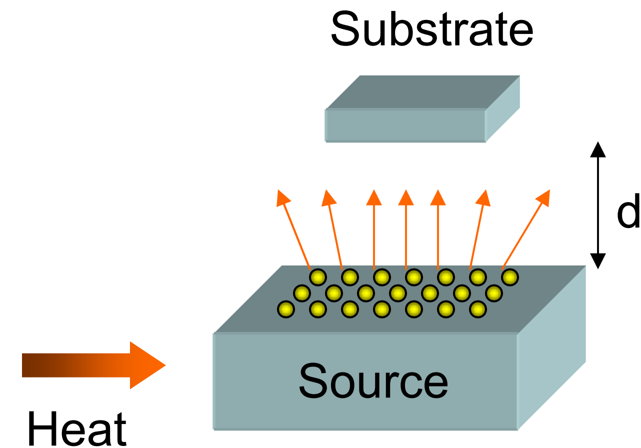
Vacuum Evaporation

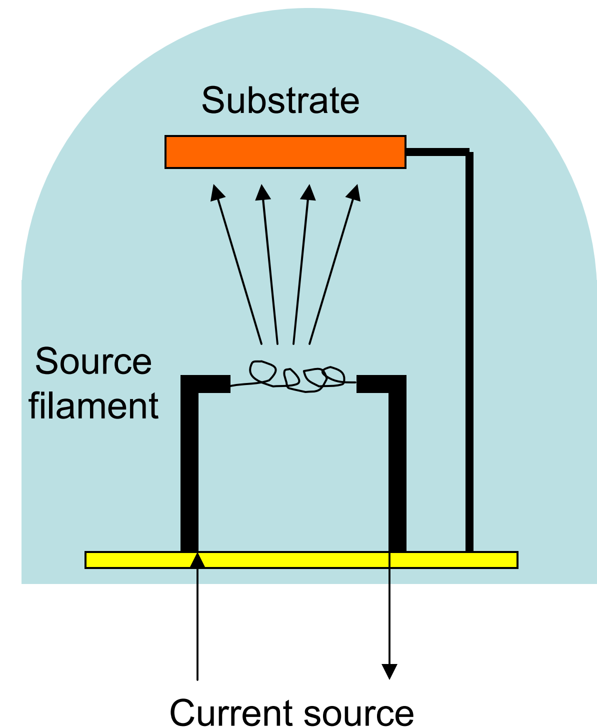
Introduction

- The objective is to controllably transfer atoms from a heated source (which can be a liquid or a solid) to a substrate located a distance away to grow a film.
- The source is heated directly or indirectly until the point is reached where it efficiently sublimes or evaporates.
- When analyzing this method, we need to start from evaporation rates and vapor pressure.
- Evaporation is normally done in the ballistic regime ($Kn > 1$).
- Other than pressure and temperature, the placement of the heater, source and substrate are important factors.



Process Summary

- Place a suitable material (the source) inside the vacuum chamber with a heater.
- Seal and evacuate the chamber.
- Heat the source. When the temperature reaches the evaporation temperature, atoms or molecules start to leave the surface of the source and travel in a more or less straight path until they reach another surface (substrate, chamber wall, instrumentation).
- Since these surfaces are at much lower temperatures, the molecules will transfer their energy to the substrate, lower their temperature and condense.
- Since the vapor pressure at the new temperature is much higher, they will not re-evaporate and adhere to the substrate.
- The deposition thickness is a function of the evaporation rate, the geometry of the source and the substrate and the time of evaporation.



Vapor Pressure

- Vapor pressure is the pressure at which the vapor phase is in equilibrium with the solid or the liquid phase at a given temperature.
- Below this pressure, surface evaporation is faster than condensation, above it it is slower.
- Theoretically, the vapor pressure can be found by the **Clausius-Clapeyron** equation.

$$\frac{dP}{dT} = \frac{\Delta H(T)}{T\Delta V}$$

where ΔH is the change in enthalpy, and ΔV is the change in volume between the solid (or liquid) and vapor phases

- Over a small temperature range, the equation can be simplified as:

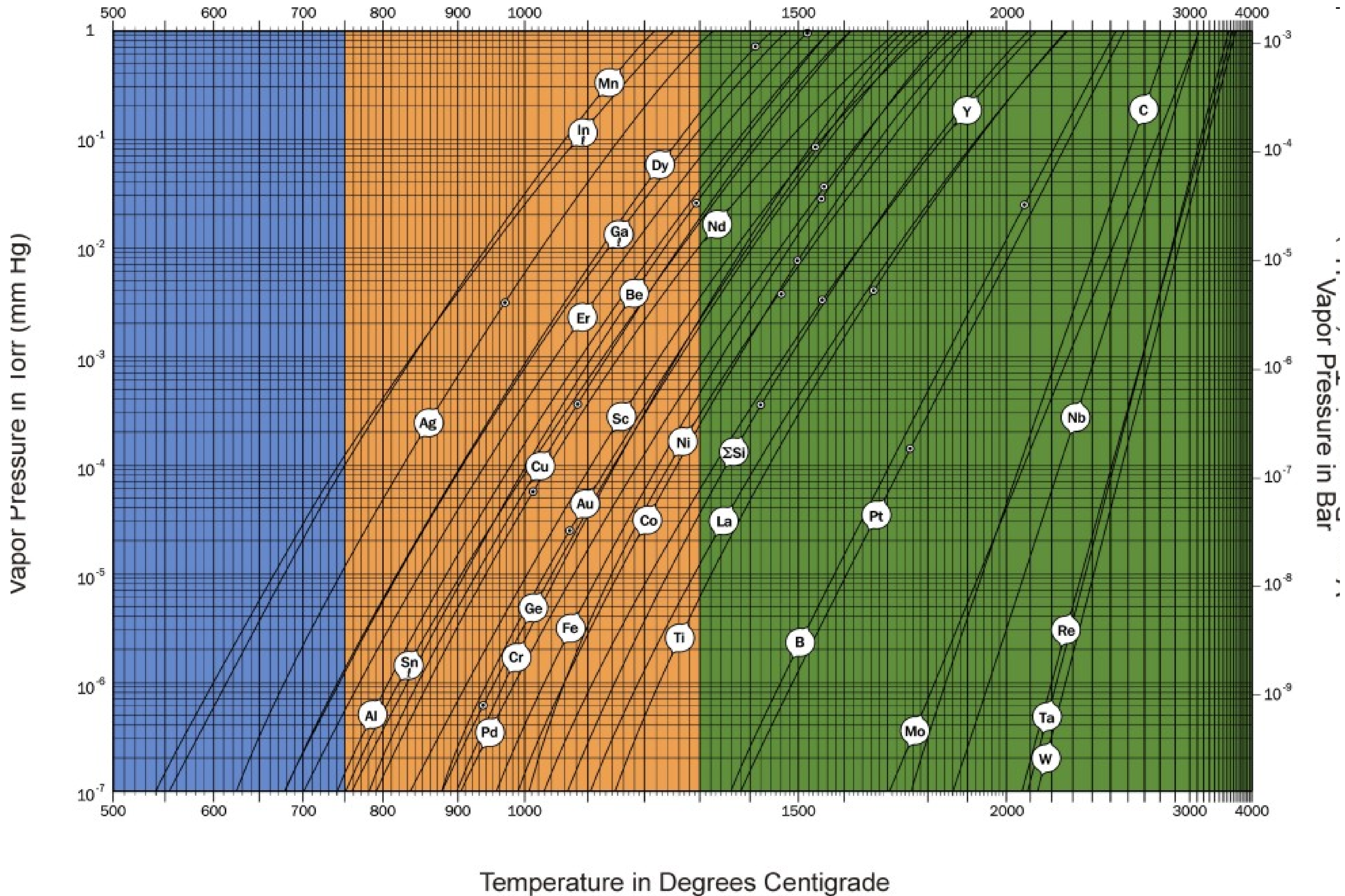
$$P = P_0 \exp\left(-\frac{\Delta H_e}{RT}\right)$$

where ΔH_e is the molar heat of evaporation

Vapor Pressure of Elements

- In reality, empirical formulas and experimental data are more useful to find the vapor pressure of an element.
- For example, the vapor pressure of liquid Al is given by:

$$\log P(torr) = \underbrace{-15993/T + 12.409}_{\text{Main Terms}} \underbrace{- 0.999 \log T - 3.52 \times 10^{-6} T}_{\text{Smaller Terms}}$$



Vapor Pressure in Torr (mm Hg)
Vapor Pressure in Bar
Temperature in Degrees Centigrade
500
600
700
800
900
1000
1500
2000
3000
4000
1
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
Mn
In
Dy
Ga
Nd
Be
Er
Y
C
Ag
Sc
Ni
ΣSi
Cu
Au
Co
La
Pt
Nb
Ge
Fe
Ti
B
Re
Sn
Cr
Al
Pd
Mo
Ta
W

Evaporation Rate

- The basic equation for evaporation flux is given by:

$$\Phi_e = \frac{\alpha_e N_A (P_v - P_h)}{\sqrt{2\pi MRT}}$$

where Φ_e is the evaporation flux, α_e is the coefficient of evaporation ($0 < \alpha_e < 1$), P_v is the vapor pressure and P_h is the ambient pressure.

- Maximum flux is obtained when $\alpha_e = 1$ and $P_h = 0$

$$\Phi_e = 3.513 \times 10^{22} \frac{P_v}{\sqrt{MT}} \frac{\text{molecules}}{\text{cm}^2\text{s}}$$

- This can also be put in mass units by multiplying flux with the atomic mass:

$$\Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{M}{T}} P_v \frac{\text{gr}}{\text{cm}^2\text{s}}$$

Aluminum Example

- For Al, M = 27 gr
- From the vapor pressure diagram, to get $P_v = 10^{-4}$ Torr, we need to heat Al to 980 °C.
- At this temperature, the mass evaporation rate is:

$$\Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{27}{980}} 10^{-4} \ \frac{\mathrm{gr}}{\mathrm{cm^2 s}} = 9.694 \times 10^{-7} \ \frac{\mathrm{gr}}{\mathrm{cm^2 s}}$$

- If the vapor pressure is chosen to be 10^{-2} Torr, then the temperature has to be increased to 1220 °C and the evaporation rate becomes:

$$\Gamma_e = 5.84 \times 10^{-2} \sqrt{\frac{27}{1220}} 10^{-2} \ \frac{\mathrm{gr}}{\mathrm{cm^2 s}} = 8.688 \times 10^{-5} \ \frac{\mathrm{gr}}{\mathrm{cm^2 s}}$$

Deposition Rate

- Of course the ultimate quantity we are looking for is a deposition rate.
- This is not only related to the evaporation rate but also the angle and distance between the source and substrate.
- Our basic assumption remains that we are in the ballistic regime and the evaporated atoms travel in a straight line from the source to the substrate.
- We start by looking at the mass lost from the source.

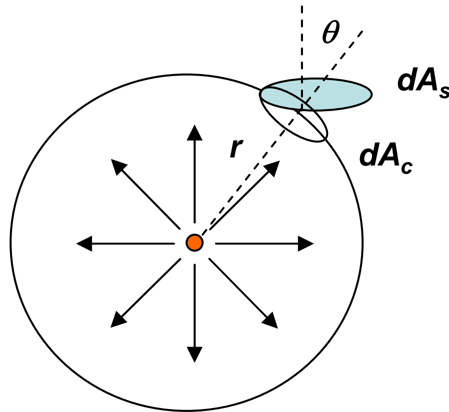
$$M_e = \int_0^t \int_{A_e} \Gamma_e \, dA_e \, dt$$

where A_e is the surface area of the source

- The expansion of that mass in the chamber depends on whether the source is a point or a surface source.
- A portion of that mass is incident on the target. The orientation of the target will determine the actual mass that is deposited.

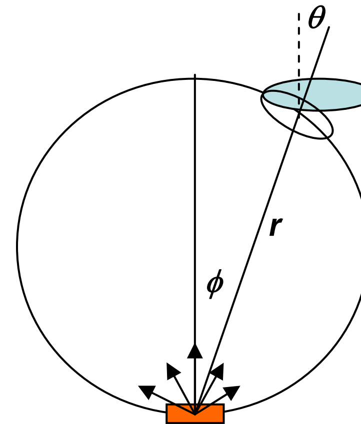
Point and Surface Sources

Point Source

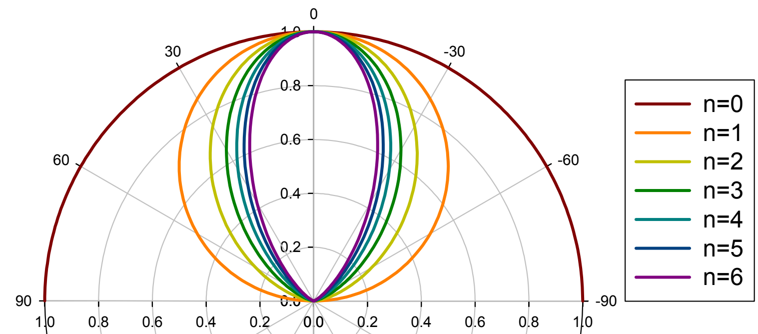


$$\frac{dM_s}{dA_s} = \frac{M_e \cos\theta}{4\pi r^2}$$

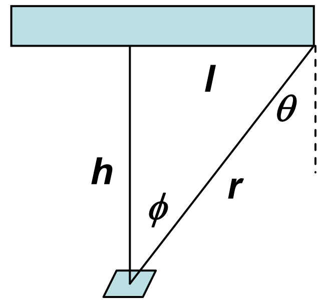
Surface Source

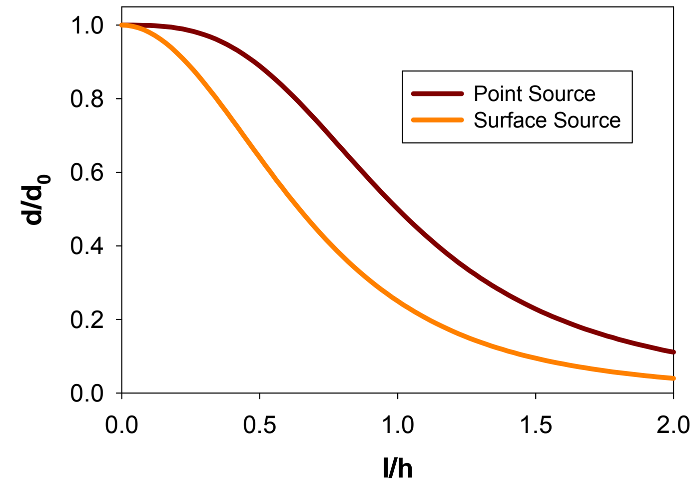


$$\frac{dM_s}{dA_s} = \frac{M_e (n+1) \cos^n \phi \cos\theta}{2\pi r^2}$$



Film Thickness Variation





Point Source

$$d = \frac{M_e h}{4\pi\left(h^2 + l^2\right)^{3/2} \rho_{density}}$$

Surface Source

$$d = \frac{M_e h^2}{\pi\left(h^2 + l^2\right)^2 \rho_{density}}$$

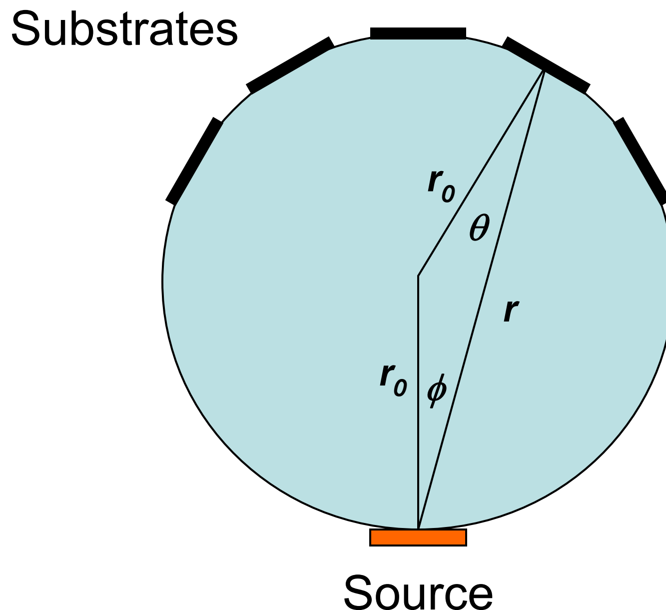
Maximum film thickness occurs at *l* = 0. If we express the thickness relative to the maximum thickness;

$$\frac{d}{d_0} = \frac{1}{\left(1 + \left(l/h\right)^2\right)^{3/2}}$$

$$\frac{d}{d_0} = \frac{1}{\left(1 + \left(l/h\right)^2\right)^2}$$

An Arrangement for Uniform Films

- If both the source and the substrate are located on the surface of a sphere, the angular dependence on θ or ϕ is eliminated.



$$\frac{dM_s}{dA_s} = \frac{M_e}{4\pi r_0^{\;2}}$$

Film Purity

There are several sources of impurity:

- Contamination of source materials
  - Use high purity (99.99999%) materials
- Contamination from the heater
  - Use materials with low diffusion
- Residual gas in chamber
  - Better vacuum
  - Higher deposition rate

Compounds

- Evaporation of multi-element materials like compounds present some problems.
- Compounds can decompose or dissociate during evaporation.
- Different components of the material can have different vapor pressure/temperature requirements leading to different vapor concentrations and different stochiometry.

Reaction Type	Chemical Reaction	Examples	Comments
No dissociation	MX(l or s)→MX(g)	SiO, CaF_2, MgF_2	Stoch. maintained
Decomposition	MX(s)→M(s or l)+½ X_2(g)	III-V semiconductors	Separate sources are required
Dissociation			
Chalcogenides	MX(s)→M(g)+½ X_2(g)	CdS, CdSe, CdTe	Separate sources are required
Oxides	MO_2(s)→MO(g)+½ O_2(g)	SiO_2, TiO_2	Deposit in O_2 partial pressure

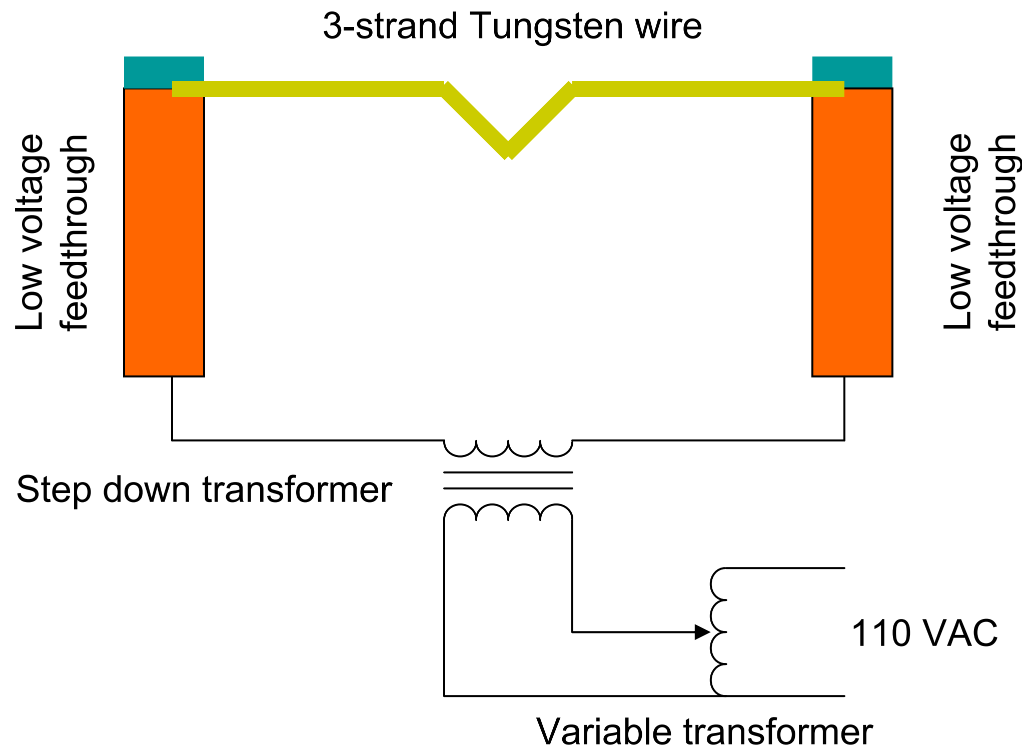
Alloys

- An alloy is a multi-component system where the constitutive elements are completely miscible in each other and can have varying stochiometry.
- The problem arises due to the different vaporization rates of the components.
- Even if initial concentration ratios are adjusted to take this into account, as evaporation proceeds, the flux of each component will vary leading to a graded film composition along the film thickness.

Vacuum Evaporation Sources

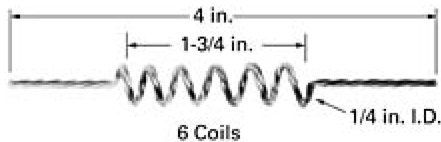
- Physical evaporation
  - A “source” container is heated.
  - The material to be evaporated is placed in or near the source.
  - The radiative and conductive heating evaporates the source.
- Electron beam evaporation
  - A filament is heated and emits electrons.
  - The electrons heat the evaporant and vaporize it.

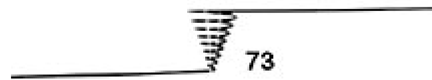
The Basic V-Groove Source

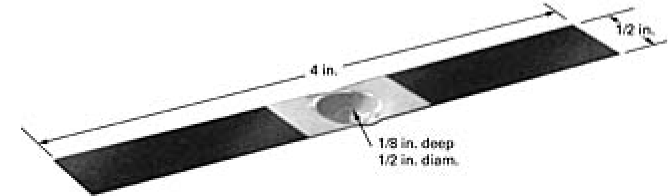


- Place the evaporant at the tip of the V.
- Uses radiative and conductive heating (through wetting) to evaporate material.
- Filament is good for one use.
- Not for depositing films thicker than 1500 A.
- Point source (fairly even coating over a spherical surface)

Other Arrangements







- **Multiple Loop Source**
- Better for heavier coatings
- As many as 15 loops, wound helically
- Need trial and error to find best position for even coating.

- **Wire basket source**
- More flexible
- Better able to handle evaporants that melt

- **Dimpled boat source**
- Made of Mo, Ta, Tu
- Can hold bigger charges
- Can deposit thicker layers
- Evaporation occurs only in the upward direction
- Higher power requirements

Closed Sources

- Evaporant is placed in dimpled volumes inside the source.
- The source is sealed creating a simple furnace.
- As current is passed through the source, evaporant vapors are emitted through the holes in the source.
- Creates speck-free vapor.

Electron Beam Sources

- Resistive heating first heats a source and then uses radiant or convection heating to heat the evaporant. This can be inefficient.
- By applying a high voltage to a filament, we can create an electron beam.
- When the beam contacts the evaporant, it will heat it directly.
- Since the evaporant is water cooled, it will not wet the source and remains pure.
- Since there are no boats, wires, etc., higher temperatures can be reached.
- Electrical arcing and discharges may occur.

Thickness Measurements

- Gravimetric Method
  - Measure substrate weight before and after coating
  - Calculate thickness from known substrate dimensions
  - Not real-time but surprisingly accurate
- Stylus Method (Profilometer)
  - A stylus is drawn across a step in the film
  - Scratching can occur
  - Needs calibration
  - Can do repeated measurements
  - Not real-time

Process Control

- Resistance monitoring
  - For metallic (conductive) films
  - Resistance is the ratio of voltage to current.
  - It is a function of the dimensions of the film (thickness and length) as well as the material it is made of (resistivity).
  - Should be calibrated against the gravimetric method.

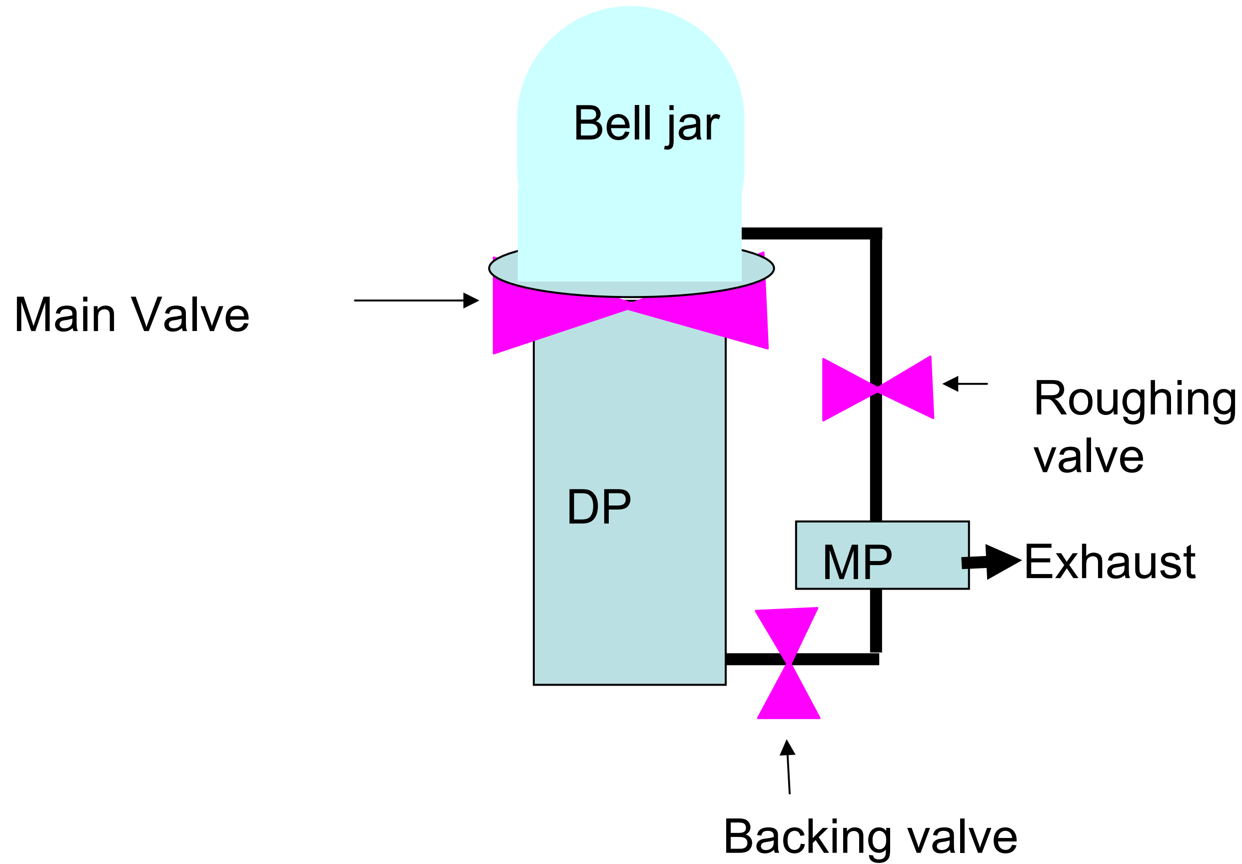
Quartz Crystal Monitors

- Install a quartz oscillator in the vacuum chamber.
- Quartz will have a specific oscillation frequency.
- Expose one side of the quartz wafer to the vapor.
- As the vapor coats the wafer, the oscillation frequency changes.
- Many assumptions are being made including proper calibration, quartz quality and proper usage.
- With a 6 MHz oscillator, it is possible to measure nanogram changes which in turn means about 0.1 A.

Substrate Cleaning

- A clean substrate is essential to achieve good film adhesion.
- The “Tape Test” is the qualitative measure for good adhesion.
- Sample cleaning for ITO:
  - 30 min ultrasonic bath in acetone
  - 30 min ultrasonic bath in methanol
  - 15 min ultrasonic bath in isopropanol
  - 90 min UV/Ozone cleaning

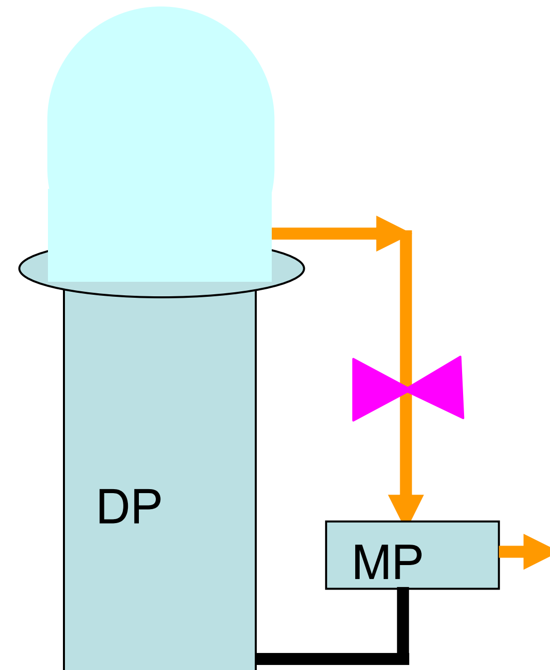
Vacuum Evaporator Diagrams



Complete vacuum evaporator

Operating situation 1: Making low vacuum in chamber

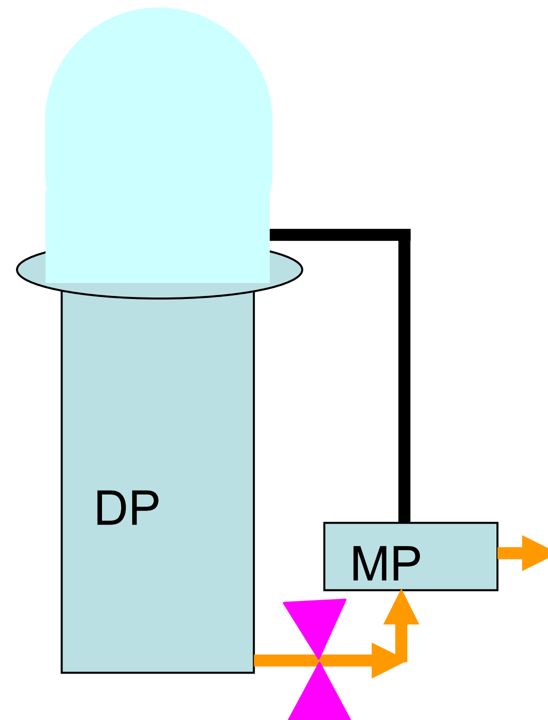
Roughing valve open:
- MP makes low vacuum in chamber



Operating situation 2: Standby situation

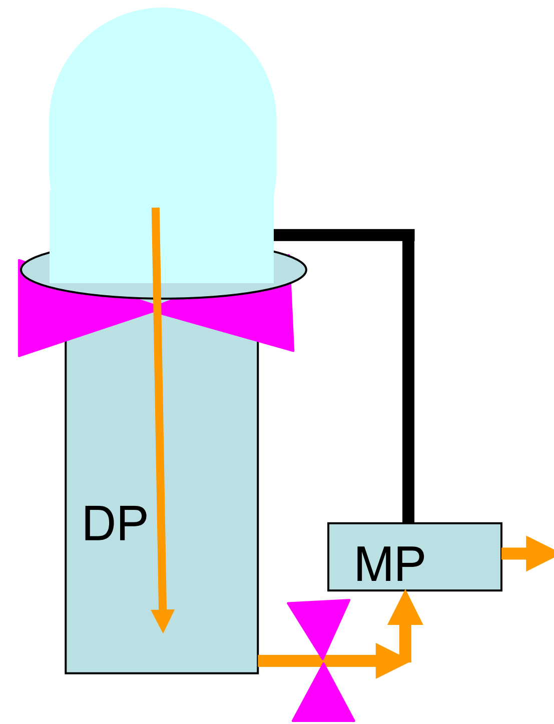
Backing valve open:

- MP removes air molecules from DP



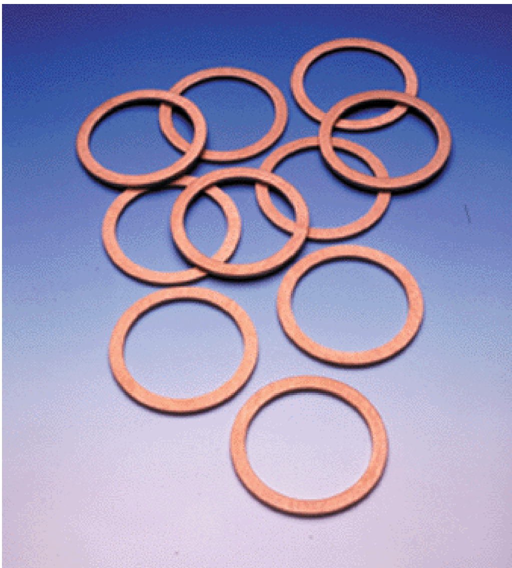
Operating situation 3: Condition for evaporation

Backing valve and main valve both open: MP removes air molecules from DP while DP removes air from main chamber



Vacuum Chamber

- 304 stainless steel base plate ~1 in. thick
- Glass bell jar: usually Pyrex
- Viton rubber boot on bottom of bell jar (greased)



SAFETY:

1. Do not handle bell jar with gloves on
2. Line inside of bell jar with aluminum foil to keep surface clean/no abrasives
3. Never touch components of chamber or interior of bell jar with bare hands

Final Words

- Vacuum evaporation is most suitable for deposition of metallic thin films.
- Compounds and alloys don’t deposit well because they tend to dissociate at the temperatures required.
- While patterning using masks are routinely done, step coverage is not very good because the vapor flows ballistically (shadowing).