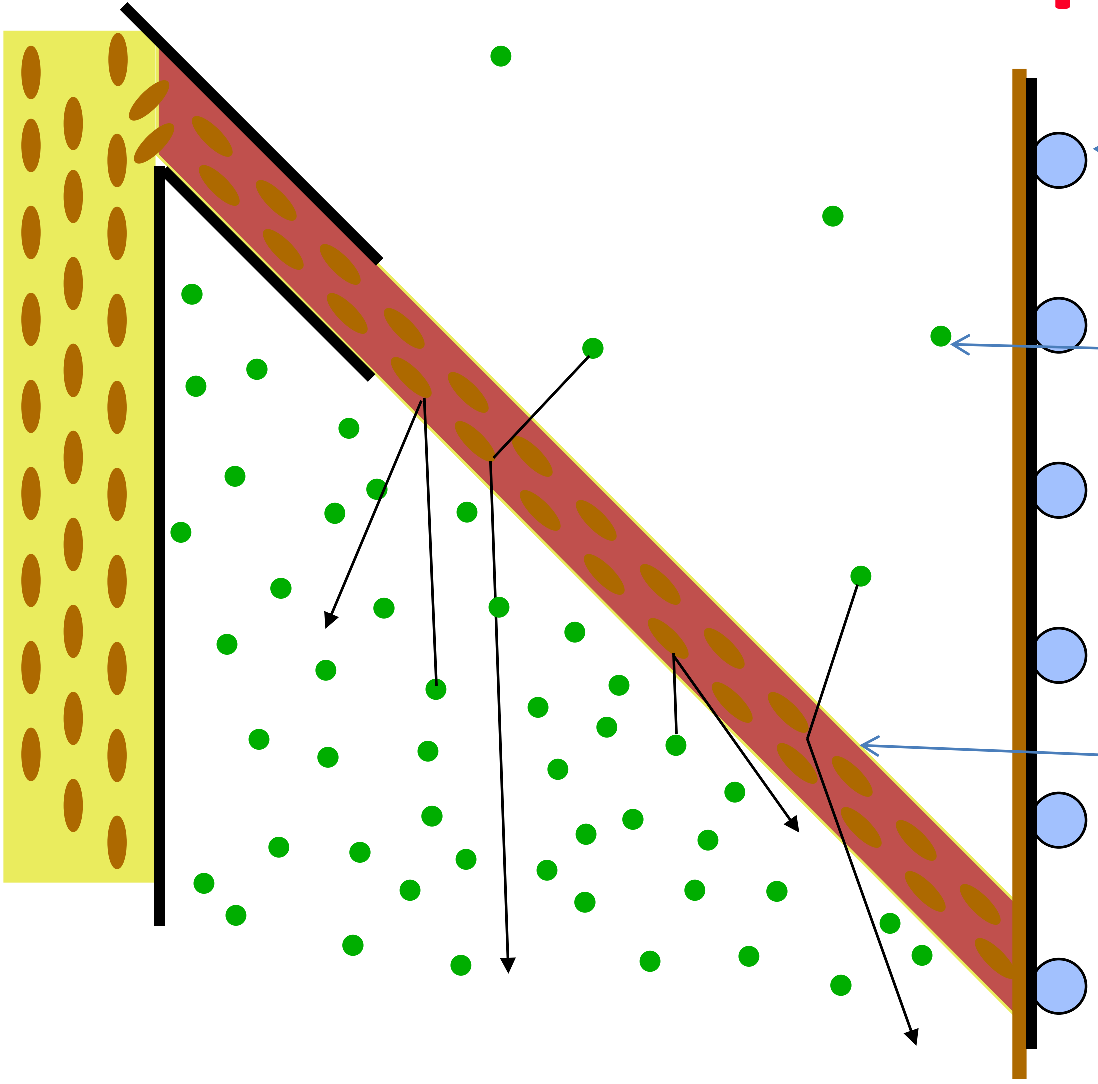


Operation

- Fluid vapourised from base of pump.
- Reflected downwards by a series of fixed vanes, Vapour speed about 750 mph.
- Downward momentum transferred to gas atoms.
- Fluid recondenses and the gas is removed by the backing pump.
- silicones (cheap) and polyphenyl ether (expensive but better) are common pump fluids.

Pump animation

How the Pump Works



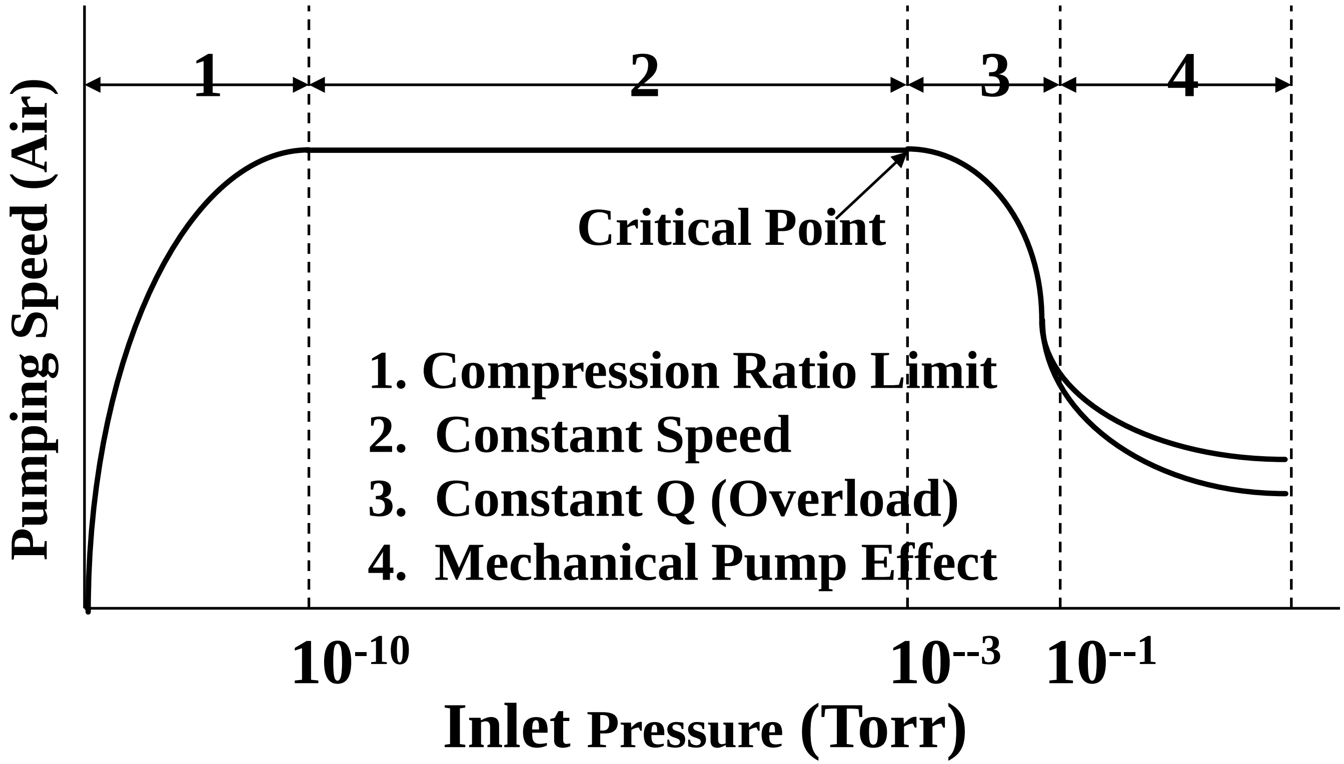
Water circulation

Air molecules

Oil vapor- It accelerates at the speed of 720 miles per hours.

Note: it works at the pressure below 1mtorr

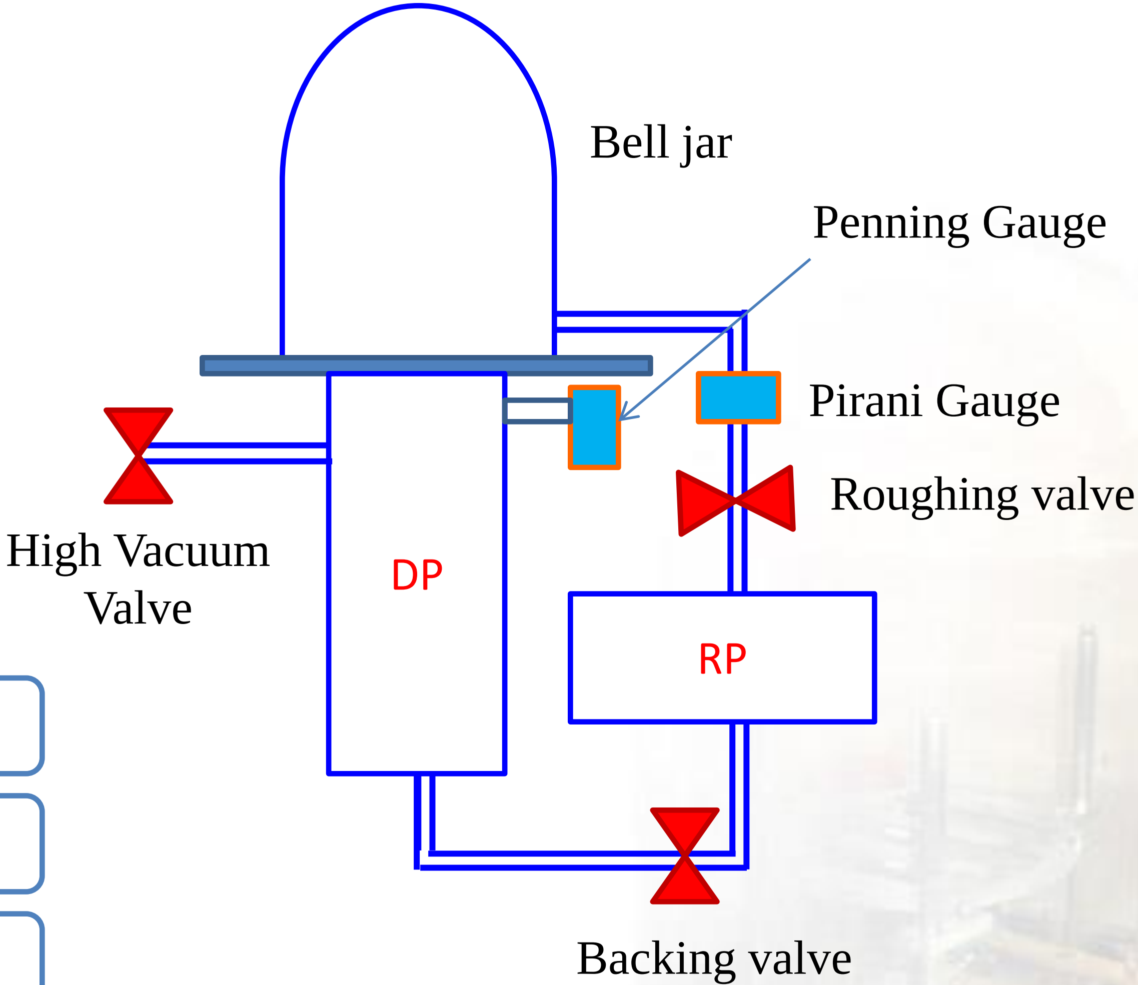
Pumping Speed:



Limitation of diffusion pump

- This is not a self-driven pump, it always require a backing pump.
- Diffusion pump cannot operate above 1000mTorr so it is necessary to use mechanical pump in conjunction with diffusion pump.

Vacuum Coating Unit



1. Chamber
2. Pumps
3. Gauges

Vacuum chamber:

- A vacuum chamber is rigid enclosure from which air and other gasses can be removed by vacuum pump.

It is made up of different materials, the strength, pressure and permeability are consideration for selecting chamber material.

Common materials are

- Stainless steel
- Aluminum
- Mild steel
- Brass
- High density ceramics
- Glass
- Acrylic

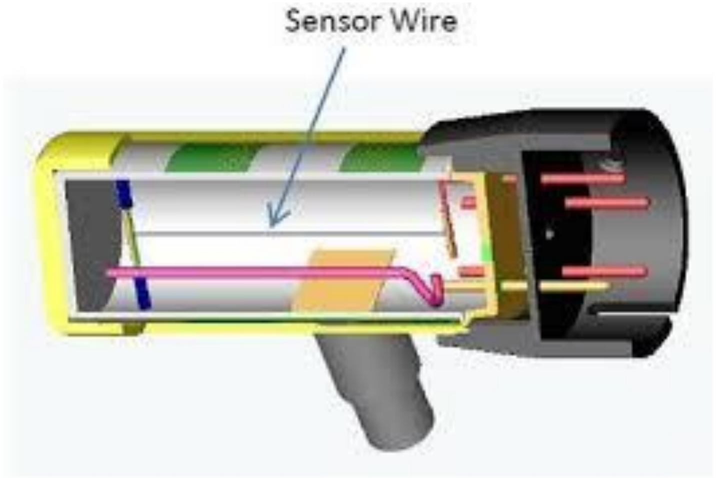
Picture does not depict actual size or shape.
Picture is for material reference only.

Vacuum gauges:

1. **Pirani gauge:** it is robust thermal conductivity gauge used for the measurement of pressure in vacuum system.

principle: A heated metal wire suspended in a gas will lose heat to the gas as its molecules collide with the wire and remove heat. If the gas pressure is reduced the number of molecules present will fall proportionately and the wire will lose heat more slowly. Measuring the heat loss is an indirect indication of pressure.

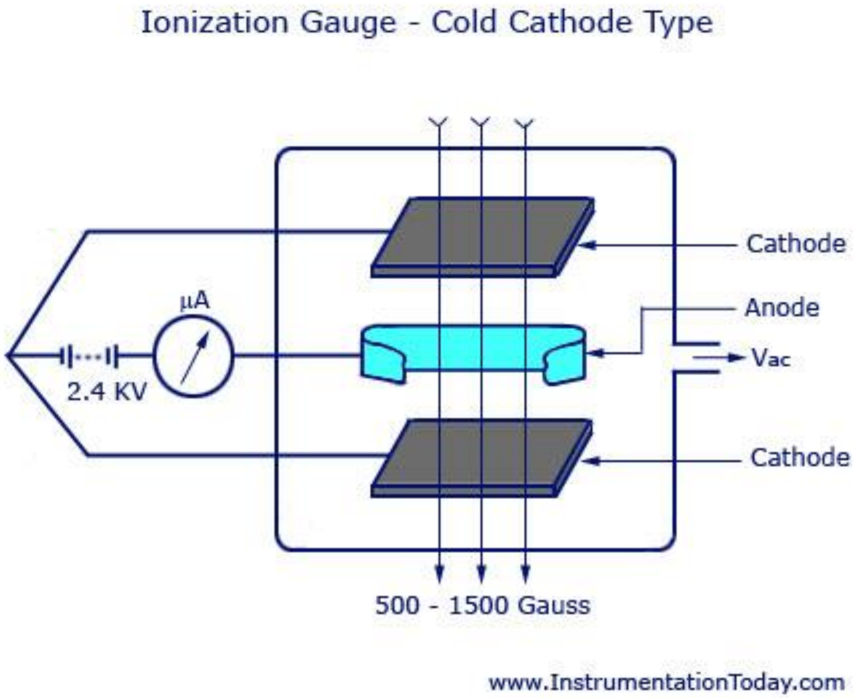
Resistance of the wire varies with the temperature so the resistance is measured to measure the vacuum.



Limit: it can measure pressure from 0.5 to 10^{-4} torr

2. Penning gauges:
It is called as ionic conductivity gauge, also known as cold cathode gauge .

Principle: High voltage between the anode and the cathode causes gas discharge and the resulting ionic current is measured with an ammeter. The measured amperes are then converted into pressure units such as Pascals or Torrs.



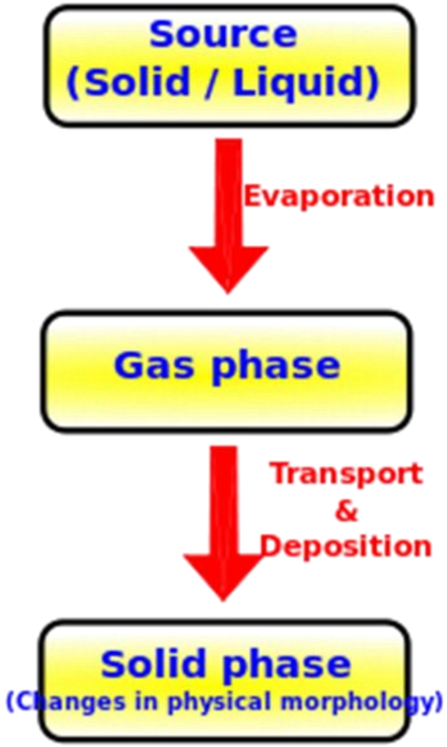
Limit: it can measure pressure from 10^{-2} to 10^{-9} torr

Physical vapor deposition technique:

Step 1: generation of vacuum.

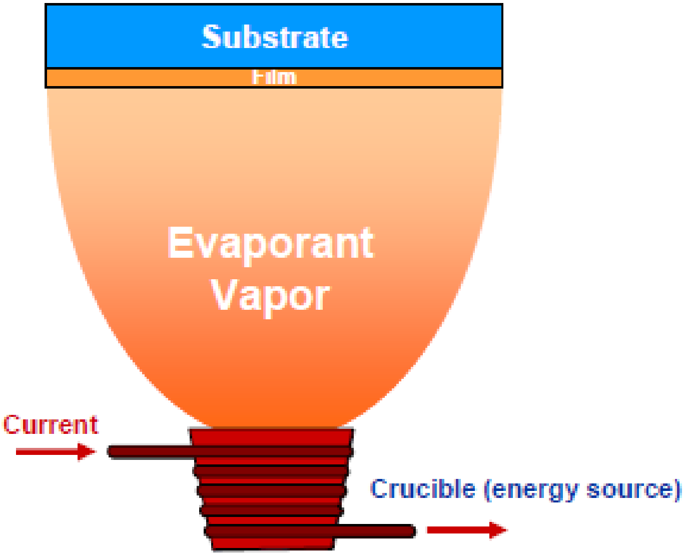
Step 2: Evaporate the source material and transport.

Step 3: condensation of evaporant on the substrate and formation of thin film.



Evaporation of source material:

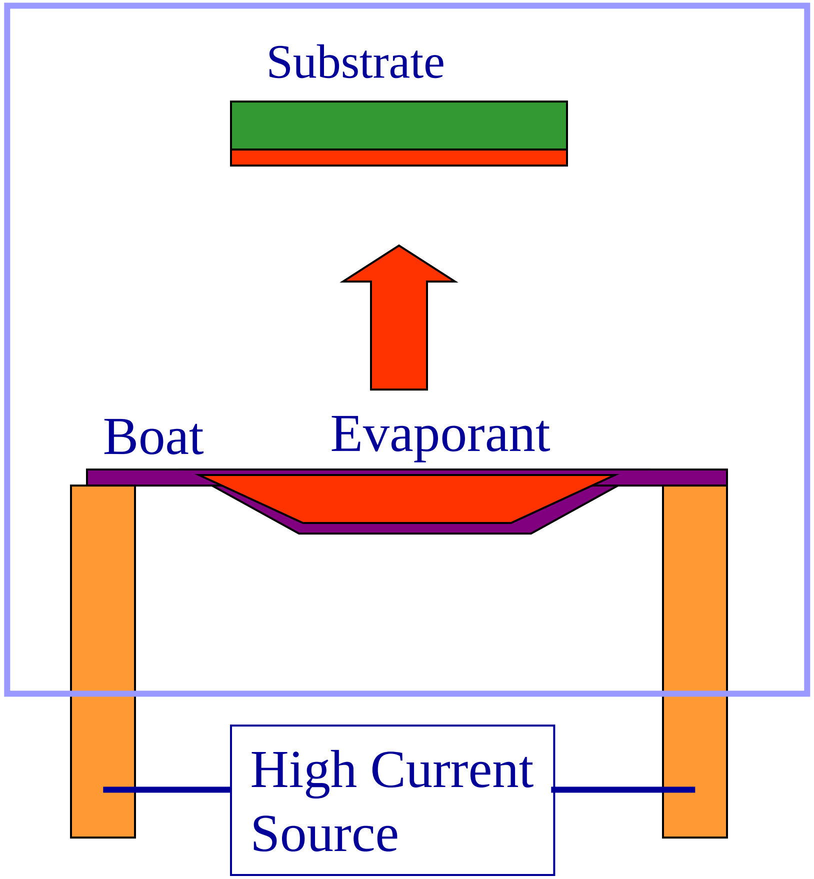
- Load the source material-to-be-deposited (evaporant) into the container (crucible)
- **Heat the source** to high temperature.
- Source material evaporates
- Evaporant vapor transports to and Impinges on the surface of the substrate.
- Evaporant condenses on and is adsorbed by the surface



Different type of heating methods:

- Resistive heating .
- E-beam
- Sputtering: DC, RF, DC magnetron sputtering

Resistive heating:



- A current I is passed through the boat to heat it.
- The heating power is I^2R, where R is the electrical resistance of the boat.
- For boats made of refractory metals (W, Mo, or Ta) temperatures upto 2000° C can be achieved.
- Materials which alloy with the boat material cannot be evaporated using this method.

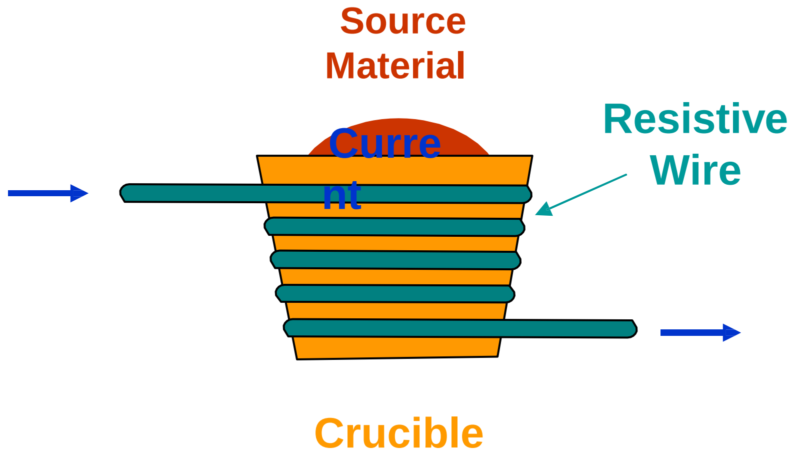
filament

Basket type

Boat & boxes

Rods & screens

Heating Method – Thermal (Resist Heater)



Foil Dimple Boat

Alumina Coated
Foil Dimple Boat

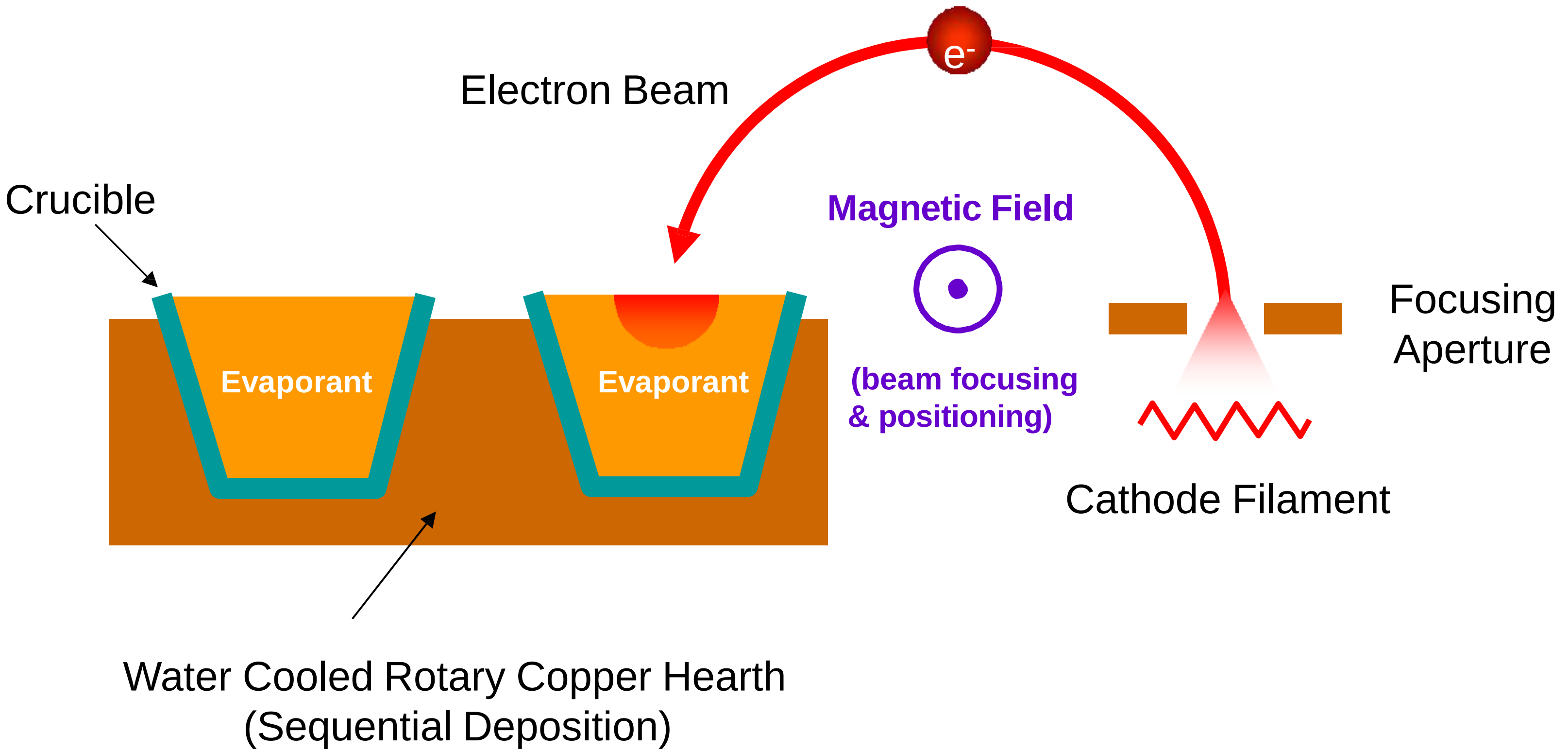
Cr Coated Tungsten Rod

Contamination Problem with Thermal Evaporation

Container material also evaporates, which

contaminates the deposited film

Heating Method – e-Beam Heater



e^-

Electron Beam

Crucible

Magnetic Field

Focusing Aperture

Evaporant

Evaporant

(beam focusing & positioning)

Cathode Filament

Water Cooled Rotary Copper Hearth
(Sequential Deposition)

Advantage of E-Beam Evaporation:

Very low container contamination

Comparison

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 ºC	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 ºC	High

Stoichiometrical Problem of Evaporation

- Compound material breaks down at high temperature
- Each component has different vapor pressure, therefore different deposition rate, resulting in a film with different stoichiometry compared to the source

Typical Boat/Crucible Material

<table>
<tr><th colspan="3">Refractory Metals</th></tr>
<tr><th>Material</th><th>Melting Point (ºC)</th><th>Temperature for 10-mtorr Vapor Pressure (P_e) (ºC)</th></tr>
<tr><td>Tungsten (W)</td><td>3380</td><td>3230</td></tr>
<tr><td>Tantalum (Ta)</td><td>3000</td><td>3060</td></tr>
<tr><td>Molybdenum (Mo)</td><td>2620</td><td>2530</td></tr>
<tr><th colspan="3">Refractory Ceramics</th></tr>
<tr><td>Graphitic Carbon (C)</td><td>3799</td><td>2600</td></tr>
<tr><td>Alumina (Al_2O_3)</td><td>2030</td><td>1900</td></tr>
<tr><td>Boron Nitride (BN)</td><td>2500</td><td>1600</td></tr>
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LASER beam evapouration

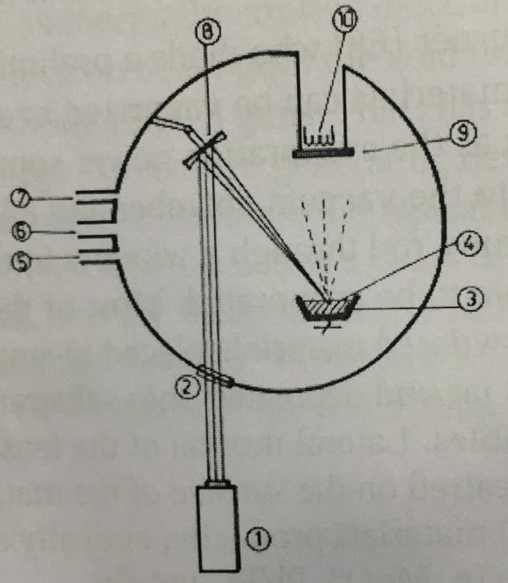


Figure 1.10
Schematic diagram of the laser evaporation system:
1, CO2 laser; 2, ZnSe window; 3, Mo boat;
4, source material; 5, to pump; 6, to vacuum gages;
7, to mass filter; 8, concave mirror; 9, substrate;
10, infrared heater.
(Data from Ref. 69.)

Arc evapouration

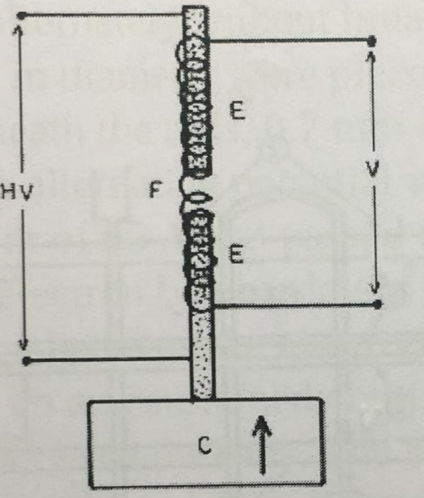


Figure 1.19
Schematic diagram of the electrode-filament arrangement for the vacuum arc method: C, gap control device; E, electrodes; F, helical filament.
(Data from Ref. 91.)

DC Diode Sputtering Deposition

- Target (source) and substrate are placed on two parallel electrodes (diode)

- They are placed inside a chamber filled with inert gas (Ar)

- DC voltage (~ kV) is applied to the diode

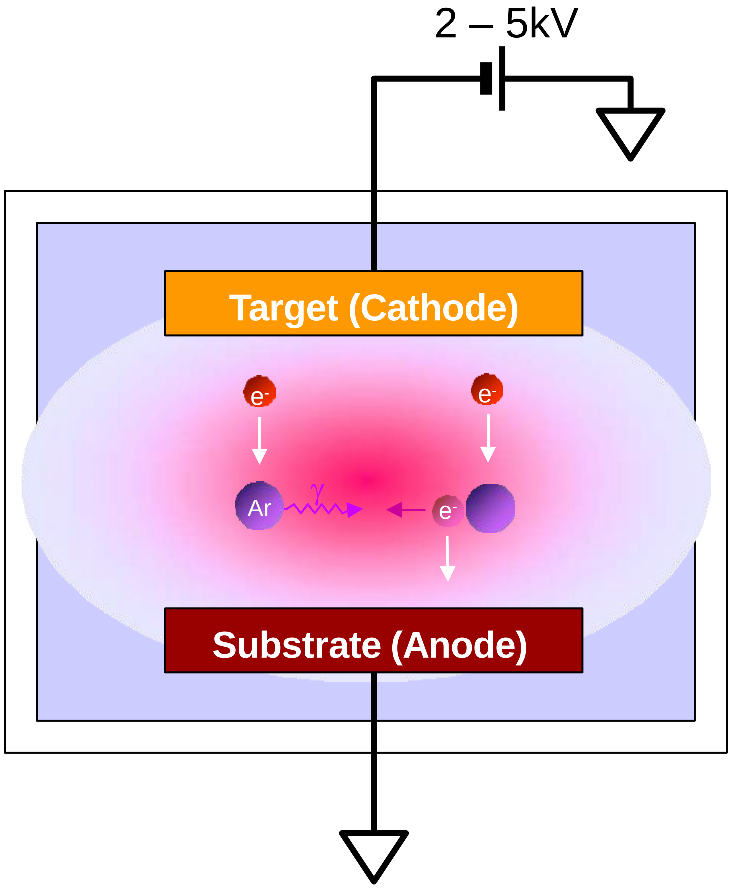
- Free electron in the chamber are accelerated by the e-field

- These energetic free electrons inelastically collide with Ar atoms
    - ◆ excitation of Ar → gas glows
    - ◆ ionization of Ar → Ar^+ + 2nd electron

- 2nd electrons repeat above process

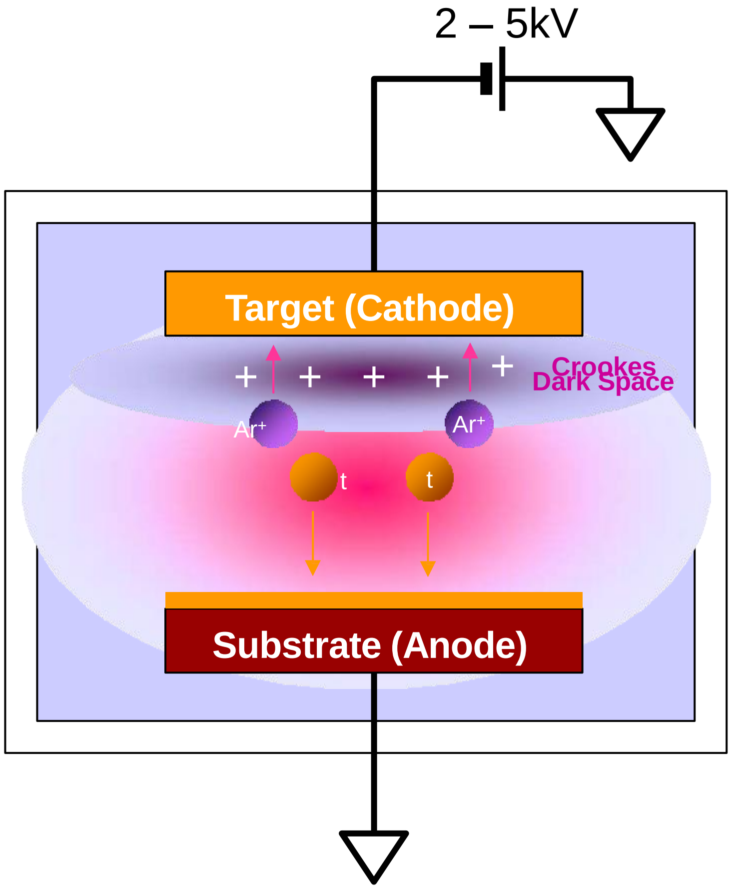
→ “gas breakdown”

→ discharge glow (plasma)



Self-Sustained Discharge

- Near the cathode, electrons move much faster than ions because of smaller mass
  - positive charge build up near the cathode, raising the potential of plasma & less electrons collide with Ar
  - few collision with these high energetic electrons results in mostly ionization, rather than excitation
  - dark zone (Crookes Dark Space)
- Discharge causes voltage between the electrodes reduced from ~10^3 V to ~10^2V, mainly across the dark space
- Electrical field in other area is significantly reduced by screening effect of the position charge in front of cathode
- Positive ions entering the dark space are accelerated toward the cathode (target), bombarding (sputtering) the target
  - atoms locked out from the target transport to the substrate (momentum transfer, not evaporation!)
  - generate 2nd electrons that sustains the discharge (plasma)



Requirement for Self-Sustained Discharge

- If the cathode-anode space (L) is less than the dark space length
  - ionization, few excitation
  - cannot sustain discharge
- On the other hand, if the Ar pressure in the chamber is too low
  - Large electron mean-free path
  - 2^{nd} electrons reach anode before colliding with Ar atoms
  - cannot sustain discharge either

Condition for Sustain Plasma: $\boxed{L \cdot P > 0.5 \ (cm \cdot torr)}$

L: electrode spacing, P: chamber pressure

For example:

Typical target-substrate spacing: L ~ 10cm

→ P > 50 mtorr

Deposition Rate vs. Chamber Pressure

High chamber pressure results in low deposition rate

Mean-free path of an atom in a gas ambient:

$$\lambda \sim \frac{5 \times 10^{-3}}{P(torr)} \quad (cm)$$

Use previous example:

L = 10 cm, P = 50 mtorr

→ λ ~ 0.1 cm

→ sputtered atoms have to go through hundreds of collisions before reaching the substrate

→ significantly reduces deposition rate

→ also causes source to deposit on chamber wall and redeposit back to the target

In fact, sputtering deposition rate R:

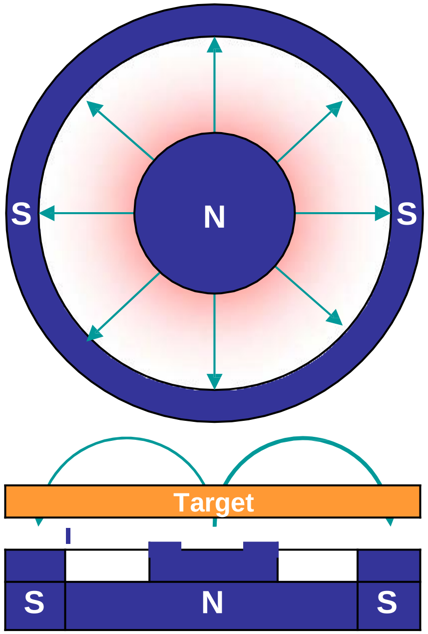
$$R \propto \frac{1}{L \cdot P}$$

- ◆ Large LP to sustain plasma
- ◆ small LP to maintain good deposition rate and reduce random scattering

?

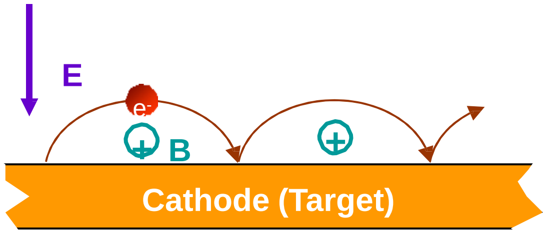
DC Magnetron Sputtering

- Using low chamber pressure to maintain high deposition rate
- Using magnetic field to confine electrons near the target to sustain plasma



Apply magnetic field parallel to the cathode surface

→ electrons will hope (cycloid) near the surface (trapped)



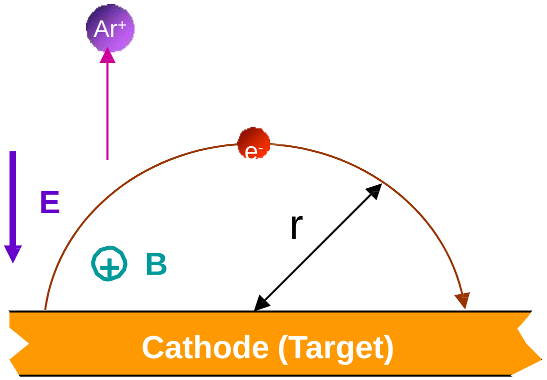
Impact of Magnetic Field on Ions

Hoping radius r:

$$r \sim \frac{1}{B}\sqrt{\frac{2m}{e}V_d}$$

V_d – voltage drop across dark space (~ 100 V)

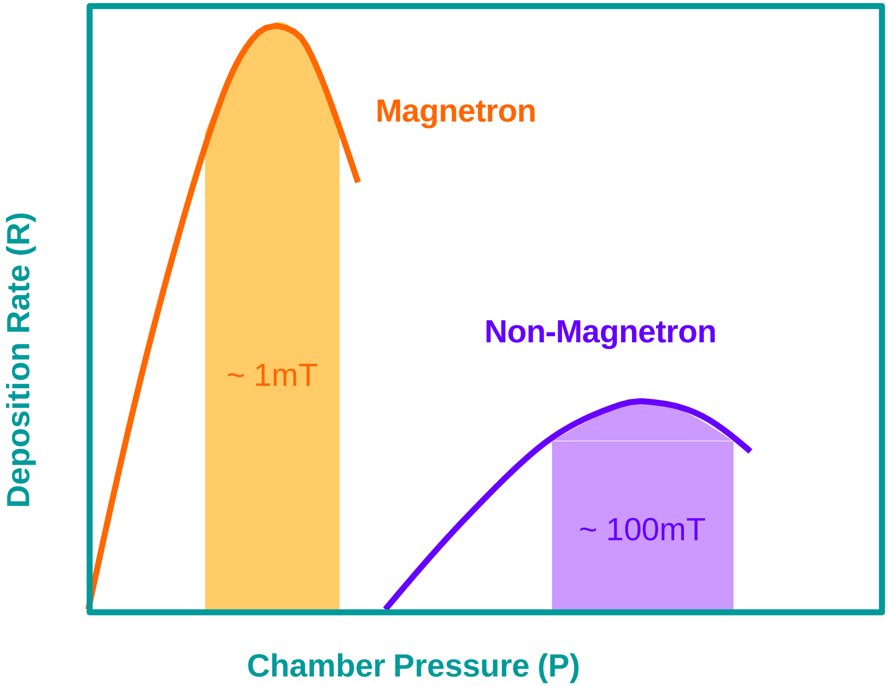
B – Magnetic field (~ 100 G)



For electron	r ~ 0.3 cm
For Ar+ ion:	r ~ 81 cm

As A Result …

- current density (proportional to ionization rate) increases by 100 times
- required discharge pressure drops 100 times
- deposition rate increases 100 times



RF (Radio Frequency) Sputtering

DC sputtering cannot be used for depositing dielectrics because insulating cathode will cause charge build up during Ar^+ bombarding

→ reduce the voltage between electrodes

→ discharge distinguishes

Solution: use AC power

•at low frequency (< 100 KHz), both electrons and ions can follow the switching of the voltage –

→ DC sputtering

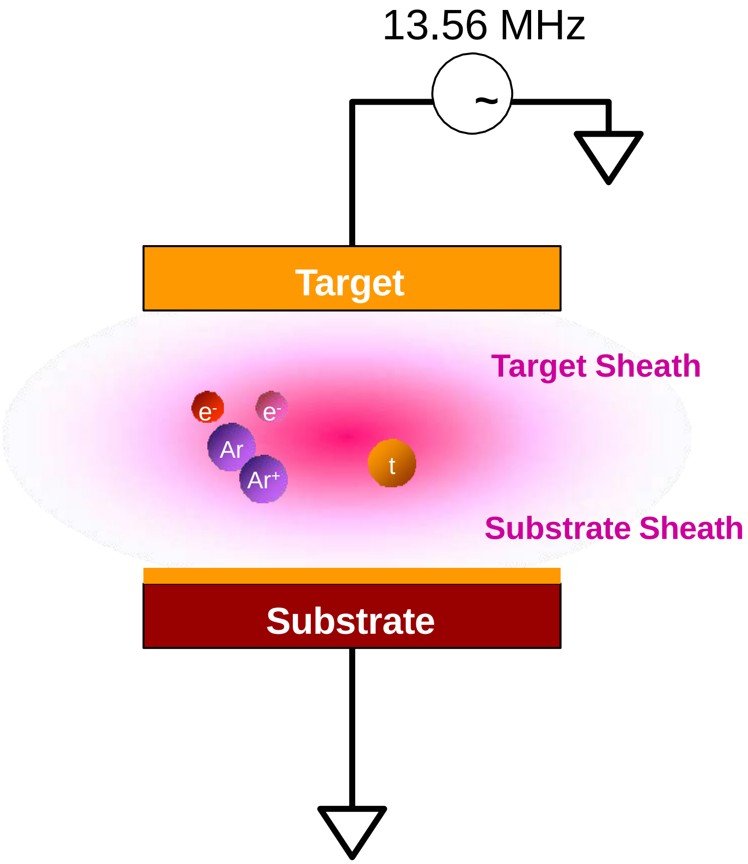
•at high frequency (> 1 MHz), heave ions cannot no long follow the switching

→ ions are accelerated by dark-space (sheath) voltage

→ electron neutralizes the positive charge buildup on both electrodes

•However, there are two dark spaces

→ sputter both target and substrate at different cycle



Comparison between Evaporation and Sputtering

Evaporation	**Sputtering**
Low energy atoms (~ 0.1 eV)	High energy atoms / ions (1 – 10 eV) • denser film • smaller grain size • better adhesion
High Vacuum •directional, good for lift-off •lower impurity	Low Vacuum •poor directionality, better step coverage •gas atom implanted in the film
Point Source •poor uniformity	Parallel Plate Source •better uniformity
Component Evaporate at Different Rate •poor stoichiometry	All Component Sputtered with Similar Rate •maintain stoichiometry

Advantages of PVD:

1. There is no specific requirement for the substrate: it means film can be deposited on any substrate such as metal, insulator, plastic, wood, cloths etc.
2. PVD coating are sometimes more harder and corrosion resistant than coatings applied by electroplating technique.
3. Most of the films are high temperature and good impact streangth, excellent abrasion resistance and are so durable.
4. Highly controlled growth.
5. Good repeatability.
6. Process is more environmental friendly than other chemical techniques.
7. Almost all type of organic material can be coated as well as some organics also can be deposited.

Dis-advantages of PVD:

1. It is line of sight technique meaning that it is very difficult to coats undercoats and complex surfaces.
2. High capital costs
3. Some processes operate at high temperature and vacuum requires skilled operator.
4. Processes requiring large amounts of heat require appropriate cooling systems.
5. The rate of coating is usually quite slow.